The Gas Chromatograph Mass Spectrometer Aboard Huygens

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The Gas Chromatograph Mass Spectrometer (GCMS) on the Huygens Probe will measure the chemical composition of Titan's atmosphere from 170 km altitude (≃1 hPa) to the surface (≃1500 hPa) and determine the isotope ratios of the major gaseous constituents. GCMS will also analyse gas samples from the Aerosol Collector Pyrolyser (ACP) and will be able to investigate the composition (including isotope ratios) of several candidate surface materials.

GCMS is a quadrupole mass filter with a secondary electron multiplier detection system and a gas sampling system providing continuous direct atmospheric composition measurements and batch sampling through three gas chromatograph (GC) columns. The mass spectrometer employs five ion sources sequentially feeding the mass analyser. Three ion sources serve as detectors for the GC columns and two are dedicated to direct atmosphere sampling and ACP gas sampling, respectively. The instrument is also equipped with a chemical scrubber cell for noble gas analysis, and a sample enrichment cell for selective measurement of high boiling-point carbon-containing constituents. The mass range is 2-141 dalton and the nominal detection threshold is at a mixing ratio of 10^{-8}.

The data rate available from the Probe system is 885 bit/s. GCMS mass is 17.3 kg and the energy required for warm-up and 150 min of operation is 110 Wh.

1. Scientific Objectives

1.1. Introduction

Titan is unique in the solar system in several respects. The dense atmosphere is still chemically reducing, even though Titan is small enough to allow hydrogen to escape readily from its gravitational field. The major constituents of the atmosphere, nitrogen and methane, are continuously broken apart by a combination of solar UV, impinging electrons from Saturn's magnetosphere, and a steady flux of cosmic rays. The resulting molecular fragments recombine to form a variety of new species, many of which were detected for the first time by Voyager 1 (Broadfoot et al., 1981; Hanel et al., 1981; Kunde et al., 1981; Samuelson et al., 1981, 1983; Lutz et al., 1983; Bézard et al., 1993). Other simple molecules must be present, while the existence of still more complex compounds is manifested by the ubiquitous, surface-hiding aerosol blanket. In addition to hydrocarbons and nitriles, the atmosphere is known to contain CO and CO_2 (see reviews by Hunten et al., 1984; Morrison et al., 1986; Lunine et al., 1989; Gautier and Raulin, this volume).

Chemical reactions are continuously converting methane, nitrogen, carbon monoxide and possibly externally-delivered H_2O into more complex substances. The origin of this atmosphere, the processes involved in its evolution, the end products and their subsequent fate as they interact with the surface remain to be elucidated. A particularly interesting aspect of this investigation is the possible relevance of the chemical evolution currently occurring on Titan to some of the prebiotic syntheses that took place on the Earth. It is the purpose of GCMS to provide an accurate analysis of Titan's atmospheric composition along Huygens' descent trajectory.

1.2 Atmospheric composition: argon, isotopes and organic compounds

Despite the great success of Voyager 1, the basic composition of Titan's atmosphere is still poorly known (Table 1). The present uncertainty in the methane mixing ratio and its variation with altitude can be resolved easily from the continuous recording of mass spectra by GCMS during the Probe's descent. The Voyager observations left open the possibility that several percent of some heavy, spectroscopically-undetectable gas might be present (Samuelson et al., 1981). Non-radiogenic argon ($^{36}Ar + {}^{38}Ar$) is the most likely candidate (Owen, 1982); the mass spectrometer can detect it down to mixing ratios of 10-100 ppb. The amount of argon that could remain undetectable in presently available observations has been steadily decreasing with improved treatment of the data, first to $\leq 10\%$ (Strobel et al., 1993), then to $\leq 6\%$ (Courtin et al., 1996), the same upper limit originally reported by Broadfoot et al. (1981). In fact, several percent of argon would be difficult to explain based on current models for the origin of Titan's atmosphere (Owen & Bar-Nun, 1995).

The full range of abundance and isotope data provided by GCMS will be employed to study atmospheric origin and evolution. For example, the ratio $^{14}N/{}^{15}N$ will permit an evaluation of atmospheric escape processes, as will the value of $^{12}C/{}^{13}C$. Once escape and chemical exchange have been studied, it will be possible to establish the original value of D/H in Titan's methane. For example, if $D/H \approx 2 \times 10^{-5}$, the value in Saturn's hydrogen, this might favour a sub-nebula origin for most of the methane. A determination of $^{40}Ar/{}^{36}Ar$ could be used to model escape of gas from Titan's rocky interior.

The oxidised compounds offer other opportunities and challenges. The production of CO_2 requires hydroxyl (OH) that may come from either outside the atmosphere (e.g. by bombarding ice particles or micrometeorites) or from internal sources, from CO plus CH_4. The external source seems likely to be more efficient, but we do not know the flux of incoming particles. If the nitrogen we now see in Titan's atmosphere was originally incorporated as N_2, one would expect a comparable amount of primordial CO. In that case, a large amount of CO_2 would have been produced and several metres of 'dry ice' could now be present on the surface (Samuelson et al., 1983; Owen & Gautier, 1989). The CO chemistry on Titan will be tested by measuring the abundance of this gas at the four altitudes at which atmospheric GC samples are taken.

The drivers for the chemistry on Titan are solar ultraviolet radiation, the charged particle-induced chemistry when Titan is immersed in Saturn's magnetosphere, and galactic cosmic rays, especially for lower atmospheric chemistry. The chemistry of

Table 1. Atmospheric composition od Titan (50°N, Voyager 1)*

Constituent	*Mixing Ratio*	
Major Species (global values)		
N_2	0.85-0.98	Hanel et al., 1981;
Ar	≤ 0.06	Broadfoot et al., 1981;
CH_4	≤ 0.15 at surface	Courtin et al., 1995.
Minor Species		
H Group		
H_2	$2\text{-}6 \times 10^{-3}$	De Bergh et al., 1988;
D/H	$0.7\text{-}2.3 \times 10^{-4}$	Coustenis et al., 1989; Orton, 1992.
CN Group		
C_2N_2	$\sim 2 \times 10^{-8}$	Coustenis & Bézard, 1995;
C_4N_2	condensed phase	Bézard et al., 1993.
C-N-H Group		
HCN	$\sim 10^{-6}$	Coustenis & Bézard, 1995;
HC_3N	$\sim 3 \times 10^{-8}$	Bézard et al., 1993.
CH_3CH	$1\text{-}5 \times 10^{-9}$ (global)	
C-O Group (global values)		
CO	$4\text{-}6 \times 10^{-5}$	Samuelson et al., 1983; Lutz et al.,
CO_2	$\sim 1 \times 10^{-8}$	1983; Gurwell & Muhleman, 1995.
C-H Group		
C_2H_6	$1\text{-}2 \times 10^{-5}$	Coustenis & Bézard, 1995;
C_3H_8	10^{-6}	Bézard et al., 1993.
C_2H_2	$2\text{-}6 \times 10^{-6}$	
C_2H_4	10^{-6}	
CH_3C_2H	$\sim 3 \times 10^{-8}$	
C_4H_2	$\sim 2 \times 10^{-8}$	

* values at other latitudes and seasons likely to be different.

CH_4 on Titan proceeds, to some extent, in a manner similar to that proposed for Jupiter, with the exception that H_2 is replaced by N_2 as the major gas. The stable hydrocarbons resulting from the CH_4 photochemistry are C_2H_6, C_2H_2 and C_2H_4. Subsequent reactions involving C_2H_2 result in the formation of methylacetylene or allene (C_3H_4) and polynes ($C_{2n}H_2$, $n = 2, 3, 4$). Propane C_3H_8, butane C_4H_{10} and other heavier hydrocarbons are expected to be formed following the reaction of the radical CH_3 with C_2H_5, C_3H_7, etc.

Lower mixing ratios are expected with an increasing number of C atoms, but available observations paint a more complex picture. Careful re-analysis of the Voyager data by Coustenis and colleagues has revealed striking variations in abundances of minor constituents with latitude on Titan (Coustenis & Bézard, 1995 and references therein). At 50°N, they find the following order of increasing abundances: C_4H_2, C_2N_2, HC_3N, C_3H_4, C_3H_8, C_2H_8, HCN, C_2H_2, C_2H_6. Abundances measured at this latitude can be more than 17 times the values at southern latitudes. The abundances measured by GCMS along the Probe trajectory can be used to calibrate the remote measurements by the Composite Infrared Spectrometer (CIRS) on the Orbiter, allowing analysis of these variations over the globe during a season different from that sampled by Voyager 1.

Unlike Jupiter, the CH_4 chemistry on Titan is not isolated, as the above list of constituents shows (cf. Table 1). Atomic nitrogen produced on dissociation of N_2 reacts with CH_4 and products of its photochemistry, CH_3 and CH_2, to produce HCN. Photolysis of HCN produces CN. The reactions of CN with CH_4, CN (or HCN) C_2H_2 and C_2H_4 yield, respectively, HCN, C_2N_2, HC_3N and C_2H_3CN (not yet detected). Reactions of CN with the other hydrocarbons result in the formation of additional nitriles such as CH_3CN. Other possible nitriles with mixing ratios in the range 10^{-8} to 10^{-9} are: C_2H_5-N, $CH_2=CH-CN$, $CH_3C\equiv C-CN$ and HC_4-CN. Lower mole fractions are expected for nitriles of higher molecular weight. For comprehensive discussions of the models of chemical pathways in Titan's atmosphere, the reader is referred to Yung et al., 1984; Atreya, 1986; Lunine et al., 1989; Toublanc et al., 1995; Lara et al., 1996.

GCMS will approach this analysis problem in two ways: by taking mass spectra continuously, thereby measuring every m/e peak within 2-141 dalton; and by making discrete GC analyses at various altitudes, including sample enrichment, thereby permitting both greater sensitivity and specificity in identification at those points. A third approach is possible in collaboration with the ACP experiment (see Israel et al., this volume).

1.3 Descent sequence

Direct measurement with the mass spectrometer will be made continuously from initiation of experiments until landing. A minimum of five GC samples will be taken, one immediately after the opening of the inlet valve, another in the lower stratosphere, a third near 60 km (where concentrations of most complex trace gases are thought to be the highest) and two more below 60 km altitude. One of the latter will be devoted to analysis of the output from the aerosol pyrolysis experiment and the other taken near the atmospheric temperature minimum to provide the best CO/N_2 separation. A sixth sample can be taken close to the surface if the nominal descent time is maintained. Its purpose is to characterise conditions near the ground, especially to search for evidence of the vapour phases of possible surface condensates. The timing will be adjusted to ensure GCMS readout before impact for the nominal descent scenario.

1.4 Surface science

Titan has the largest unexplored surface in the solar system. This surface is currently being studied at very low spatial resolution (~ 300 km) by ground-based and Hubble Space Telescope observations through near-IR windows (Smith et al., 1996 and references therein) and by means of radar (Muhleman et al., 1995). Owing to the presence of Titan's thick, chemically active atmosphere, the surface of this satellite must be one of the most unusual we are ever likely to see. This surface must contain or conceal a reservoir for atmospheric methane, since the present atmospheric abundance of this gas will be destroyed by photochemistry in just 10^7 years. Unless we just happen to be living at the time when Titan's original methane comes to an end, the surface (or subsurface) must provide a means for replenishing this gas. The products of atmospheric chemistry will accumulate on Titan's surface over geologic time, with the potential of producing deposits with depths on the order of a kilometre or more. If liquids are present, one can imagine their influence on the landscape through erosion, and the possibility that further chemical processing also occurs in them (Raulin et al., 1995).

Three extreme models for Titan's surface have been proposed:

- a global ocean of hydrocarbons dominated by ethane but containing methane, nitrogen, carbon monoxide and many other dissolved species;
- a global covering of precipitated aerosols;
- an icy landscape dominated by impact craters, perhaps including rocky debris.

It is now clear that the first of these models cannot be correct. A solid surface with lakes or seas of liquid hydrocarbons and some areas dominated by aerosol deposits is more consistent with existing data (Lunine, 1993, 1994; Lorenz, 1993; Smith et al., 1996).

If Huygens lands in a liquid, a compositional analysis with GCMS is straightforward. Mass spectra of evaporating liquid showing the relative abundances of nitrogen, ethane, methane, argon and other noble gases, simple hydrocarbons, nitriles and oxides would be an outstanding contribution to understanding the origin and evolution of the atmosphere. If the Probe settles into a deposit of aerosols, one needs to extrapolate the accumulated information from the descent measurements to interpret the data. This would offer an opportunity to determine the level of chemical complexity achieved by chemical synthesis in the atmosphere, as even rare aerosols may accumulate in measurable concentrations on the surface. Here the GCMS heated inlet will ensure that the more volatile components of such aerosols reach the instrument. Landing on exposed ice could still permit a measurement of H_2O ice 'bedrock' and a search for condensed CO_2, measurements of fundamental importance to an understanding of atmospheric evolution. A determination of D/H in H_2O on the surface would be of great interest for comparison with atmospheric values in CH_4 and other species. It is recognised, however, that this is the most challenging landing scenario, both for Probe survival and for a good interface between the gas inlet and the surface.

2. Instrument Description

2.1 General

Mass spectrometry as the principal chemical identification technique is ideally suited for an exploratory mission such as Huygens. All atoms and molecules within the mass and sensitivity range of the mass spectrometer will be detected. No a priori knowledge of the composition is required. The simultaneous occurrence of species of similar composition can sometimes lead to difficulties in species identification. Multiple electron beam energies in electron impact ionisation usually remove the difficulties by generating energy-dependent fractionation patterns. Further improvement of species separation and more accurate species identification is achieved with a gas chromatographic system coupled with the mass spectrometer. Gas chromatograph mass spectrometer systems are among the most powerful analytical tools for chemical analysis of many types of compounds, and especially of gas mixtures. The added complexity, compared to standalone gas chromatographs or mass spectrometers, is recognised but the benefits resulting from a combined instrument outweigh the possible disadvantage of increased instrument complexity. The advantage offered by combining gas chromatography and mass spectrometry is best illustrated in Fig. 1. In this 3D display, the detector signal obtained from a gas mixture using only a mass spectrometer *vs* mass is plotted at the origin of the time axis, and the detector signal using only a gas chromatograph *vs* time is plotted at the origin of the mass axis. The mass spectrum shows a mass overlap at many mass values for the mixture and the gas chromatograph shows distinct peaks without species identification. The advantage of this combination is illustrated in the display allowing time-dependent separation of the components by the gas chromatograph and molecular identification of the mass spectrometer.

The main elements of the instrument are:

- a mass spectrometer system consisting of ion sources, mass analyser and ion detector;
- a gas sampling system consisting of a direct atmospheric sampling system to introduce atmospheric gas into the ion source and to enrich trace species and noble gases;
- a gas chromatograph for batch sampling at specific altitudes in the atmosphere and subsequent time separation of species and identification by the mass spectrometer;
- a sample transfer system for gas mixtures, generated by the aerosol pyrolyser, to the mass spectrometer sample inlet systems.

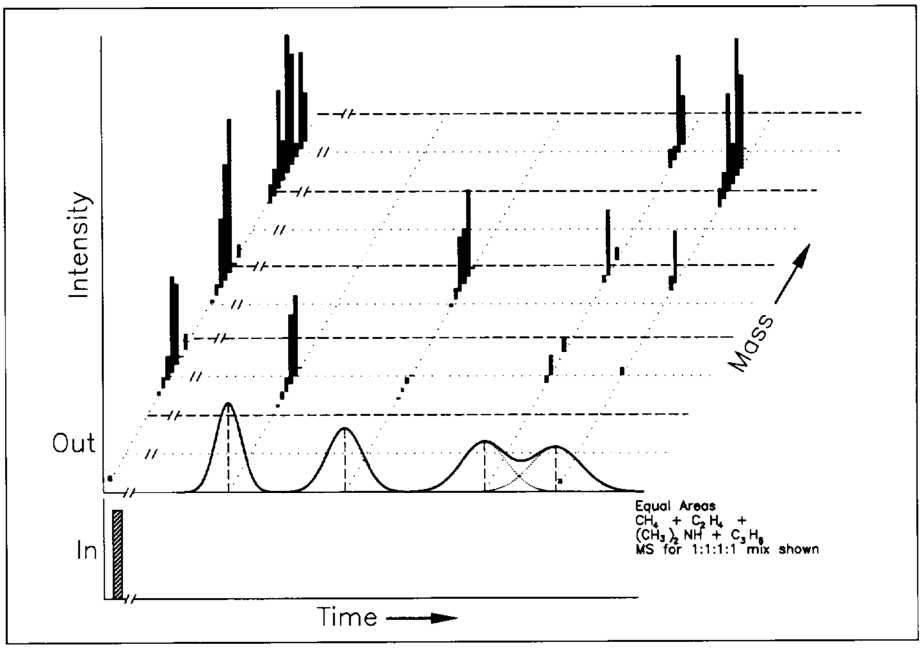


Fig. 1. Illustration of the Gas Chromatograph Mass Spectrometer operational principle. Signal intensities are shown in the ordinate *vs* time in the abscissa. Column sample injection time is shown in the first trace. The 3D plot shows signal intensities of column elutents for a 4-component sample on the abscissa and the corresponding mass spectra of the elutents in the third coordinate. The simultaneous mass spectra of all four components, i.e. without chromatographic separation, is shown at the origin and illustrates the significant signal overlap in the mass spectra.

A functional block diagram of the GCMS/ACP system is shown in Fig. 2; a schematic for the GCMS systems is shown in Fig. 3.

The mass spectrometer has five ion sources feeding a common mass analyser one ion source at a time. The first source, IS1, samples the atmosphere continuously. The second ion source, IS2, samples the ACP output, and the IS3, IS4 and IS5 ion sources are detectors for three gas chromatographic columns (GC columns). The choice is prescribed for the descent by a preprogrammed sequence.

The source connected to the direct atmospheric sample, IS1, is selected during the descent's first 30 min and at any time when no peaks are present at the output of any of the GC columns. For the analysis of the gas mixture from the ACP, the associated source will be selected and during the GC analysis of these mixtures the sequence will be identical to that associated with the atmospheric GC samples.

2.2 Gas sampling system

The gas sampling system has three subsystems: direct atmospheric sampling, the gas chromatograph and the ACP sample line. The direct atmospheric sampling and the gas chromatograph are self-contained units sharing only the mass spectrometer. The ACP sample line is connected from outside the instrument to a Pyrolyzer Transfer Line (PTL) and interfaces with both the gas chromatograph and the mass spectrometer. The direct atmospheric sampling and gas chromatograph share gas flow lines with a gas inlet port in the fore dome at the Probe apex near the stagnation point and an outlet port at the minimum pressure point at the Probe rear. Inlet and outlet ports are sealed by metal ceramic devices. All lines are evacuated after instrument calibration prior to shipment. They will be opened in sequence by redundant pyrotechnic actuators after Probe entry and ejection of the Probe Front Shield.

2.2.1 Direct atmospheric sampling

Most of the composition measurements will be obtained from direct atmospheric sampling during descent. Ambient atmospheric gas is conducted through pressure-reducing devices into the ion source, and a sample enrichment and scrubber cell will enhance trace constituent detection and rare gas analysis.

At an altitude of approximately 170 km when the Probe is ready for instrument deployment, i.e. all protective devices are jettisoned, the Atmospheric Inlet and Outlet

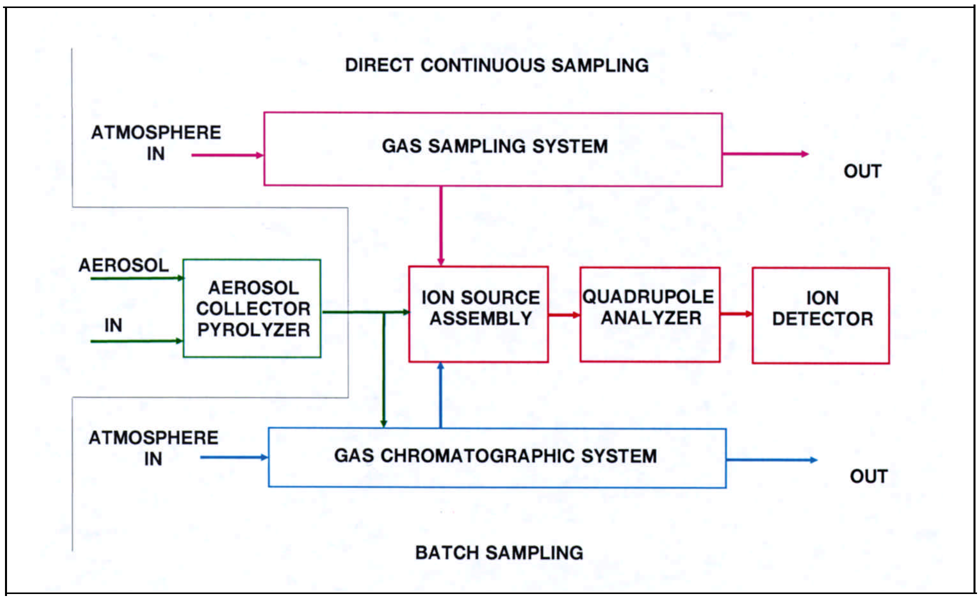


Fig. 2. System block diagram of the Gas Chromatograph Mass Spectrometer/Aerosol Collector Pyrolyser, showing the major components of the sample collection, processing and mass analyser subsystems.

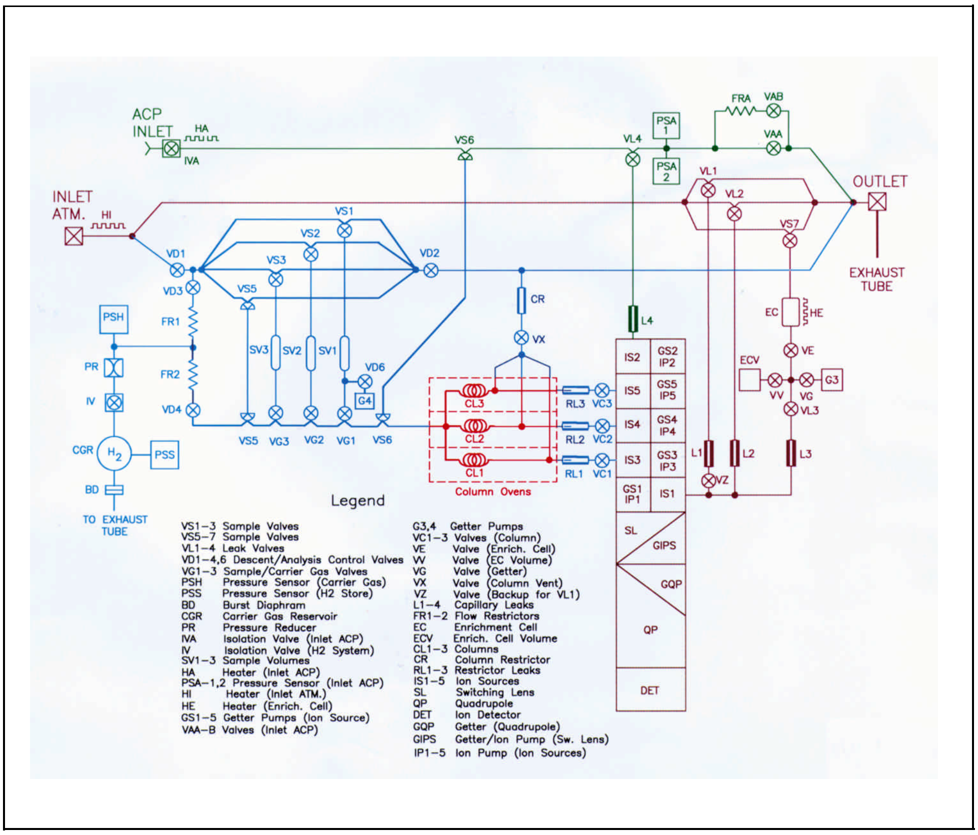


Fig. 3. Schematic of the Gas Chromatograph Mass Spectrometer. The colour scheme is used to identify the major subsystems corresponding to the block diagram shown in Fig. 2. Details of the Aerosol Collector Pyrolyser are shown in an accompanying paper in this volume.

will be opened to the atmosphere. A dynamic pressure of about 70 Pa before parachute jettison and 10 Pa after will force atmospheric gas to flow close to the ion source through the sample system tubulation and manifolds. Small quantities of atmospheric gas will be introduced from the sample system into the ion source through fixed size leaks and removed at a constant rate by chemical getters and a sputter ion pump. Noble gases will be pumped only by the sputter ion pump and at a slower rate than the reactive gases, increasing the noble gas mixing ratio in the ion source relative to the atmosphere. Laboratory calibration will establish exactly the relationship between ambient and ion source partial pressures.

The gas leaks are arrays of glass capillaries located in the ion source. Typically, seven capillaries per leak are used, with inside diameters ranging from 2 μm for the lowest conductance leak to 20 μm for the largest. Capillary arrays instead of single capillaries were chosen in order to reduce the chance of blocking by small aerosol particles. The gas conductances are selected so that the pressure in the ion source does not exceed 10^{-4} hPa in a nominal descent.

The full dynamic range of the mass spectrometer is best used when the ion source pressure is kept at the maximum operating value. Fixed size leaks do not allow this because the ambient pressure increases during descent. To prevent a large pressure change in the ion source and to accommodate a purified noble gas and an enrichment cell measurement, the direct sampling is divided into two sections. A pressure-time profile and measurement sequence are shown in Fig. 4. In Fig. 4a the change in ambient pressure is shown and predicted cloud or haze levels are also indicated. Nominal values from the Lellouch-Hunten model of the atmosphere of Titan were used. The pressure variation in ion source IS1 is shown in Fig. 4b. From time t_0 to time t_1, approximately 36 min, leak L1 will be opened by switching the microvalves VL1 and VZ (see schematic Fig. 3). While the ambient atmosphere is sampled through leak L1, the enrichment cell EC will be charged for a brief period. The enrichment cell adsorbs trace gases, e.g. high boiling point hydrocarbons and nitriles, but no nitrogen or noble gases. By opening valves VS7, VE and VV, gas flows through the cell until the evacuated volume ECV is filled. All remaining reactive gases except methane will then be removed by getter G3 after closing of valves VS7 and VV and opening VG.

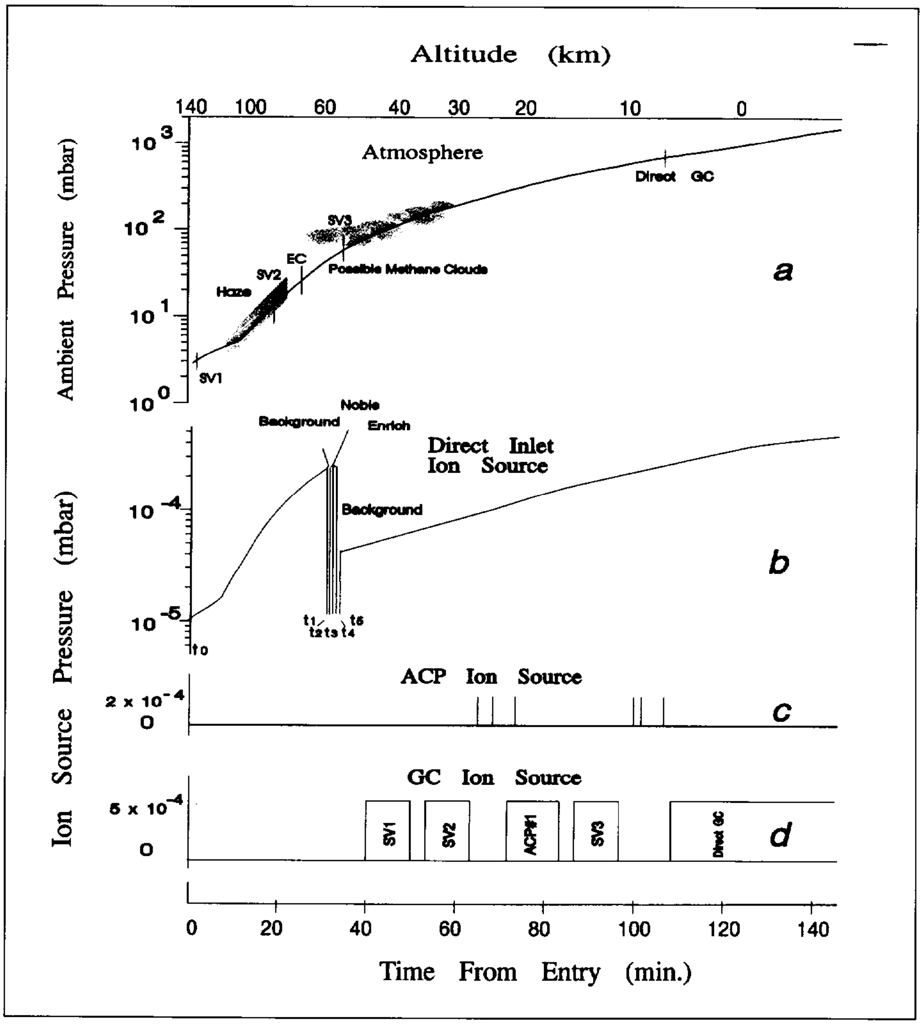


Fig. 4 Pressure *vs* time profiles of the ambient atmosphere and in the mass spectrometer ion sources during the Probe descent through Titan's atmosphere.
a: Ambient atmospheric pressure, possible cloud locations and sample enrichment cell and gas chromatograph sample collection times are also indicated.
b: Pressure in the direct sampling ion source. Noble gas and sample enrichment gas analyser times are also indicated.
c: ACP ion source dedicated sampling time.
d: Operating times of the three ion sources dedicated to the gas chromatographic columns.

The gas flow through leak L1 is discontinued after 36 min by closing valves VL1 and VZ and remaining gas in the ion source is pumped out, leaving only background pressure. Following the background pressure measurement, the enrichment cell will be isolated by closing valve VE and heated to desorb the collected trace gases. Simultaneously, the gas mixture residing between the valves VV, VE, VG and VL3 will be introduced into the ion source IS1 through L3 for noble gas analysis. The gas content of the enrichment cell will then be added to the gas mixture for analysis by opening valve VE. When the enrichment cell and noble gas analysis are complete, the subsystem will be isolated from the ion source by closing valve VL3 and background pressure is observed again. At time t_5 direct leak L2 will be activated until the end of the mission. Sampling for the first 36 min through leak L1 will be continuous and at a high rate. The direct atmospheric sampling through leak L2 will be interrupted repeatedly by sampling sequences for the analysis of elutents from the gas chromatographic columns and ACP products.

2.2.2 *Gas chromatographic analysis*

Gas chromatography allows, under suitable conditions, the gas phase separation of complex mixtures of hydrocarbons, nitriles and permanent gases, including carbon monoxide.

A small amount of a mixture of gases is introduced into a carrier gas stream that flows continuously through the column. Each component in the mixture, in the ideal case, elutes from the column outlet at a different time. A detector at the outlet gives a signal related to the quantity or concentration of the components of the gas mixture.

Difficulties in data interpretation result when universal detectors are used because the exact chemical composition of the elutent is not known. A mass spectrometer eliminates most of the difficulties (see illustration in Fig. 1). Advantages and disadvantages of combined GCMS instrument techniques have been discussed in great detail in the technical literature and the arguments apply to this application as well. One disadvantage is the increased complexity of the instrument which must be of particular concern here because of the specific mission environment. The short time available for sampling and analysis, long time reliability and severe limits placed on mass and power require special considerations.

The use of open capillary columns (Do & Raulin, 1989, 1990, 1992; de Vanssay et al., 1994; Aflalaye et al., 1995) and of packed columns (de Vanssay et al., 1994) has been considered. Best instrument performance and moderate instrument complexity have to be balanced in this design. Three chromatographic columns with different properties are used and operated in parallel to cover the range of expected atmospheric species. One column will separate CO and N_2 and other permanent gases. A second column will separate nitriles and other organics with up to three carbon atoms. A third column will provide the separation of C3 to C8 saturated and unsaturated hydrocarbons and nitriles of up to C4. A silica steel micropacked GC column 2 m in length with 0.75 mm internal diameter (for column 1) and silica steel wall coated open tubular (WCOT) GC capillary columns 10 m and 14 m in length with 0.18 mm internal diameter (for columns 2 and 3), were found to be most suitable. The columns are wound in a 178 mm diameter coil on high temperature foil heaters. A thermally isolated oven will enclose each column to allow efficient heating. The columns will be operated at 0.18 MPa inlet pressure and the outlet is vented through a flow restrictor to the ambient atmosphere.

Hydrogen was selected as carrier gas because of efficient storage and pumping. It is stored in a hydride metal alloy enclosed in a stainless steel housing. The amount of hydrogen required for the GC operation, approximately 3 litres, is stored in 100 g of hydride metal alloy, assuming 180 min descent time and a 50% reserve.

The hydrogen carrier gas reservoir CGR will be equipped with an injection valve IV, shown schematically in Fig. 3. The valve is solenoid-operated and similar in design to the microvalves. The valve plunger punctures a diaphragm and initiates carrier gas flow. A pressure regulator PR controls the flow through the flow restrictors and columns. For safety, a burst diaphragm BP installed in the CGR is set to burst at 3 MPa.

The Probe does not spend sufficient time in the altitude region between 176 km and 60 km for repeated gas chromatographic analysis. To overcome this difficulty, samples will be collected at specified times during the descent through the upper region of the atmosphere in sample volumes SV1 to SV3 for later analysis. Samples will also be injected directly from the atmosphere into the carrier gas flow path of the GC near the surface.

At system initiation, hydrogen carrier gas flows from the hydrogen reservoir CGR (see Fig. 3), through the injection valve IV, the pressure regulator PR, flow restrictor FR2, valve VD4 past the sample injection valves VS5, VG 1, 2, 3, then splits into the three GC columns. A fraction of the flow exiting the columns will be split off and conducted through capillary leak arrays into the ion sources.

The atmospheric samples collected in the sample volumes will be analysed one at a time by first flushing the inlet manifold between valves VD1 and VD2 with carrier gas and then operating valve pairs VS1, VG1, etc for several milliseconds to allow the sample volume to be discharged into the carrier gas stream. The GC analysis time allowed per sample is about 10 min. Direct sample injection will be accomplished in a similar fashion by first closing VD1 and VD2 and injecting part of the trapped sample gas through valve VS5 by redirecting the carrier gas flow through VD3 for a short time interval. Injection of the ACP sample from the sample transfer manifold into the GC column will be accomplished through valve VS6 in a similar manner. A time profile of the complete GC sampling sequence is shown in Fig. 4d.

2.3 Aerosol Collector Pyrolyser analysis

ACP operation and details of the sample transfer are described in a separate paper in this volume. The pyrolysis products will be provided through a sample transfer line made of 0.5 mm internal diameter nickel tube connected to an injection valve IVA (ACP Inlet in Fig. 3) at the centre of the instrument housing. Internally, a feed tube connects to the GC inlet valve VS6, the direct inlet valve VL4 and to the outlet via valves VAA, VAB and flow restrictor FRA.

The ACP line will be opened just prior to the first sample transfer. After gas flow stabilisation, direct gas analysis begins using the dedicated ion source IS2. After analysis is completed, sample gas in the ACP line is vented through the outlet and the line is refilled with the next sample. The sample for the gas chromatograph is injected by opening valve VS6 for a short time interval to superimpose the sample on the carrier gas stream as described in the previous section. The time line for the ACP sampling is shown in Fig. 4c.

2.4 Post surface impact analysis

It is likely that Huygens will continue to operate for a short time after surface impact. As the nature of the surface is not known, it is hard to predict the specific contact the Probe will make. The most probable landing position is expected to be upright, which is also optimum for the instrument. In case of a landing on a liquid surface, the heated inlet tube will be submerged in the liquid, which will rapidly evaporate in the inlet tube and the vapours will flow through the inlet lines. Rapid direct sampling through leak L2 will provide composition measurements of the vapour. In case of a landing on a solid surface, the surface will be heated locally by the inlet tube and volatised gases will flow through the inlet lines and be available for analysis.

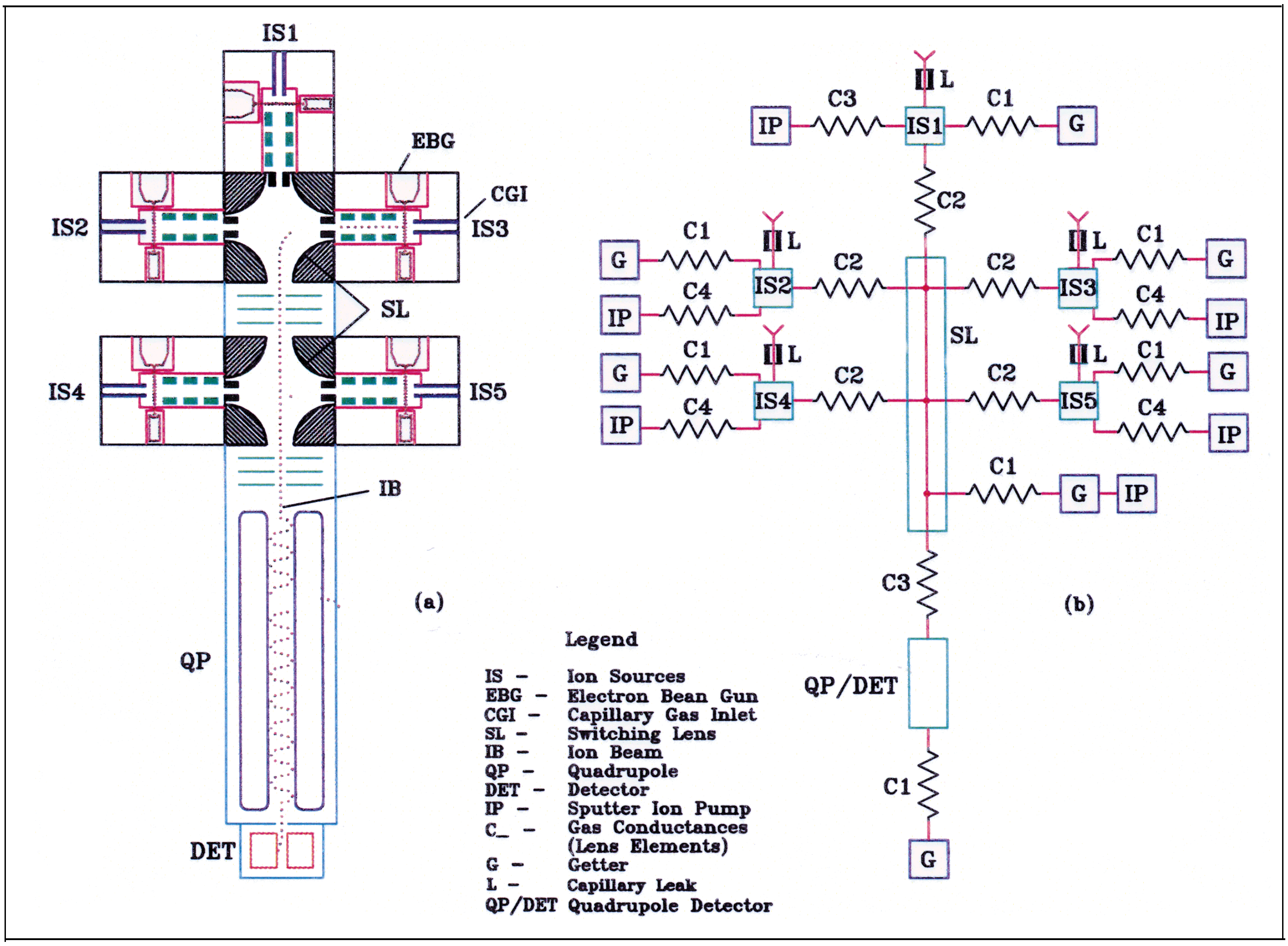
GC analysis will be initiated through valve VS5 as described above if the Probe survives for more than 2 min. The surface sampling mode will be initiated by an altimeter signal shortly before surface impact.

2.5 Ion sources

Electron impact ionisation is used in the miniaturised ion sources. A well collimated electron beam is directed through the ionisation region into which the gas stream is conducted by the capillary leaks. The flow paths are short because the valves and capillary leaks are mounted directly on the ion sources. The electron guns have heated filaments of 0.075 mm-diameter 97% tungsten, 3% rhenium wire and require approximately 1 W of power. The electron beam energies can be chosen from two preselected values (25 eV or 70 eV) to permit species identification and discrimination by observing energy dependent fractionation. A typical electron beam current is 80 µA. Ions are focused and transmitted into a quadrupole switching lens assembly by multi-element ion lenses of small aperture. Quadrupole switching lenses are operated as ion beam deflectors. Any one of the five ion beams can be deflected by the switching lens into the quadrupole mass analyser at any time. Switching is accomplished in microseconds by changing the bias voltages to the appropriate values for the ion source of choice. The ion source arrangement and the switching lens system are shown schematically in Fig. 5a.

Sample gas decoupling of the ionisation regions is achieved by differential pumping. The principle of sample decoupling is shown in a schematic diagram in Fig. 5b. By

Fig. 5. Illustrations of the ion source configuration and the differential vacuum pumping system.



designing the gas conductances C such that their ratios Cl/C2 and Cl/C3 are approximately 10^3 and 10^2, respectively, the separation in partial pressures between ionisation regions is 10^6. For example, gas in ion source IS1 with a partial pressure of 10^{-6} hPa will be seen by the other ion sources as a partial pressure of 10^{-12} hPa, and the pressure in the quadrupole mass filter and detector region is below 10^{-6} hPa to eliminate ion scattering. The size of conductances C2 is determined by the ion lens apertures, which are designed to be long and narrow. The pumping speed of the getters and the sputter ion pumps determine the size of conductances Cl and C4. An ion source, showing the electron and ion lens arrangement, and an ion source system, showing the individual ion source and the switching lenses in the partially assembled ion source housing, are seen in Fig. 6 and Fig. 7, respectively.

2.6 Quadrupole mass filter and ion detector

The quadrupole mass filter accepts the ion beam generated by the ion sources transmitting only ions of a chosen charge to mass ratio. The selected ion beams are focused on two secondary electron multiplier ion detectors. The nominal mass range measured by the instrument is 2-141 dalton. The quadrupole rods are excited by radio frequency (VAC) and direct current (VDC) potentials which together create a dynamic electric field within the quadrupole region that controls the transmitted mass (m/e value) and the resolution. A mass scan is executed by varying the radio frequency potential VAC to satisfy the relationship $M=0.55\ VAC/f^2$ where VAC is in volts, f in

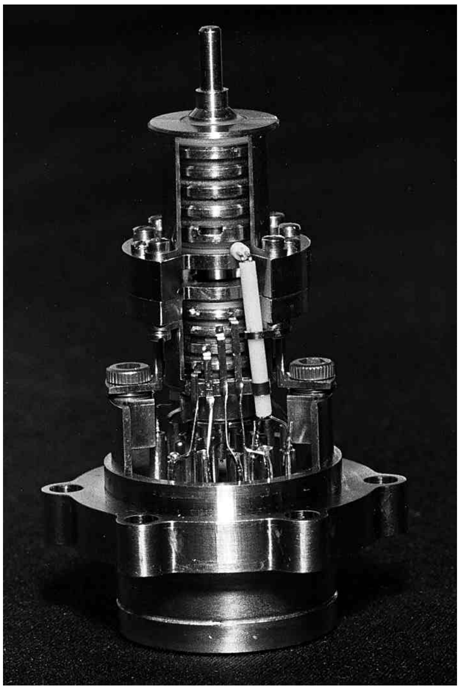


Fig. 6. An ion source, showing the electron and ion focusing lenses. The overall height is 63 mm.

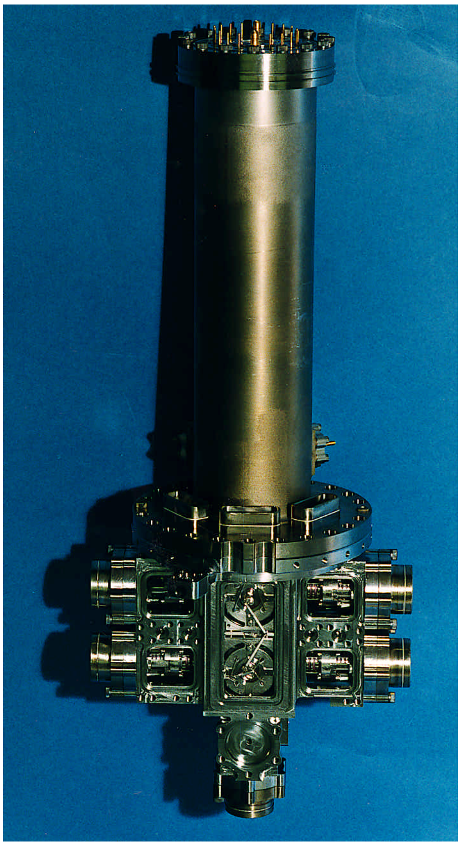


Fig. 7. The ion source system, showing the individual ion sources and the switching lenses in the partially assembled ion source housing before installation of the getter housings and the gas inlet manifolds. The overall length is 357 mm.

MHz, and M in dalton. The resolution will be controlled over the mass range by programming the ratio of VDC to VAC to maintain the resolving power defined by a crosstalk criterion appropriate for that mass range. More information about the operating principle of quadrupole mass filters can be found in the technical literature (e.g. Dawson, 1976).

The transmission efficiency will be 100%, resulting in flat top mass peaks over the mass range of interest. This allows a mass scan mode in which each mass is monitored by a single step.

In another operating mode, the DC voltage will be reduced to zero, which creates a high pass filter giving the sum of all masses greater than, for example, 2 or 141 dalton. This feature allows the use of the mass spectrometer as a non-specific GC-detector excluding the detection of the abundant hydrogen ions produced by the GC carrier gas.

The ions passing the mass filter will be detected by a pair of continuous dynode secondary electron multipliers with effective entrance aperture sizes differing by a factor of $3x10^3$. Charge pulses at the anodes of the secondary electron multipliers are amplified and counted. The background noise of the secondary electron multipliers is approximately one count per minute. The upper count rate is limited to approximately $3x10^7$ count/s by the pulse width of the anode pulses of the secondary electron multipliers. The instrument sensitivity for 100% ion transmission is approximately $1x10^{14}$ count/s per hPa. Secondary electron multiplier background count rates of one count per minute or less yields a detection threshold of $1.7x10^{-16}$ hPa partial pressure in the ion source region for a signal to background count ratio of unity. The maximum pressure level in the ionisation region is limited by free path conditions to about 10^{-3} hPa. In the low mass range (<46 dalton), the lower detection limit is often not realisable because of background gases emitted from the surrounding surfaces or because of interference at some mass numbers from other gases present in high concentrations. Typical background gases in the ion source are H_2, CH_4, H_2O, CO and CO_2. The exact sensitivity is established by calibration and varies with species because of differing ionisation efficiencies for neutrals, and the conversion efficiency at the secondary electron multiplier. The detector assembly, consisting of the entrance lenses, support structure and the continuous channel secondary electron multiplier, is shown in Fig. 8.

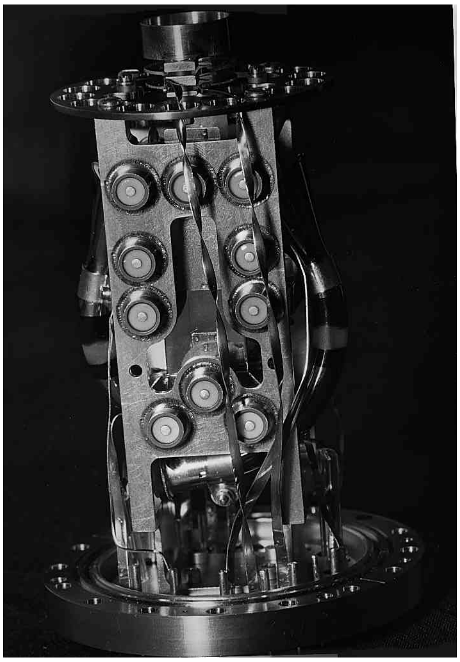


Fig. 8. The ion detector assembly, showing the entrance lenses, the support structure and the location of the continuous channel secondary electron multipliers. Overall length is 110 mm.

2.7 Pumping systems

The pumps establish a flow of sample gas through the ion sources when a sampling device is opened and they remove the gas from the ion source regions after analysis and closure. Non-evaporable getters and sputter ion pumps are used because of simple adaptation to space flight systems. The sputter ion pumps depend only on electrical power for operation and work without moving parts. Hydrogen is sorbed reversibly at a very high rate and in very large quantities by the getter material, while nitrogen is efficiently pumped by irreversible bonding. The getter material is sintered titanium and molybdenum powder. The sorption capacity for hydrogen is ~20 hPa litre/g for an equilibrium pressure of 10^{-4} hPa at a worst-case temperature of 200°C. More favourable conditions exist at the expected operating temperature of <100°C. The getters, after activation in a vacuum, will remain activated indefinitely at room temperature. The components of a getter pump assembly consisting of the getter wafers, heat shields and the housing are shown in Fig. 9.

Uncertainties exist about the concentration of argon and methane in Titan's atmosphere. These gases will be pumped by sputter ion pumps. Synthesis of hydrocarbons in the sputter ion pumps is eliminated by special processing of the cathodes. A partially assembled sputter ion pump, the anode, cathode and housing without magnet assembly, is shown in Fig. 10.

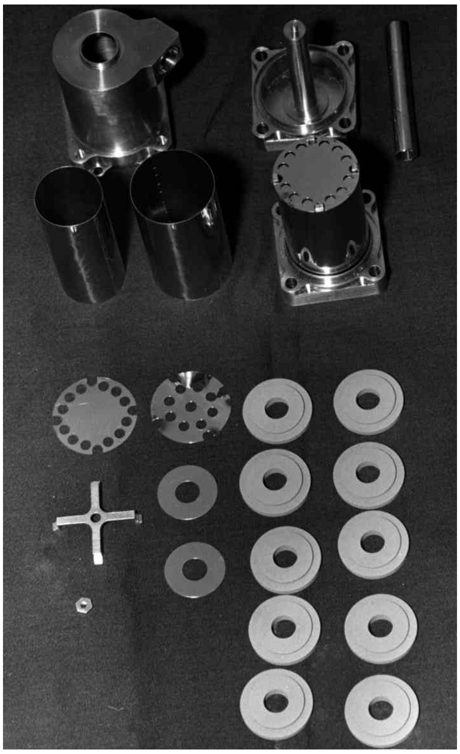


Fig. 9. Components of a getter pump assembly consisting of getter wafers, heat shields and housing. The wafer diameter is 25 mm.

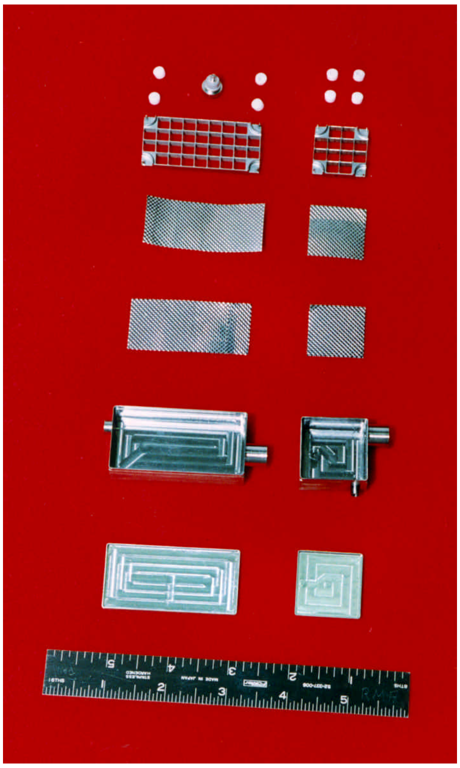


Fig. 10. A partially assembled sputter ion pump, showing the anode grid structure, the cathode and the housing. (Indicated dimensions are in inches.)

2.8 Electronic system

The electronics system block diagram is shown in Fig. 11. The various subsystems required to control the sample flow, to power the sensor and ion detectors and to process the output signal are under the control of a microcomputer. Instrument potentials are produced by a number of programmable, floating-secondary DC-DC converters that are configured for each measurement. Telemetry and command streams connect to the spacecraft through redundant serial interfaces. The electronics system provides the flexibility to accommodate the diverse measurement and testing requirements.

The pyrotechnic devices used to break the ceramic seal in the sample inlet and outlet systems are fired by the Probe pyro bus. The sample-sequencing microvalves are powered by switching circuits under microcomputer control. Each of the five ion source supplies contains a filament emission regulator and electrode supply to provide the required voltages and currents. Fast switching of the ion beam deflectors is accomplished by high speed bipolar electronic switches.

The quadrupole VAC and VDC potentials are generated in a dedicated supply. Before each measurement, the microcomputer calculates the proper amplitudes and frequency step for the VAC potential. An auto-tune algorithm is incorporated into the control software to ensure that changes such as component ageing in the supply do not affect mass tuning and resolution.

Current pulses from the secondary electron multiplier are amplified by a low noise trans-resistance amplifier and counted. The counts are held in a 32-bit register, which is then read by the microcomputer. A parallel electrometer channel measures

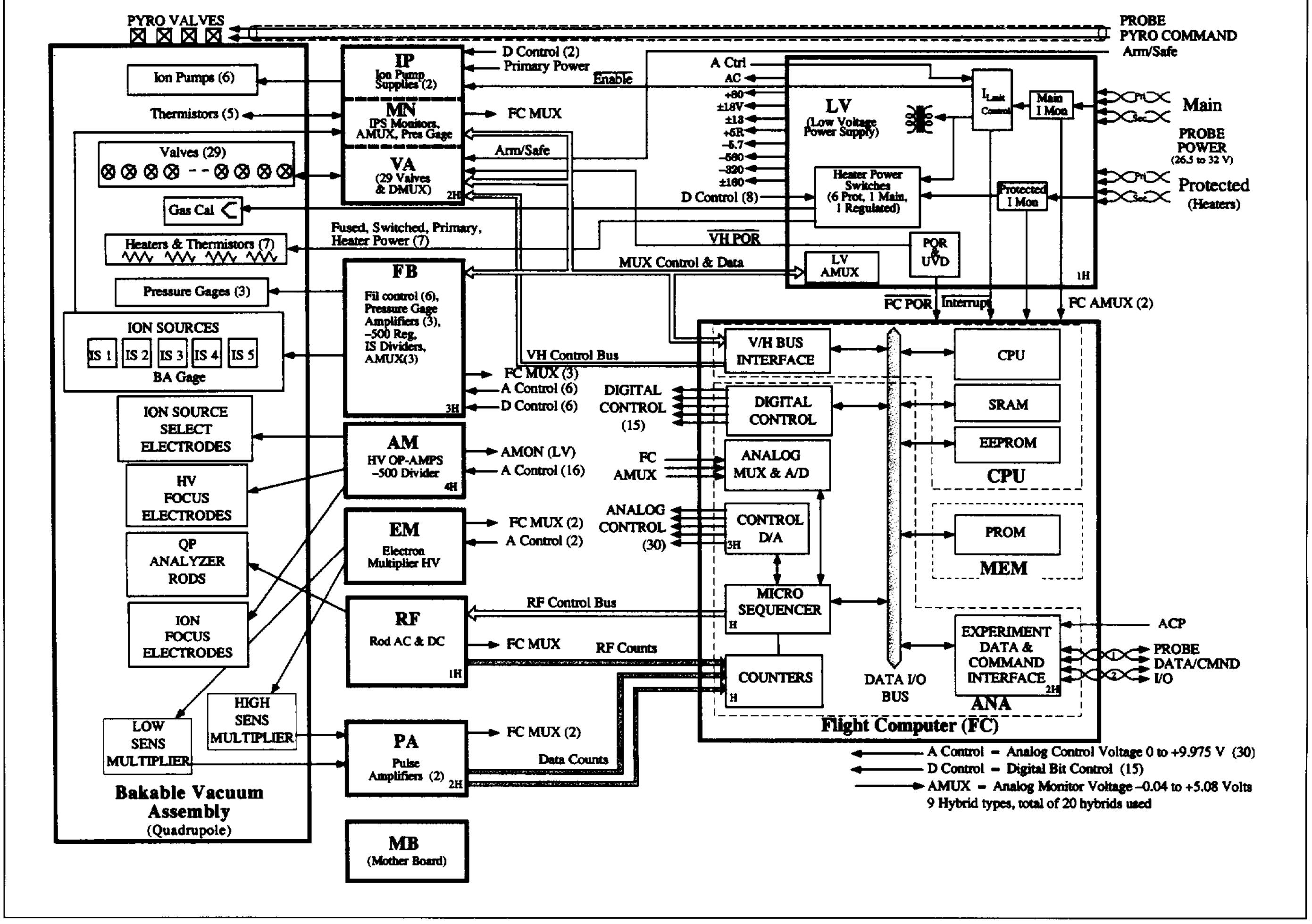


Fig. 11. Electronics block diagram showing major digital and analogue circuit subsystems.

multiplier current when the maximum count rate is approached, allowing an inflight gain check.

A 1750A microprocessor controls and sequences the instrument in accordance with software instructions contained in programmable read-only memory (PROM). Control of the many subsystems is accomplished by writing to a separate, high speed sensor data bus. The instrument software was written in a high level language (ADA) whenever possible and in assembly language when speed is crucial. Code has been developed in a modular, top-down manner to increase testability and improve maintainability. The instrument will receive commands and transmit (science and housekeeping data) through the Probe Command and Data Management System (CDMS) interfaces.

Power to the instrument is derived from the common +28 V spacecraft bus; inrush current limiting and overload protection is provided in the main power converter. The spacecraft bus voltage is transformed by a DC-DC converter to a number of standard secondary potentials that power the subsystems. To minimise size and mass of the electronics system, approximately 80% of the electronic circuits are packaged in hybrids. A typical hybrid circuit, the microsequencer, is shown in Fig. 12.

2.9 Mechanical configuration

The mechanical layout of the instrument is shown in Fig. 13 and Fig. 14. The ion source and mass analyser assembly constitute the main body of the sensor system. Getter pumps and sputter ion pumps are directly mounted to the ion sources at the

Fig. 12. An unsealed electronics circuit packaged in hybrid form. The circuit is the microsequencer subsystem. Side dimension is 57 mm.

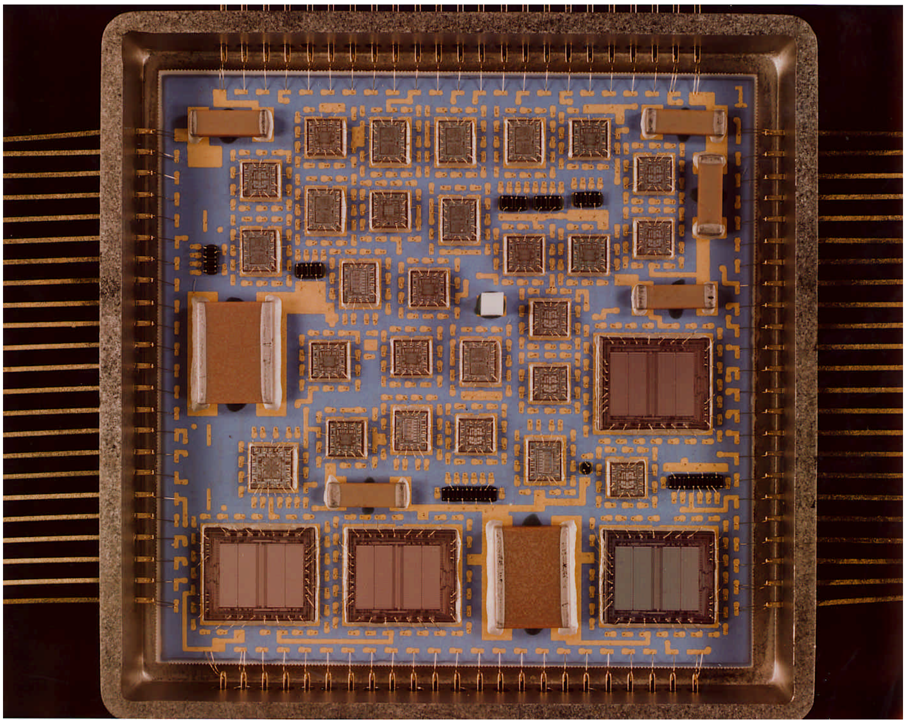
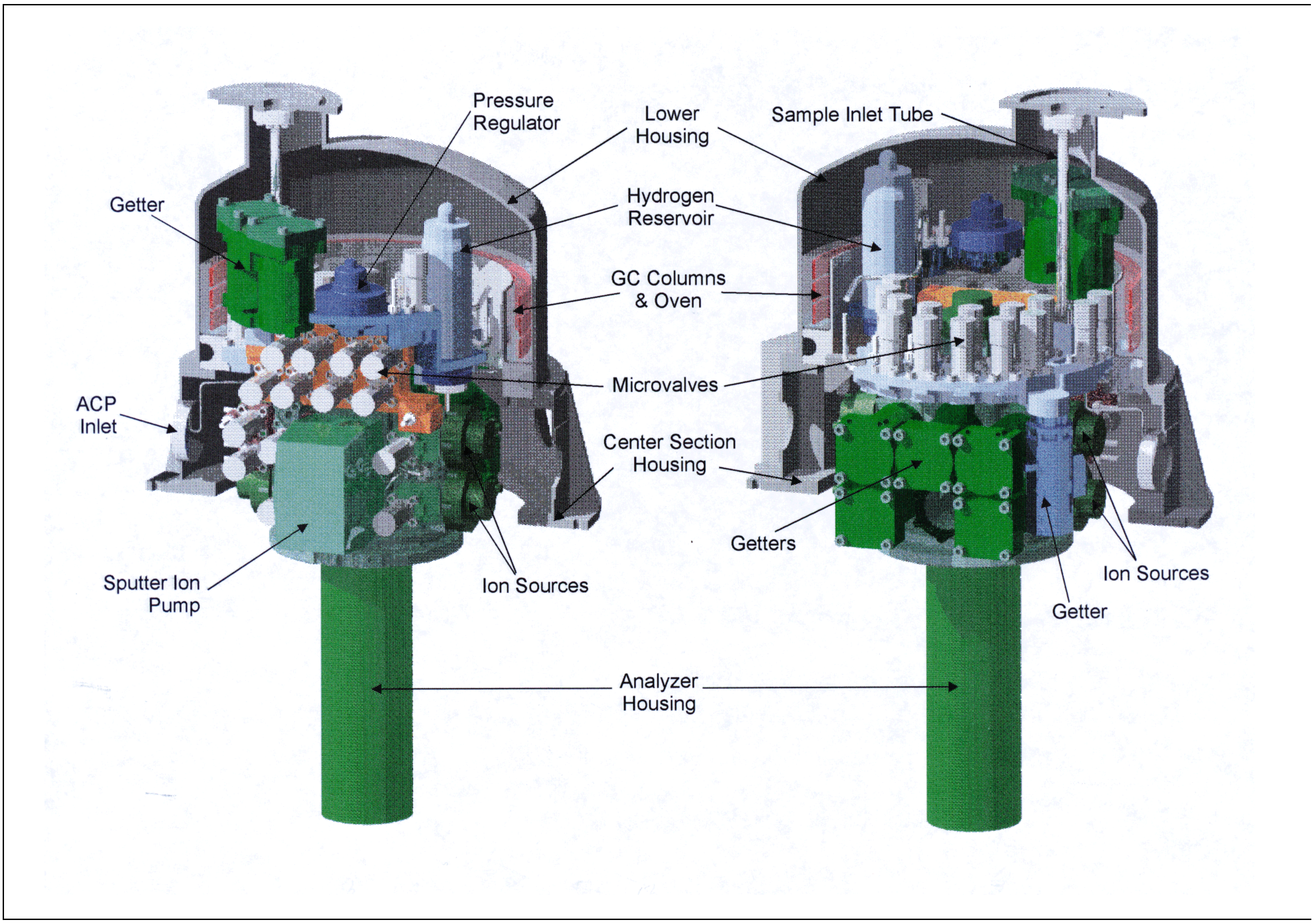


Fig. 13. Computer-generated cutaway views of the Gas Chromatograph Mass Spectrometer, gas sampling, mass analyser and vacuum pumping systems. Major components are identified in the figure and highlighted by artificial colour.



upper part of the assembly for compactness. The GC columns and the gas sampling system are concentrically arranged around the ion source assembly. The gas inlet tube, shown in Fig. 13, extends forward to penetrate the fore dome. The electronics system is located below the gas sampling system. The electronics support structure and the electronic circuit boards are shown in Fig. 14. The structure is made of aluminium alloy and is attached to the centre section of the instrument housing.

The instrument housing is also made of aluminium alloy and consists of three sections, as shown in Fig. 15. The lower housing encloses the sampling system and the ion sources. It also provides the inlet port interface with the fore dome. The upper housing covers the electronics system. The centre housing provides the mounting support for all instrument components and most external interfaces. It is hermetically sealed by metal seals. The overall helium leak rates of <10^{-8} cm^3/s is sufficient to maintain the housing pressurised for more than ten years. The housing is designed to withstand 0.15 MPa internal pressurisation and an external pressure of 0.15 MPa above the internal pressure. For flight, the housing will be filled with dry nitrogen to 0.12 MPa.

The instrument is mounted on the Experiment Platform of the probe via a flange at the centre housing. The sample inlet line penetrates the fore dome near the stagnation point outside of the boundary layer of the gas flow around the Probe body. The sample outlet port is at the rear section of the housing. ACP's mounting position on the Experiment Platform is adjacent to the GCMS for efficient sample transfer.

2.10 Sampling strategy

Throughout the entire descent of Huygens through Titan's atmosphere, GCMS will perform a measurement each 5.008 ms and select from one of the five ion sources and process that measurement for telemetry. The mass range measured for each ion source is determined by a stored sequence. The sequence also determines which ion sources are enabled for sampling during various stages of the descent. The sequence of measurements is shown in Fig. 4. During the first 36 min of the descent, the direct inlet into a mass spectrometer ion source is analysed and atmospheric samples are collected for subsequent analysis by GCMS. During the same interval, an atmospheric sample is processed to enrich the noble gas content to extend the sensitivity of the noble gas ratio analysis. During the descent interval at 40-95 min, the collected samples are analysed sequentially by the GCMS, as indicated in Fig. 4, panel 'd'. The ACP output is analysed both directly by MS and by GCMS during intervening periods. In each of these analyses, the characteristics of the mass scan can be programmed.

Each integral mass number from 2 to 141 dalton is sampled sequentially. During all mass scans, the total output from each ion source (with carrier gas rejected) will be

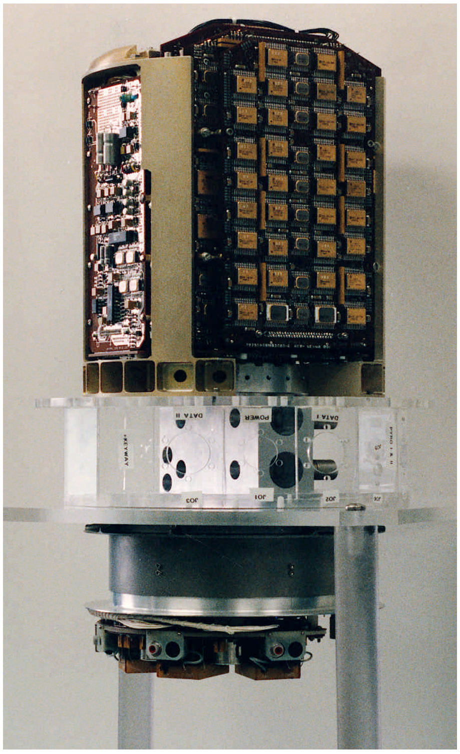


Fig. 14. The Engineering Model electronics package and support structure. Shown in front is the Programmable Read-Only Memory (PROM) board.

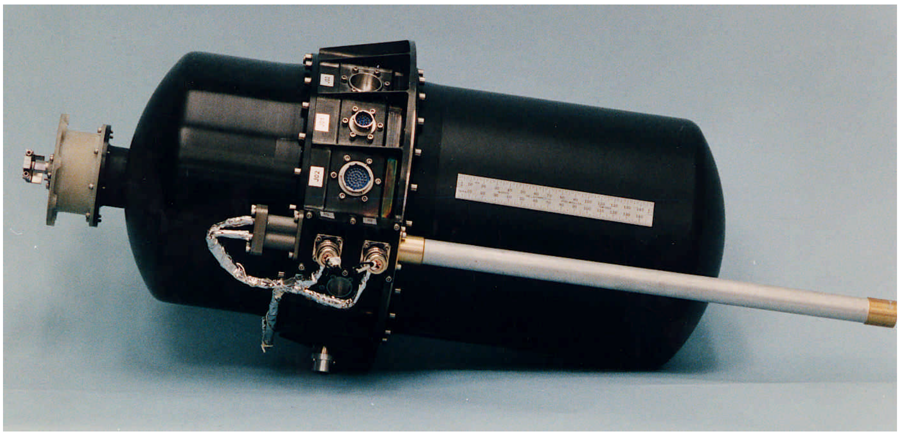


Fig. 15. The assembled Engineering Model GCMS. The lower housing encloses the sampling system and the ion sources, while the upper housing covers the electronics system. The gas inlet port is at the dome of the lower housing. The sample gas is vented through a glassfibre tube toward the rear of the Probe. The housing is hermetically sealed and pressurised to 0.12 MPa during flight. (Indicated dimensions are in mm.)

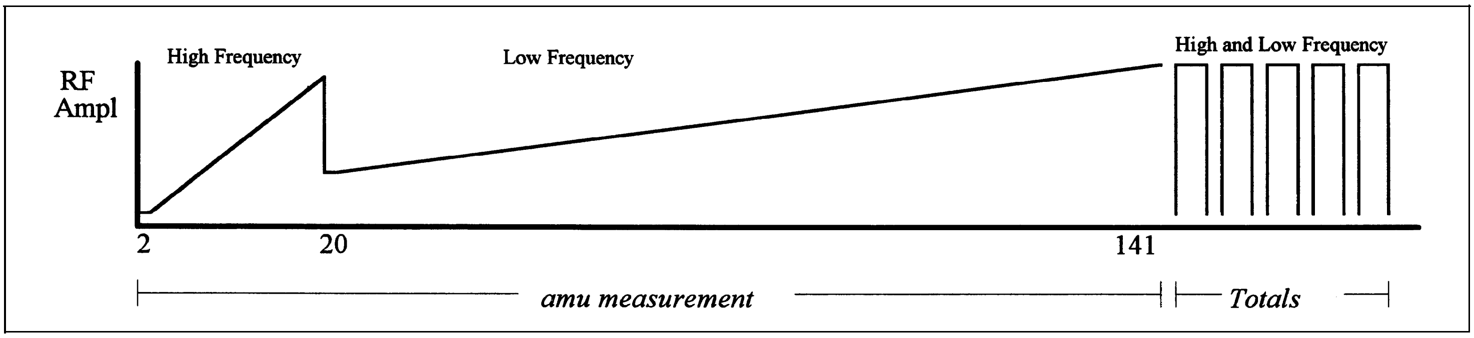


Fig. 16. Illustration of a 'Full Scan' of the mass analyser from 2 to 141 dalton.

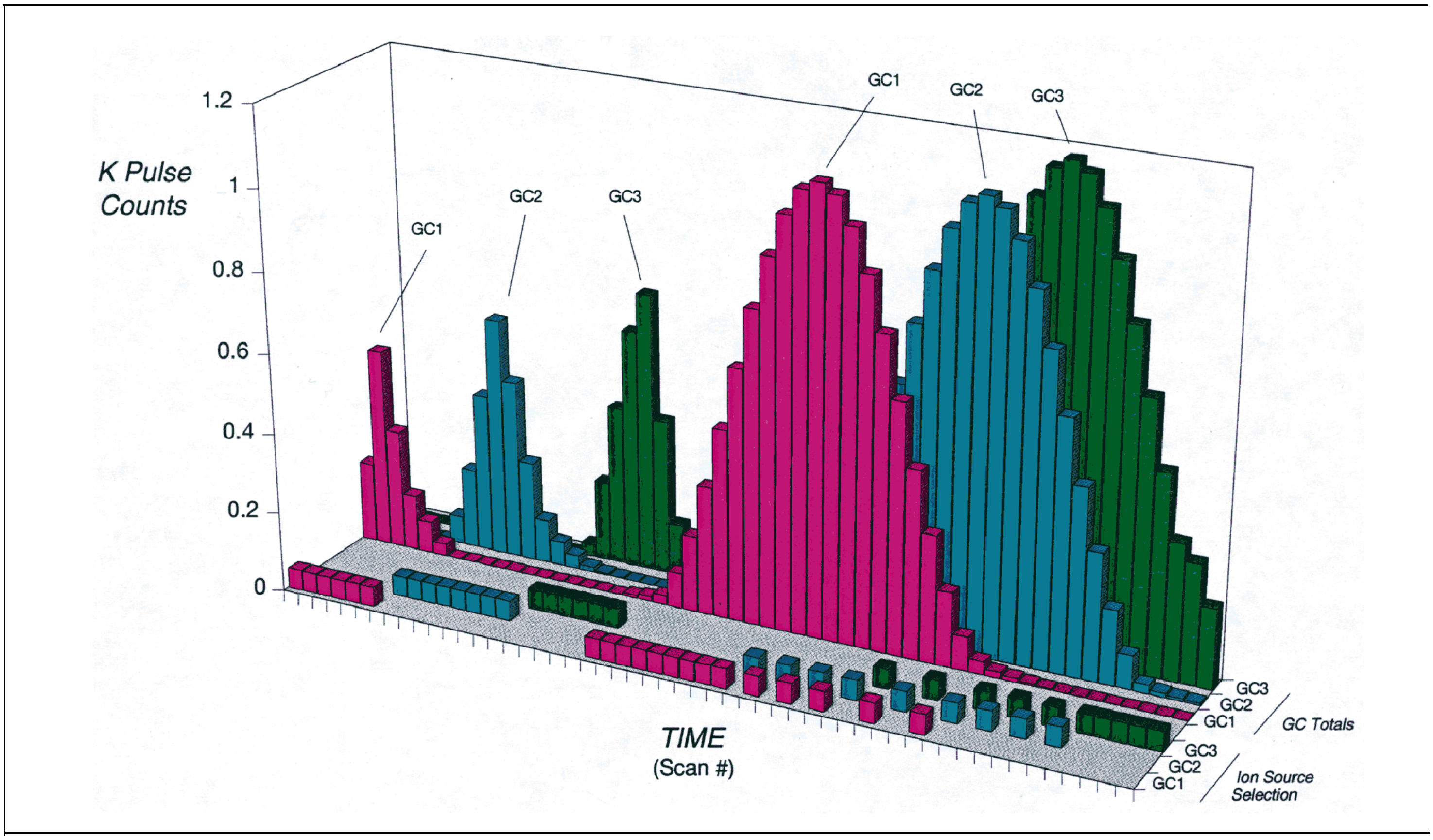
measured both for the purpose of providing a continuous record of the total density in each ion source and for the purpose of selecting the ion source to be sampled when an unknown gas mixture is flowing through the GC columns. An illustration of the Full Scan is shown in Fig. 16.

For the direct mass spectrometer measurements, 936.5 ms are required to complete a Full Scan. This resolution is more than adequate to define the atmospheric profile defined by the descent rate and will be used. The operation of the instrument when three GC columns are' simultaneously on range is shown in Fig. 17.

A diagnostic scan of the full mass range in l/8 dalton increments will be made at times during the descent when the rate of change of the atmospheric samples is lowest. This diagnostic scan and others will be interleaved with the atmospheric measurements.

The ACP output will be sampled both directly and through one of the GC columns at the appropriate time in the descent, as outlined in the accompanying paper describing the ACP and its operation. The same mass scan capabilities available for GCMS measurements are available to the ACP instrument.

Fig. 17. An illustration of the operation of the instrument when three GC columns are simultaneously on range.



2.11 Data format

GCMS is intrinsically capable of generating much more data than can be transmitted within the bandwidth allocated to it. Counter data are produced as two 16-bit words each integration period, one from the high sensitivity and one from the low sensitivity secondary electron multiplier. Only data from one counter are selected for telemetry. The data are compressed by taking the square root above a pulse count rate of 2.56×10^4/s to yield 8 bits of counter data per integration period, and one bit is added for counter identification.

Even with data compression, data are produced at approximately twice the available rate of a single telemetry channel assigned to the instrument. For this reason, the data will be sent alternately to the two (redundant) channels. If both telemetry channels function, all data will be recovered. If one channel fails, the effect will be to reduce the temporal resolution of the science data.

The data are configured as subpackets within the standard Huygens Probe telemetry packet. The GCMS is allotted 15 telemetry packets per 16 s cycle; each packet is 126 octets in length, but seven of those are reserved for packet header and error correction. This results in an actual data rate available to the GCMS of 885 bit/s per channel.

- Science Data Subpacket: data from one mass scan is packetised along with time tag information and is sent to telemetry once every 936.5 ms. This subpacket contains 1488 bits, for a data rate of 1589 bit/s.
- Housekeeping Data Subpackets: three different subpackets are used for low, medium and high speed housekeeping data. The total of the three types is approximately 100 bit/s.
- Acknowledge Subpackets: these are used to send confirmation of external events such as ACP sync pulses and telecommands. Each subpacket consists of 32 bits.

Subpacket synchronisation and descent sequence monitoring data consume an additional 52 bit/s (for both channels). This results in a total GCMS data production rate of approximately 1741 bit/s, versus the available telemetry of 1770 bit/s for two channels used alternately. If the Probe retrieves data faster than science data are being produced, GCMS will insert idle subpackets containing housekeeping data.

3. Instrument Calibration

In order to determine the overall system transfer characteristics, the instrument was calibrated on a dynamic flow system where the time, pressure and temperature profile encountered during descent was simulated. Gas mixtures containing known mixing ratios of gases were introduced into the high pressure flow system of the sample inlet system of the flight instrument. The design of the sample inlet system allows complete instrument calibration as it is used in flight. Components with limited operational life time, i.e. getter materials and the sputter ion pumps, were replaced after calibration. All pumps are designed to operate in a conductance limited mode so that small changes in pump performance will have a negligible effect on the instrument transfer function.

The calibration system consists of two parts: the high pressure gas flow and sample mixing system and the ultra high vacuum pumping stand. The flight instrument inlet and outlet ports are connected directly with vacuum flanges to the appropriate terminals of the high pressure gas flow system. All lines are thermally isolated and the gas temperature is controlled by heaters and heat exchangers. Absolute system pressure and the differential pressure across the inlet are monitored with precision pressure gauges. The gas flow will be adjusted so that the differential pressure is equal to the Probe stagnation pressure expected in flight. Trace gas mixtures were added through the calibration gas line. The exact quantity of added calibration gas is determined by measuring the gas flow with flow meters and the pressure at the injection port.

4. Instrument Summary

Science objectives, instrument operating characteristics and the required Probe resources are summarised in Tables 2-4.

Table 2. GCMS science objectives.

Objective	*Measurement*
1. Atmospheric Composition	Abundances of all constituents within the mass range of the instrument with mixing ratios $>10^{-8}$, selected species to 10^{-10}.
2. Atmospheric Origin.	Discrimination between primordial and radiogenic argon. Surface composition. Other noble gas abundances. Value of D/H.
3. Atmospheric and Interior Evolution.	Major element isotopes. Surface composition. Noble gas abundances. CO vertical distribution.
4. Chemical Evolution.	Abundances of organic compounds. Variations with altitude. Surface composition.

Table 3. GCMS operating characteristics.

Gas Sampling:	1. Continuous direct atmospheric gas sampling. 2. Batch sampling for GCMS analysis, distributed over descent altitude. 3. Sample enrichment for MS (100-1000× enrichment).
Ambient Pressure Range:	1-1500 hPa.
Altitude Above Surface:	176-0 km.
GC System:	3 parallel columns with H_2 carrier gas. Independent MS ion source detection.
Mass Analyzer:	Quadrupole Mass Filter.
Ion Source:	Five sources, electron impact ionisation. Maximum operating pressure 1×10^{-3} hPa H_2, 5×10^{-4} hPa N_2.
Ion Detector:	Dual Secondary Electron Multipliers, pulse counting and analogue current mode.
Background Noise:	1 count/min.
Mass Range:	2-141 dalton.
Sensitivity:	1×10^{14} count/s/hPa source pressure.
Dynamic Range:	$\geq1\times10^{8}$.
Resolution/Crosstalk:	1×10^{-6} for adjacent half mass up to 60 dalton, less for higher mass.

Table 4. Probe resources required for GCMS.

Data Rate:	15 packets per cycle.
Viewing Requirements:	1. Sample inlet near stagnation point. 2. Sample outlet near minimum pressure point (e.g. inside Probe body).
Deployment Mechanisms:	1. Metal ceramic breakoff caps, pyrotechnically operated. 2. Valves, solenoid operated.
Altitude Information:	Obtained from altimeter data provided by Probe or ambient pressure desired near surface.
Temperature Range:	-20°C to +50°C operating, -20°C to +60 storage.
Power:	41 W average, 71 W peak.
Energy:	110 Wh.
I (Max):	1.68 A (main), 1.32 A (protected).
Mass:	17.3 kg.
Size:	Cylindrical, 198 mm diameter, 470 mm high. Mounting flange bolt circle 248 mm.

Acknowledgements

The dedication and effort of many people have made this complex and difficult experiment possible. The Experimenter Team wishes to acknowledge particularly the contributions of the engineers and technicians at the Goddard Space Flight Center for the design, fabrication, assembly and testing of the gas sampling system, the analyser system and the digital electronics; the engineers and technicians at the University of Michigan for the design, fabrication and testing of the analogue electronics system; and the personnel at the Laboratoire Interuniversitaire des Systèmes Atmosphériques of the University of Paris for their contribution to the definition, design and testing of the gas chromatographic columns.

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