Gas chromatography in space exploration
Capillary and micropacked columns for in situ analysis of Titan's atmosphere

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Abstract

The gas chromatography–mass spectrometry (GC–MS) experiment using capillary and micropacked columns is one of the main instruments of the Huygens probe of the Cassini–Huygens mission launched in October 1997 for the in situ analysis of Titan's atmosphere. Because of its composition and density the study of the atmosphere of Titan is of primary interest for understanding the prebiotic chemistry in the primitive Earth's environment. We describe here the GC subsystem of the GC–MS instrument with a particular emphasis on its exobiological implications. The GC subsystem includes three columns which operate in parallel: a carbon molecular sieve micropacked column is used for the separation of CO, N_2 and other permanent gases; a capillary column will separate the light hydrocarbons up to C_3; a second capillary column with a cyanopropyl dimethyl polysiloxane stationary phase will analyze the C_4–C_8 hydrocarbons and the low-molecular mass nitriles up to C_4. These heavier compounds will mainly result from the pyrolysis of the aerosols present in the atmosphere of Titan by using the aerosol collector pyrolyser instrument.   © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Capillary columns; Stationary phases, GC; Titan's atmosphere; Hydrocarbons; Nitriles

1. Introduction

Comparative planetology is a powerful mean for a better understanding of our own planet. Study of the physics and chemistry of various planetary environments beside the Earth's can provide important information on that of the Earth. Such studies use common tools, such as sensors for in situ chemical analysis. Since the beginning of the space adventure, most of the many probes which have been sent to explore other planetary atmospheres and surfaces carried instruments to determine their elemental, isotopic and molecular–inorganic as well as organic–compositions. Since they fulfil the severe constraints of space instrumentation (mass, size, mechanical strength, automation and energy consumption), mass spectrometry (MS) and gas chromatography (GC) have been and remain the most frequent techniques for in situ chemical analysis [1]. They have been already used for the in situ analysis of Mars [2,3] and Venus [4,5] and will be used in the future missions to Saturn and comets.

With a mean radius of 2575 km, Titan is the largest satellite of Saturn. It is the only satellite in

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the solar system having a dense atmosphere. On the surface, where the temperature is about 94 K, the atmospheric pressure is 1.5 bar; this is approximately 4.5 times denser than the atmosphere on the surface of Earth. The data collected by Voyager missions, 1980–1981, have shown that the major component of Titan's atmosphere [6] is nitrogen with a few percent of methane and with the presence of many organic compounds as minor constituents (Table 1). The atmosphere is also rich in aerosols and hazes, which obscure the surface of the satellite. Such a chemically reducing atmosphere is favourable to the formation of organic compounds [7], both in the gas and in aerosol phases. Almost all organic compounds that have been detected in the atmosphere by remote sensing techniques were also predicted to be present from the results of simulation experiments in the laboratory [8–10]. Several of these organics are of the same nature as the organic compounds involved in terrestrial prebiotic chemistry. In spite of many differences with the Earth, such as lower temperature and absence of liquid water, Titan appears as a

natural laboratory to study prebiotic evolution of organic systems in a real planetary environement over a long period. Therefore, in situ analysis of the composition of Titan's atmosphere is one of most important goals of the Cassini–Huygens mission.

This paper presents the GC–MS instrument [11] of the Huygens probe with a particular emphasis on the exobiological aspects and implications of its objectives. The three chromatographic columns used for the separation of the constituents present in gaseous and solid phases of Titan's atmosphere are described, with chromatographic analysis of complex samples from models of Titan's atmosphere.

2. The Cassini–Huygens mission

The Cassini–Huygens mission is a joint project between NASA and the European Space Agency (ESA). It includes a US (NASA) spacecraft named Cassini which will carry a European (ESA) probe named Huygens [12]. After having been successfully

Table 1
Chemical composition of Titan's atmosphere (adapted from Ref. [6])[a]

Detected compounds			Expected compounds		
	Stratospheric mixing ratio	Simulation experiment	Hydrocarbons	Nitriles	O-Compounds
N_2	0.90–0.99				
Ar	<0.06				
CH_4	0.017–0.045				
	0.017–0.12 T				
CO	5.0×10^{-5}				HCHO
CO_2	1.3×10^{-8} N				CH_3OH
H_2	0.00060–0.0014				
H_2O	8.0×10^{-9}				
C_2H_6	1.6×10^{-5} N	Maj.	Propene		
C_2H_2	6.5×10^{-6} N	Maj.	Allene		
C_2H_8	1.2×10^{-6} N	++	Cyclopropane		
C_2H_4	1.5×10^{-5} N	++	Triacetylene		
C_3H_4	3.7×10^{-8} N	+	Tetraacetylene		
C_4H_2	2.7×10^{-8} N	+	C_4H_4		
HCN	1.5×10^{-6} N	Maj.	1,2-C_4H_6	C_2H_5–CN	
HC_3N	4.5×10^{-8} N	++	1,3-C_4H_6	CH_2=CH–CN	
C_2N_2	2.2×10^{-8} N	+	C_4H_8	CH_3–C_2–CN	
CH_3CN	Detected	++	n-C_4H_{10}	n-C_3H_7–CN	
C_4N_2	Solid phase		iso-C_4H_{10}	iso-C_3H_7–CN	
			C_6H_6	cyclo-C_3H_6–CN	
				HC_5N	

[a] T, troposphere; N, north pole.

launched in October 1997, it will fly by Venus twice and Earth once to gain gravity-assisted acceleration, then the spacecraft will fly by Jupiter in 2000 and reach the Saturn system in 2004. It will be placed into orbit around Saturn, and after completion of the first orbit in mid-2004, it will release the probe into Titan's atmosphere. The Huygens probe will carry out six scientific experiments designed to determine the physical and chemical properties of the atmosphere and the surface of Titan. One of the instruments is a GC–MS system, the main objective of which is to measure the chemical composition of the stratospheric and tropospheric gas phase (from 170 km to the surface) during the 2.5-h descent time. Coupled with a second instrument, the aerosol collector and pyrolyser (ACP) [13], it will also determine the nature and the abundance of the organic and inorganic compounds present in the atmosphere, in the gas phase and in the aerosols. If the probe survives the surface impact, the instrument will also gather information about the surface composition.

3. Experimental

3.1. GC–MS instrument

Built at the Atmospheric Experimental Branch Laboratory for Atmospheres (NASA/GSFC, Greenbelt, USA) with Hasso Niemann as principal investigator, the GC–MS instrument is the most important in term of mass (about 18 kg) and is also the most important for the expected scientific return relating to organic chemistry. It includes a gas chromatograph and a mass spectrometer. The GC system will allow the separation of the chemical constituents of Titan's atmosphere. It uses the MS system as the detector. The MS system can operate in two modes, coupled to the GC system or independently (by direct injection of the samples). It provides a qualitative and quantitative analysis of the constituents eluted from the GC columns or of the directly injected samples. Identification is obtained through the mass spectra (range 2–150 amu) provided by MS. The MS system is a quadrupole derived from the MS instrument of the Galileo mission to Jupiter, lighter and very

sensitive. It will be able to determine atmospheric composition of gas and aerosols, providing abundance of all constituents, within the mass range of the instrument, with mixing ratio as low as 10 ppb, even 0.1 ppb for selected species. These include argon and other noble gases, but also many organics, major element isotopes and the vertical profile of their concentration.

A schematic diagram of the GC–MS instrument is given in Fig. 1 and its main characteristics are summarized in Table 2.

The main elements of the instrument are [11]:

(i) The gas sampling system which consists of three subsystems: the direct atmospheric sampling system to introduce atmospheric gas into the ion source and to enrich trace species and noble gases, the GC sampling system and the ACP sample line which is connected with both the GC and the MS systems.

(ii) The GC system which performs analysis at specific altitudes in the atmosphere and subsequently separates the species identified by MS.

The hydrogen selected as carrier gas (3 l required for GC operation) is stored in a hydride metal alloy tank enclosed in a stainless steel housing. Samples will be collected during the descent in sample volumes (SV1-3) for later analysis. Others will also be injected directly from the atmosphere, near the surface. At least four GC samples will be taken, one after opening the inlet valve, a second in the lower stratosphere, a third near 60 km and one below this altitude and the ACP output will be analyzed.

(iii) The MS system consists of five miniaturized ion sources, with switching systems to deflect the ion beams into the quadrupole mass analyzer and ion detector.

The ACP instrument [13] coupled to GC–MS is devoted to the collection of Titan aerosols and preparation for their analysis. This instrument releases a protruding tube, equipped with a filter, outside the boundary layer of the probe. The sampling is achieved by direct impaction and filtering of the gas flowing through the filter, with the help of an internal fan. After a few minutes of sampling, the filter with the collected sample is retracted through the protruding tube and isolated in an oven. Then the oven is heated successively at low and medium temperatures for release of volatiles and higher
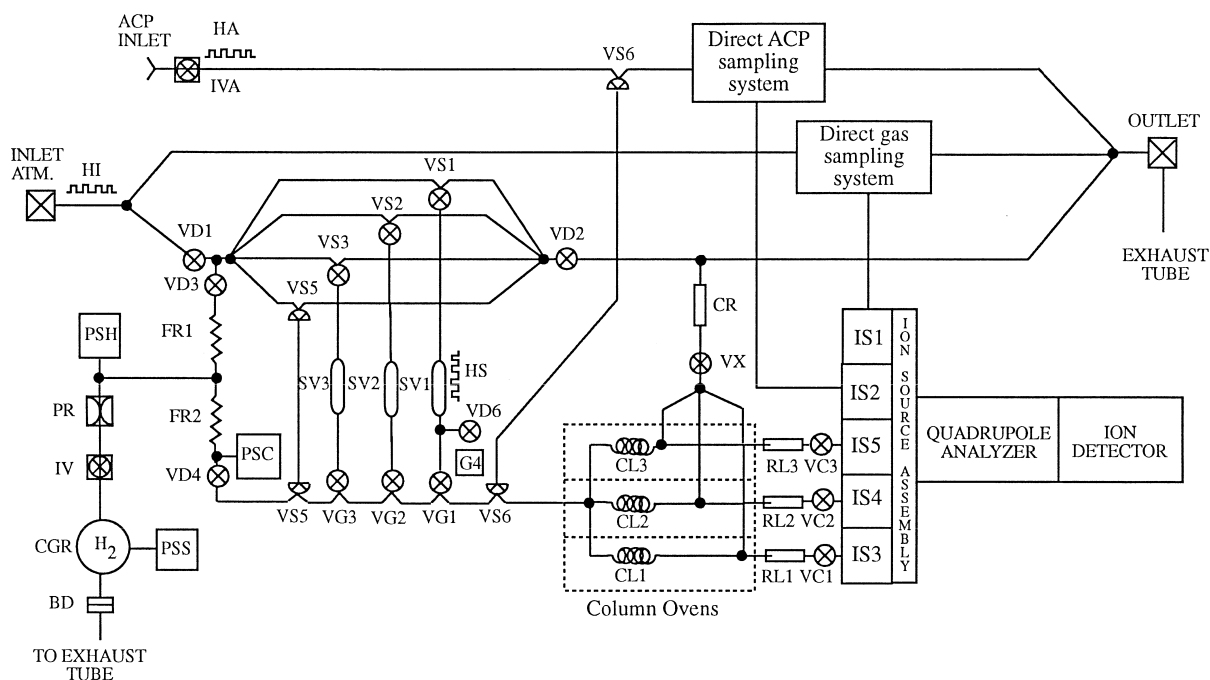
Fig. 1. Schematic diagram of the GC–MS instrument (adapted from Ref. [11]). ACP, Aerosol collector pyrolyser; BD, burst diaphragm; CL, column; CR, column restrictor; CGR, carrier gas reservoir; FR, flow restrictor; G, getter pump; HA, heater (inlet ACP); HI, heater (inlet atm.); HS, heater (sample volume); IV, isolation valve (H2 system); IVA, isolation valve (inlet ACP); PR, pressure reducer; PSH, pressure sensor (H2 store); PSC, pressure sensor (column); RL, restrictor leak; SV, sample volume; VC, valve (column); VD, descent/analysis control valve; VG, sample/carrier gas valve; VS, sample valve.

temperature (up to 600°C) for pyrolysis of oligomers. The produced gases are systematically sent to the GC–MS system for chemical analysis.

3.2. Chromatographic columns

Three chromatographic columns are used and

Table 2
GC–MS instrument characteristics (adapted from Ref. [11])

Mass	17.3 kg
Size	Cylindrical, 198 mm diameter, 470 mm high
Temperature range	−20 to +50°C, operating
	−20 to +60°C, storage
Power	41 W average, 71 W peak
Energy	110 Wh
Temperature range	−20 to +50°C, operating
	−20 to +60°C, storage
GC system	Three parallel columns, H_2 carrier gas
	Independent MS ion source
Mass analyzer	Quadrupole mass filter
Ion source	Five sources, electron impact ionisation.
	Max. operating pressure: 0.1 Pa (H_2)
Mass range	2–141 amu

operate in parallel to cover the range of expected atmospheric species.

The first column is a carbon molecular sieve micropacked metallic column (2 m×0.75 mm I.D.) packed with Carboxen 1000 (60–80 mesh) from Supelco (Bellefonte, PA, USA). This column will separate CO from N_2, other permanent gases and CH_4.

The second column is a laboratory-made glassy carbon capillary column (14 m×0.18 mm I.D.) with a coating of 0.6 μm thickness immobilized on the metallic tubing in order to whithstand the vibrations during the launch. It will separate organic species up to three carbon atoms in size.

The third column is a MXT 1701 silcosteel capillary column (10 m×0.18 mm I.D.) from Restek (Bellefonte, PA, USA) with a cyanopropyl di-methylpolysiloxane intermediate polar stationary phase of 0.6 μm film thickness. This column will analyze higher molecular weight compounds (hydrocarbons up to C_8 and nitriles up to C_4), and particularly pyrolysis products from the ACP experiment.

The columns are wound in a 178-mm diameter coil on high temperature foil heaters. A thermally isolated oven encloses each column to allow efficient heating. The columns will be operated at 1.8 bar inlet pressure and the outlet is vented through a flow restrictor to the ambient atmosphere. Hydrogen was selected as the carrier gas because of its efficient storage and pumping feasibility.

In addition to the scientific objectives, the GC subsystem must fulfil the imposed conditions (carrier gas inlet pressure, 1.8 bar; total outlet flow-rate, <1 ml/min; isothermal analysis temperature range, 30–60°C; analysis time cycle, <10 min) and the general requirements of space instrumentation such as high mechanical strength, long-term stability under vacuum and radiation resistance.

4. Results

Several species of Titan's atmosphere were detected by Voyager 1 (1980) and others are suspected to be present from laboratory simulations and photochemical modelling [8–10]. On the basis of these results, a model of Titan's atmosphere was used as a calibration mixture to test the GC columns.

4.1. Analysis of CO, N_2 and other permanent gases

Several gases are expected to be present such as Ar, CH_4 and CO. Argon has never been detected but its presence has been speculated from the mean molecular mass in the atmosphere. The MS can detect it at a mixing ratio of 10–100 ppb. A particular emphasis will be given to the problem of GC analysis of CO. The determination of its vertical concentration profile will provide information about the source of oxygen atoms on Titan and consequently, about the complexity of its organic chemistry.

To analyze CO, with N_2 as the major gas and with important concentrations of CH_4, we have tested several type of columns. Fast analyses with good resolution were achieved [14] with molecular sieve 5A porous layer open tubular (PLOT) columns. However, these columns are not suitable for GC in space because of their poor mechanical stability. The analysis could be achieved with a molecular sieve 5A micropacked column [15], but CO is strongly retained with a broad and tailing peak. Moreover, because of the hydrophilic character of the adsorbent, the reproducibility of retention time varies with column conditioning.

An alternative was to use a microcolumn packed with a non-specific adsorbent such as carbon molecular sieve [16]. A column of this type was selected because of the good resolution between N_2 and CO. Fig. 2a illustrates the separation of CO in the presence of other compounds of Titan's atmosphere. The sample contains a mixture of gases with a composition similar to that expected in Titan except for CO. Its concentration is 10 000 times larger in order to visualise the good resolution achieved between N_2 and CO. The major gas of Titan's atmosphere is N_2 and CO is eluted in the tailing of the N_2 peak (Fig. 2b). The MS detection of a low CO concentration is thus difficult in the presence of N_2 and a large separation factor between CO and N_2 is needed.

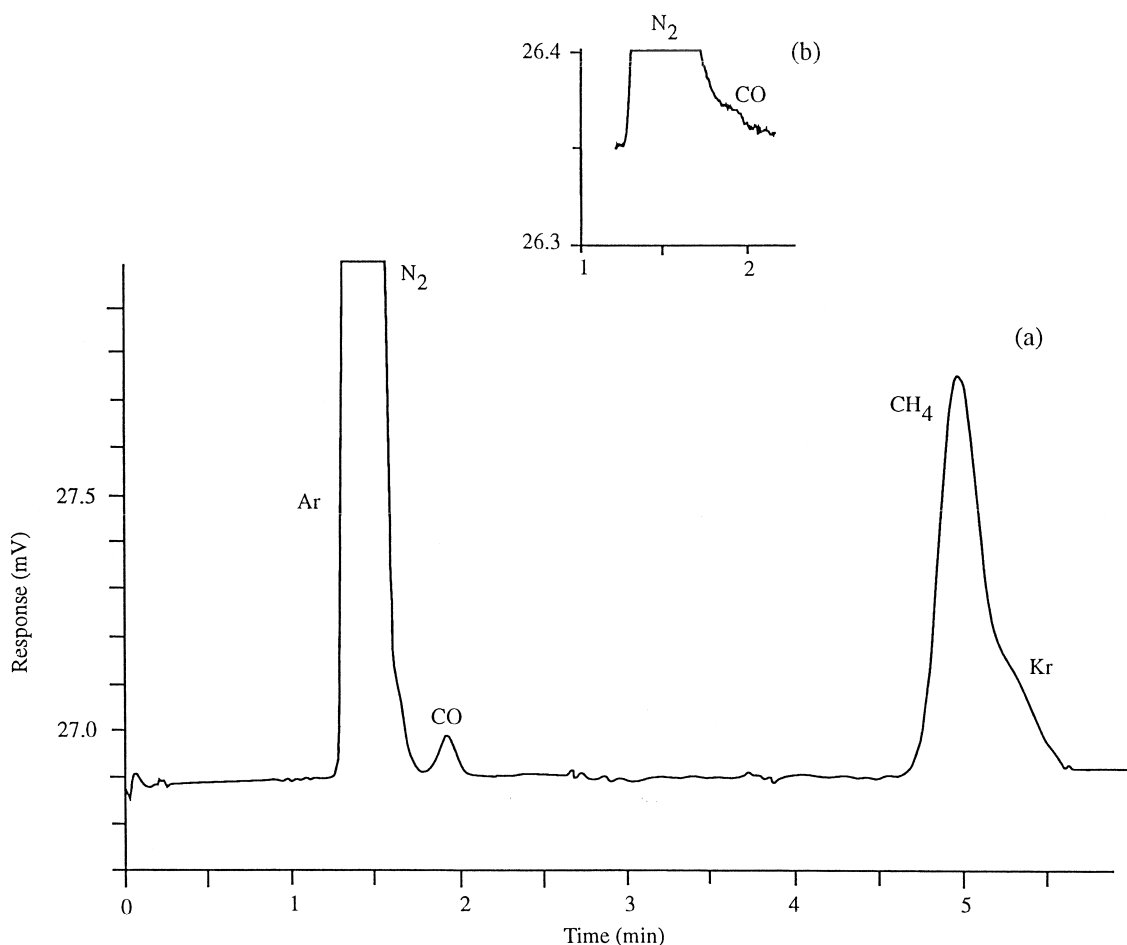Considering the pressure drop (1.8 bar) and tem-

Fig. 2. Example of analysis of the gases present in Titan's atmosphere with a micropacked carbon molecular sieve column (a) 0.5% CO; (b) 100 ppm CO Column (2 m×0.75 I.D. mm) packed with Carboxen 1000 (175–200 μm). Thermal conductivity detector as in Ref. [16]. Carrier gas, H_2; temperature, 50°C; flow-rate, 2.2 ml/min; pressure drop, 0.45 bar.

perature (30°C) constraints, the analysis time is short, less than 10 min. This carbon molecular sieve column is also able to analyze the C_2 hydrocarbons at higher temperature (in less than 10 min at 100°C). Because of the limited energy available the temperature needed for such a separation is too high. Another column was devoted to the separation of the low-molecular mass hydrocarbons.

4.2. Analysis of the hydrocarbons up to C_3

In Titan's atmosphere the photolysis of CH_4 produces C_2H_6 (main product), C_2H_4 and C_2H_8.

Therefore, a consumption of CH_4 is expected. As its mixing ratio is important (a few percent), an important reservoir of methane should exist (for instance surface liquid bodies).

A column was specially selected for the analysis of the low-molecular mass hydrocarbons up to three carbon atoms, in the temperature range (30–60°C) compatible with the instrumentation constraints. For this purpose, several types of column and stationary phases were investigated. A wall-coated open-tubular (WCOT) capillary column with a chemically bonded stationary phase (dimethyl polysiloxane) was tested [17] for the separation of C_1–C_6 hydrocarbons and

C_1–C_4 nitriles, at 20°C. With these isothermal conditions, several solutes are co-eluted such as ethene with ethyne.

Micropacked columns can also be used for such applications. A column of this type, packed with a porous polymer, a copolymer of divinylbenzene and ethylene glycol dimethacrylate was tested in our laboratory [18]. An easy separation of methane and C_2 hydrocarbons was achieved in less than 3 min at 90°C. This temperature is too high for the energy constraints, but a reasonable analysis time is to be expected at lower temperatures. For future space missions Akapo and co-workers [19,20] reported the use of bonded-phase silica columns for the separation of C_1–C_4 hydrocarbons at 25°C. Packed micro-columns of this type are thus good candidates for the analysis of low-molecular mass hydrocarbons. However, the relatively large flow-rate needed with the micropacked column leads to important problems regarding the coupling with the MS instrument. Moreover, an important gas consumption is to be expected.

Due to the instrument constraints, a capillary column was thus selected for the analysis of light hydrocarbons. The analysis is achieved at low temperature and flow-rate, when using a glassy carbon capillary column of 14 m length (Fig. 3).

4.3. Analysis of C_4–C_8 saturated and unsaturated hydrocarbons and nitriles up to C_4

From the data of photochemical models [7], heavier hydrocarbons and nitriles are expected to be formed in Titan's atmosphere. Atomic nitrogen produced from N_2 dissociation, reacts with CH_4 and other hydrocarbons to yield several possible nitriles. Moreover a complex abundance of these species is to be expected as laboratory simulations have produced solid polymeric substances (named tholins).

For the analysis of C_4–C_6 hydrocarbons and nitriles and specially for the analysis of the pyrolysis products of tholins (models of Titan's aerosols), our group has tested different commercial WCOT capillary columns with chemically bonded films: a 100% dimethylpolysiloxane (DMPS) stationary phase [21], one with 5% phenylpolysiloxane substituted groups [22] and stationary phases containing, respectively, 6 and 14% of cyanopropyl phenyl (CPP) substituted
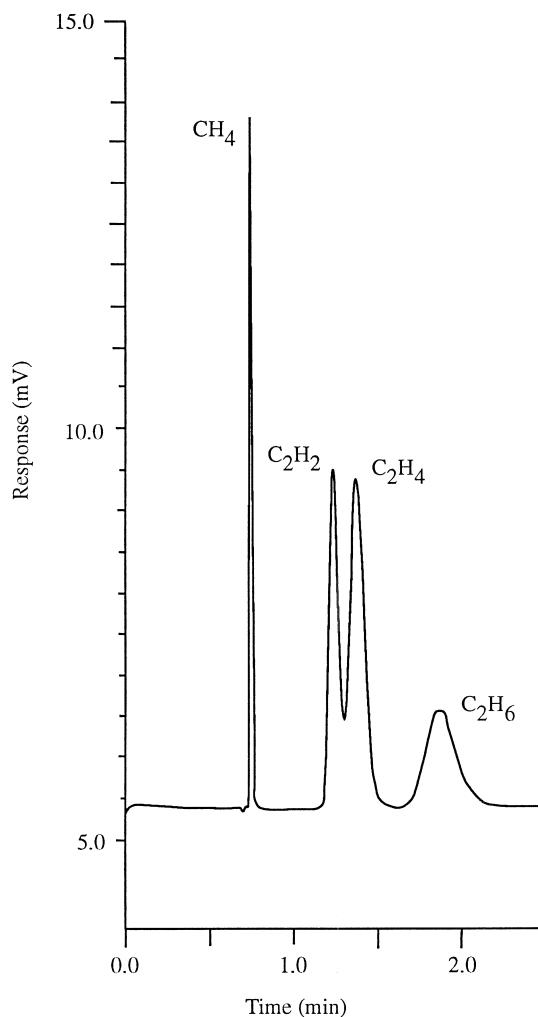

Fig. 3. Chromatogram of a mixture of low-molecular mass hydrocarbons with a WOTC capillary column. Glassy carbon capillary column (14 m×0.18 I.D. mm) Flame ionization detector as in Ref. [23]. Carrier gas, H_2; temperature, 30°C; flow-rate, 0.4 ml/min; pressure drop, 0.45 bar.

groups [23]. Systematic studies as a function of film thickness have shown that the best efficiencies in the shortest analysis time are achieved with columns of small internal diameter, having a thin film coating. The WCOT capillary columns with a CPP–DMPS (14:86) ratio are slightly more polar, allowing a good separation for the simultaneous analysis of C_4–C_8 hydrocarbons and low-molecular mass nitriles.

A silanized stainless-steel WCOT capillary column (14 m×0.18 mm I.D.) bonded with a CPP–DMPS (10:86) ratio was selected. Stainless steel capillary columns of this type present various advantages in space applications over the conventional silica columns: they are mechanically resistant, while offering low bleeding properties and a high degree of inertness. To optimize the performances and reduce the separation time at the temperature of analysis (40°C), a column of low film thickness (0.6 μm) and small internal diameter (0.18 mm) was found most suitable for the Cassini–Huygens mission. With this stationary phase of relatively high polarity, the nitriles are more retained and well separated from the hydrocarbons. As shown in Fig. 4, the analysis is achieved in about 10 min with a limited number of overlapping peaks. The problem of co-elutions is solved with MS detection that will differentiate these components from their mass fragments. The separation of C_2 hydrocarbons is not possible with capillary columns of this type and was achieved by the glassy carbon capillary column.

5. Conclusion

GC techniques have demonstrated their efficiency for analyzing extraterrestrial environments aboard atmospheric probes or surface landers. GC systems with packed columns have been used for analyzing the atmosphere and surface of Venus and Mars. Future space missions to comets and Mars will use powerful miniaturized pyrolysis–GC–MS instrumentation, with high resolution multi-GC columns and time-of-flight or ion trap mass spectrometers.

In the Cassini–Huygens mission, capillary columns will be used for the first time for in situ analysis of an extraterrestrial planetary atmosphere. Operating in parallel and coupled to the mass spectrometer detector, the GC columns should allow during the probe descent and landing to determine the vertical concentration of the organic and inorganic compounds present in the gaseous and solid phases of Titan's atmosphere. This could provide crucial information about the origin and evolution of Titan's atmosphere and also by comparative
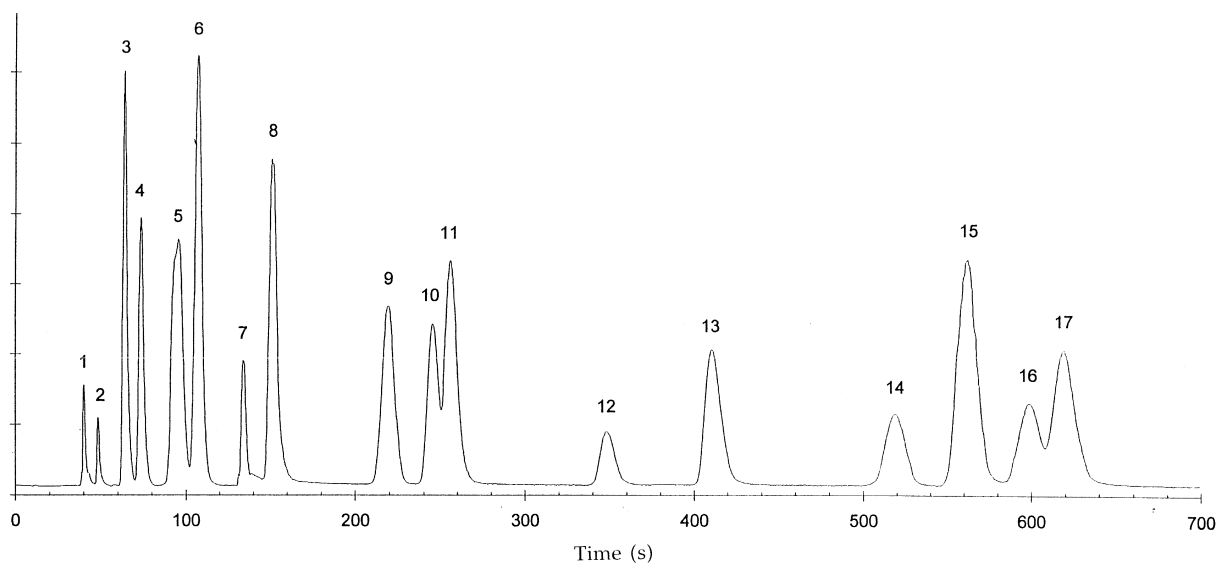

Fig. 4. Chromatogram of a mixture of hydrocarbons (C_1 to C_6) and nitriles (C_1 to C_4) with a CPP–DMPS (14:86) capillary column. Capillary column MXT 1701 (10 m×0.18 I.D. mm). MS ion trap detector as in Ref. [16]. Carrier gas, He; temperature, 30°C; pressure drop, 0.3 bar. (1) Methane, (2) 1-butene, (3) n-pentane+1-pentene, (4) 2-methyl-2-butene, (5) cyclopentane+3-methylpentane, (6) n-hexane+1-hexene, (7) acetonitrile, (8) acrylonitrile, (9) n-heptane+cyclohexene, (10) benzene+methacrylonitrile, (11) propionitrile, (12) iso-butyronitrile, (13) cis- or trans-crotonitrile, (14) n-octane, (15) butyronitrile, (16) toluene, (17) cis- or trans-crotonitrile.

planetology, about the prebiotic chemistry of the primitive Earth.

Like Titan, comets are also of prime importance for exobiological studies. With their nuclei rich in C, H, N and O containing compounds, cometary impacts may have largely contributed to the build up of organic matter on the primitive earth.

Two very ambitious missions are under development for in situ analysis of cometary surface (nucleus) and atmosphere (coma).

The European Rosetta (ESA) and the American Deep Space 4 (NASA) missions, are both planned to be launched in 2004 for a rendezvous with short period comets, and will carry landing probes with GC based experiments for in situ analysis. The cometary sampling and chemical analysis experiment (COSAC) of Rosetta (Helmut Rosenbauer as principal investigator, MPAe, Lindau, Germany) will use a pyrolysis–GC–MS system made up of eight capillary columns coupled to nano thermal conductivity detectors and a time-of-flight mass spectrometer. The chemical analysis of released gas experiment (CHARGE) of Deep Space 4, will also use a pyrolysis–GC–MS system with one capillary column associated to chemical and cryofocusing traps and coupled to a quadrupole MS system derived from the MS of the Huygens probe.

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