ION NEUTRAL MASS SPECTROMETER MEASUREMENTS FROM TITAN. Science Team: J. H. Waite, Jr.[1], H. Niemann[2], R. V. Yelle[3], W. Kasprzak[2], T. Cravens[4], J. Luhmann[5], R. McNutt[6], W.-H. Ip[7]; Data Analysis Team: D. Gell[1], I.C.F. Muller-Wordag[8], S. Ledvina[5], B. Magee[1], N. Borggren[3]; Operations Team: G. Fletcher[1], E. Walter[1], R. Miller[1], J. Xu[1], B. Block[1], K. Arnett[1], [1]University of Michigan, Department of Atmospheric, Oceanic, and Space Sciences, Ann Arbor, MI 48109-2143, USA, hunterw@umich.edu, [2]NASA Goddard Space Flight Center, Greenbelt, MD, USA, [3]University of Arizona, Lunar and Planetary Laboratory, Flagstaff, AZ, USA, [4]University of Kansas, Department of Physics and Astronomy, Lawrence, KS 66045, USA, [5]University of California, Berkeley, CA, USA, [6]Johns Hopkins University, Applied Physics Laboratory, Laurel, MD 20723, USA, [7]National Central University, Chung-Li, Taiwan, [8]Imperial College, Space and Atmospheric Physics Group, London, UK.

Introduction: The Ion Neutral Mass Spectrometer (INMS) aboard the Cassini orbiter has obtained the first in situ composition measurements of the neutral densities of molecular nitrogen, methane, argon, and a host of stable carbon-nitrile compounds in its first flyby of Titan. The bulk composition and thermal structure of the moon's upper atmosphere do not appear to be changed since the Voyager flyby in 1979. However, the more sensitive techniques provided by modern in-situ mass spectrometry also give evidence for large-spatial-scale large-amplitude atmospheric waves in the upper atmosphere and for a plethora of stable carbon-nitrile compounds above 1174 km. Furthermore, they allow the first direct measurements of isotopes of nitrogen, carbon, and argon, which provide interesting clues about the evolution of the atmosphere. The atmosphere was first accreted as ammonia and ammonia ices from the Saturn sub-nebula. Subsequent photochemistry likely converted the atmosphere into molecular nitrogen. The early atmosphere was 1.5 to 5 times more substantial and was lost via escape over the intervening 4.5 billion years due to the reduced gravity associated with the relatively small mass of Titan. Carbon in the form of methane has continued to outgas over time from the interior with much of it being deposited in the form of complex hydrocarbons on the surface and some of it also being lost to space.

INMS is a dual-ion-source quadrupole mass spectrometer covering the mass range 0.5-8.5 and 11.5-99.5 Daltons [1, 2]. The dual-source design combines classic closed and open ionization source configurations designed to measure inert species and reactive species/ions, respectively. The primary data reported in this paper were obtained with the closed ion source, which is designed to measure non-reactive atmospheric gases. In the closed source the neutral gas flows into a bulbous antechamber where it thermally accommodates with the walls of the antechamber before flowing through a transfer tube where the gas is ionized by an electron ionization source operating at an energy of 70 eV. The high flyby velocity of the Cassini spacecraft with respect

to Titan (6 km s^{-1}) produces a dynamic pressure enhancement in the antechamber, which increases sensitivity but must be taken into account to determine the proper ambient environmental density [1, 2].

The spectrum (acquired every 4.6 seconds between the altitudes of 1230 and 1174 km and co-added to enhance the signal-to-noise ratio) includes a full-mass scan covering the range 1 to 99 Daltons (see Fig. 1). The signal in any mass bin is the combination of the signal due to each species, including fragments formed due to dissociative ionization. Calibration data provides the sensitivity and the distribution of the dissociation products. Spacecraft velocity and attitude are used to compute the ram enhancement factor. From this data, a matrix is formed, each column of which describes the relative distribution of counts in the various mass channels due to a species. This kernel matrix forms the forward model relating the instrument response to the atmospheric composition. Given a measured spectrum, this model may be inverted to obtain the abundances of the species.

The inversion is performed using singular value
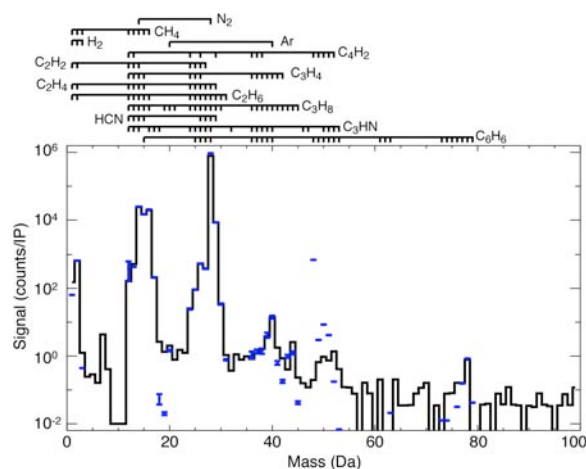
Fig. 1. The average mass spectrum from 1 to 99 Daltons measured by INMS on Ta between the altitudes of 1174 and 1300 km. The spectrum includes both inbound and outbound values in the average.

decomposition [3]. Both the measurements and the kernel are weighted by the reciprocal measurement error. The resulting matrix is factored into three matrices, using the SVD algorithm. The densities and the standard deviations are computed via products of the appropriate matrix factors.

Atmospheric Structure: The derived volume-mixing ratio of methane was found to be between 2.0 and 2.7% in the upper atmosphere using the two independent methods. The first method involves determining the average ratio from the series of ratios as a function of altitude taking into account the statistical weighting, and the second simply ratios the number of nitrogen molecules measured to the number of methane molecules within the well-mixed region of the atmosphere measured on this flyby (1174 to 1230 km). The measured temperature structure between 1174 and 1500 km was best fit by an isothermal profile with a value of 148.6 Kelvin (Fig. 2). From Fig. 2 we also note the close agreement of the reanalysis of the Voyager ultraviolet spectrometer data set by Vervack [4]. The extension to lower altitudes in this case is performed with an isothermal profile down to 900 km.

Carbon-Nitrile Compounds in the Upper Atmosphere: Deconvolution of a co-added time series of spectra acquired at a cadence of 4.6 s between the altitudes of 1230 km and the closest approach altitude of 1174 km allowed us to determine a probable list of carbon-nitrile compounds and their abundances. The spectral fit is shown in Fig. 1 and the table of compounds can be found in Table 1.
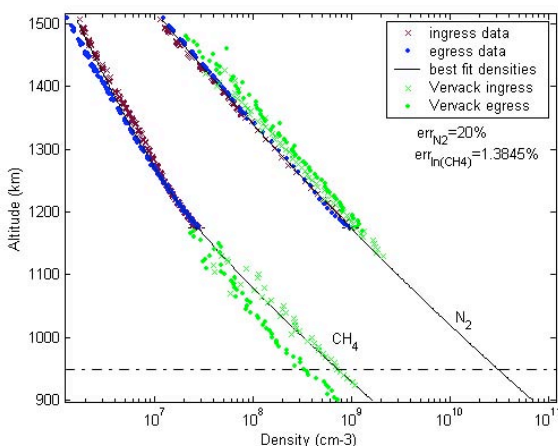
Fig. 2. The INMS-derived densities of methane (mass channel 16) and molecular nitrogen in blue (ingress) and red (egress) from Ta compared to the Vervack-derived [4] values from Voyager UVS (green). The isothermal temperature is 149 K and the methane mixing-ratio is 2.7%.

Table 1. Minor species determined from the mass spectral deconvolution with one sigma error.

Species	INMS-Derived Values	Stratospheric Values [1]
H_2	$4.28 \pm 0.04 \times 10^{-3}$	1.1×10^{-3}
C_2H_2	$2.02 \pm 0.04 \times 10^{-4}$	2.2×10^{-6}
C_2H_4	$5.84 \pm 0.06 \times 10^{-4}$	9.0×10^{-8}
C_2H_6	$1.17 \pm 0.05 \times 10^{-4}$	9.4×10^{-6}
C_3H_4	$4.10 \pm 0.80 \times 10^{-6}$	4.4×10^{-9}
C_3H_8	$3.00 \pm 0.30 \times 10^{-6}$	7.0×10^{-7}
C_4H_2	$6.70 \pm 0.02 \times 10^{-6}$	1.4×10^{-9}
HCN	$7.00 \pm 6.00 \times 10^{-6}$	3.5×10^{-7}
HC_3N	$4.40 \pm 0.10 \times 10^{-7}$	$<=1.5 \times 10^{-9}$
C_6H_6	$3.66 \pm 0.01 \times 10^{-7}$	not measured

Isotopic Ratios of Carbon, Nitrogen, and Argon: This general deconvolution procedure also leads to a determination of isotopic ratios for nitrogen ($^{14}N/^{15}N$) and carbon ($^{12}C/^{13}C$), as well as upper limits on the ^{36}Ar and ^{40}Ar mixing ratios in the upper atmosphere. Since the lowest altitudes sampled by INMS on this first Titan flyby were below the homopause (<1230 km), these volume mixing ratio values should be representative of the well-mixed atmosphere at all altitudes below. To verify and refine the deconvolution approach, another method was also used to determine the isotopic abundances. This method used altitude profiles of the respective species fit by using the hydrostatic approximation below 1230 km, determined the integrated sum of observed material and determined the ratios and the error bars from the integrated sums with their appropriate error bars. The results of the two approaches are given in Table 2.

Table 2. Key isotopic ratios measured by INMS (errors are three sigma).

Isotopic ratio	Integration Method	Deconvolution Method
$^{14}N/^{15}N$	--	223 ± 1
$^{12}C/^{13}C$	94.8 ± 0.1	96.8 ± 3.8
^{36}Ar	mixing ratio (mr) $<6 \times 10^{-7}$	mr $<6 \times 10^{-7}$
^{40}Ar	mr $8.3 \pm 0.1 \times 10^{-7}$	mr $7.3 \pm 2.1 \times 10^{-7}$
H/D	2020 ± 200	--

References:
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