

**MEASURING THE MARTIAN ATMOSPHERIC COMPOSITION WITH THE SAMPLE ANALYSIS AT MARS (SAM) QUADRUPOLE MASS SPECTROMETER.** M. G. Trainer<sup>1</sup>, H. B. Franz<sup>1,2</sup>, M. H. Wong<sup>3</sup>, H. L. K. Manning<sup>4</sup>, J. C. Stern<sup>1</sup>, E. Raaen<sup>1</sup>, S. K. Atreya<sup>3</sup>, L. A. Leshin<sup>5</sup>, P. R. Mahaffy<sup>1</sup>, T. C. Owen<sup>6</sup>, and the MSL Science Team. <sup>1</sup>NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771, [Melissa.Trainer@nasa.gov](mailto:Melissa.Trainer@nasa.gov), <sup>2</sup>University of Maryland Baltimore County, Baltimore, MD 21228, <sup>3</sup>University of Michigan, Ann Arbor, MI 48109, <sup>4</sup>Concordia College, Moorhead, MN 56562, <sup>5</sup>Rensselaer Polytechnic Institute, Troy, NY 12180, <sup>6</sup>University of Hawaii, Honolulu, HI 96822.

**Introduction:** The Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) “Curiosity” rover was designed to perform chemical and isotopic analysis of volatile compounds from atmospheric and solid samples to address questions pertaining to habitability and geochemical processes on Mars [1, 2]. Here we report quadrupole mass spectrometer (QMS) measurements of volume mixing ratios of major atmospheric constituents.

**SAM Instrument Overview:** The analytical components of the SAM suite include the QMS, the tunable laser spectrometer (TLS), and six gas chromatograph (GC) columns. Of the three primary SAM instruments, the QMS is tasked with measuring the volume mixing ratios of major atmospheric constituents and isotope ratios of nitrogen and noble gases. The TLS is targeted specifically to measure abundances and isotope ratios of carbon, oxygen, and hydrogen in CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>O. The composition of the atmosphere and isotope ratios of other compounds not accessible to the TLS may be determined only with the QMS, which can scan continuously over m/z values of 1.5 to 535.5.

Gases are introduced to the SAM analytical components through a gas processing system (GPS), which includes two turbomolecular pumps, oxygen and helium tanks, a hydrocarbon trap, gas scrubbers and getters, heated manifold and transfer lines, and valves [2]. Measuring some key species that occur at low concentrations, including nitrogen and noble gases, may require specialized enrichment experiments utilizing the scrubbers and getters. The GC may be invoked in future atmospheric experiments focused on examining trace gases.

**Experimental Methods:** SAM performs three types of atmospheric experiments that involve QMS analysis [2]. The experiment that will be used most frequently on Mars introduces atmospheric gas directly into the GPS manifold for sampling by the QMS and TLS. Prior to the experiment, the QMS and TLS are evacuated, followed by “QMS” and “TLS empty-cell” background measurements. The gas manifold and transfer lines are heated to a specified target temperature, nominally 135 °C, and evacuated. Additional QMS background measurements are then taken after opening the microvalve that connects the QMS to the manifold through a glass capillary inlet (the “manifold background”). Gas is introduced to the manifold by

opening a valve that directly accesses the martian atmosphere through an inlet in the rover wall. With martian ambient pressure in the manifold, gas leaks into the QMS ion source through the capillary tube, while the QMS scans continually across m/z values from 1.5 to 149.9 for a parameterized duration. The entire measurement sequence may be repeated by pumping out the QMS and manifold, obtaining new background measurements, and then introducing a fresh aliquot of atmospheric gas into the instrument.

Three QMS scanning modes are utilized during both background and analytical segments, through control of the quadrupole rod voltages [2]. In unit mass scan mode, the selected range of m/z values is sampled by stepping between integer mass values. In high-resolution or “fractional” scan mode, the mass scan is nominally performed with steps of 0.1 Da. Additionally, a high-speed or “smart scanning” mode samples a range (band) of m/z values in a single integration period. All ratios for atmospheric experiments described here were computed from integrated fractional scan peak areas at each m/z ± 0.4, averaged over multiple scans. Data were corrected for dead time effects, as described in [3], prior to background subtraction and further processing.

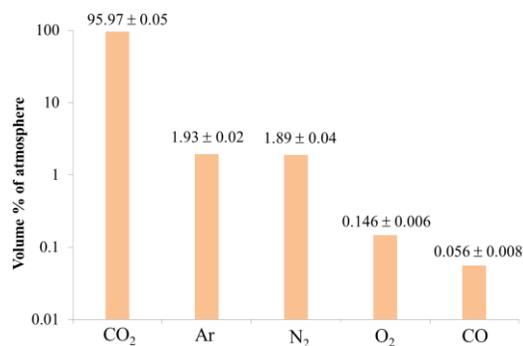
**Calibration Constants:** The direct atmospheric experiment sequence was performed multiple times during pre-flight testing, using a commercially-prepared gas tank of martian atmospheric composition [4]. To facilitate computation of the volume mixing ratios (VMR) of the four main atmospheric constituents on Mars, empirical calibration constants were prepared through analysis of a separate gas mixture comprising CO<sub>2</sub>, N<sub>2</sub>, Ar, and O<sub>2</sub> in equimolar proportions. The calibration constants for these four gases were derived by taking the ratio of a key “marker” fragment of each molecule to <sup>40</sup>Ar.

The marker for each species was determined through consideration of expected abundances and potential isobaric interferences from other compounds. Due to the high concentration of CO<sub>2</sub> in the martian atmosphere, the major molecular ion at m/z 44 saturates the QMS detector under nominal operating conditions of the direct atmospheric experiment. However, the CO<sub>2</sub><sup>++</sup> ion at m/z 22 occurs in a region of the spectrum free of expected interferences and has appropriate signal strength on Mars for accurate atmospheric

measurements. The major molecular ion of  $N_2$  at  $m/z$  28 incurs interferences from  $CO^+$  fragments of  $CO_2$  as well as molecular  $CO^+$  ions. The  $m/z$  28 signal also saturates the QMS detector under atmospheric experimental conditions. For these reasons, the signal at  $m/z$  14, which includes contributions from both  $N_2^{++}$  and  $N^+$  ions, was selected as the marker for  $N_2$ . The contributions of  $CO^{++}$  ions at  $m/z$  14 are considered negligible and are ignored. For  $O_2$ , the major molecular ion at  $m/z$  32 was selected as the marker fragment, since the low abundance of  $O_2$  in the martian atmosphere does not predict issues with detector saturation.

The final constituent for which a calibration constant was derived was CO, predicted to occur at  $<0.1$  vol% abundance [4]. The CO calibration constant was computed from combined results of ground tests performed with the Mars gas mix and equimolar gas mix. The equimolar mix (with no CO) was used to determine the contribution of  $CO_2$  to  $m/z$  12 in the SAM QMS, which was then used to correct for  $CO_2$  interference in the Mars mix run, yielding the CO calibration constant.

**Preliminary Results:** Figure 1 illustrates average preliminary VMR of major martian atmospheric constituents obtained during sols 0-100. Uncertainties shown are for statistical error only, computed as the standard deviation divided by the square root of the number of observations. Systematic error will be refined with further analysis. Interpretation of these measurements is discussed in another abstract at this meeting [5].



**Figure 1. Average martian atmospheric composition determined during sols 0-100. ( $1\sigma$  errors computed from standard deviations of the mean.)**

**References:** [1] Mahaffy (2008) Space Sci. Rev. 135, 255. [2] Mahaffy et al. (2012) Space Sci. Rev. 170, 401. [3] Franz et al. (2013) LPSC XLIV. [4] Owen et al. (1977) J. Geophys. Res. 82, 4635. [5] Atreya et al. (2013) LPSC XLIV.