

Analytical Chemistry Cumulative Examination

Professor M. Trenary

February 7, 2019

The most accurate measurements of the methane concentration in the atmosphere of Mars have been made with the tunable laser spectrometer on the Curiosity rover. These measurements have been described in recent articles in *Science* (vol 324, p. 355; vol 347, p. 415). One motivation for the measurement is that on Earth atmospheric methane is almost entirely biological in origin and so if any methane is found it would indicate that there are living organisms on Mars. Given the importance of the question, highly accurate measurements are essential. This examination concerns the analytical chemistry involved in the measurement.

100 points total

- (15 pts) The methane concentrations were measured with tunable laser spectroscopy (TLS) based on infrared absorption lines in the asymmetric C–H stretch region. Routine chemical analyses often use gas chromatography mass spectrometry (GC-MS). Give some possible reasons why NASA chose TLS over GC-MS for the methane measurements.
- (20 pts) The apparatus carried to Mars included infrared lasers, detectors, beam splitters, a foreoptics area, and a Herriott cell. Sketch this apparatus, labeling all of the key components.
- (20 pts). The infrared absorption spectra can be measured in different ways, including direct absorption and second harmonic detection. Explain how second harmonic detection is achieved and the advantages it offered in this case.
- (20 pts). The authors noted that a Beer's law calculation using known spectra line parameters can, in theory, determine the methane abundance without the need for a calibration gas.
 - (10 pts) Explain what Beer's law is and how it could be used in this way.
 - (10 pts) What are the advantages of using a calibration gas instead of relying on Beer's law?
- (20 pts) Multiple choice. (Write the answers in the exam book).
 - The spectral resolution of the TLS is:
 - 2 cm^{-1}
 - 0.2 cm^{-1}
 - 0.02 cm^{-1}
 - 0.002 cm^{-1}
 - 0.0002 cm^{-1}
 - What kind of pump is used to evacuate the Herriott cell?
 - An ion pump
 - A diffusion pump
 - A turbomolecular pump
 - All of the above
 - No pump was needed because the pressure on Mars is low enough already.

c. From the measurements, the authors of the 2013 article reached which of the following conclusions.

- i) There is an upper limit with 95% confidence of 1.3 ppbv (parts per billion by volume) in the methane abundance in the Martian atmosphere.
- ii) The measurement was inconclusive because of a leak on the launch pad that allowed some methane-containing air from Earth into the foreoptics chamber, which then leaked into the Herriott cell.
- iii) The measured methane abundances were substantially the same as those reported from Mars remote sensing spacecraft.
- iv) Although the absolute methane abundance could not be measured, the $^{12}\text{C}/^{13}\text{C}$ isotope ratio was measured and provided strong evidence of significant methanogenic microbial activity on Mars.
- v) Although a measureable amount of methane was detected, the $^{12}\text{C}/^{13}\text{C}$ ratio was found to be substantially different than the ratio for methane in Earth's atmosphere, proving that the methane on Mars cannot be due to significant methanogenic microbial activity on Mars.

d) Two different lasers are included in the infrared spectrometer on Opportunity. Which of the following was the purpose of having two lasers?

- i) The technique is an example of sum frequency generation, in which light from a fixed visible laser, with a frequency of ν_{vis} , is combined with light from a tunable infrared laser, with frequency ν_{ir} , to generate light through a non-linear process at frequency $\nu_{\text{vis}} + \nu_{\text{ir}}$.
- ii) Two lasers are needed for the 2nd harmonic detection method used.
- iii) The laser used in the methane measurements was an interband cascade laser at 3.27 μm . The second laser was a near-IR tunable diode laser at 2.78 μm , which is used for measurements of CO_2 and H_2O .
- iv) The second laser was identical to the first and was included as a back-up in case the first laser failed.
- v) Because the output power from a single laser was insufficient, it was necessary to combine the output of two lasers in order to achieve the required signal-to-noise ratio.

6. (5 pts). Has methane been definitively, i.e, outside the measurement error, found in the Martian atmosphere from the TLS on Curiosity?