Review

Gas chromatography in space

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Abstract

Gas chromatography has proven to be a very useful analytical technique for in situ analysis of extraterrestrial environments as demonstrated by its successful operation on spacecraft missions to Mars and Venus. The technique is also one of the six scientific instruments aboard the Huygens probe to explore Titan's atmosphere and surface. A review of gas chromatography in previous space missions and some recent developments in the current environment of fiscal constraints and payload size limitations are presented.   © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Reviews; Space research; Hydrocarbons

Contents

1. Introduction

A detailed knowledge of the history and abundance of the biogenic elements and their compounds throughout the solar system can provide scientists with a basis for understanding the conditions necessary for chemical evolution and the origin of life. Clearly, the acquisition of such information requires the use of different analytical techniques including

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visual imagery, α-proton-X-Ray (APX), γ-spectros-copy, mass spectrometry, gas chromatography, thermal analysis, neutron activation analysis, Raman spectroscopy, Mössbauer spectroscopy etc. [1]. However, for successful operation, the technique must satisfy the requirements placed on analytical instruments aboard planetary probes such as small mass and size, low power consumption, high mechanical and shock strength, high sensitivity and accuracy, and reliability of operation under extreme space conditions [2,3]. To a great extent, gas chromatography (GC) fulfils these requirements and has been part of the analytical repertoire of space research programs for quite some time.

GC was at first in the domain of space biologists who used it to study the problem of the generation and buildup of toxic gaseous contaminants in closed systems such as simulation chambers and manned spacecraft [4,5]. The use of GC began to acquire great significance with studies of methods to remove toxic mixtures from spacecraft atmospheres by means of chemical bonding, conversion into non-toxic mixtures, or adsorption on appropriate adsorbents during the circulation of cabin gases in a closed system [2,6,7].

GC space research related to exobiology started in 1962 when it was first considered for a possible early Mars Lander Mission [8]. The first time a GC system was successfully developed and flown on a planetary mission was in 1976 on the Viking mission in a search for extant life [9]. Even though life was not discovered on Mars, interesting soil chemistry was found indicating the highly oxidative nature of the Martian soil [10,11]. Another GC system was developed and successfully flown in 1978 on the Pioneer Venus mission. This comprehensively determined the composition of the Venusian atmosphere [12,13]. With a few exceptions, the results obtained compared favorably with those obtained by Venera 11 and 12 missions launched in the same month by the former Soviet Union to the surface of Venus which carried a mass spectrometer and a gas chromatograph [14–16]. The Vega mission sent two more GC instruments to Venus in 1985 [17] to further analyze the gas phase content of the Venusian atmosphere and provide a quantitative estimate of the sulfuric acid content of the clouds.

2. Planetary missions

2.1. Viking mission

There is substantial evidence that the climate of early Mars, the red planet, was more Earth-like at some time in its past, with a warm, dense atmosphere and abundant liquid water [18]. Consequently, Mars remains the most promising for further elucidation of current concepts about chemical evolution and the origin of life amongst all the other planets in our solar system. The Viking mission, therefore, was designed to orbit Mars and to land and operate on the surface of the planet. Among the instruments on board each of the two Viking spacecraft that landed on the surface of Mars in 1976 were two scientific instruments with GC systems, one for the Viking gas chromatography–mass spectrometer (GC–MS) experiment and the other for the Viking biological experiments.

2.1.1. Viking GC–MS experiment

The scientific goals of this experiment were to determine the composition of the Martian atmosphere, and to detect and identify chemical compounds released from Martian soil when heated or pyrolyzed [19]. The major features of the instrument are a sample oven, a gas chromatograph, an effluent divider that protected the mass spectrometer from excessive gas pressure, a carrier gas separator, a mass spectrometer and the associated electronics and logic systems [20]. The GC column (2 m×0.75 mm stainless steel) was filled with 60–80 mesh Tenax-GC (2,6-diphenyl-*p*-phenylene oxide) coated with polymetaphenoxylene and held isothermally at 50°C for 10 min. It was then ramped linearly to 200°C at 8.3°C/min and held at that temperature for a predetermined period of 18, 36 or 54 min. A hydrogen stream was used to transfer the products into the gas chromatograph, the effluent of which was monitored every 10 s by the mass spectrometer. The mass range of the spectrometer was from m/z 10–220 with a resolution of ≈1:200. Under these conditions, any organic compound expelled out of a soil sample at Martian atmospheric pressure passed through the chromatograph and was detected by the mass spectrometer. While the Poly MPE–Tenax column ex-

hibited good chromatographic performance with alcohols, hydrocarbons and amines, it also allowed efficient separation of trace amounts of organic compounds in the presence of a large excess of water and carbon dioxide [21].

2.1.2. Viking biological experiments

The gas-exchange (GEX) experiment was one of the three modules in the biology instrument on the 1976 Viking Landers. The experiment was designed to determine if Martian life could metabolize and exchange gaseous products in the presence of water vapor at high activity or liquid water containing organic compounds commonly used as food by heterotrophic microorganisms [22]. The composition of the gases evolved from the moistened Martian soil samples was determined with a miniaturized and automated GC system consisting of a gas sampling device, a helium carrier gas system, two stainless steel columns filled with 100–200 mesh Porapak Q and a thermal conductivity detector. Both columns were operated with a carrier gas flow-rate of 13.5 ml/min at 24°C, with one of the columns serving as a reference. The GC conditions allowed good separation of permanent gases including hydrogen, nitrogen, oxygen, krypton, carbon dioxide and methane, while carbon monoxide and argon could not be resolved.

Although the three biology experiments provided no clear evidence for the presence of living microorganisms, interesting soil chemistry was found indicating the highly oxidative nature of the Martian soil [22]. For instance, the slow oxidation of the nutrient in the GEX experiment followed by the release of carbon dioxide is likely caused by the presence of an oxidant in the Martian soil. While the Landers' GC–MS instruments failed to detect organic compounds at the landing sites, they did provide a precise and definitive analysis of the composition of the Martian atmosphere and found previously undetected trace elements. The composition of the Martian atmosphere is listed in Table 1.

2.2. Pioneer-venus mission

In spite of its hostility to life, Venus, our closet neighbor, has been the target of more unmanned,

Table 1
Chemical constituents of Martian atmosphere (surface pressure=7 mbar; surface temperature=140–295 K) (adapted from [24])

Constituents	Mol fraction
Major constituents (%)	
CO_2	95.3
N_2	2.7
^{40}Ar	1.6
O_2	0.13
CO	0.27–0.08
H_2O	0.03
Minor constituents (ppm)	
Ne	2.5
^{36}Ar	0.5
Kr	0.3
Xe	0.08
O_3	0.03–0.003

scientifically equipped interplanetary spacecraft than any other object in the solar system. The Pioneer-Venus mission carried both a stand alone mass spectrometer and a gas chromatograph on the sounder probe that entered the atmosphere of Venusian in December 1978. The Pioneer-Venus gas chromatograph [13] was designed to obtain samples at three pre-selected altitudes (51.6, 41.7 and 21.6 km) in the Venus atmosphere and then perform individual detailed compositional analyses. The instrument was specifically designed to accept without impediment both gases as hot as 160°C and cloud particles or aerosols. This approach gave assurance that accurate water analyses could be made. Ne, N_2, O_2, Ar, CO, H_2O, SO_2, and CO_2 were directly measured and upper limits for H_2, CS_2, H_2S, CH_4, Kr, NO, CH_3CH_3, $CH_2=CH_2$, and $CH_3CH_2CH_3$ were established. Indirect evidence was also obtained for the presence of sulfuric acid aerosols.

The miniaturized instrument including external sampling port, carrier gas supply, and electronics was built to withstand an acceleration of nearly 300 *g* and had a mass of less than 10 kg. The heated sampling port extended through the wall of the Sounder Probe pressure vessel and led to an arrangement of six extremely small, on–off valves which could simply grab or transfer appropriate samples to the analytical train upon command. The instrument had two sets of miniature stainless steel columns. The first set was a pair of 15.8 m×1.1 mm I.D.

columns packed with 100–120 mesh Porapak N that allowed the separation of H_2, Ne, N_2, O_2, Ar, CO and Kr under isothermal conditions ($\approx 18°C$) with a flow-rate of 35 ml/min. The second set was a pair of 2.3 m×1.1 mm I.D. columns filled with 180–220 mesh specially prepared polydivinylbenzene (poly-DVB) to resolve the remaining gases in the presence of water and sulfur dioxide. This column was also operated isothermally at 62°C with a carrier gas flow-rate of ≈ 40 ml/min. Each column pair led to a differential, thermistor-bead, thermal conductivity detector giving a dynamic range from a few parts per million to the 10s of percent level. The identification of the eluting components was based on retention time, but an internal standard of freon was added to the last sample to confirm the measurements.

The instrument design allowed a continuous and relatively large flow of the Venus atmosphere into a plenum for the entire mission through the inlet valve. This arrangement provided that any absorptive or reactive sample path sites would be constantly saturated minimizing effects on the sample ''injected'' into the GC column.

The Pioneer-Venus gas chromatograph's findings [12] for the basically inert species, e.g., Ne, N_2, Ar and CO_2 were fundamentally consistent with the all other Venus measurements most especially from the Venera missions 11 and 12 conducted by the former Soviet Union [14–16]. Carbon dioxide concentration was 96% and nitrogen was 3.4%. However, higher levels of water, oxygen and sulfur dioxide were found by the Pioneer-Venus gas chromatograph than those obtained by other instruments. The oxygen and water measurements were particularly controversial, as they did not match predicted levels. At this writing new missions are being planned for Venus to gather more data on our closest neighbor. The major and minor constituents of the atmosphere of Venus are listed in Table 2.

2.3. Cassini-Huygen mission

Titan is the largest satellite of Saturn with a mean diameter greater than that of Mercury and an atmosphere denser than that on Earth's surface. Saturn is best known for its complex ring system, and the study of these rings together with Saturn's moons, is expected to provide useful information on the com-

Table 2
Chemical constituents of Venus atmosphere (surface pressure=90 bar; surface temperature=730 K) (adapted from [24])

Constituents	Mol fraction
Major constituents (%)	
CO_2	96
N_2	3.4
Minor constituents (ppm)	
H_2O	1000–1
CO	200–20
Ne	2.5
SO_2	200–0.1
H_2S	80–1
COS	40–0.35
H_2	25
Ar	70
Ne	7
HCl	0.4
HF	$5 \cdot 10^{-3}$
S_3	$4 \cdot 10^{-5}$

position and evolution of the planetary masses from which planets form. The results of the Voyager mission showed that the Titan atmosphere is primarily nitrogen and is rich in hydrocarbons, resembling the early atmosphere of Earth. The Voyager data also confirm the abundance of aerosols and cloud droplets in the atmosphere, which mask the surface of the satellite. Theoretical modeling of this surface from the atmospheric data strongly suggests the presence of oceans of liquid methane–ethane mixture at the surface. In addition to the already detected organic molecules, laboratory simulation experiments has predicted the presence of many more organic compounds including other light hydrocarbons (saturated and unsaturated), nitriles, dinitriles and O-organics at a very low mol fraction [23,24]. The observation of two independent water lines at 43.9 and 39.4 μm using the short wavelength spectrometer (SWS) of ISO recently showed evidence for water vapor in the atmosphere of Titan [25]. With this result, all the three major oxygen compounds (CO, CO_2 and H_2O) seem to be present in Titan and Saturn atmospheres. The composition of Titan's atmosphere from Voyager, ground-based and ISO observations is listed in Table 3.

One of the most important objectives of the Cassini–Huygen mission, a joint NASA/ESA mission to Saturn and its moon Titan launched in

Table 3
Chemical composition of Titan's stratosphere (adapted from [26])

Constituents	Stratosphere mixing ratio			
Major constituents				
Nitrogen, N_2	0.90–0.99			
Argon, Ar (?)	<0.06 (at 3σ)			
Methane, CH_4	0.017–0.045			
	0.017–0.12	T		
Hydrogen, H_2	0.00060–0.0014			
Hydrocarbons				
Ethane, C_2H_6	$1.3 \cdot 10^{-5}$	E	$1.65 \cdot 10^{-5}$	N
Acetylene, C_2H_2	$3.0 \cdot 10^{-6}$	E	$6.5 \cdot 10^{-6}$	N
Propane, C_3H_8	$5.0 \cdot 10^{-7}$	E	$1.2 \cdot 10^{-6}$	N
Ethylene, C_2H_4	$1.5 \cdot 10^{-7}$	E	$1.5 \cdot 10^{-5}$	N
Propyne, C_3H_4	$5.0 \cdot 10^{-9}$	E	$3.7 \cdot 10^{-8}$	N
Diacetylene, C_4H_2	$1.4 \cdot 10^{-9}$	E	$2.7 \cdot 10^{-8}$	N
N-Organics				
Hydrogen cyanide, HCN	$1.7 \cdot 10^{-7}$	E	$1.5 \cdot 10^{-6}$	N
Cyanoacetylene, HC_3N	Detected	D	$4.5 \cdot 10^{-8}$	N
Cyanogen, C_2N_2			$2.2 \cdot 10^{-8}$	N
Acetonitrile, CH_3CN	Detected			
Dicyanoacetylene, C_4N_2			Solid phase	N
O-Compounds				
Carbon dioxide, CO_2	$1.4 \cdot 10^{-8}$	E	$1.3 \cdot 10^{-8}$	N
Carbon monoxide, CO	$5.0 \cdot 10^{-5}$	D	$6.0 \cdot 10^{-5}$	D,T
Water, H_2O[a]	$0.4–1.4 \cdot 10^{-8}$			

Abbreviations: E, equator; N, north pole; D, disc-averaged; T, troposphere.
[a] Taken from [25].

October 1997, is the analysis of the atmosphere of Titan. Designed to employ a Venus–Venus–Earth–Jupiter gravity assist trajectory, the Cassini spacecraft is expected to reach the Saturn system in 2004. At the end of the first orbiting tour in mid-2004, the Orbiter will release the Huygens probe for its 2.5-h descent, via parachute, into Titan's dense and intriguingly Earth-like atmosphere, while the former continues to explore Saturn and its rings.

Onboard the Huygen probe are six science instruments all of which will take measurements during its spectacular descent, providing details on the chemical composition of Titan's atmosphere, its weather and clouds, and then the surface itself. Amongst these instruments is a GC–MS system, which is expected to identify and quantify various atmospheric constituents during the probes descent as well as measuring the composition of Titan's surface at the impact location in the event of a safe landing [23,24]. Based on the present models of Titan's atmosphere, the instrument will determine the major

isotopes of carbon, nitrogen, hydrogen, oxygen and argon as well as the detection of neon and the other noble gases from 10 to 100 ppb levels.

The GC–MS instrument consists of a gas sampling system, a carrier-gas supply (hydrogen), a GC column assembly, and a mass spectrometer. The gas sampling system has three inlets: one for direct analysis of the atmosphere by MS, one for GC–MS analysis and a third for the analysis of the aerosol collector pyrolyzer (ACP) gaseous products. The GC column assembly is made of three parallel columns. One column, a Silcosteel tubing (Restek, Bellefonte, PA, USA) packed with carbon molecular sieve (Supelco, Bellefonte, PA, USA), is for the separation of permanent gases particularly nitrogen and carbon monoxide. The second column, a MXT capillary column (Restek) is for the analysis of nitriles and higher-molecular-mass compounds or gas mixtures released from the ACP experiments. The third column, which is a glassy carbon capillary column, is for the analysis of low-molecular-mass hydrocar-

bons, mainly C_2–C_3. Table 4 shows some organic compounds not yet detected in Titan's stratosphere but expected to be present at concentrations detectable from Cassini–Huygens.

The mass spectrometer employs a quadrupole mass filter [27] with a secondary electron multiplier detection system covering the range 2–146 u. It also employs five ion sources selectively feeding a common mass analyzer. The first source is connected to the atmospheric input manifold, the second to the output of the ACP, and the last three sources are connected to the three GC columns. The GC–MS instrument is also fitted with gas samplers, which will be filled at high altitude for analysis later in the descent when more time is available. The successful operation of this instrument will be considered as a remarkable achievement as it will mark the second time a gas chromatograph–mass spectrometer is

flown and landed for in situ analysis of extraterrestrial planetary environments.

3. Advances in GC for space exploration

3.1. Columns

Porous polymer columns were first used in GC by Baum [28], who studied the characteristics of microporous polyethylene as an adsorption and support medium for the separation of alcohols, ketones, acetates, paraffins and aromatic compounds. Thereafter, Hollis developed porous polymer columns for the separation of possible Martian atmospheric constituents [29,30]. These columns allowed good resolution of a wide variety of compounds such as H_2, N_2, O_2, Ar, CO, CO_2, SO_2, CH_4 and H_2O. In

Table 4
Organic compounds in Titan's stratosphere that are likely to be present at concentrations detectable from Cassini–Huygen (adapted from [26])

Constituents	Expected mean mol fraction
Hydrocarbons	
Propene, C_3H_6	10^{-7}–10^{-8}
Allene, C_3H_4	10^{-7}–10^{-8}
Cyclopropane, C_3H_6	10^{-8}–10^{-10}
Triacetylene, C_6H_2	10^{-8}–10^{-10}
Tetraacetylene, C_8H_2	10^{-9}–10^{-10}
The above compounds may play a major role in Titan's photochemistry	
C_4H_4	10^{-8}–10^{-10}
1,2-C_4H_6	10^{-8}–10^{-10}
1,3-C_4H_6	10^{-8}–10^{-10}
C_4H_8	10^{-8}–10^{-10}
nC_4H_{10}	10^{-8}–10^{-10}
iso-C_4H_{10}	10^{-7}–10^{-9}
C_6H_6	$<$about 10^{-9}
(related to C_2H_2 polymerization)	
Nitriles	
C_2N_5–CN	$<5\cdot10^{-7}$ (likely to be in the range 10^{-8}–10^{-9})
CH_2=CH–CN	$<2\cdot10^{-7}$ (likely to be in the range 10^{-8}–10^{-9})
CH_3–CC–CN	$<2.5\cdot10^{-7}$ (likely to be in the range 10^{-8}–10^{-9})
n-C_3H_7–CN	$<6\cdot10^{-8}$ (likely to be in the range 10^{-8}–10^{-10})
iso-C_3H_7–CN	$<2\cdot10^{-8}$ (likely to be in the range 10^{-8}–10^{-10})
cyclo-C_3H_6–CN	$<1.5\cdot10^{-8}$ (likely to be in the range 10^{-8}–10^{-10})
HC_5N	$<1.5\cdot10^{-8}$ (likely to be in the range 10^{-8}–10^{-10})
O-Compounds	
HCHO	10^{-10}–10^{-12}
H_2O	10^{-10}–10^{-12}
CH_3OH	10^{-10}–10^{-12}

addition, Hollis [29,30] noticed that the polymer beads were mechanically stable, not destroyed by vacuum or radiation, and had sufficiently high temperature stability (up to 250°C). These characteristics made them very promising for use in space research and they were subsequently employed on various missions including Viking (Porapak Q), Pioneer (Porapak N), and Vega (Porapak T) [19,31]. Another noteworthy column in space exploration is Poly MPE–Tenax developed by Novotny et al. [21]. This column, which formed part of the Viking lander assembly, exhibits good chromatographic properties for alcohols, hydrocarbons and amines with minimal

tailing and provides efficient transmission and resolution of sub-ppb organic compounds in the presence of large amounts of water and carbon dioxide.

Even though the aforementioned columns were successfully used for in situ analyses of the target atmospheres, they are, however, presently considered unsuitable for GC experiments in future planetary missions due to their relatively long analysis times and lack of selectivity for complex mixtures. For example, the GC experiment aboard Huygens must, in a relatively short time (<15 min), be able to simultaneously analyze light hydrocarbons (C_1–C_8) and nitriles (C_1–C_4), CO, H_2, and CO_2, in the
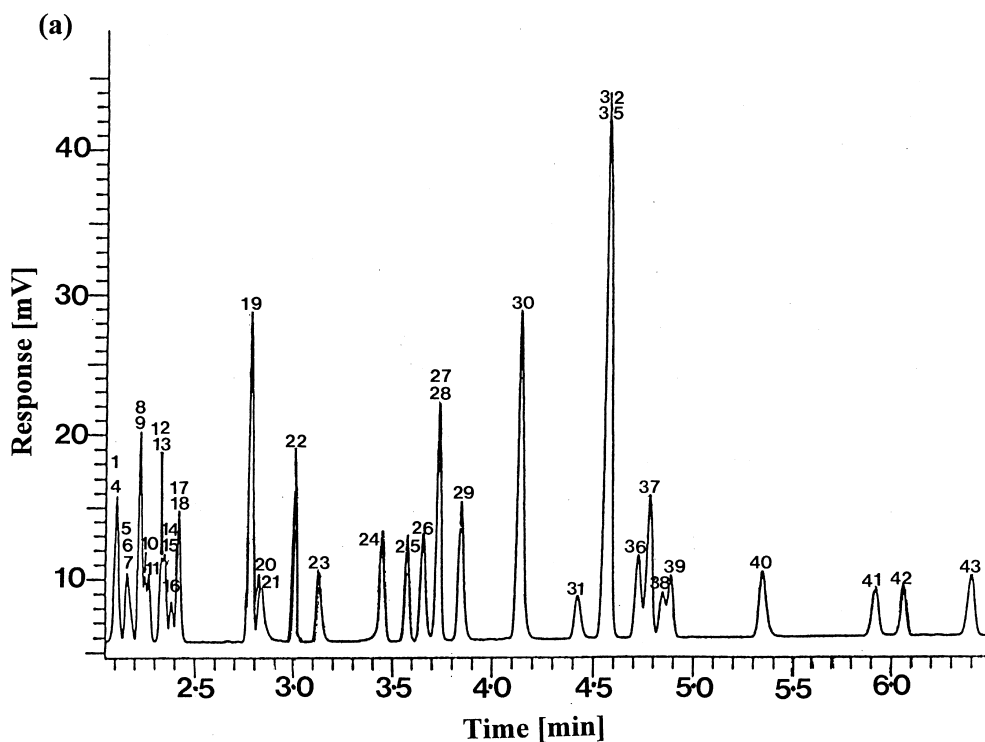

Fig. 1. GC analysis of a gaseous mixture of C_1–C_6 hydrocarbons, polycyclic aromatic hydrocarbons and C_1–C_4 nitriles. (a) On a 25 m×0.15 mm I.D. BPX5 (d_f=0.25 μm) fused-silica WCOT column. Temperature, isothermal for 1.5 min at 30°C, then increased to 100°C at 30°C/min; carrier gas, H_2; outlet flow-rate, 0.33 ml/min; inlet pressure, 0.8 bar. (b) On a 25 m×0.15 mm I.D. BPX5 (d_f=2 μm) fused-silica WCOT column. Temperature, isothermal for 1.6 min at 40°C, then increased to 100°C at 45°C/min; carrier gas, H_2; outlet flow-rate, 0.44 ml/min; inlet pressure, 0.70 bar. Peaks: 1=methane; 2=ethene; 3=ethyne; 4=ethane; 5=cyanogen; 5′-hydrocyanic acid; 6=propene; 7=propane; 8=propyne; 9=allene; 10=cyclopropane; 11=isobutane; 12=1-butene; 13=isobutene; 14=butadiene; 15=butane; 16=trans-2-butene; 17=butyne; 18=cis-2-butene; 19=1-pentene; 20=acetonitrile; 21=pentane; 22=2-methyl-2-butene; 23=acrylonitrile; 24=cyclopentane; 25=3-methylpentane; 26=propionitrile; 27=1-hexene; 28=hexane; 29=methacrylonitrile; 30=isobutyronitrile; 31=cis- or trans-crotononitrile; 32=3-butenenitrile; 33=2-butynitrile; 34=benzene; 35=cyclohexane; 36=butyronitrile; 37=cyclohexene; 38=cis- or trans-crotononitrile; 39=n-heptane; 40=cyclopropanecarbonitrile; 41=toluene; 42=1-octene; 43=cycloheptane; 44=octane; 45=ethylbenzene; 46=xylene. (Reprinted with permission from [35]). *(continued on next page)*

presence of large amounts of nitrogen and argon, all of which are plausible constituents of Titan's atmosphere [32]. To solve some of these problems and in the preparation of the GC experiment for the NASA/ ESA Cassini mission that was launched in October 1997, Do and Raulin [32,33] systematically investigated porous-layer open-tubular (PLOT) capillary columns for the analysis of light hydrocarbons and nitriles. This same research group studied the suitability of other commercially available GC columns including wall-coated open-tubular capillary columns (WCOT) [34,35], Molsieve PLOT capillary columns [36], molecular sieve micropacked columns [37] and carbon molecular sieve packed capillary columns [38] for the analysis of various gases in Titan's atmosphere. Their results generally showed the good separation efficiency of the columns for the target compounds at conditions compatible with flight instrumentation constraints. Typical chromatograms are shown in Figs. 1 and 2 for the analyses of light hydrocarbons and nitriles on BPX5 capillary columns and permanent gases (in the presence of

hydrocarbons and nitriles) on Molsieve PLOT capillary column, respectively.

While the superior resolution and overall performance of PLOT columns over conventional columns were expected, other factors such as mechanical strength and column bleed were not as impressive [34–37]. To overcome these drawbacks, the potential importance of chemically bonded micropacked GC columns for the analysis of light hydrocarbons in future space missions were investigated by Akapo et al. [39–42]. These types of columns were considered as suitable alternatives to PLOT or WCOT capillary columns because of their high resolving power, large sample capacity, and high stability, which make them more capable of withstanding the rigors of launch and space flight. A typical chromatogram for the separation of a ten-component mixture of C_1–C_4 saturated and unsaturated hydrocarbons on a mixed cyclic siloxane-alkyl bonded phase under isothermal conditions is shown in Fig. 3. Even though the test solutes were retained longer on the transition metal-containing columns presumably due to specific sol-
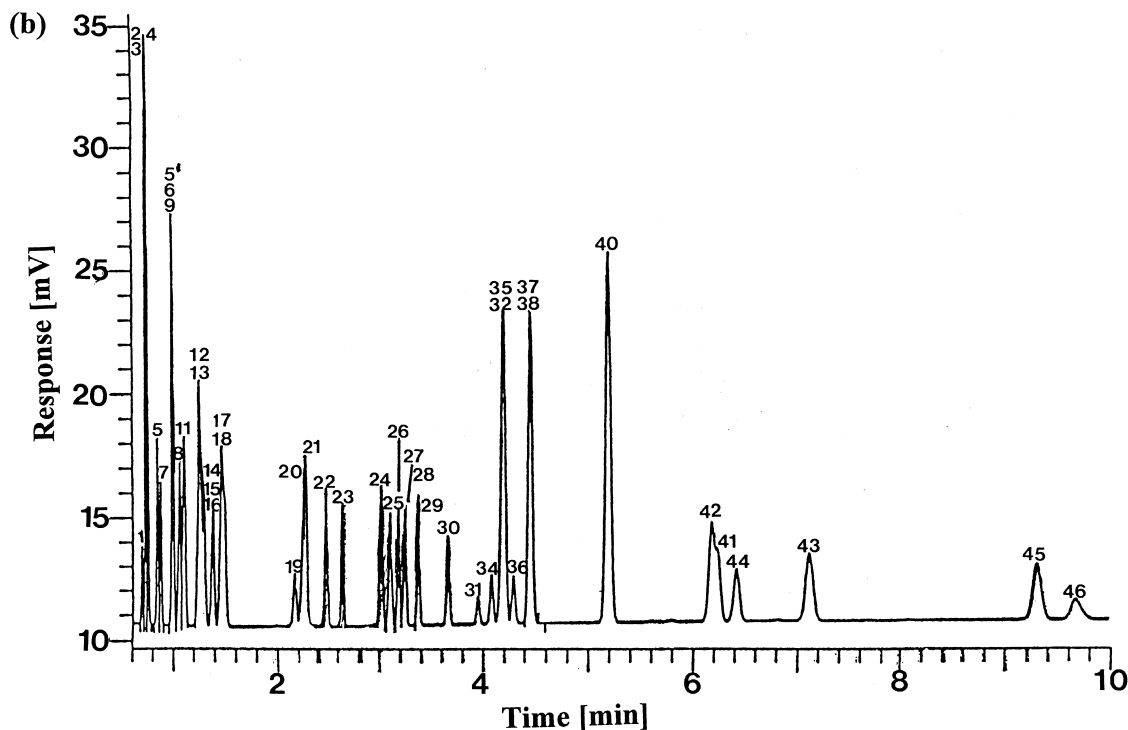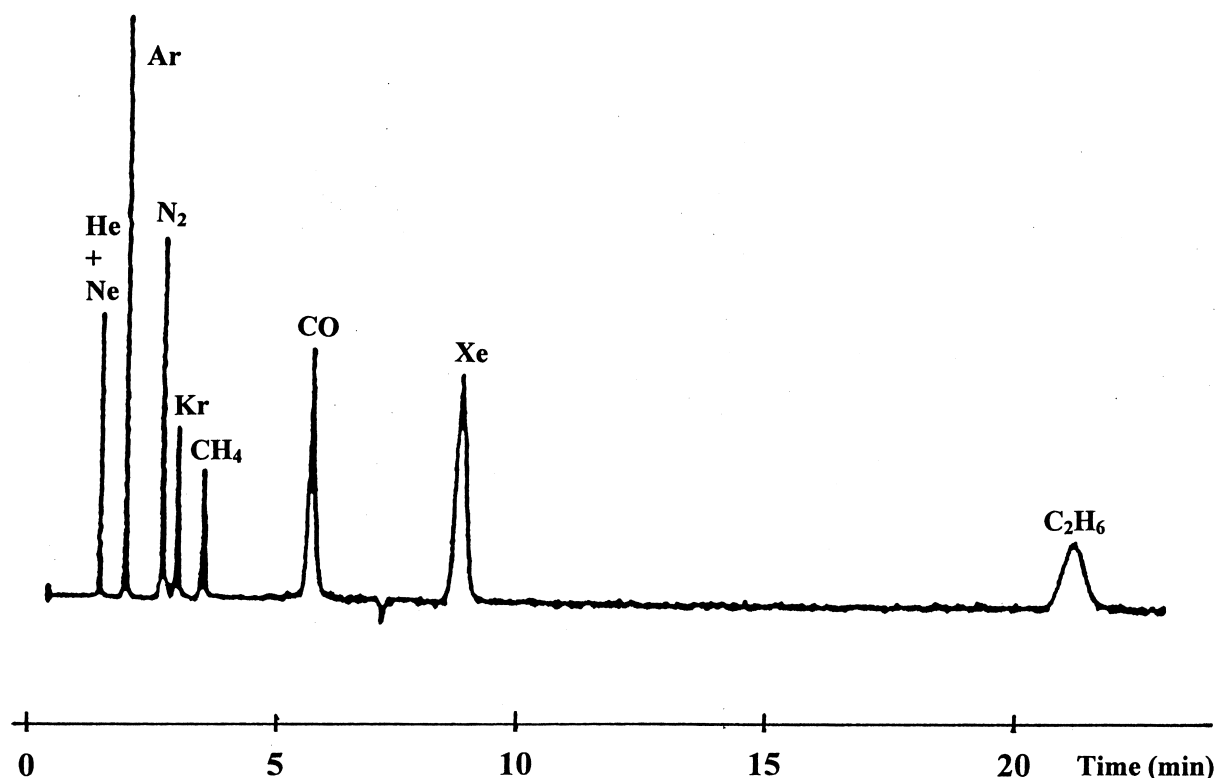

Fig. 1. (*continued*)

Fig. 2. Gas chromatography of a gaseous mixture of He, Ne, Ar, N$_2$, Kr, CH$_4$, CO, Xe and C$_2$H$_6$ on a 10 m×0.53 mm I.D. Molsieve 5A (film thickness 50 μm) fused-silica PLOT column at 90°C. Carrier gas, H$_2$; outlet flow-rate, 2 ml/min; amount injected, ~3 nmol of each constituent; splitting ratio, 40:1; thermal conductivity detector. (Reprinted with permission from [36]).

ute–metal interactions, the cobalt (II) complex of aminopropylsilyl-dithiooxamide bonded phase showed a noticeable improvement in the separation of C$_2$ hydrocarbons over molecular sieve 5A [38,43].

Additional efforts in GC column development at NASA-Ames for future planetary missions include the production of PLOT columns by in situ polymerization as described by Shen et al. [44,45]. This method, which uses direct polymerization of monomer inside the metal column, produced relatively stable PLOT column over the conventional ones with high separation efficiency for light gases, particularly permanent gases at low flow-rates (3 ml/min) [45].

3.2. Detectors

The need for complete chemical analysis of the volatile species present in the atmospheres and surfaces of various bodies within our solar system requires continual improvement of existing or development of new sensitive, miniaturized detectors, having both selective and universal response for GC. Even though the thermal conductivity detectors (TCDs) flown on the Viking and Pioneer Venus missions performed well [11–13], TCDs are vulnerable to g-stresses, require high precision thermal control and only provides about 1 ppm sensitivity. Because they measure small changes in thermal conduction, stringent thermal stabilization is required.

A review of other types of detector for exobiology flight experiments revealed the metastable ionization detector (MID) as a likely candidate because of its superior thermal stability and high sensitivity. Commercially available as the helium ionization detector, the MID combines universal response with high sensitivity (ppb), wide response range ($>10^6$), particularly when used with voltage modulator, and
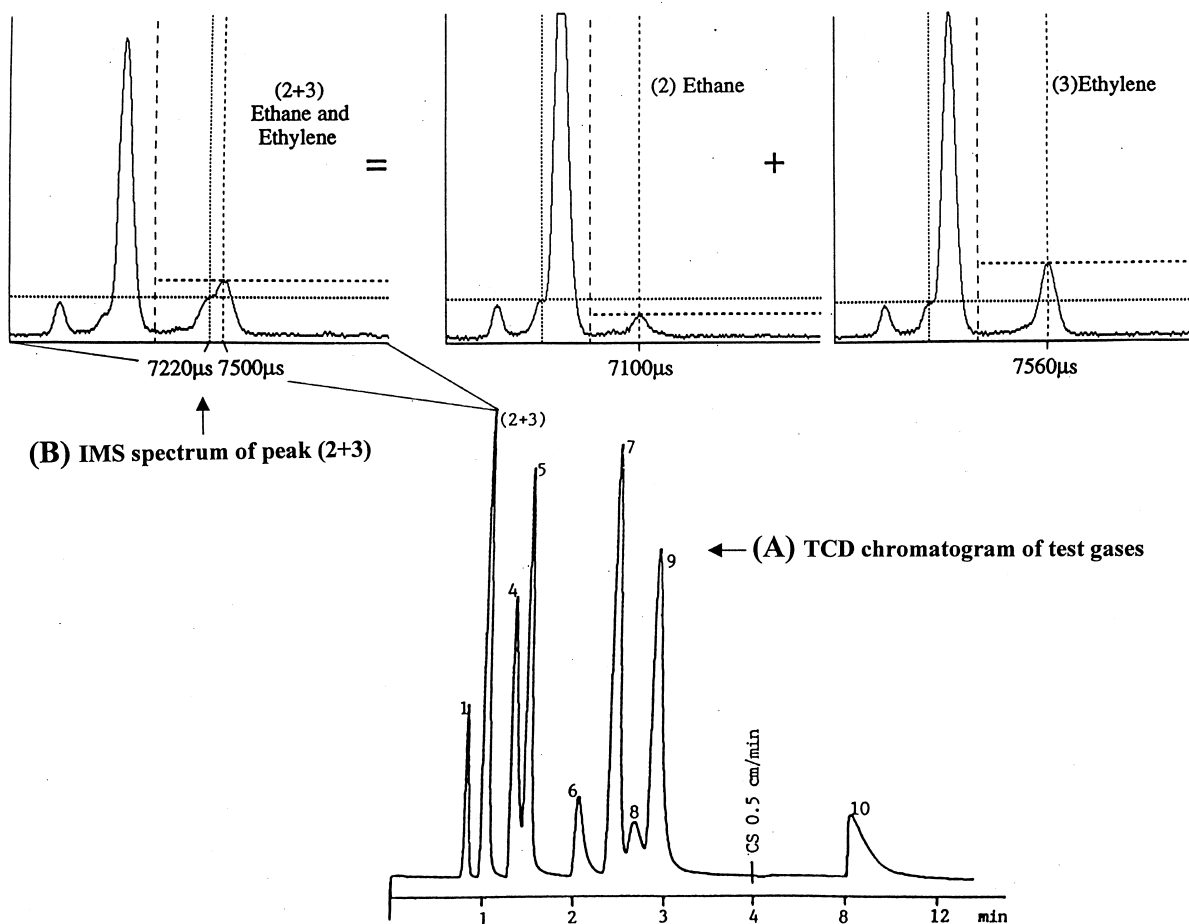
Fig. 3. (A) Analysis of a ten-component mixture of C_1–C_4 saturated and unsaturated hydrocarbons on a 2 m×1.07 mm I.D. hexamethylcyclotrisiloxane–octadecylsilyl stainless steel column at 25°C. Carrier gas, He; flow-rate, at 5.20 ml/min; 100 µl injection loop; thermal conductivity detector. (B) IMS spectra of peak (2+3) showing the presence of both ethane and ethylene product ions from single component spectra (upper middle and right). Peaks: 1=methane; 2=ethane; 3=ethylene; 4=acetylene; 5=propane; 6=propylene; 7=isobutane; 8=propadiene; 9=butane; 10=propyne.

ruggedness, thus making it an ideal detector for analysis of complex mixtures [46]. The mini-Triaxial MID shown in Fig. 4 weighs about 1 g and has been used in all breadboard systems for proposed exobiology flight experiments at NASA-Ames. This detector and voltage modulation system were incorporated into the baseline cometary ice and dust experiment (CIDEX) for the comet rendezvous asteroid flyby mission (CRAFT) [47]. Additional research efforts have led to the development of microvolume MIDs (µMID) having internal volumes of 12 µl with similar sensitivity as the mini-MID at carrier gas

flow-rates below 2 ml/min, and compatible with the voltage modulator [48].

Although tiny and highly sensitive with wide response range and universal response, MIDs do not provide any sample identification information other than the GC retention time [48,49]. To fulfill this sample identification role, an ion mobility spectrometry (IMS) system is being developed as a flight instrument [50]. IMS is an ion reaction chamber connected to an ion drift tube, all operated at or near one atmosphere pressure. The reactant ions produced by the action of a radioactive source on the carrier

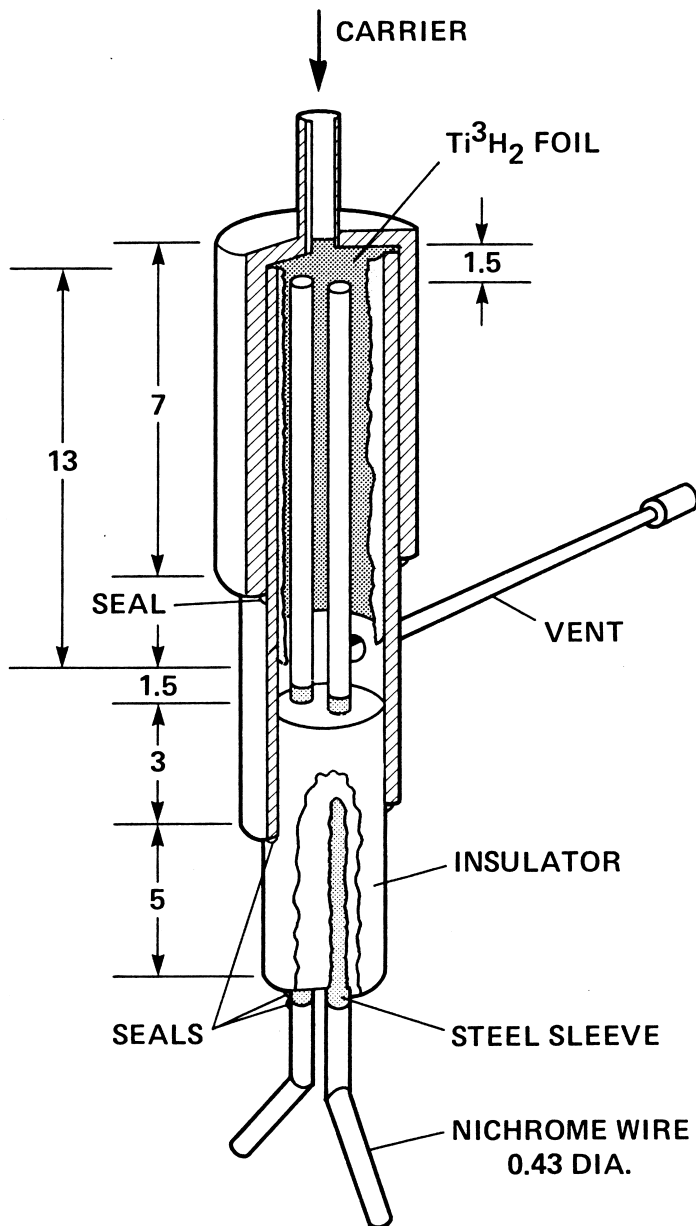# TRIAXIAL MINI METASTABLE IONIZATION DETECTOR

Fig. 4. Triaxial mini-metastable ionization detector.

gas ionize the sample molecules in the reaction region and both the reactant and product ions pass through an ion gate into the drift region. An electric field moves the ions through the drift region against the flow of a drift gas flow. The ions, separated by differences in structure and charge distribution, are detected at the end of the drift tube by a collecting electrode. The sample components are identified by the resultant ion intensity vs. drift time data, the IMS spectra.

A typical analysis of a ten-component mixture of light hydrocarbons at ppm levels using the mini-CIDEX breadboard GC is shown in Fig. 5. The center chromatogram is the mini-MID response, while the surrounding boxes show the spectra of the GC peaks as identified by IMS. This flight prototype detector uses very high purity dry helium and employs a 2×10 cm reaction region/drift tube. In

addition, the use of helium as drift gas make it very compatible with the GC columns and MIDs that use helium as a carrier gas. The former is demonstrated in Fig. 3 where the IMS provides separate analyses of ethane and ethylene, which co-eluted on a chemically bonded micropacked column using a TCD detector. Each component gives a unique product ion peak, which can be seen in the IMS spectrum of the unresolved ethane–ethylene peak (see upper left).

3.3. Signal processing

The main goal of signal processing techniques in chromatography is the efficient extraction of useful information from the raw chromatogram. In this technique, the chromatographic system is viewed as a combination of several components including a modulator (injection), a filter (column), and a sensor
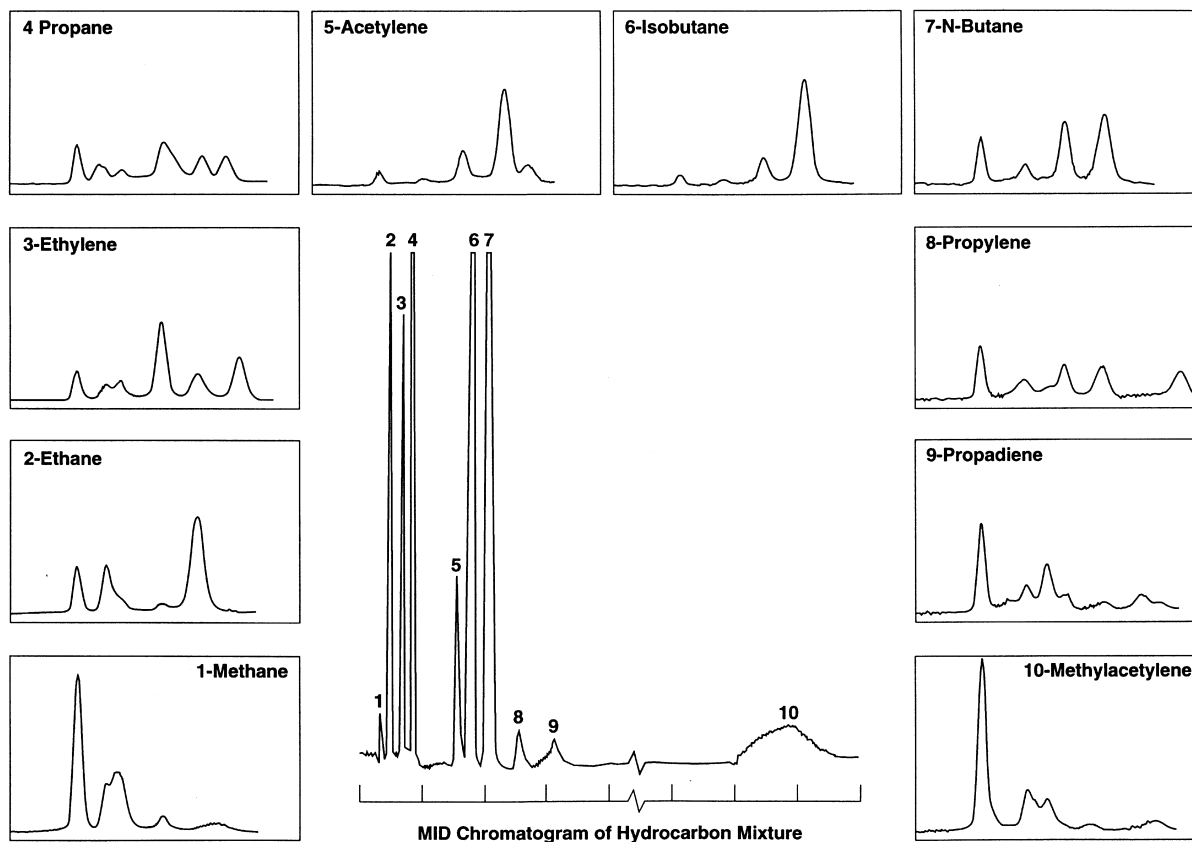

Fig. 5. Mini-CIDEX GC–IMS analysis of a ten-component hydrocarbon mixture.

Chemical Signal Input

Modulator

**Modulation Signal
Current**

**Signal Filter
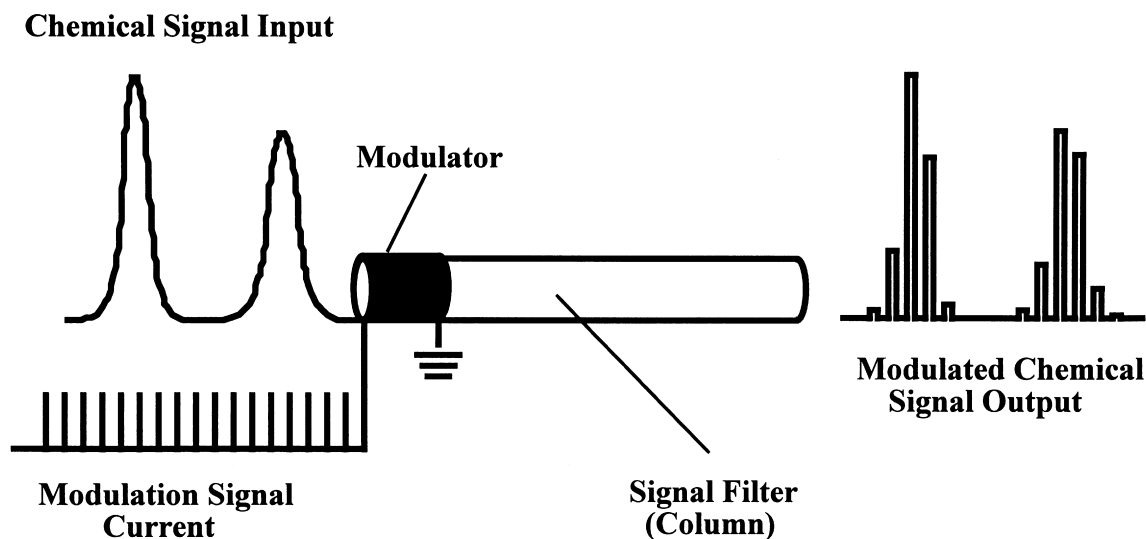(Column)**

**Modulated Chemical
Signal Output**

Fig. 6. GC as a signal processing device. The modulator chops the chemical signal into a series of pulses, which take on the form of the modulation signal. In this case the chemical signal is the profile of one compound that changes as a function of time.

(detector) [51]. As illustrated in Fig. 6, modulation is the direct result of sample injection and has the form of a concentration pulse. Signal processing computational techniques has proven very useful in multiplex gas chromatography (MGC) [52,53].

4. Multiplex gas chromatography

MGC was developed as an alternative concept for GC analysis of planetary atmospheres most importantly because of the limited time available to perform the analysis and the extremely low level of analytes that would be introduced into the instrument during the flight [51,52]. In MGC, multiple samples are introduced into a gas chromatograph independently of the migration rate of each sample. Thus, large sample volume could be analyzed without increasing the data-acquisition requirements. The chromatograms from the detector output data are obtained through the use of appropriate computational techniques since the output signal from an MGC experiment is not directly interpretable (see Fig. 7) [52]. By performing some analyses at sub-atmospheric pressure, Valentin and Hall [54] have demonstrated the potential application of this technique in restricted environments, such as that which can be

encountered in planetary environments. These authors also investigated the limitations of the technique in an environment where the sample composition changes during the sampling period.

Concurrently with MGC, various modulation techniques were also developed and used when necessary to simplify flight instrumentation in terms of size, mass, and amount of consumables needed [53]. A modulator is a device that has been viewed as an excellent substitute for the established GC sampling methods because it allows the use of only one carrier gas (the sample gas). Thus, a target planetary atmosphere could be used as its own carrier gas thereby avoiding the need for any consumables except power. Other recent developments in this area includes MGC in non-stationary systems, a sample storage system using GC columns to store a profile, and thermal modulators to selectively measure moisture in a gas mixture and soil samples [53,55].

5. Conclusion

GC has developed into a powerful analytical instrument for solar system exploration even though the technology onboard spacecraft has always lagged behind the state-of-the-art techniques that exist on
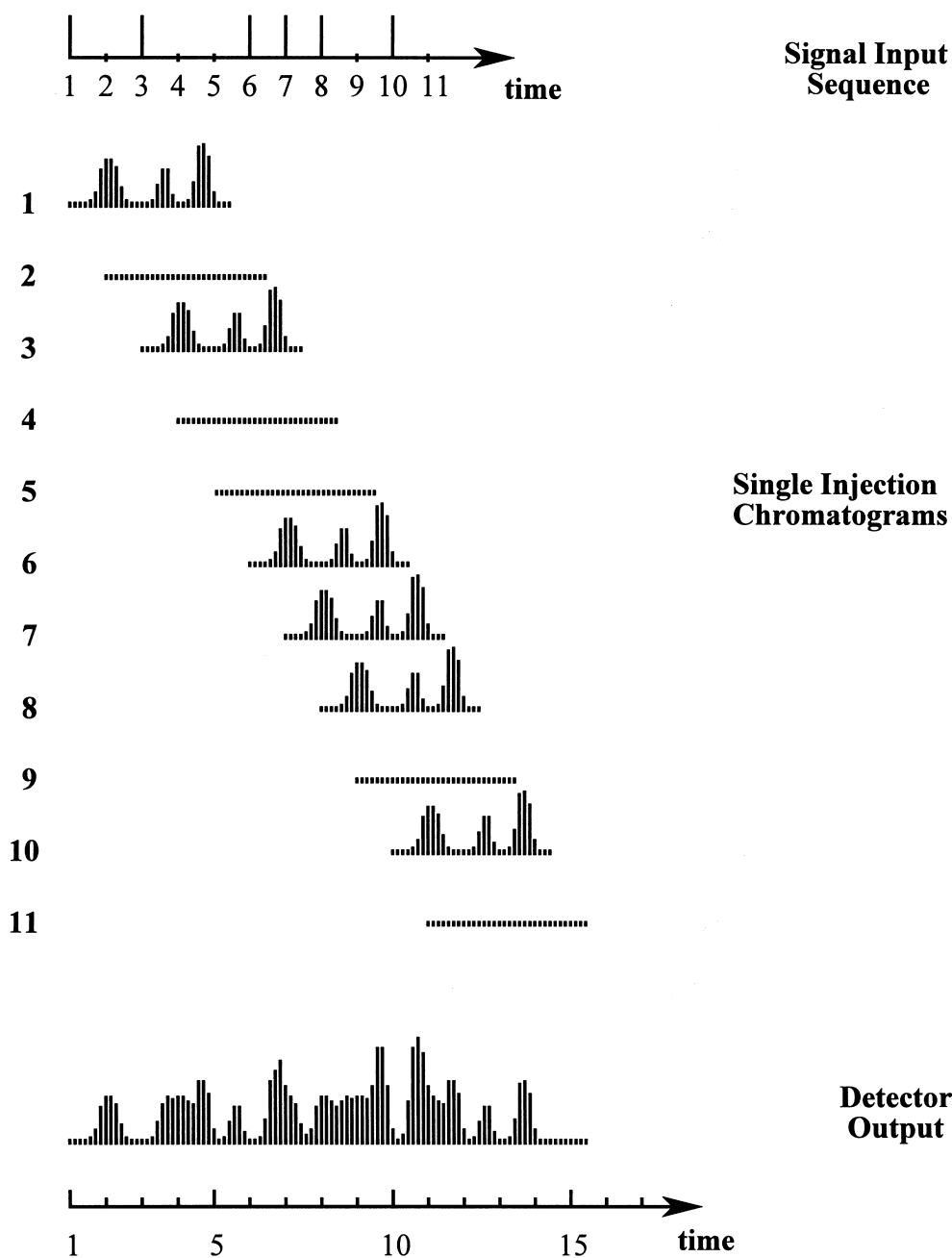
Fig. 7. Detector output of a multiplex GC experiment. The chromatogram is obtained through demodulation of the output signal with the signal input sequence signal.

Earth. This is because space flight instruments need to have been tested and optimized over several years on the ground to guarantee high reliability. For GC,

the development of different parts of the system in support of future exobiology flights has remained a continuous exercise in order to satisfy NASA's new

mantra of ''faster, better, cheaper'' for flight instruments. In this case, new columns, detectors, signal processing techniques and different forms of GC methods directly focused on exobiology science goals have been undertaken. As has been done in the past and present, GC will continue to play a prominent role in solar system exploration either alone or as part of integrated analytical instruments such as GC–MS, GC–IMS, differential scanning calorimeter (DSC)–GC and differential thermal analyzer (DTA)–GC.

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