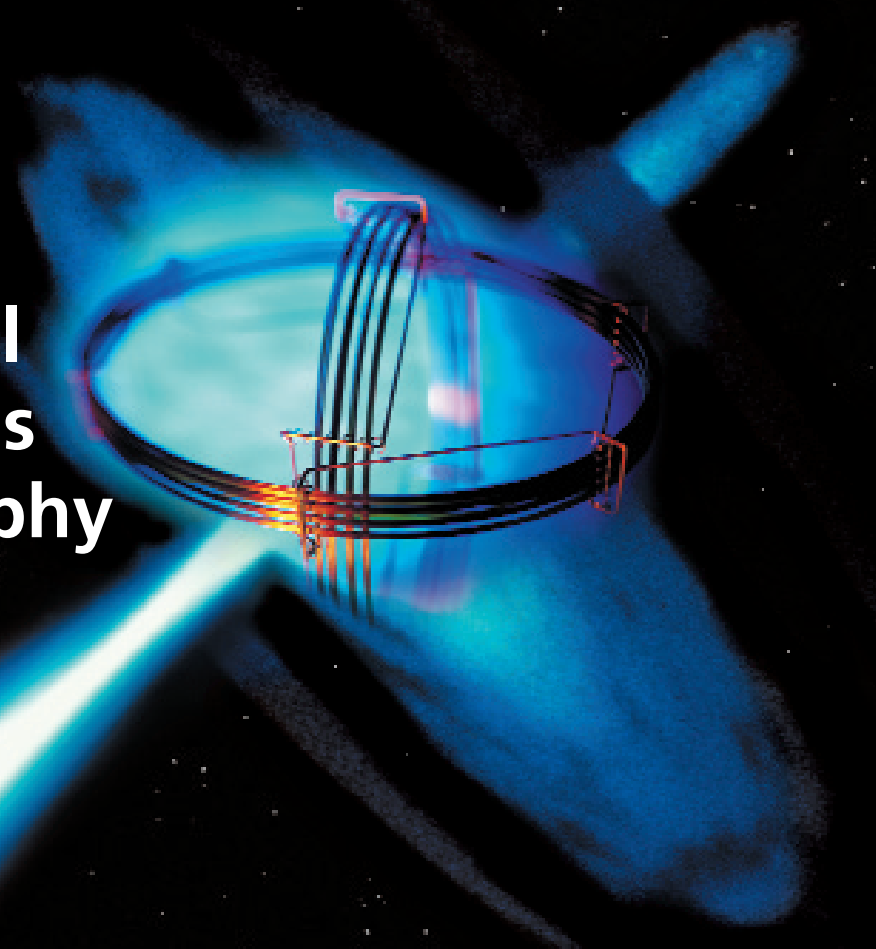


Development and Analytical Aspects of Gas Chromatography for Space Exploration



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Introduction

Gas chromatography (GC) has been used in space exploration for 25 years, since investigations of the atmosphere and soil composition of Mars in 1976 by the Viking space probe (Table 1) (1, 2). This analytical technique has been selected for characterizing the chemical composition of complex extraterrestrial environments because of its straightforwardness and efficiency, but also because of its suitability to space applications. As a result of space mission constraints (robustness, operating conditions, storage for long durations under extreme conditions etc.), a specially designed gas chromatograph is required. The development stage of the instrument is critical because once the spacecraft is launched, hardware configuration cannot be changed and no significant modification of its working conditions can be implemented. The aim of this article is to highlight the parameters that must be considered before developing a gas chromatograph for use in space, together with their influence on the design and

operation of the instrument. As an application, the COmetary Sampling And Composition (COSAC) experiment development is described, with emphasis on the chromatographic columns used. Finally, we will postulate on future improvements in space GC.

This article relies on the skills developed at LISA that have led to the development of on-board GC systems for the Cassini-Huygens (3–11) and Rosetta lander probes (12–14), as well as new chromatographic techniques for future Mars exploration (15).

Development of a Space GC Experiment

Scientific requirements: First, the physical and chemical nature of the sample to be analysed by the instrument must be defined. This “scientific” objective has a strong influence on the selection of chromatographic columns and detectors, as well as on the sampling system definition and, therefore, the whole instrument itself. As a consequence, it is vitally important to comprehensively define

the nature of the samples as hardware configuration cannot be changed after the probe launch.

Whereas the physical nature of the sample is rather well known (gas, aerosol or soil), estimation of its chemical composition is much more complicated. Fortunately, there are several means to identify “candidate” compounds that could form part of future analysed samples:

- Remote sensing observations (spectroscopy) performed from Earth or orbital telescopes provide information about the studied bodies, but this chemical characterization is limited to the high atmosphere zones (16).
- In situ measurements previously performed can be used, as was the case for the Pioneer (1978) and Vega (1984) missions to Venus (Table 1) (17, 18).
- Simulations of the investigated bodies’ compositions by simulating their chemistry in the laboratory usually generate a lot of products that are seldom detected by observations, as is the case for Titan (19) and the cometary nuclei (20).

Table 1: An Overview of GC Instruments for In Situ Planetary Missions.

Mission/ Target body	Launch/ Arrival	Experiment/ Sample nature	Analytical columns/ Column nature	Temperature/ Carrier gas	Detectors
NASA Viking/ Mars	1975/1976 1978/1978	GEx/gas GC-MS/soil	Two Porapak Q (7.6 m × 1 mm)/ Packed One Tenax coated with polymetaphenoxylene (2 m × 0.76 mm)/ Packed	24 °C/He 50 °C (12 min) + linear prog. to 200 °C/H ₂	One Thermistor TCD (32 °C) MS
NASA Pioneer- Venus/ Venus	1978/1978	GC/gas	In parallel: one pair of Porapak N (15.85 m × 1.1 mm); one pair of PDVB (2.13 m × 1.1 mm)/Packed	18 °C and 62 °C/ He	In parallel: two thermistors/TCD
USSR Venera 11 to 14/ Venus	1978/1978	Sigma GC/gas	In series: one Polysorb (2 m), one molecular sieve (2.5 m) and one reduced manganese/Packed	70 °C/Ne	In series: three Ne ionization
USSR Vega/ Venus	1984/1985	Sigma-3 GC/ gas and aerosol	In parallel: one Porapak QS+N, one Porapak QS+N and one Porapak T/Packed	70 °C/He and N ₂	He ionization + TCD; ECD
NASA/ESA Cassini-Huygens/ Titan, largest satellite of Saturn	1997/2004	GC-MS/ gas and aerosol	In parallel: one carbon molecular sieve (2 m × 0.75 mm), one glassy carbon (14 m × 0.18 mm) and one CNPP-DMPS (10 m × 0.18 mm)/one Packed and two WCOT	Isothermal 30-60 °C/H ₂	Ion trap MS with one ion source connected to each column
ESA Rosetta Comet Wirtanen	2003/2011	COSAC/ gas, ice and dust	In parallel: carbon molecular sieve (15 m × 0.25 mm), a DVB-styrene (10 m × 0.18 mm), a DMPS (10 m × 0.18 mm), a CNPP-DMPS (15 m × 0.18 mm), a DP-DMPS (15 m × 0.18 mm) three chiral columns (10 m × 0.25 mm)/ two PLOT and six WCOT columns	Isothermal 30-60 °C/He	Eight nano-TDCs (one for each column) and TOF- MS (only one ion source)

Once the candidate compounds are defined, the sampling system must be selected. For gas analysis, a direct sampler is relatively "easy" to conceive even though the system can become complex in the case of atmospheric probes (17, 21, 22) because of the incompatibility between the descent duration and the analysis time of the instrument. Moreover, the sample to be analysed can be treated to remove compounds in order to either improve the sensitivity of the analysis, or prevent an unwanted interaction with the columns' stationary phases and the removed compounds, which could disturb the analysis. Until now, only the Viking GC-mass spectrometry (MS) experiment (23) had used such a process, to enrich a sample from the Martian atmosphere by removing carbon monoxide, carbon dioxide and water with hydroxide, silver oxide and magnesium perchlorate adsorbents. With refractory materials such as aerosols (Titan's atmosphere) or soil (Mars), the sample can be either heated at medium (vaporization) or high temperature (pyrolysis), or chemically treated in order to make it more volatile. Whereas pyrolysis has been commonly used since the Viking mission, chemical treatments by

derivatization have only recently emerged with the need to identify amino acids in extraterrestrial environments, particularly Mars (see below). Indeed, the detection of these molecules is very important for evaluating the presence or absence of past life in Martian soil. However, analysis by pyrolysis is difficult because amino acids are thermally fragile.

Moreover, the defined range of candidate compounds is used to select the most appropriate stationary phases and column dimensions for separation with the maximum resolving power. Finally, detector selection also depends on the nature and abundance of targeted compounds because there exist numerous detectors dedicated to the analysis of a specific range of compounds. However, only universal detectors (thermal conductivity detectors (TCD), mass spectrometers, ionization detectors (ID)) have been used so far (1, 2, 24) because of their capability to analyse a wide range of volatile species. **Technological constraints:** The launch of high mass out of the Earth's atmosphere is currently difficult and expensive. This is the reason why space probes suffer from mass and size restrictions, which directly influence the scientific payload design and

operation. First, it limits the size and mass of the electric batteries that can be boarded in the probe and, therefore, the energy available for the different operating systems. Whereas for missions to Mars, solar cells were able to provide enough energy to allow the system to work for about one year, for cometary lander probes such as for the Rosetta mission, the amount of light received from the Sun is too low to generate electrical power. Moreover, the chromatographic system itself must be compact in size and have low mass. Therefore, carrier gas tanks suffer from the same limitations, thus significantly reducing the amount of carrier gas available for analyses. This is one of the reasons why flame ionization detectors are not used (even though the presence of a flame is the strongest argument) because they would require supplemental tanks of H₂ and air for the flame.

However, the most important criterion is the robustness of the individual instrument parts, which must resist vibrations and shocks generated during launch, temperature variations that can be harsh in space, vacuum conditions and space radiation including high-energy particles and γ rays. For the columns, this means

selecting a sturdy wall and until now, only metallic columns were used in space GC. Moreover, the link between the stationary phase and the wall must be strong enough to prevent bleeding, which would have a dramatic effect on the analysis. This is the reason why columns used for the 1970s and 1980s missions were packed ones. Indeed, at that time, capillary column external walls were mainly made of glass or polyimide, and processes of phase bonding had not been developed. Now, with metallic capillary development, cross-linked and bonded phases are preferentially selected to strengthen robustness to vibrations and temperature variations, and to prevent stationary phase evaporation under vacuum storage. For detector selection, the main criterion is resistance to shocks and vibrations. This is the reason why all the detectors used in space probes until now have been relatively simple. Thus, TCDs, electron capture detectors and IDs have been preferentially used in space GC. However, the mass spectrometers used in the Viking (23), Cassini–Huygens (21) and Rosetta lander (25) probes are the exceptions to this rule. Nevertheless, the information given by such a detector for peak identification is of great importance, and progress in MS design over the last 10 years has provided on-board miniaturized mass spectrometers (25).

“temperature programming is not used because of its high power consumption.”

Operating constraints: The space operating conditions cannot be the same as on Earth, because of the restricted power and carrier gas amount available for the instrument. The major consequence of this is an analysis time limited to less than 30 min.

As energy consumption must be low, relatively low operating temperatures are used compared with those reachable in the laboratory. They have historically been in the range 20–70 °C. Moreover, temperature programming is not used because of its high power consumption. It would also be time-consuming because the instruments are thermally isolated to avoid energy loss and therefore, the analytical cycle would be very long because of the cooling phase. The only exception to this rule was the GC–MS experiment on Mars, which used temperature programming up to 200 °C (23), but in this instance, time was not a restrictive factor, as explained above. As with energy, carrier gas consumption must also be low. Thus, low

carrier gas flow-rates in the columns are required, which significantly influences their characteristics. It also helps explain the evolution of the flight columns for space missions. Indeed, the columns used for the Venus and Mars missions were packed ones because of their robustness (metallic column walls and sturdy packing material). As capillary columns were restricted to glass wall material, packed columns were the only possible alternative. But today, metallic capillary columns with sturdy stationary phases exist and these are preferentially used because of their lower carrier gas consumption, higher efficiency and shorter time of analysis compared with packed columns. Another advantage is having flow-rates compatible with MS, thus removing the need for a split between the gas chromatograph and mass spectrometer, which could bias the analysis. For the stationary phases, and more particularly the liquid ones, resolving power is strongly dependent on the operating temperature. The liquid stationary phases are required to operate above a temperature corresponding to their crystallization point, which depends on the composition of the phase and which is generally in the range –30 to 40 °C (Restek Catalogue 2000, Restek Corp., Bellefonte, Pennsylvania, USA). More generally, the defined operating conditions combined with the

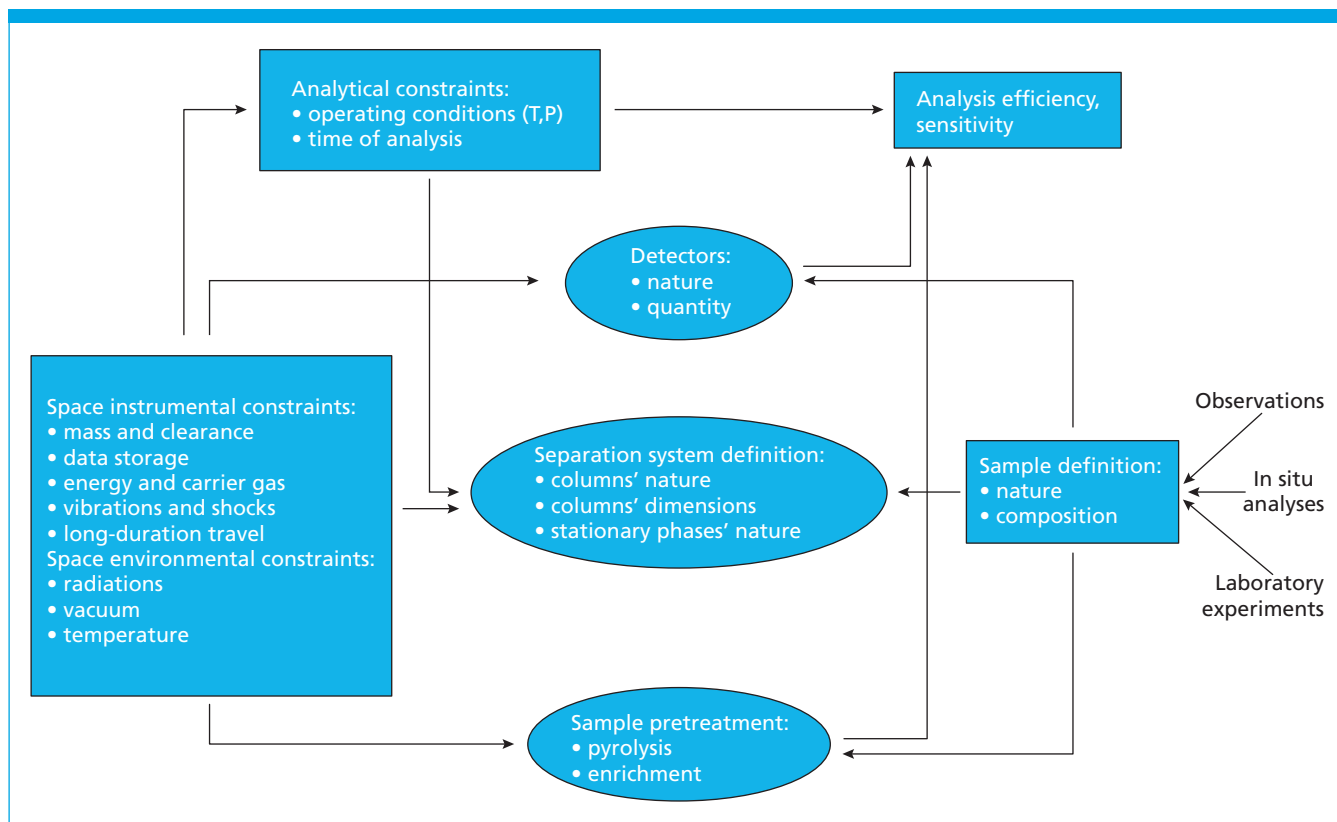


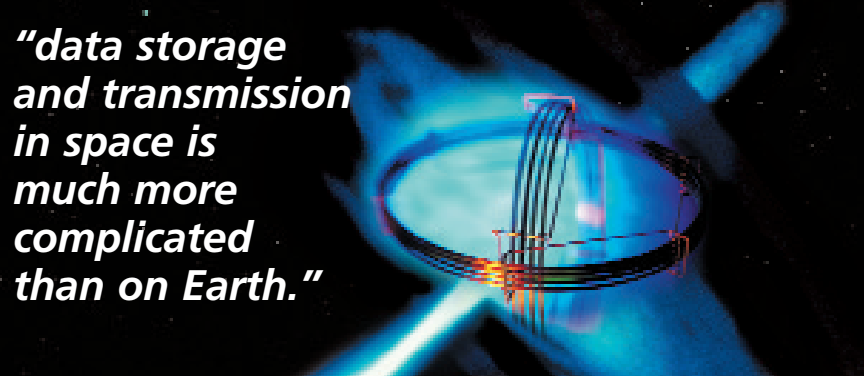
Figure 1: Scheme summarizing the influence of space requirements on the analysis and design of the instrument.

time of analysis limitation strongly constrain the selection of the columns' dimensions and stationary phases. Indeed, it is well known that porous layer open tubular (PLOT) columns have high retention properties (26), which generally require high temperatures to achieve the separation usually expected in the laboratory. Therefore, if selected for space exploration, PLOT column length and polymer film thickness must be optimized for lower analysis temperatures.

In addition to these GC problems, data storage and transmission in space is much more complicated than on Earth because on-board electronic and data handling systems suffer from the same restrictions as the scientific hardware. This mainly affects the time of analysis (generally limited to 10–20 min) and the bunching rate, which is of primary importance for chromatogram definition and interpretation. A simplified scheme allowing better visualization of all the interactions between the different exposed parts is presented in Figure 1.

The COSAC Experiment

The COSAC experiment (principal investigator being H. Rosenbauer/MPAe, Lindau, Germany), presented in Figure 2, is the latest space gas chromatograph and is to be flown in the next Rosetta European Space Agency (ESA) mission to comet 46/P Wirtanen (25). Its goal is the molecular and chiral characterization of the cometary material, assumed to be composed of grains made of refractory materials with a



core of silicate, and volatile organic, inorganic and water ices. For this reason, the sampling system will use micro-ovens to heat solid samples from -150 up to 200 °C and vaporize them. The chemical compounds potentially present in the cometary nucleus have been defined from data provided by:

- remote sensing observations of cometary atmospheres and the interstellar medium (26)
- in situ chemical analyses of the cometary grains released from the comet Halley by the MS experiments of the Giotto (27) and Vega (28) missions in 1986
- the chemical composition of ices irradiated in the laboratory (29).

Considering the wide range of targeted compounds and the technical constraints presented above, the COSAC GC subsystem will use several columns in parallel: five dedicated to the analysis of general molecular composition and three

for the separation of enantiomers.

All column tubing is metallic in order to improve column robustness and to simplify their integration into the flight gas chromatograph. The stationary phases of the general purpose columns, selected according to the nature of the targeted compounds, are bonded to the internal capillary wall. In order to evaluate the columns' resistance to vibrations, radiations, vacuum and thermal cycles, they were submitted to environmental tests in the laboratory. Chromatographic analyses performed prior to and after the tests proved their ability to resist these harsh constraints (Sternberg, submitted). The columns' lengths were fixed in the 10–15 m range because of heat capacity and clearance in the instrument. The selected detectors were nano-TCDs, all columns having their own, and a time-of-flight (TOF)-mass spectrometer, which could be used separately or coupled to the gas chromatograph. Nano-TCDs are of new silicon technology equivalent to microchips (small size and low mass) and the TOF-mass spectrometer was specially designed to be miniaturized and to respect the limitations in size and mass of the instrument. Both of these detectors were selected for their robustness and their detection limits, which are in the range 1–10 ppm.

Isothermal analyses in the range 30 – 60 °C will be performed. In order to limit the carrier-gas consumption and improve the resolving power of the gas chromatograph, columns' internal diameters were reduced as much as possible (0.18 mm and 0.25 mm), taking into account the manufacturing technology limitations. An example of the separation obtained with one of the selected columns, and showing the influence of the space operating conditions, is presented in Figure 3.

Future Developments

Sampling systems including chemical treatments are of primary importance for organic chemical characterization in space

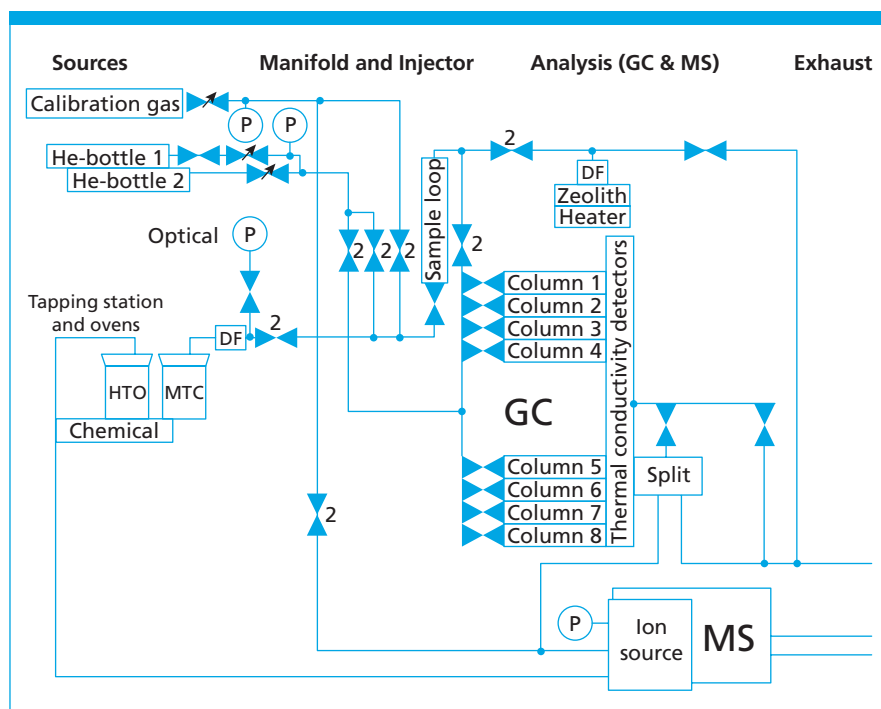


Figure 2: Principal schemes of the GC-MS of the COSAC experiment (2003). (From reference 34.)

exploration. This is the reason why derivatization techniques and their adaptation to space application are currently under development. These techniques can cause cleavage or "chemolysis" of certain functional groups so that compounds can be easily recovered and transformed, in a chemical reactor, into volatile compounds able to be directly analysed by GC-MS techniques. Thus, they can be used to transform either compounds that interact strongly with the stationary phases commonly used in GC (such as carboxylic acids and amines), or non-volatile compounds (amino acids) into compounds that can be analysed directly by GC. Currently, these techniques are being developed for the analysis of amino acids possibly present on Mars (Figure 4), which could indicate past or present life on the red planet (15, 30). Besides the liquid handling difficulties, the main problem to adapting this technique to space application is the extraction of organic matter from the solid matrix before derivatization.

From a separation viewpoint, improvements can be made to reduce the inlet columns' diameters to 0.1 mm. However, the main improvement is expected from the use of higher temperatures and temperature programming. Indeed, it would enable the elution time for most of the analysed compounds to be shortened, thus increasing the sensitivity of the gas chromatograph, and allowing more retained compounds to be reached. Moreover, the number of columns, currently used in space gas chromatographs, that has significantly grown for 25 years with the number of compounds to be detected, could be decreased, resulting in simplification of the experimental design, and savings in mass and carrier gas. At last, elaboration of stationary phases specifically adapted to the range of compounds targeted by the missions could be achieved, thus allowing better separations. Computer modelling (31, 32) and experimental work (12) allow the prediction of retention properties of mixed liquid phases that are not currently commercialized. However, the production of these phases remains difficult because of problems raised by the manufacturing processes (bonding techniques etc.) and obviously, the cost of their development.

The last main point is the sensitivity improvement of the system. Whereas sample enrichment by trapping and thermal desorption should be explored in the future, improvements in detector

sensitivity in space appear to be much more important. Indeed, the currently preferred detectors are mass spectrometers because they give more information than a traditional detector. However, sensitivity is low because of their restricted design. Conventional sturdy detectors such as nano-TCDs suffer from a lack of response to trace species injected. Therefore,

improving the dynamic range of analysis using more sensitive detectors would be a real breakthrough in space GC. Such an approach has already been used in the Vega probe to Venus, which combined a helium ionization detector using a radioactive source for trace compounds detection, and a TCD for major compounds analysis. However,

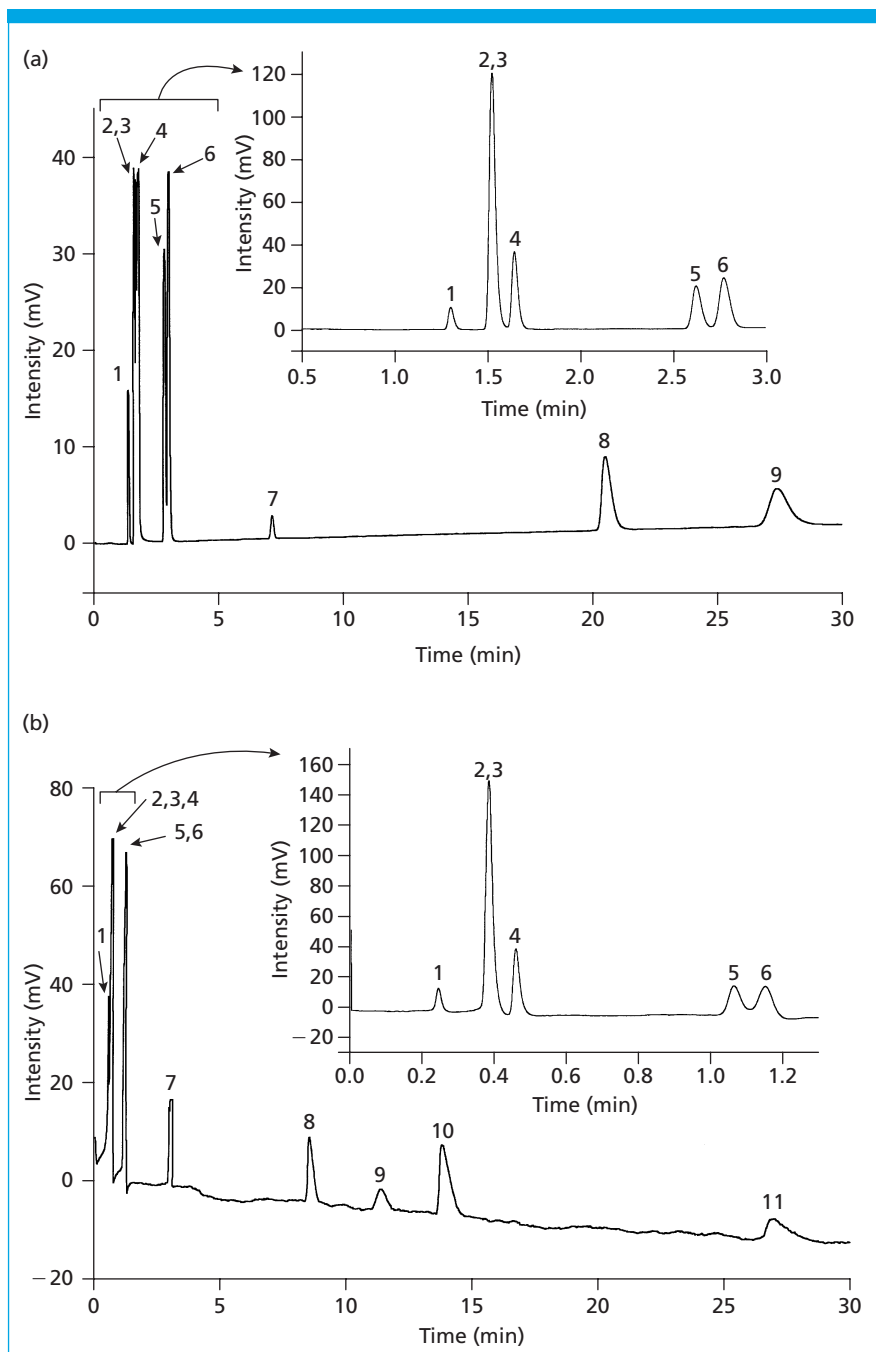


Figure 3: Comparison between the analyses of light hydrocarbon, noble and permanent gases with a Carbobond PLOT capillary column (15 m × 0.25 mm, Varian Inc., Palo Alto, California, USA) under (a) atmospheric column outlet pressure and (b) 10 mbar of column outlet pressure. Carrier gas: He; injection: sampling valve (splitless mode); detector: nano-TCD; temperature: 30 °C; columns inlet pressure: 150 kPa. Peaks: 1 = neon, 2 = nitrogen, 3 = argon, 4 = carbon monoxide, 5 = methane, 6 = krypton, 7 = carbon dioxide, 8 = acetylene, 9 = xenon, 10 = ethylene, 11 = ethane. (From reference 13.)

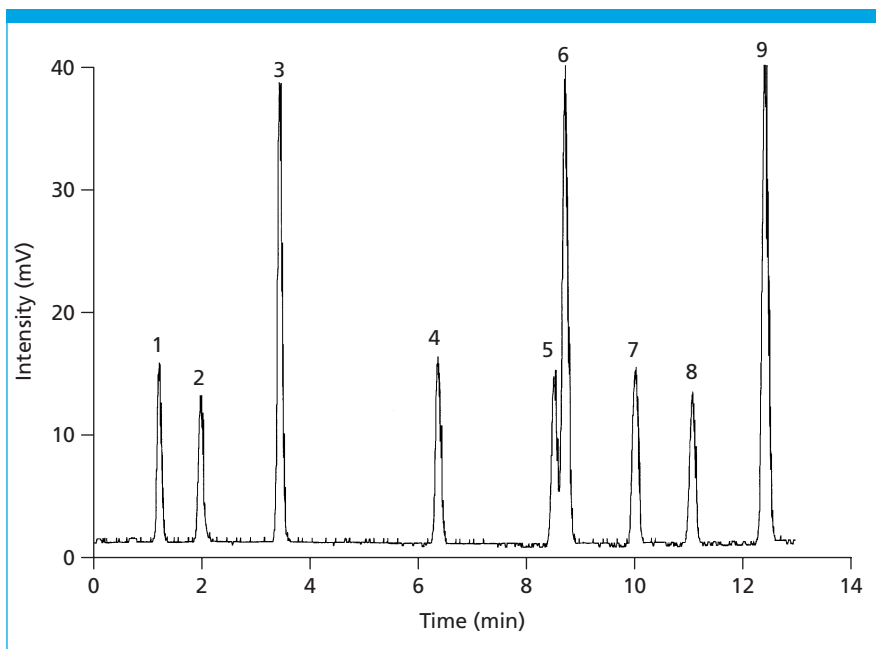


Figure 4: Chromatogram of an amino acids standard mixture and two puric acids, obtained with a CPSil 5CB WCOT column (15 m × 0.25 mm, Varian Inc.) after derivatization treatment. Carrier gas: He; detector: quadrupole MS; temperature: programmed at 3 °C/min from 120 °C to 270 °C; columns inlet pressure: 120 kPa. Peaks: 1 = alanine, 2 = glycine, 3 = isobutyric acid (AIB), 4 = valine, 5 = N-methyl-N-terbutyl-(dimethyl silyl) trifluoroacetamide (derivative agent), 6 = leucine, 7 = isoleucine, 8 = proline, 9 = α-methyl leucine.

miniaturization and new instrumental constraints (with no radioactive source) only allow the use of nano-TCDs today, because it is the only detector meeting these requirements. Studies are currently under way on miniaturization of high-sensitivity detectors, particularly on ionization detectors (30) without a radioactive source.

Conclusions

Gas chromatography has proven to be a very powerful technique for the analysis of extraterrestrial environments, in particular for analysing simple organic molecules. The drastic improvements in space instrumentation (miniaturization, energy consumption etc.) have induced several technological developments in classic GC, and should result in the best data ever obtained in space GC with the Cassini–Huygens and the Rosetta probes. However, there is clearly a growing need for new and more sensitive space instrumentation, able to perform molecular analyses of non-volatile organics, in addition to pyrolysis. Therefore, new breakthroughs are required to further enhance space GC techniques, but over the long term, complementary techniques such as high performance liquid chromatography, capillary electrophoresis and supercritical fluid chromatography

should also be adapted to space applications (33).

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