MEASUREMENTS OF MARS METHANE AT GALE CRATER BY THE SAM TUNABLE LASER SPECTROMETER ON THE CURIOSITY ROVER.

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Summary: We report on the search for methane in the Martian atmosphere using the Tunable Laser Spectrometer (TLS) in the Sample Analysis at Mars (SAM) instrument suite on the Curiosity Rover [1]. After three separate searches on Martian sols 79, 81 and 106 days after landing in August 2012, we have no definitive detection of methane, with a measured value of 0.55 ±1.46 ppbv at the 1-sigma level. This corresponds to a 95% confidence interval (CI) for methane abundance of -2.4 to 3.5 ppbv. This value will be updated at the LPSC meeting as more observations are made, and we will present results of implementing a methane-enrichment experiment to lower our detection limit by at least an order of magnitude.

Introduction: Since 2004, the detection of methane on Mars has been reported from spectroscopic observations in the infrared by ground-based telescopes [2,3] and Mars orbital spacecraft [4,5]. The SAM-TLS data reported here represent the first direct measurements carried out in situ from the surface of Mars at Gale Crater. The Mars Express data are most extensive but were done with poor spectral resolution. They yield a global average methane of 10-15 ppbv [4,6], with similar values for equatorial region in spring. The ground-based observations were done with a relatively large spectral resolution [3] but through the earth's atmosphere that contains at least a million-times more abundant methane gas than Mars. These data yield a maximum methane of 50 ppbv. Although no data exist for Gale Crater region, interpolations beween existing data predict on the order of 20 ppbv CH_4. The pre-Curiosity data on methane led to either a geological (water-rock reactions) or biogenic origin of methane with possibly a small contribution from comets, micrometeoritic dust or IDP [7]. The photochemical lifetime of methane was found to be several hundred years, and the time for uniformly distributing the gas over Mars less than three months [7]. However, the pre-TLS data reported a much shorter lifetime of <4 years, leading to speculations of surface loss [7]. Monitoring methane over time with the SAM-TLS will reveal any seasonal or temporal variations in methane.

Measurement Method: TLS is a two-channel tunable laser spectrometer that uses direct and second harmonic detection of IR laser light absorbed after multi-passing a sample cell [8]. One laser source is a near-IR tunable diode laser at 2.78 µm that can scan two spectral regions containing CO_2 and H_2O isotopic lines (reported in a second presentation); the second laser source is an interband cascade (IC) laser at 3.27 µm used for methane detection alone. For the results reported here, the IC laser makes 81 passes of a 20-cm long Herriott cell fitted with high-vacuum microvalves that allow evacuation with a turbomolecular pump for "empty cell" scans, or filled to Mars ambient pressure (~7 mbar) for "full cell" runs. During data collection, the Herriott cell and other optics are kept at 47±3 ^oC using a ramped heater that spoils any interference fringes during the 2-minute sample period.

The laser scans every second through the methane spectral region (see Figure 1). Each spectrum is co-added on board to downlink sequential 2-minute spectra during a given run, ~1-2 hours in duration. Typically, we record and download twenty-six 2-minute "empty cell" spectra followed by twenty-six 2-minute "full cell" spectra, then finally five additional 2-minute empty cell spectra. This experiment has been repeated on three separate Martian Sols (days) to date (Martian Sols 79, 81, & 106) after landing in August 2012.

Spectral regions. TLS scans over individual rovibrational lines in two spectral regions near 2.78 µm; one centered at 3590 cm^{-1} for CO_2 isotopes, and a second centered at 3594 cm^{-1} for both CO_2 and H_2O isotopes (see Figure 1). The lines used in both regions have no significant interferences. In the 3057.5 to 3058.2-cm^{-1} region, CH_4 lines have no significant spectral interferences, allowing determination in both atmospheric and evolved gas experiments.

Difference Method: As discussed earlier, the methane measurement is made by differencing the "full cell" spectrum from the "empty cell" spectrum. However, prior to entering the 81-pass (16.8 m pathlength) sample cell, the IC laser beam passes through ~9 cm of a foreoptics chamber containing beamsplitters and steering mirrors. That foreoptics chamber contains terrestrial methane at a mixing ratio of about 5 ppmv and an initial pressure of about 46 mbar. During earli-

Observation	Method	Mixing Ratio (ppbv)
Mars Express PFS[4,5]	Mars orbital remote sensing	10-15 (global)
IRTF telescope[3]	Earth telescope	~20 (interpolated)
SAM-TLS	Mars in situ	0.55 ± 1.46 (1-σ) Gale Crater

Table 1. Results to date.

er observations, a difference of a few ppbv methane was detected that was observed to increase with time over the 1 hour measurement period, and this was identified as terrestrial methane that had leaked from the foreoptics into the Herriott cell during the run. For the measurements reported here, the foreoptics pressure was reduced from 46 to 7 mbar, thereby reducing any foreoptics leak (whether driven by pressure difference or by molecular diffusion) to the point that no detectable increase in the empty cell or full cell measurements was seen. The terrestrial methane signal from the foreoptics is equivalent to a Herriott cell signal of about 80 ppbv, close to the value of 88 ppbv in our calibration gas. Rather than evacuate the foreoptics chamber completely, we chose (prefer) to leave this residual gas in the foreoptics since it provides a clear methane spectrum that can be monitored precisely during the run and allows us to make any minor changes to adjust for small motion left or right of the spectral lines during the run. In this way, we are co-adding the spectra accurately and not dealing with non-observable spectral lines.

Preliminary Results: After three separate searches on Martian sols 79, 81 and 106 days after landing in August 2012, we have no definitive detection of methane, with a measured value of 0.55 ±1.46 ppbv at the 1-sigma level. This corresponds to a 95% confidence interval (CI) for methane abundance of -2.4 to 3.5 ppbv. This value will be updated at the LPSC meeting as more observations are made, and we will present results of implementing a methane-enrichment experiment to lower our detection limit by at least an order of magnitude.

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Acknowledgements: The research described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration (NASA).

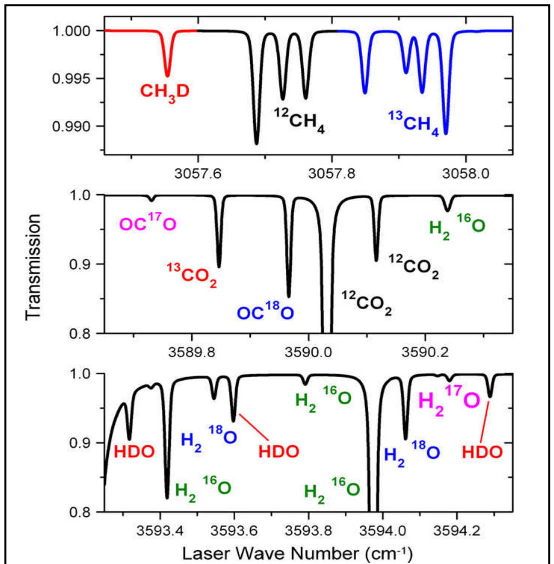

Fig. 1. Spectral scan regions used by MSL-SAM's TLS instrument for measuring gas abundances and isotope ratios. For the methane scan, the vertical axis for $^{13}CH_4$ and CH_3D is multiplied by 100, 500.

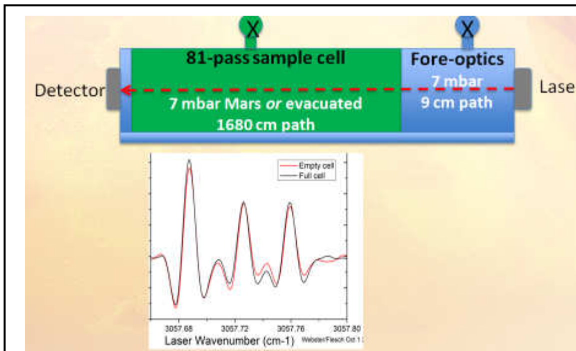

Figure 2. The methane detection configuration (above) with sample spectra for full and empty cell (below).