The composition of Titan’s lower atmosphere and simple surface volatiles as measured by the Cassini-Huygens probe gas chromatograph mass spectrometer experiment.

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Abstract

The Cassini-Huygens Probe Gas Chromatograph Mass Spectrometer (GCMS) determined the composition of the Titan atmosphere from \(~\text{140 km}\) altitude to the surface. After landing, it returned composition data of gases evaporated from the surface. Height profiles of molecular nitrogen (N\textsubscript{2}), methane (CH\textsubscript{4}) and molecular hydrogen (H\textsubscript{2}) were determined. Traces were detected on the surface of evaporating methane, ethane (C\textsubscript{2}H\textsubscript{6}), acetylene (C\textsubscript{2}H\textsubscript{2}), cyanogen (C\textsubscript{2}N\textsubscript{2}) and carbon dioxide (CO\textsubscript{2}). The methane data showed evidence that methane precipitation occurred recently. The methane mole fraction was \((1.48 \pm 0.09) \times 10^{-2}\) in the lower stratosphere (139.8 km to 75.5 km) and \((5.65 \pm 0.18) \times 10^{-2}\) near the surface (6.7 km to the surface). The molecular hydrogen mole fraction was \((1.01 \pm 0.16) \times 10^{-3}\) in the atmosphere and \((9.90 \pm 0.17) \times 10^{-4}\) on the surface. Isotope ratios were 167.7 \(\pm\) 0.6 for \(^{14}\text{N}/^{15}\text{N}\) in molecular nitrogen, 91.1 \(\pm\) 1.4 for \(^{12}\text{C}/^{13}\text{C}\) in methane and \((1.35 \pm 0.30) \times 10^{-4}\) for D/H in molecular hydrogen. The mole fractions of \(^{36}\text{Ar}\) and radiogenic \(^{40}\text{Ar}\) are \((2.1 \pm 0.8) \times 10^{-7}\) and \((3.39 \pm 0.12) \times 10^{-5}\) respectively. \(^{22}\text{Ne}\) has been tentatively identified at a mole fraction of \((2.8 \pm 2.1) \times 10^{-7}\). Krypton and xenon were below the detection threshold of \(1 \times 10^{-8}\) mole fraction. Science data were not retrieved from the gas chromatograph subsystem as the abundance of the organic trace gases in the atmosphere and...
on the ground did not reach the detection threshold. Results previously published from the GCMS experiment are superseded by this publication.

1. Introduction

The GCMS instrument [Niemann et al., 2002] was designed to measure the composition of the ambient atmosphere of Titan during the descent of the Huygens Probe. Atmospheric data were received for 148 minutes beginning at an altitude of 146 km down to the surface. Although not designed to survive surface impact, the probe and the instruments did survive the impact undamaged and returned gas composition data for another 72 minutes until contact was lost with the Cassini orbiter. [Lebreton et al., 2005]
Preliminary results presented in [Niemann, et al., 2005] have been refined based on further laboratory calibration of the spare flight unit sensor and more detailed analysis of the flight data.

Voyager remote sensing instruments had already identified the major and several minor constituents above Titan’s tropopause [Kunde et al., 1981; Hanel et al., 1981; Coustenis et al., 1989; Coustenis et al., 1991]. These measurements were made in the stratosphere. Height profiles, isotope ratios and noble gas concentrations were not retrieved from these data. Thus, the fate of the photochemically produced trace gases in the upper atmosphere remained obscure. Several of the Cassini orbiter instruments, e.g. the Ion and Neutral Mass Spectrometer (INMS), the Composite Infrared Spectrometer (CIRS) and the Ultraviolet Imaging Spectrometer (UVIS) have provided a wealth of information on the composition of organic trace gases in the stratosphere, and the upper atmosphere and ionosphere, i.e. in the regions where they were first formed [Waite et al., 2005, 2007; Cui et al., 2009; Magee, et al., 2009; Flasar et al., 2005; Coustenis et al., 2007; Shemansky et al., 2005]

One of the objectives of the Huygens probe experiments was to determine the extent to which the simpler trace gases can form complex molecules, condensates or aerosol particles that ultimately precipitate onto the surface. N₂, CH₄, H₂, and ⁴⁰Ar were measured in-situ in the lower atmosphere by the GCMS and altitude profiles were obtained. ²²Ne and ³⁶Ar were detected in a batch sample in a noble gas enrichment cell. Kr and Xe were below the detection limit of the instrument for those species and their abundances are estimated to be less than 1x1⁸ mole fraction.

Isotope ratios were determined for hydrogen from H₂ and HD, for nitrogen from ¹⁴N¹⁴N and ¹⁴N¹⁵N, and for carbon from ¹²CH₄ and ¹³CH₄. These GCMS measurements provide important constraints on models for the formation of Titan and its atmosphere. After landing CH₄, C₂H₆, C₂H₂, C₂N₂, and CO₂ were detected as they evaporated from the surface directly below the probe. Benzene (C₆H₆) may also have been evaporating but its abundance was too low to be separated unambiguously from the permanent C₆H₆ background in the instrument.

The GCMS was also used to analyze the aerosol pyrolysis products from the Cassini-Huygens Aerosol Collector Pyrolyser (ACP) experiment [Israel et a., 2002]. Results obtained from that experiment were reported and discussed separately [Israel et al., 2005; Biemann, 2006; Israel et al., 2006].
Identification of organic trace constituents with the three-column gas chromatograph subsystem (GC) was not possible because concentrations in the atmosphere were too low to reach the GCMS detection threshold.

At the altitude of 74 km, when the probe passed through a region of extensive turbulence, ion source number 5 failed. This ion source was dedicated to obtaining data from a GC column specifically designed for the measurement of carbon monoxide (CO) since the flight mass spectrometer was not designed to separate directly N₂ and CO at m/z = 28.

2. Experiment Description

The experiment has been described in detail by Niemann et al. (2002). It was designed to measure the chemical composition of the atmosphere of Titan and to determine the isotope ratios of the major gaseous constituents. It was able to also detect gases evaporating from the surface. The GCMS analyzed gas samples from the Aerosol Collector Pyrolyser (ACP). A detailed description of the ACP instrument is given by Israel et al., 2002.

2.1 Instrument

A simplified block diagram of the instrument is shown in Figure 1. The instrument consists of a gas inlet and distribution system, a system for pressure reduction, a gas processing system (sample enrichment and chemical scrubber cell), a three column gas chromatograph system (GC 1,2,3) and a quadruple type mass filter with a secondary electron multiplier ion detector. The interface points of the ACP with the instrument are also indicated in Figure 1. The chemical scrubber cell was used to facilitate interference free noble gas measurements and the sample enrichment cell was intended for enriching high boiling point hydrocarbons.

The mass spectrometer had five electron-impact ion sources with electron energies of 70 eV. Lower electron energy of 25 eV was used for short periodic intervals. Three ion sources served as detectors for the GC columns, one was dedicated to direct atmosphere sampling, and one for analyzing the gas samples transferred from the ACP. The multiple ion source approach allowed rapid electronic switching between sample systems and prevented cross contamination from the multiple sample sources.

The gas crosstalk between ion sources was less than 1x10⁻⁶. The separation was achieved by pumping each ion source and the analyzer/detector regions with separate sets of chemical getters and sputter ion pumps. In addition the ion lenses of the ion sources were especially designed for low gas conductance between the ionization regions and the common mass analyzer region. The system is described in detail by Niemann et al. (2002).

The mass filter produced flat top mass peaks that allowed rapid scanning with 5 milliseconds per data sample. Unit step values of mass to charge ratios (m/z) from 2 to 141 were used with occasional 0.125 interval sweeps for diagnostics. The nominal detection threshold was at a mole fraction of 10⁻⁸. The actual detection threshold for individual species varied depending on interference from other species and chemical noise in the ion sources. The three GC columns were selected to separate C₃ to C₈ hydrocarbons and, nitrogen and carbon monoxide.
respectively. Micron sized capillary arrays were used to reduce the ambient pressure during the Probe descent, ~3hPa to 150 kPa, to the required ion source pressure as well as to reduce the operating pressure of the GC columns to180 kPa. Two sets of capillary arrays with different gas conductance were used in sequence for the direct atmosphere ion source in order to cover the wide ambient pressure range traversed during the descent. Gases were removed from the ion sources by conductance limited getter and sputter ion pumps. The maximum ion source operating pressure was 1x10^-4 hPa. The pressure in the mass filter was always below 1x10^-6 hPa.

The gas inlet was near the apex of the probe fairing and the outlet was at the rear of the probe. The sample inlet and outlet locations on the probe body are shown in Figure 2. Gas flowed through a several millimeter diameter sampling tube, driven by the dynamic pressure. The dynamic pressure is the pressure differential between the stagnation pressure at the tube entrance and the ambient pressure at the tube exit. A small amount of the atmospheric gas was diverted from the flow line through the capillary leaks into the ionization region of the ion source. To minimize surface losses of trace and chemically active constituents, the capillary leaks were located so that the exit flow from the capillaries could enter the ionization region with minimal surface collisions. Upstream from the capillary leaks, the inlet line was heated to prevent condensation and to cause rapid evaporation of condensates that might flow through the sampling line. This also caused a small convective gas flow through the inlet line after landing. The mass flow through the inlet line varied with altitude during the descent from several hPa cm\(^3\) per minute to several hundred hPa cm\(^3\) per minute. The gas sampling system and mass spectrometer were sealed before launch and maintained under ultra high vacuum until jettison of the probe heat shield when the inlet and outlet seals of the sampling tube were broken and the system was exposed to the ambient atmosphere of Titan.

Figure 3 shows the dynamic pressure, ambient pressure and descent velocity versus time from sampling initiation at 147 km. The ambient pressure, mass density and the descent velocity data are from the HASI experiment [Fulchignoni et al., 2005] and the Descent Trajectory Working Group [Kazeminejad et al., 2007]. The dynamic pressure shown in Figure 3, \(P_d\), was not measured directly. It was computed using the familiar relation, \(P_d = \frac{1}{2} \rho V^2\), where \(\rho\) is the in situ mass density of the atmosphere and \(V\) is the descent velocity. The abrupt change of the dynamic pressure occurred when the descent velocity increased after jettison of the second parachute.

### 2.2 Measurement Sequence

The measurement sequence was preprogrammed. The atmosphere was sampled nearly continuously during the entire descent, interrupted only when the contents of the noble gas and the sample enrichment cells were analyzed and when ACP samples were transferred. GC samples were collected in storage volumes in the upper atmosphere for later analysis when the descent slowed and more time was available for analysis. At lower altitudes, close to the surface, GC samples were injected directly from the atmosphere.

The measurement sequences are shown in Figure 4. The change of the ambient pressure and temperature are shown in panel a. The ambient pressure and temperature were measured by the HASI experiment [Fulchignoni et al., 2005]. The events in ion source 1 are indicated in panel b and the times when ACP samples were analyzed are
shown in panel c. Finally, the GC sample collection and analysis times of the batch
samples with ion source 3, 4 and 5 as detectors are plotted in panel d.

The mass spectrometer was scanned continuously in unit mass steps over the mass
range (m/z = 2 to 141) with a dwell time of 4.592 msec per step. Periodic high-resolution
spectra, eight steps per unit mass, were taken to verify correct mass tuning. With a small
time fraction allowed for settling of transients after each sample step, the period of a full
unit mass scan cycle was 937.5 msec. In flight, the time doubled to 1.875 sec between
samples because the instrument data stream was split on two quasi-redundant
transmission links from the Huygens probe to the Cassini orbiter and one receiver
channel was inadvertently not turned on.

The preprogrammed measurement sequence was properly executed during the
mission. Ion source 5, which served as a detector for the N2-CO separation column
failed to operate normally at 74 km altitude. This resulted in the loss of the data from
this column and the measurement of the CO concentration. A simultaneous sensitivity
change of ion source 1 occurred, likely related to the ion source 5 failure. The sensitivity
change was mass independent which is consistent with a bias potential change at one or
more of the ion focusing lenses. This did not affect the mole fraction and isotope data
since absolute ambient partial pressure measurements by the GCMS were not intended.
Large atmospheric turbulence affected the probe motion at the same time and it likely
triggered the event. The exact cause of that failure in the instrument could not be
determined but an examination of the housekeeping data pointed to an electrical
malfunction in the ion source supply circuit.

As indicated in Figure 4, data were collected from 146 km altitude to the surface for
8871 seconds (2 hours and 27 minutes). From 146 km to 65 km, only atmospheric gases
were analyzed directly, introduced through leak L1 into ion source 1. Direct atmosphere
sampling was interrupted for 6 minutes from 65 km to 56 km to analyze the contents of
the noble gas scrubber cell followed by the analysis of the content of the sample
enrichment cell. The gas samples for the scrubber and enrichment cell were collected
from 77 km to 75 km. Direct atmosphere sampling was resumed at 56 km altitude using
the second, lower conductance, leak L2 for ion source 1. The GC analysis was also
initiated at this time scanning ion sources 3, 4 and 5. Ion source 2 was operated for two
short periods for the analysis of the transferred ACP samples. The Probe and the
instrument survived the surface impact although this was not an objective of the mission.
Data were collected for an additional 70 minutes from gases evaporating from the
surface.

The ion arrival rate at the detector during each measurement step constituted the
primary measurement. Pulse counting rates per time sample varied from 0 to an
equivalent of $10^8$ counts per second. Because of pulse pile up and a finite recovery time
of the pulse counting system after a pulse was received, a correction needed to be applied
to the raw count rates up to $7x10^6$ counts per second. The corrected count rate was
derived from the expression

$$[R] = \frac{[n]}{(1-[n][T])}$$

where $[R]$ is the corrected count rate and $[n]$ is the measured count rate. The value of $[T]$
was empirically determined as $2.8x10^8$ sec using cruise checkout data from the
background argon present in the sensor at that time.
At pulse count rates higher than $7 \times 10^6$ counts per second the correction could no longer be applied. In that case a proxy mass peak can be used such as the fractionation peak of the parent mass peak, which is at a lower magnitude. This occurred only for molecular nitrogen where the $N^+$ peak, at $m/z = 14$, with a peak height ratio of 0.0467 relative to the parent $m/z = 28$ peak, was used as a proxy for the $m/z = 28$ peak. This ratio was determined from dead time corrected flight data when both pulse count rates were sufficiently low in signal to allow the determination, (from 100 to 1000 seconds descent time). The results were consistent with the laboratory calibration data.

Data rate limitations for the link between the Huygens probe and the Cassini orbiter restricted the available data rate for the GCMS to 1770 bits per second for combined science and housekeeping data. To cover the full range of available data from the instrument it was necessary to compress the data. Square root data compression was chosen for this purpose. Maximum resolution for low count rate science data from the detector was maintained, however, by transmitting counts uncompressed from 0 to 127 counts per integration period (0 to 27657 counts per second).

Figure 5a shows sample mass spectra from the stratosphere averaged from ~ 130 to 120 km altitude and ~ 4 to 6 hPa ambient pressure, Figure 5b from the troposphere at ~ 20 to 10 km altitude and ~ 500 to 900 hPa ambient pressure and Figure 5c from the surface at 1500 hPa.

### 2.3 Calibration

The instrument was calibrated on a dynamic flow system where the time, ambient pressure and the ambient temperature profile were simulated as expected during the descent of the Huygens probe. [Niemann et al., 2002] have described details of the calibration facility and the calibration process. The objective of the calibration was to determine the overall system transfer characteristics for molecular species expected to be in the atmosphere of Titan. The transfer function of the instrument is species dependent. The transmission of the gas mixtures through the capillary leaks is pressure dependent and mole fraction dependent. The ionization cross sections and, to a lesser degree the conversion efficiencies of the ion detector, are species dependent. The effective pumping speeds of the vacuum pumps are different for inert and reactive gases. Although the vacuum pumps were conductance limited, i.e. their effective pumping speed was nearly constant for the time of the descent and on the surface, the specific pump properties needed to be determined. While the getters pump reactive gases only, except methane, the sputter ion pumps remove all gases and hence the mole fraction in the ion source was different from that of the ambient atmosphere.

Static calibration runs were conducted with hydrocarbon mixtures and noble gas mixtures, introduced at several fixed pressure levels. Dynamic descent simulations verified the system response prior to instrument delivery for flight.

The calibration of the flight instrument was not completed before launch. Limitation of the lifetime of the chemical getters and the sputter ion pumps, which needed repeated replacement during the calibration period required more time than was available before launch. After Titan encounter, work continued on the flight spare unit, which was built to be identical to the flight instrument. The effect of unavoidable differences between the two instruments on the measurement accuracies is assumed to be small. The calibration data are expressed as pressure dependent calibration factors. The dead time and
background corrected count rates of ions are multiplied by the calibration factors to produce the mole fractions of species in the ambient atmosphere. Calibration factors are pressure dependent because transmission of molecular species through the capillary leaks depends on the molecular properties, mass and viscosity, and on the mole fractions. The diameter and length of the capillaries needed for correct pressure reduction from the ambient pressure to the ion source pressure resulted in the gas flow through the capillaries to be in the transition regime between free molecular and viscous flow.

Calibration data were obtained for CH₄ and H₂ in N₂ using certified premixed gas mixtures of 2%, 5% and 10% methane and 1% and 3% hydrogen in molecular nitrogen. When normalized, the differences in the calibration results for the different mole fractions were smaller than the calibration errors. Polynomials were fitted to the calibration curves and were applied to the flight data. For gas species not directly calibrated in either the flight unit or flight spare unit, literature ionization cross sections were used relative to N₂.

The laboratory calibration data showed an inconsistency between the flight and the flight spare instrument in the system pump down of hydrogen. This was observed during the transition period from the leak L1 to the leak L2 measurement phase when ion source 1 was isolated from the atmosphere for 90 seconds for pump down to remove residual gases from the leak L1 operating period. Different from the results for all other gases, the hydrogen remained at a higher background level in the flight unit than what was observed before flight and in the flight spare unit in the laboratory. The discrepancy can be resolved if it is assumed that the getter pumps for ion source 1 in the flight instrument did not pump hydrogen during the descent and only the sputter ion pump was effective for ion source 1. This would be possible if a small hydrogen leak in the isolation valve from the gas chromatograph hydrogen reservoir to the sample inlet system had developed during or shortly after launch. The leak rate would have been too small (less than 1x10⁻⁶ std.cc/sec) to detect after launch, but over a time of 7 years would have gradually saturated the getters of ion source one.

Since the gettering process for hydrogen is different from the other gases (going into solution reversibly rather than chemical bonding), the hydrogen present in the getter has only a small effect on the pumping speed of the getters for the other gases. The hydrogen loading on the getters for the other ion sources was only small because they are decoupled and the gas flow from the sample inlet system is six orders of magnitude lower than the flow to the getters in ion source 1. However, the getter in the noble gas and sample enrichment cells was also exposed to a higher gas flow. The possible effect on the enrichment cell data is still being evaluated. The assumption is also consistent with theoretical and experimental data obtained in our laboratory of the getter capacities and equilibrium vapor pressure values for the getter mass and material. With that caveat the hydrogen data are presented with the assumption that the hydrogen in ion source one was pumped by the sputter ion pump only. The ratio of the total pumping speed, with fully activated getters, to that of the sputter ion pump only was determined to be 9.02 in the laboratory calibration for the flight spare instrument. The indicated H₂ mole fraction was corrected by that factor. Since it can not be determined with certainty, based on the flight and laboratory calibration data, that the effective pumping speed for hydrogen of the ion source 1 getter in the flight instrument was exactly zero, the hydrogen mole fraction presented is considered to be a the lower limit.
Ambient pressure data from the HASI experiment [Fulchignoni et al., 2005] and the Descent Trajectory Working Group [Kazeminejad et al., 2007] were used to correlate the flight data with the calibration data.

Simulation experiments of the interaction of the instrument sample inlet line with the surface are needed for a more thorough understanding of the data obtained on the surface of Titan.

3. Data

3.1 Methane

As already observed from the ground for methane [Kuiper, 1944] and from Voyager 1 for nitrogen, [Broadfoot et al., 1981; Tyler et al., 1981], molecular nitrogen (N_2) and secondarily methane (CH_4) are the major constituents of the atmosphere of Titan. The GCMS measurements confirmed this and determined the mole fraction of methane from 140 km altitude to the surface during the probe descent.

In the mass spectra received during the descent, the contributions to the mass peak intensities at m/z = 28 and 16 were primarily from N_2 and CH_4 respectively. Contributions from other species were negligible because their parent peak intensities were much lower.

Calibration data were applied as described in section 2.3. At m/z = 14, the peak intensity needed to be corrected for the contribution from methane fractionation in the ion source, ^12CH_2^+ . The fraction was 0.0506 of the m/z = 16 (CH_4) count rate. It was determined from the noble gas scrubber cell data obtained in flight where methane was the only non-noble atmospheric gas that was not removed by the chemical getters.

The mole fractions were computed using

\[
CH_4/(N_2+CH_4) = \frac{[16]/[28]/[cf_{16,28}]}{1+[16]/[28]/[cf_{16,28}]}
\]

or where m/z = 14 due to N_2 is used as a proxy for m/z = 28

\[
CH_4/(N_2+CH_4) = \frac{[16]/[14]/([28]/[14]r)/[cf_{16,28}]}{1+[16]/[14]/([28]/[14]r)/[cf_{16,28}]}
\]

where [16], [28], [14] are the actual pulse count rates at the respective mass values, corrected for dead time. Residual background counts were subtracted. [cf_{16,28}] is the calibration factor for the CH_4/N_2 ratio. [28]/[14], is the dead time corrected count ratio at m/z = 28 and 14 in the range where both are valid.

The results are shown in Figure 6 as function of time from sequence initialization. The section where the mass 14 proxy was used is marked in red. To improve the statistical accuracy, data points were averaged over approximately 50 sample points also shown in Figure 6. The error bars show the standard deviation. The vertical red dashed line marks the time of surface impact. The variation of the mole fraction with altitude is shown in Fig. 7. A gradual increase in the mole fraction is noticed starting at 3000
seconds, about 40km above the surface, to 7500 seconds and about 7 km above the surface. It then remained nearly constant until surface impact. After landing, it again increased rapidly and remained nearly constant until close to the end of the data transmission (Figure 6). The time averaged numerical data as shown in Figures 6 and 7 are tabulated in Table 1. The errors shown are one-sigma statistical errors only. Additional systematic errors resulting from calibration and differences between the flight instrument and the flight spare instrument are estimated to be ± 5%.

The increase of the mole fraction with decreasing altitude down to approximately 7 km is evidence for cloud formation (see section 4.1) and, after landing on the surface, of evaporation of methane from the soils beneath the heated probe.

3.2 Non-Methane Hydrocarbons and other Trace Gases

Hydrocarbons of C₂ and higher order, and nitrogen containing species were not reliably detected above the surface by the GCMS. Numerous heavy hydrocarbons and nitriles, produced by photochemical reactions and energetic particle collisions, however, were detected in situ on ionospheric altitudes above 900 km by the Cassini Ion and Neutral Mass Spectrometer (INMS) [Waite et al., 2007] during Titan flybys of the Cassini Orbiter and in the stratosphere remotely by the Cassini Composite Infrared Spectrometer (CIRS) [Coustenis et al., 2007]. As the newly formed species descend, they undergo additional chemical reactions to form more complex compounds and aerosols while their parent mole fractions decrease. Ultimately, most gases condense or change to aerosols as they reach the tropopause due to the decreasing temperature with decreasing altitude between the stratosphere and troposphere [Wilson and Atreya, 2004].

When the GCMS measurements were initiated (below 146 km), only traces of C₂H₆ and C₂H₂ were near the detection threshold of the instrument but could not be quantified. Evaporation of these materials from the surface was observed, however, after the probe landed. In Figure 5c the mass spectra show more high mass peaks on the surface. Still most of the count rates at higher mass values are close to the detection threshold and only a few mass peaks stand out.

The probe came to rest on the surface in an upright position. In this position, the sample inlet port of the GCMS could have been touching the surface or was inside of a small cavity around the inlet port created by the settling motion. The interface geometry of the inlet sample port and the surface is illustrated in the drawing shown in Figure 8. The sample inlet line heated the inlet port on the surface either by conduction (direct contact) or by conduction and radiation through the surrounding atmosphere. The exact nature of the thermal contact of the inlet port with the surface is not known, nor is the exact temperature or temperature distribution known of the surrounding surface area. It can, however, be safely assumed that the temperature inside the probe and downstream in the sample line was higher than the temperature of the surface and in the vicinity of the capillary leak. The temperature at the entrance port of the inlet tube was not monitored. On the surface, a value of 140 K was estimated from temperature modeling of the sample inlet line [Lorenz et al., 2006].

The inlet port temperature, being higher than the ambient temperature, caused the evaporation of low boiling point surface condensates followed by convective gas flow through the heated sample line. In addition to methane, which showed the highest evaporation rate and fastest time response, a number of other species were also
evaporating at different rates and with different starting times. This is shown in Figure 9. Increases in vapor concentrations after landing were identified for C$_2$H$_6$, C$_2$H$_2$ and C$_2$N$_2$, in addition to CH$_4$. A small increase in the C$_6$H$_6$, m/z = 78, 51 and 50 mass peaks, also occurred but it could not be identified unambiguously as originating from the surface. C$_6$H$_6$ was permanently present in the instrument as a trace background gas and the observed very small increase, which occurred before impact, could have been surface outgassing from the sampling system stimulated by the incoming atmospheric gas. The upper limit for the C$_6$H$_6$ mole fraction is 1x10$^{-7}$. The list above is ordered in decreasing level of confidence of correct species identification. Pulse count rates were used from either parent and/or fractionation peaks and with application of the respective calibration factors, mole fractions were calculated. All reached quantifiable levels only after landing. The dashed vertical lines indicate the time of surface impact. The finite values above the surface seen in the figures are residuals at the detection threshold and are not valid numerical quantities. The detection threshold for C$_2$H$_6$ and C$_2$H$_2$ is relatively high with respect to the full dynamic range of the instrument because the mole fractions were derived by subtracting pulse count rates of interfering species from the total at m/z = 30 and 26 respectively to obtain the plotted values. The upper limits of the mole fractions of the species in the atmospheric portions during the descent are estimated to be 1x10$^{-5}$ for C$_2$H$_6$, 2x10$^{-6}$ for C$_2$H$_2$ and 1x10$^{-7}$ for C$_2$N$_2$.

### 3.3 Carbon Dioxide

Carbon dioxide, CO$_2$, is not expected to be present in any detectable abundance in the lower atmosphere of Titan. Evaporation from the surface, from CO$_2$ ice, is plausible and was observed from monitoring the peak intensity at m/z = 44. The m/z = 44 peak contained also contributions from a constant CO$_2$ background in the ion source and from propane, C$_3$H$_8$. Contributions from propane can be separated by observing the fractionation peaks of propane at m/z = 43 and 42. The CO$_2$ background, where measured, was constant and was subtracted. The result for CO$_2$ verses time is shown in Figure 9. Surface impact time is indicated in the figure by a vertical dashed line. As with the solid organic compounds on the surface the CO$_2$ mole fraction monotonically increases with time until the end of data transmission.

### 3.4 Hydrogen

Molecular hydrogen in the atmosphere was detected by the GCMS by observing the count rates at m/z = 2. The mole fraction was then calculated using the relation:

$$\frac{H_2}{(N_2+CH_4)} = \frac{([2] - [16][cf^{2,16}])/[28]/[cf^{2,28}]}{1+[16]/[28]/[cf^{16,28}]}$$

When the m/z = 28 counts were saturated the counts at m/z = 14 were used as proxy for mass 28 (corrected for CH$_4$ contributions)

$$\frac{H_2}{(N_2+CH_4)} = \frac{([2] - [16][cf^{2,16}])/[14]/([28]/[14])}{1+[16]/[14]/([28]/[14])}$$


where [2], [16], [28], and [29] are the pulse count rates at the respective mass values, corrected for dead time, GC H₂ carrier gas crosstalk (leak L2 only) and residual ion source background counts. \([cf_{2,28}]\) is the calibration factor for the H₂/N₂ ratio at \(m/z = 2\) to \(m/z = 28\). \([cf_{16,28}]\) is the calibration factor for the CH₄/N₂ ratio at \(m/z = 16\) to \(m/z = 28\) and \([28]/[14]_f\) is the dead time corrected count ratio at \(m/z = 28\) and \(14\) in the range where both are valid.

Contributions to the \(m/z = 2\) count rate from dissociative ionized H₂⁺ ions of CH₄ were evaluated from laboratory calibration with CH₄ using the flight spare instrument. The H₂⁺ ion fraction of the CH₄⁺ ion count rate was:

\[
[cf_{2,16}] = \frac{[2]}{[16]_{lab}} = 1.05 \times 10^{-3}
\]

Species other than N₂ and CH₄ were not included in the mole fraction calculations. Their contributions are negligible compared to other measurement errors.

The fixed (static) background in the ion source was determined for the leak L1 region before the sample inlet system was opened to the atmosphere. Fixed background contributions in the leak L2 region were determined at the beginning of the leak L2 measurement phase when ambient hydrogen contributions were negligible. The carrier gas contribution was determined by observing the increase in the \(m/z = 2\) count rate at the time when the hydrogen gas flow was started. It results from crosstalk of the hydrogen pressure in the GC dedicated ion sources 3, 4 and 5 into ion source 1. The increase was of the order of the residual ion source background. It does not vary with time since the carrier gas pressure and hence the pressures in the GC dedicated ion sources were constant. Contributions from other hydrogen carrying compounds were negligible.

The calibration factor \([cf_{2,28}]\) was determined from laboratory calibration of the flight spare instrument with representative gas mixtures of H₂, CH₄ and N₂. As described in section 2.3 this calibration factor includes the pressure and mole fraction dependent transmission through the capillary leak arrays of species with different molecular weight, the ionization cross sections, the ion transmission through the mass filter and ion lens system and conversion efficiency of the secondary electron multiplier ion detector. The calibration factor was expressed in a closed form by fitting the laboratory calibration data as function of pressure.

The mole fraction of hydrogen versus time from entry (all sampling points) is shown in Figure 10 for the high altitude region (144 km to 66 km), leak L1, and the low altitude and ground region (45 km to the ground), leak L2. Averaged data over approximately 50 sample points are also presented in Figure 10. The error bars shown are the standard deviations. Figure 11 shows the altitude dependence of the mole fractions. On the surface, the mole fraction remains constant until about 10000 seconds or 1300 seconds after impact. The mole fraction then decreases gradually until the end of the mission. Similar gradual decrease in mole fraction was observed also for methane. The cause is not explained at this time. An instrument effect or a gradual change in the gas flow through the sample inlet line because of the changes in temperature over time could be contributing. The 50-point average data are tabulated in Table 2.

### 3.5 Noble Gases
$^{36}\text{Ar}$ and $^{22}\text{Ne}$ were the only non-radiogenic or "primordial" noble gases detected by the instrument and only in sufficient abundance in the noble gas cell for quantitative evaluation. Interference with peaks produced by organic molecules makes it impossible to isolate them in the direct measurement sequence during the descent.

Noble gas cell data were collected during the descent from 77 km to 75 km and analyzed during the descent from 64 to 61 km. Figure 12 shows the mass spectrum from the noble gas cell. The function of the noble gas cell was to remove, or significantly reduce, the concentration of the reactive gases in the cell that minimized the mass spectral interference from these gas species, and enhanced the noble gas concentration relative to molecular nitrogen. This was accomplished with a chemical getter that pumped all reactive gases except methane. Mixing ratios of the noble gases with respect to methane in the cell were then converted to mole fractions using the methane mole fraction measured at the time when the noble gas and enrichment sample collection occurred. More details on the operation of the noble gas cell can be found in Niemann et al. (2002). Molecular nitrogen was only reduced in concentration. It could not be removed completely from the cell. The pumping capacity of the getter is not sufficient to remove all nitrogen. Carbon dioxide ($\text{CO}_2$), benzene ($\text{C}_6\text{H}_6$) and some other traces in the low mass range were permanent background gases in the ion source which could not be removed during the pre-flight processing. They did not originate from the cell. Molecular hydrogen was not removed because of the diminished getter pumping presumably due to the gas leak from the GC carrier gas reservoir as described in section 2.3.

As in all other cases, laboratory calibration data for the instrument transmission function were applied involving ionization cross sections, pulse counter dead times, gas conductance of capillary leaks and effective pumping speed.

The $^{36}\text{Ar}$ mole fraction from the noble gas cell data is:

\[(7) \quad ^{36}\text{Ar}/(\text{N}_2+\text{CH}_4) = (2.1 \pm 0.8) \times 10^{-7}\]

The presence of $^{38}\text{Ar}$ was confirmed qualitatively. The small number of pulse counts collected was approximately correct for an isotope ratio for $^{38}\text{Ar}/^{36}\text{Ar}$ of 0.2. It also provided assurance that the mass peak at $m/z = 36$ was not a residual hydrocarbon peak.

The $^{38}\text{Ar}$ upper limit is $\sim 5 \times 10^{-8}$.

The mole fraction of $^{20}\text{Ne}$ could not be determined at $m/z = 20$. Much larger peaks of doubly ionized $^{40}\text{Ar}$ mask the peaks. The upper limit of the mole fraction for $^{20}\text{Ne}$ is $\sim 4 \times 10^{-5}$.

The detection threshold of the isotope $^{22}\text{Ne}$ was also raised because of doubly ionized $\text{CO}_2$ background interference at the $m/z=22$ peak. Although the interference peak value was of the same order as the total peak count value ($^{22}\text{Ne}^+$ and $\text{CO}_2^{2+}$) it could be subtracted from the total.

The remaining pulse count values were converted to a mole fraction of $^{22}\text{Ne}$:

\[(8) \quad ^{22}\text{Ne}/(\text{N}_2+\text{CH}_4) = (2.8 \pm 2.1) \times 10^{-7}\]

This result should be considered tentative because the signal level is low, close to the detection threshold at $m/z=22$, which is also reflected in the large statistical error shown.
Doubly ionized $^{20}\text{Ne}$ at m/z = 10 and $^{22}\text{Ne}$ at m/z = 11 were not detected. They occur in an interference free region but their intensity would still be below the detection threshold of the instrument.

$\text{CO}_2$ resided in the ion source as low-level permanent background gas. It is a common contaminant in flight mass spectrometers and results from slow outgassing from microscopic surface cracks and trapping volumes in the evacuated regions of the instrument. Prolonged bake out periods, on a high vacuum pumping speed processing system prior to launch, reduce it and other background gases but never do completely eliminate them in the time available for processing.

Radiogenic $^{40}\text{Ar}$ was detected in the noble gas cell and directly during the descent. The average mole fraction from 18 km altitude to the surface is:

$$^{40}\text{Ar}/(\text{N}_2+\text{CH}_4) = (3.35 \pm 0.25) \times 10^{-5}$$

Above 18 km altitude the direct measurement was obscured by the $^{40}\text{Ar}$ instrument background. The mole fraction computed from the noble gas cell measurement is:

$$^{40}\text{Ar}/(\text{N}_2+\text{CH}_4) = (3.39 \pm 0.12) \times 10^{-5}$$

The mole fractions were computed from the m/z = 40 mass peak intensities. Laboratory calibration data and corrections were applied for dead time and contributions from a permanent $^{40}\text{Ar}$ instrument background. Contributions of hydrocarbons in the same mass range, for example, C$_3$H$_4$ are negligible based on heights of the fractionation peaks.

Kr and Xe concentration levels were below the detection threshold of the instrument as can also be seen from the mass spectrum shown in Figure 12. The upper limit is at a mole fraction of $1 \times 10^{-8}$.

### 3.6 Isotope Ratios for the Major Gas Constituents

#### 3.6.1 $^{14}\text{N}/^{15}\text{N}$ in Molecular Nitrogen

The isotopic ratio of nitrogen was derived from the pulse count ratio at, m/z = 29, $^{14}\text{N}^{15}\text{N}$, and m/z = 28, $^{14}\text{N}_2$. The count ratios plotted versus time from entry are shown in Figure 13 which also shows the count ratios plotted with m/z = 14, $^{14}\text{N}^+$, used as proxy for $^{14}\text{N}_2$. The regions where leak L1 and leak L2 were used are shown in different colors as indicated in the legend. At times later than 1500 seconds for leak L1 and later than 7000 seconds for leak L2 the m/z = 28 counts are no longer valid due to counter saturation as can be seen by the slope changes. The species and molecular weight dependent gas transmission through the capillary leaks was verified to be negligible for the difference of one mass unit and the differential count resolution of the instrument. Corrections were applied for the molecular weight depending on pumping speed of the vacuum pumps.

The results are listed in Table 3 from regions where the statistical fluctuations were low and dead time corrections for the m/z = 28 peaks were also small. The average is:

$$^{14}\text{N}/^{15}\text{N} = 167.7 \pm 0.6.$$
As mentioned above, the range of usable data points during the descent was extended by using dissociative ionized nitrogen $^{14}\text{N}^+$ at $m/z = 14$ as proxy for $^{14}\text{N}_2$. The contributions from dissociative ionization of methane, $\text{CH}_2^+$ at $m/z = 14$ were subtracted. The dissociation fractions were determined from flight data to be 0.0467 for $\text{N}_2$ and from the noble gas cell data to be 0.0506 for $\text{CH}_4$. The result is shown in Figure 14 where the appropriately scaled pulse counts are plotted and the slope of the least square fit is the isotope ratio $^{14}\text{N}/^{15}\text{N}$, after multiplication by the pumping speed ratio of $(29/28)^{0.5}$. The results are $167.1 \pm 3.9$ for the leak L1 and $167.5 \pm 2$ for the leak L2 region. These numbers are not listed in Table 3 and are presented only to show consistency of the data.

### 3.6.2 $^{12}\text{C}/^{13}\text{C}$ in Methane

The carbon isotopic ratio was determined from methane, the major carbon-carrying molecule in the atmosphere of Titan. Data were analyzed from all regions of the atmosphere, the noble gas cell and the surface. As mentioned above, methane is retained in the noble gas cell and it serves as reference gas to determine noble gas mixing ratios. Pulse count ratios of $m/z = 17$ to $m/z = 16$ are plotted versus time from descent initiation in Figure 15, for the upper atmosphere region sampled through leak L1 and the lower atmosphere region and surface through leak L2. Methane ($^{12}\text{CH}_4$) is assumed to be the only significant contributor to the $m/z = 16$ counts. Contributions of fractionations from higher molecular weight species at $m/z = 16$ are negligible because of the high abundance of methane. The counts at $m/z = 17$ are the sum of counts from $^{13}\text{CH}_4$ and $^{12}\text{CH}_3\text{D}$. Both compounds cannot be separated by the mass spectrometer but the $^{12}\text{CH}_3\text{D}$ contribution can be obtained from the results for the $^{12}\text{CH}_3\text{D}/^{12}\text{CH}_4$ ratio of the CIRS experiment on the Cassini orbiter. A D/H ratio of $1.32 \times 10^{-4}$ [Bezard et al., 2007] was used to compute the $^{12}\text{CH}_3\text{D}$ contribution to the $m/z = 17$ counts. Fractionations from high molecular weight constituents do not add noticeably to the $m/z = 17$ count because none were seen by the mass spectrometer in high enough concentrations to matter. Ammonia, NH$_3$ either from the atmosphere or as chemical background is not expected to contribute to the $m/z = 17$ peak because its atmospheric mixing ratio would be too low and the detection would further be impeded by surface absorption in the instrument. A permanent ammonia background in the ion source has never been observed. The regions from which the isotopic ratios were computed are from 127 km to 67 km altitude for leak L1, from a grab sample taken at 76.5 km for leak L3 (noble gas cell) and from 23 km to the surface and on the surface for leak L2. The values are listed in Table 3.

The average atmospheric value is $^{12}\text{CH}_4/^{13}\text{CH}_4 = 91.1 \pm 1.4$, the noble gas cell value is $91.7 \pm 1.5$ and the value for methane evaporated from the surface is $92.0 \pm 0.5$. These values are approximately 10% greater than the earlier preliminary results [Niemann et al., 2005].

### 3.6.3 Deuterium in Molecular Hydrogen

The D/H ratio in hydrogen in the atmosphere was determined from molecular hydrogen $\text{H}_2$ and deuterated hydrogen HD. The D/H isotope ratio is numerically very low since the $\text{H}_2$ abundance in the atmosphere is also small. The low pulse count rate at $m/z = 3$ (DH) reduces the time during the descent when the $m/z = 3$ pulse counts were sufficiently above the detection threshold to yield a valid measurement. The leak L1 region was generally preferred because it was free from possible interference from the
molecular hydrogen that was used as a carrier gas later for the gas chromatograph subsystem. It was determined, however, that the carrier gas interference was small, and could be subtracted. The data were averaged for all of the leak L1 regions and all of the leak L2 regions. Corrections were made for instrument carried hydrogen background, not associated with the H\textsubscript{2} carrier gas for the GC, and contributions of dissociative ionized H\textsuperscript{2+} and HD\textsuperscript{+} from methane. The methane contributions were determined from post-flight laboratory calibration of the flight spare GCMS instrument. The D/H ratios are listed in Table 3.

Although it is of interest to see a height profile of the D/H ratio, the count rates at m/z = 3 were too low to derive a meaningful profile.

3.7 Oxygen

Oxygen-bearing constituents e.g. H\textsubscript{2}O and CO\textsubscript{2} were not in sufficient abundance in the atmosphere for an oxygen concentration and oxygen isotopic ratio measurement. CO could not be separated from N\textsubscript{2}, as discussed previously. However, as is shown in Figure 9 and discussed in section 3.3, CO\textsubscript{2} was observed on the surface.

4. Discussion

Preliminary results from the GCMS have been reported previously [Niemann et al., 2005]. All the preliminary results provided in that report have changed to various degrees and are now superseded by the data provided in this paper. Calibration data applied from a thorough calibration of the flight spare instrument, a more accurate accounting of mass peak sizes (e.g. species interference) and dead time corrections of the pulse counting system and a more thorough examination and better use of the complete data set led to the results reported here.

Molecular nitrogen is the most abundant gas in the atmosphere of Titan followed by a few percent in mole fraction of methane. The total pressure on the surface is 1500 hPa. This was determined by many experiments using various techniques and refinements of the measurements.

The GCMS results contributed a detailed altitude profile of the CH\textsubscript{4} and H\textsubscript{2} mole fractions in the lower atmosphere, the isotope ratios of \textsuperscript{14}N/\textsuperscript{15}N in molecular nitrogen, \textsuperscript{12}C/\textsuperscript{13}C in methane and D/H in molecular hydrogen.

4.1 Methane (CH\textsubscript{4})

The current CH\textsubscript{4} mole fraction of 5.5x10^{-2} just above the surface is subsaturated, at a relative humidity of approximately 50%. While the mixing ratio of CH\textsubscript{4} remains nearly uniform with altitude up to approximately 7 km, its saturation vapor mixing ratio decreases rapidly with decreasing temperature above the surface (saturation vapor pressure of CH\textsubscript{4} above a mixture of N\textsubscript{2} dissolved in liquid CH\textsubscript{4} was based on Kouvaris and Flasar (1991)). Consequently, CH\textsubscript{4} reaches its lifting condensation level, or 100% relative humidity, at an altitude of approximately 7 km. This represents the base of condensation of CH\textsubscript{4} as liquid. The GCMS CH\textsubscript{4} data are consistent with saturation above liquid CH\textsubscript{4} with N\textsubscript{2} dissolved in it up to about 13-14 km. Above this altitude, a phase change to solid particles is expected, with the possible presence of supercooled droplets of a two component (methane-nitrogen) liquid as well. The nearly constant CH\textsubscript{4} mole fraction of 1.48x10^{-2} at the tropopause and above in the stratosphere is consistent with
saturation above CH$_4$ ice and with the departure of the measured CH$_4$ mole fraction from
the predicted Kouvaris and Flasar (1991) saturation values above approximately 14 km,
as discussed previously by Atreya et al. (2006), and confirmed recently by laboratory
simulation experiments [Wang et al., 2009].
The GCMS value is in agreement with the CIRS measurement of methane in the
stratosphere [Flasar et al., 2005]. Only at very high altitudes of ~600 km and higher does
photochemistry begin to erode methane, thus depleting its mole fraction [Wilson and
Atreya, 2004].

4.2 Molecular hydrogen, (H$_2$)
The H$_2$ mole fraction determined from the GCMS data is in good agreement with
previous determinations of the H$_2$ mole fraction in Titan by Voyager IRIS and Cassini
CIRS experiments. The Voyager determination by Courtin et al., (2005) from S$_0$(0) and
S$_0$(1) transitions of the H$_2$-N$_2$ dimers indicated a mole fraction of (1.0 $\pm$ 0.4) x10$^{-3}$. The CIRS-Cassini determination is equal to (9.6 $\pm$ 2.4) x10$^{-4}$ [Courtin et al., 2007].
Since Titan’s atmosphere is mainly composed of N$_2$ and CH$_4$, substantial amounts of
atomic hydrogen are produced by photochemical reactions during the formation of
organic products. Theoretical models predict that atomic hydrogen recombines to form
H$_2$ molecules [Yung et al., 1984; Wilson and Atreya 2004; Strobel et al., 2009; Cui et al.
2008; Strobel, 2009]. The models predict a constant volume mixing ratio of H$_2$ in the
homosphere, consistent with the 1Myr photochemical lifetime of H$_2$
In laboratory measurements, Sekine et al (2008a) investigated heterogeneous
reactions of atomic hydrogen with synthetic Titan tholins. Results suggested to the
authors that these reactions might remove atomic hydrogen in the stratosphere and
mesosphere of Titan. In a subsequent work, Sekine et al. (2008b) proposed a model of
the total H$_2$ production and loss rate in the stratosphere, with an H loss peaking around
500 km altitude. As a consequence, the H$_2$ mixing ratio might not be constant with
height. Thus, it may be premature to conclude that the INMS measurements of H$_2$ made
at altitudes above 900 km [Waite et al., 2005; Yelle et al., 2006, 2008; Cui et al., 2008]
can be extrapolated monotonically to those measured in the lower atmosphere in situ
by the Huygens GCMS and remotely by CIRS from the Cassini orbiter.

4.3 Carbon Dioxide, (CO$_2$)
Carbon dioxide was first detected in the atmosphere of Titan by the Voyager
Infrared Radiometer Spectrometer at 667 cm$^{-1}$ in the v 2 band of the Q branch
[Samuelson et al., 1983]. These observations yielded an average mole fraction
of 1.5 (+1.5,-0.8) ppbv above 110 hPa, later revised to approximately 14 ppbv between
100-200 km altitude following further analysis of the same data [Coustenis et al., 1991].
This revision agrees with the Cassini CIRS results at the peak of the contribution function
at 6.2 hPa [Coustenis et al., 2007]. The CIRS data showed little change in CO$_2$ with
latitude. While CO$_2$ remains subsaturated down to low stratospheric altitudes [Baines et
al., 2006], it is expected to condense at the tropopause where the temperature is 74 K,
provided that some unknown process does not deplete it in the lower stratosphere. Some
re-evaporation of dry ice particles is expected during sedimentation below the tropopause
down to the 94K surface of Titan but, some CO$_2$ could be expected to survive in
condensed form at the surface. The presence of solid CO$_2$ in the surface of Titan was
reported from an analysis of the Cassini Visible and Infrared Mapping Spectrometer
[McCord et al., 2008].

The GCMS detected CO\(_2\) on the surface of Titan as described in section 3.3. This CO\(_2\) could have originated from one or more of the following sources: A reaction in the atmosphere between CO and externally delivered water vapor by way of CO+OH → CO\(_2\)+H [Samuelson et al. 1983] where OH is derived from water vapor detected in Titan’s upper atmosphere by ISO [Feuchtgruber et al., 1999]; or it could have been trapped as condensate on planetesimals that made Titan [e.g. Hersant et al. 2008]; or left over and outgassed from the interior if methane was produced in Titan’s interior [Atreya et al., 2006].

CO is uniformly mixed in Titan’s atmosphere, and believed to be primordial and outgassed from the interior in cryovolcanic events [Baines et al., 2006]. A detailed height profile for CO\(_2\) is not yet available. The measured CO/CO\(_2\) ratio in Titan’s stratosphere is approximately 2300, with CO at 33 ppm based on the Cassini Visual and Infrared Mapping Spectrometer (VIMS) measurements [Baines et al., 2006; Bellucci et al., 2009] and 32 ppm from ground based measurements [Lellouch et al., 2004]. This is nearly a factor of 2000 greater than the value of 1.3 estimated for comets [Boice and Huebner, 1997].

Any outgassing of CO\(_2\) (and CO) from the interior might be expected to be associated with traces of other volatiles, especially H\(_2\)O, NH\(_3\) and H\(_2\)S. The GCMS surface data do not show evidence of these gases. This does not imply that they are not present on the surface. The GCMS only samples the warmed area of Titan’s surface in the immediate vicinity of the inlet. The H\(_2\)O saturation vapor pressure at the suspected evaporation temperature of 145 K [Lorenz et al., 2006] is only 1.3x10\(^{-8}\) hPa, or a mole fraction of 8.7x10\(^{-12}\) relative to the 1500 hPa atmospheric pressure at the surface. This is well below the normal GCMS detection capability. The NH\(_3\) vapor pressure is 67.7 hPa, or a mole fraction of 4.5x10\(^{-5}\), which is within the detection range of the GCMS.

However, the m/z = 17 peak is masked by much higher contributions from \(^{13}\)CH\(_4\) and \(^{12}\)CH\(_3\)D that made the detection impossible. Although a saturated mole fraction of H\(_2\)S (2x10\(^{-5}\)) would be detectable by the GCMS, the measured H\(_2\)S at m/z = 34 was below the detection threshold of the GCMS in this mass range. The GCMS derived upper limit is 5x10\(^{-8}\). The threshold is raised above 1x10\(^{-8}\) because of background counts occurring at high ion source pressures.

### 4.4 Protosolar noble gases

The Huygens GCMS spectra clearly show the presence of the protosolar isotope of argon, \(^{36}\)Ar, with a mixing ratio of (2.1 ± 0.8) x10\(^{-7}\). There are no indications of Kr and Xe with their upper limits being 10 ppb [Niemann et al., 2005; this paper]. This led several investigators to suggest models for the evolution of the atmosphere that would account for the absence of these two gases. These models included formation of clathrates on the surface of Titan [Thomas et al., 2007; Osegovich and Max, 2005] or formation and sequestration of clathrates in a putative sub-surface ocean [Tobie et al., 2006], or capture by aerosols with subsequent precipitation. [Jacovi and Bar-Nun, 2008].

However, Owen and Niemann (2009) demonstrated that the relative abundances of noble gases in known reservoirs in the solar system -- the Sun, Venus, Earth, Mars and meteorites -- would allow the Huygens GCMS to detect \(^{36}\)Ar, but not the other two gases.
The instrument simply did not have the sensitivity to detect Kr and Xe given the observed
abundance of $^{36}\text{Ar}$ in any of these reservoirs. Although the processes proposed for the
non-detection of krypton and xenon may be operating on Titan, the available data do not
reveal or require them [Owen and Niemann, 2009]. Of course, Titan might have collected
its noble gases from a completely different mixture from those we know. The only
constraint we can offer on such unknown mixtures is that the depletion of argon relative
to krypton could not be greater than it is on Mars or the Earth.

The origin of argon on Titan can be explored by comparing the solar value of
$^{14}\text{N}/^{36}\text{Ar}$ with the values in the atmospheres of Titan, Mars and Earth, once they have
been reconstructed for escape [Lunine et al. 1999]. The solar value of $^{14}\text{N}/^{36}\text{Ar}$ is 30
[Grevesse et al., 2007]. On Earth and Mars it is $\sim 4 \times 10^4$ while on Titan it is $\sim 1 \times 10^7$.
There are several ways of explaining these differences but a detailed treatment of
appropriate models is beyond the scope of this paper.

The discovery of $^{22}\text{Ne}$ provides yet another perspective. On Titan, $^{22}\text{Ne}/^{36}\text{Ar} \sim 1$,
but with the caveat that the $^{22}\text{Ne}$ is tentative and has a large uncertainty (Section 3.5). On
the Sun it is 3, on Earth and Venus 0.04, in the C3V meteorite Allende the ratio is 0.02. It
is virtually impossible to trap Ne in ice except in amorphous ice at ambient temperatures
of about 20 to 25 K [Laufer et al., 1987]. There are not yet any detections of Ne or any
other noble gases in comets [Weaver et al., 2002]. The implications of the detection of
neon in Titan's atmosphere require further investigation.

The cold outer solar nebula should duplicate chemical conditions in the interstellar
cloud from which it formed. The basic features of these conditions should be captured in
comets. Yet comets do not reveal either the abundances or molecular species in the
interstellar medium as expected. In the ISM, $\text{N}_2$ is typically ten times more abundant than
$\text{NH}_3$ whereas in the comae of comets $\text{NH}_3$ is the dominant carrier of N. There is only an
upper limit on $\text{N}_2$ that is orders of magnitude below the expected abundance. Argon was
not detected either, with an upper limit of about 10% of the solar value for $\text{Ar}/\text{O}$
[Weaver et al., 2002] The presence of $\text{NH}_3$, and the strong depletion of $\text{N}_2$ are clear and
striking [Cochran et al., 2000; Bockelee-Morvan et al., 2004]. This suggests that an
efficient process precluded the trapping of detectable (so far!) amounts of $\text{N}_2$ and Ar in
cometesimals.

However, $^{36}\text{Ar}$ was clearly measured in Titan’s atmosphere by the Huygens GCMS
and $\text{N}_2$ has been known to be the major atmospheric constituent since Voyager
discovered it. The tiny amount of $^{36}\text{Ar}$ must be primordial, but $\text{N}_2$ is currently assumed to
be the product of $\text{NH}_3$ photodissociation in the warm early atmosphere of Titan [Atreya et
al., 2009]. There are several possible processes that could lead to the value of $^{36}\text{Ar}/^{14}\text{N}$
that is observed in Titan’s atmosphere today, both in the capture of these gases from the
solar nebula and in their pre-appearance histories on Titan [Bar-Nun et al., 1988;
Huebner and McKay 1991;Iro et al., 2003; Hersant et al., 2008]. The discovery of $^{36}\text{Ar}$
therefore provides a new basis for future studies of Titan. The acquisition of new noble
gas data from Titan must wait a decade or more. Meanwhile our best hope for some
enlightenment is perhaps the measurement of noble gases and nitrogen from Comet
Churyumov-Gerasimenko by the Rosetta mission.

4.5 Radiogenic Argon
Radiogenic $^{40}\text{Ar}$ is a decay product of potassium 40 ($^{40}\text{K}$), which has a half-life of 1.28 billion years. Thus, over the age of the solar system most of the radiogenic argon on Titan has been produced and its abundance in the atmosphere is potentially an indicator of the extent to which outgassing of volatile elements has occurred from the deep interior, where the rock (hence the potassium) should reside. If the rocky component of the interior of Titan has the same composition as that of the Earth and has outgassed to the same extent, $^{40}\text{Ar}$ should be much more abundant than measured, comprising $\sim0.05\%$ of the atmosphere [Owen, 1982] (corrected for loss of N). Evidently the outgassing or cycling of volatiles to the surface was not as much as on the Earth. Nevertheless the presence of the $^{40}\text{Ar}$ at the levels seen in Titan’s atmosphere is a strong indication that Saturn’s largest moon has had a geologically active past, and is consistent with the view that methane has been outgassed from Titan’s interior over geologic time, replacing that depleted in the atmosphere by chemistry energized by ultraviolet photons and by charged particles.

4.6 Nitrogen $^{14}\text{N}/^{15}\text{N}$ isotope ratio

The revised GCMS result confirms that the $^{14}\text{N}/^{15}\text{N}$ ratio of 167.7 in N$_2$ on Titan today is substantially different from the telluric value of 272 [Anders and Grevesse, 1989]. This is additional information to help understand the isotope ratios measured in the solar system that suggests large scale isotope heterogeneity in the early solar nebula [Marty et al., 2010]. Using data from the Cassini Ion and Neutral Mass Spectrometer (INMS) Mandt et al. (2009) arrive at a value of $^{14}\text{N}/^{15}\text{N} = 143$ for the lower, mixed, atmosphere. The discrepancy between the GCMS and the INMS could be the result of model-dependent extrapolation of the INMS data from the region of measurements above 1000 km to the homosphere.

It is difficult to determine the value of $^{14}\text{N}/^{15}\text{N}$ in the primitive atmosphere of Titan. There is a large consensus for the hypothesis that NH$_3$ not N$_2$ was the dominant form of nitrogen in the solar nebula and in the Saturn sub nebula where Titan was formed [Atreya et al., 2009]. The nitrogen isotope ratios in NH$_3$ in comets and representative protosolar bodies which contributed nitrogen to the atmosphere e.g. in icy grains have not yet been measured so that we do not know the value in NH$_3$ on early Titan.

Several scenarios for interpreting the $^{14}\text{N}/^{15}\text{N}$ ratio measured on Titan today can be envisaged. The first scenario was to assume that a very large nitrogen escape occurred during the evolution of Titan [Lunine et al. 1999; Lammer et al., 2000]. This permits us to assume a large initial isotopic ratio, even the telluric ratio of 272 [Anders and Grevesse, 1989]. However, Mandt et al. (2009) have calculated that, considering the large amount of N$_2$ that must be fractionated, the initial $^{14}\text{N}/^{15}\text{N}$ cannot have changed much due to atmospheric processes and the initial isotopic ratio should have been close to 167. A detailed treatment of the subject is given by Atreya et al. (2009).

4.7 Carbon $^{12}\text{C}/^{13}\text{C}$ isotope ratio

The value of $^{12}\text{C}/^{13}\text{C}$ determined in the local interstellar medium is $43 \pm 4$ [Hawkins and Jura, 1987]. In evaluating this determination it is important to remember that the Sun has revolved around the center of the galaxy 15-20 times since the origin of the solar
system. Thus the “local” Interstellar Medium today is not the one in which the solar system formed. Furthermore, galactic evolution will lower the ratio with time. There is, however, a remarkable uniformity of $^{12}\text{C}/^{13}\text{C} = 90 \pm 5$ in every solar system object that has been measured with sufficient precision (Table 4). Accordingly, we adopt the solar value of 90 as our standard reference [Anders and Grevesse, 1989]. This choice is strongly supported by the most recent observations of the coma of comets. Manfrid et al., (2009) give $91.0 \pm 3.6$ for the ratio in 23 comets of various dynamical classes. We therefore expect to find a value of $^{12}\text{C}/^{13}\text{C}$ close to 90 in Titan’s hydrocarbons. Indeed the GCMS found $^{12}\text{C}/^{13}\text{C} = 91.4 \pm 1.5$ for methane in Titan’s atmosphere and 92.0 $\pm$ 0.5 at the surface. [Niemann et al. this work].

These values can be compared with measurements made by remote sensing. Analyses of 15 IR spectra covering bands of CH$_4$, C$_2$H$_2$ and C$_2$H$_6$ with the Cassini orbiter Composite Infrared Spectrometer (CIRS) by Nixon et al. (2008a) produced an average value of $^{12}\text{C}/^{13}\text{C} = 80.8 \pm 2$. Individual measurements were CH$_4$: $76.6 \pm 2.7$; C$_2$H$_2$: 84.8 $\pm 3.2$; C$_2$H$_6$: 89.8 $\pm 7.3$. Nixon et al. (2008b) found a value of $84 \pm 17$ for this ratio in CO$_2$. Jennings et al., (2009) reported $^{12}\text{C}/^{13}\text{C} = 89 \pm 8$ from ground-based observations of C$_2$H$_6$. It is too soon to attempt an analysis of the reason(s) for the disagreement among these different measurements.

The preliminary reported value of $^{12}\text{C}/^{13}\text{C}$ in methane derived from GCMS data was $82.3 \pm 1$. [Niemann et al., 2005]. This value is noticeably lower than the terrestrial value of the reference inorganic standard value of 89.4 (NIST or Vienna-Pee Dee Belemnite – V-PDB). Since terrestrial carbon-based biological activity is usually associated with an isotopic fractionation that favors light carbon [Farquhar et al., 1989], we suggested that this preliminary value of $^{12}\text{C}/^{13}\text{C}$ did not support a possible biological origin for CH$_4$. It is now clear that the stand alone ratio $^{12}\text{C}/^{13}\text{C} = 91.4 \pm 1.5$ [Niemann et al., this work] in Titan’s methane does not allow any conclusions to be drawn on the existence of biological activity on Titan past or present.

4.8 Deuterium - hydrogen isotope ratio

The D/H ratio in hydrogen obtained by the GCMS is $(1.35 \pm 0.3) \times 10^{-4}$. As outlined in section 3.6, the D/H ratio is determined from the measurement of the ratio of HD to H$_2$ present in the atmosphere of Titan. These gases are presumably products of photolysis of CH$_4$. Therefore, it may not be too surprising that the ratio derived from GCMS measurements agrees with the value of $1.32(+0.15/-0.11) \times 10^{-4}$ derived from CH$_3$D/CH$_4$ measured by the CIRS instrument in the stratosphere of Titan [Bezard et al., 2007].

The low enhancement of this Titan D/H ratio for hydrogen relative to the protosolar D/H ratio in hydrogen of $(2.1 \pm 0.5) \times 10^{-5}$ [Geiss and Gloeckler, 1998] or $(2.6 \pm 0.7) \times 0^{-5}$ [Mahaffy et al., 1998] is, however, difficult to interpret. The Titan D/H ratio is lower than the D/H ratios in cometary water, which varies from $2.9 \times 10^{-4}$ to $4.1 \times 10^{-4}$ as measured in four comets [Villaneuva et al., 2009], and in the water plumes escaping from Enceladus, as measured by the INMS experiment, which is $2.9(+/1.5/-0.7) \times 10^{-4}$ [Waite et al; 2009]. A more efficient deuterium exchange between water and protosolar hydrogen relative to methane with H$_2$ is unattractive because laboratory measurements have provided evidence that in a neutral environment the isotopic exchange is weaker than that of water with hydrogen [Lecluse and Robert, 1994].
The D/H ratio in cometary methane might be smaller than the D/H ratio in cometary water [Mousis et al. 2002] implying a similar behavior in the protosolar cloud. According to available isotope chemistry models, this seems unlikely. Our best chance to improve the situation would be to determine the D/H ratio in methane in a comet from ground-based observations or from the Rosetta mission. Equally of value would be to measure the D/H ratio in water ice at the surface of Titan [Coustenis et al. 2009].

4.9 Organic species evaporating from the surface.

The different volatilities of each component either in pure form or in mixtures with other species including nitrogen and the large uncertainty about the surface contact parameters make it difficult to relate the observations quantitatively to surface concentrations. It is noticeable though, that those molecules which would be on the surface at the landing site in liquid form as possibly droplets, reach a constant partial pressure. CH₄ and C₂H₆ fall into that group. The others, which would be sublimating from solids (ices), never reached a constant level through the end of the GCMS surface measurements. This indicates that the temperature environment in the sampling area on the surface was transient for the duration. A reservoir of the evaporating liquids must have been able to hold enough liquids to last for the duration of the surface sampling. Flash evaporation from thin layer condensation on stable aerosols is less likely because the rate would vary more with time. It is thus likely that there was a reservoir of condensed species on the surface at the Huygens landing site.

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Figure Captions.

Figure 1. Schematic of the Huygens GCMS gas sampling and mass spectrometer assembly. The subsystems and their interfaces and functions are indicated on the left. The multi ion source mass spectrometer subsystem is shown on the right. IS 1 to IS5 are the ion sources. GC1 to GC3 are the gas chromatograph channels.

Figure 2. Illustration of the locations of the atmosphere sample inlet and outlet ports on the Huygens probe.

Figure 3. Ambient pressure, descent velocity and probe dynamic pressure versus altitude during probe descent. The descent velocity and dynamic pressure share the common left-hand ordinate while the ambient pressure uses the right-hand ordinate as indicated by the
horizontal arrows next to each curve. The ambient pressure was measured by the HASI experiment. The descent velocity was determined by the DWE experiment and the Descent Trajectory Working Group (DTWG). The dynamic pressure was computed from the ambient mass density and the descent velocity.

Figure 4. Ambient pressure-temperature-altitude and event profiles versus time from measurement sequence initiation. Panel a: Ambient pressure and temperature. Panel b: Raw count rates, uncorrected for pulse-pileup and/or dead-time, from ion source 1 for m/z = 28 and 16. The gaps in the m/z = 28 trace are events when the rare gas (Rg) and enrichment cell (EC) were analyzed and the ACP data were transferred and analyzed with ion source 2. Panel c: The time intervals when the inlet leaks L1 and L2 were used are shown in the shaded areas. Panel d: The gas chromatograph cycles.

Figure 5. Examples of averaged mass spectra obtained at high and low altitude and on the surface. 5a: Average from 130 to 120 km, ~4 to 6 hPa ambient pressure (leak L1). 5b: Average from 20 to 10 km ~500 to 900 hPa ambient pressure (leak L2). 5c: Average surface spectra (leak L2) from 9000 seconds to 13000 seconds.

Figure 6. Methane mole fraction all sample points, diamonds and squares averaged over 50 sample points versus time from sequence initiation. The analysis was divided into regions for leak L1 and leak L2. N_2 m/z = 14 counts, (corrected for methane contribution) are a proxy for m/z =28 for the leak L2 data because at lower altitudes the pulse counts at m/z = 28 are no longer valid. The regions are marked in the figure and the legend. The time of surface impact is also marked. The error bars are the standard deviation.

Figure 7. Methane mole fraction averaged over 50 sample points versus altitude. The error bars are the standard deviation. Leak L1 data are blue diamonds and leak L2 data are red squares.

Figure 8. A schematic of the GCMS sample inlet and its mounting in the Huygens Probe.

Figure 9. Mole fractions of CH_4, C_2H_6, C_2H_2 C_2N_2 and CO_2 versus descent time. Error bars are standard deviation. The time of surface impact is indicated by a vertical dashed red line.

Figure 10. The mole fraction of molecular hydrogen versus time from sequence initiation. All data points and 50 sample points averages are shown for the leak L1 and leak L2 regions. The error bars are standard deviations. The time of surface impact is indicated by a vertical dashed red line.
Figure 11.
The mole fraction of molecular hydrogen versus altitude. The data points shown are 50 sample point averages. The error bars are standard deviations.

Figure 12.
Average mass spectrum of the rare gas cell contents. CO₂ (at m/z=44) and C₆H₆ (at m/z = 78) were permanent background gases in the ion source.

Figure 13.
Pulse count ratios of m/z = 29 (¹⁵N¹⁴N⁺) to m/z = 28 (¹⁴N₂⁺) (red and blue) and m/z = 29 to m/z = 14 proxy (black and red) versus time from sequence initiation shown for the leak L1 and leak L2 regions. The increase in the m/z =29 to m/z =28 count ratios at ~1500 seconds and 7000 seconds results from counter saturation at high count rates for m/z = 28.

Figure 14.
M/z = 28 counts multiplied by two (m/z = 14 is used as proxy) versus m/z =29 counts. Leak L1 counts are dark blue diamonds and leak L2 counts are red squares. The straight lines are least square fits. The m/z=29 counts were multiplied by molecular mass ratio (28/29)¹/² to account for the gas flow difference in free molecular flow to the pumps.

Figure 15.
Pulse count ratios of all sample points of m/z =17 to m/z =16 due to CH₄, versus time from sequence initiation. Dark blue is from the leak L1 region and red is from the leak L2 region. Surface impact is indicated by the vertical dashed red line.

Table 1. CH₄ mole fraction, 50 data point averages. The grayed area indicates the data points averaged near the surface as noted in the table at the bottom. Pressure and temperature derived from the HASI experiment.

Table 2. H₂ mole fraction, 50 data point averages. Pressure and temperature derived from the HASI experiment.

Table 3. Isotope ratios and noble gas abundances

Table 4. Carbon isotope ratios ¹³C/¹²C in the solar system