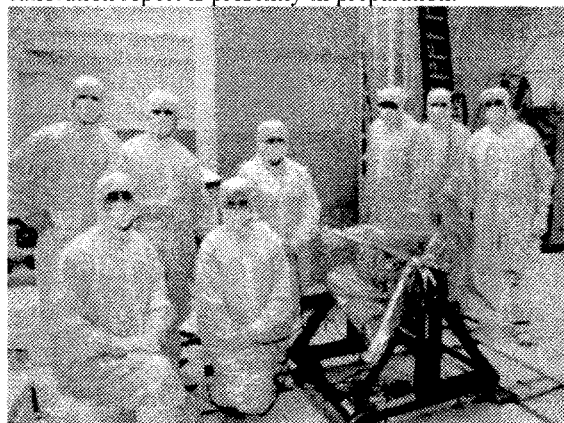


**CALIBRATION OF THE QUADRUPOLE MASS SPECTROMETER OF THE SAMPLE ANALYSIS AT MARS INSTRUMENT SUITE.** P. R. Mahaffy<sup>1</sup>, M. G. Trainer<sup>1</sup>, J. L. Eigenbrode<sup>1</sup>, H. B. Franz<sup>1</sup>, J. C. Stern<sup>1</sup>, D. N. Harpold<sup>1</sup>, P. G. Conrad<sup>1</sup>, E. Raaen<sup>1</sup>, E. Lyness<sup>1</sup>, and the SAM Team, <sup>1</sup>NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771 ([Paul.R.Mahaffy@NASA.gov](mailto:Paul.R.Mahaffy@NASA.gov))

**Introduction:** The SAM suite of instruments on the “Curiosity” Rover of the Mars Science Laboratory (MSL) is designed to provide chemical and isotopic analysis of organic and inorganic volatiles for both atmospheric and solid samples [1,2]. The mission of the MSL investigations is to advance beyond the successful search for aqueous transformation in surface environments at Mars toward a quantitative assessment of habitability and preservation through a series of chemical and geological measurements [3]. The SAM suite was delivered in December 2010 (Figure 1) to the Jet Propulsion Laboratory for integration into the Curiosity Rover. We previously [4] outlined the range of SAM solid and gas calibrations implemented or planned and here we discuss a specific set of calibration experiments to establish the response of the SAM Quadrupole Mass Spectrometer (QMS) to the four most abundant gases in the Martian atmosphere CO<sub>2</sub>, N<sub>2</sub>, Ar, and O<sub>2</sub>. A full SAM instrument description and calibration report is presently in preparation.



**Figure 1.** SAM is shown after delivery from Goddard Space Flight Center in December 2011 into the spacecraft assembly facility at the Jet Propulsion Laboratory for subsequent integration into the Curiosity Rover.

**The SAM Instrument Suite:** SAM’s instruments are a Quadrupole Mass Spectrometer (QMS) from Goddard, a 6-column Gas Chromatograph (GC) from the SAM French partners, and a 2-channel Tunable Laser Spectrometer (TLS) from JPL. Gas Chromatography Mass Spectrometry implemented with integrated GC/QMS operation enables definitive identification of organic compounds to sub part-per-billion sensitivity while the TLS [5] obtains precise isotope ratios for C,

H, and O in carbon dioxide and water and measures trace levels of methane and its <sup>13</sup>C/<sup>12</sup>C ratio. The solid phase materials are sampled by transporting sieved materials delivered from the MSL sample acquisition and processing system to one of 59 cups of the Sample Manipulation System (SMS) that can then be inserted into one of 2 ovens for thermal processing and release of volatiles for chemical and isotopic analysis. Nine other hard sealed cups contain liquid solvents and chemical derivatization agents that can be utilized on Mars to extract and transform polar molecules such as amino acids, nucleobases, and carboxylic acids into compounds that are sufficiently volatile to transmit through the GC columns. Six other cups contain calibration materials to be used *in situ*. The SAM Chemical Separation and Processing Laboratory (CSPL) consists of valves, heaters, pressure sensors, gas scrubbers and getters, traps, and gas tanks used for calibration or combustion experiments[2].

**The SAM Quadrupole Mass Spectrometer:** The SAM QMS utilizes 6” hyperbolic rods. A three-frequency RF circuit enables a mass range of 2-535 Da with *m/z* values selected by DAC control of the DC and RF amplitude and DC bias on the rod pairs. The high, medium, and low RF frequencies cover the mass ranges of 2-19, 20-149, and 150-535 Da respectively. Thus the parent peaks of the major Mars atmospheric gases are found in the mid frequency scan region with fragment peaks in the high frequency scan region. The electron emission from the filament of the electron gun of the QMS ion source is controllable by SAM command in the 2 – 200 μAmp range and the detector is a high gain channeltron operated in a pulse counting mode. The detector saturates as it approaches 10 million ions/second and a detector dead time correction of the form  $o = n \exp(-\tau n)$  [where *o* represents the observed counts and *n* the corrected count rate] represents the data well up to the point where the detector counts begin to decrease with increasing ion current. The best fits to the calibration data are obtained with  $\tau$  itself set to be a function of *o* ( $\tau = a \exp(b o)$ ) where *a* and *b* are constants determined by securing the best linear fit to the count rate at a selected *m/z* with pressure. Independent of the electron multiplier, a faraday cup can also be utilized at high ion currents to extend the dynamic range of the QMS.

**The QMS Calibration Configuration:** Most of the SAM Flight Model (FM) calibration experiments were carried out in the chamber that was developed for

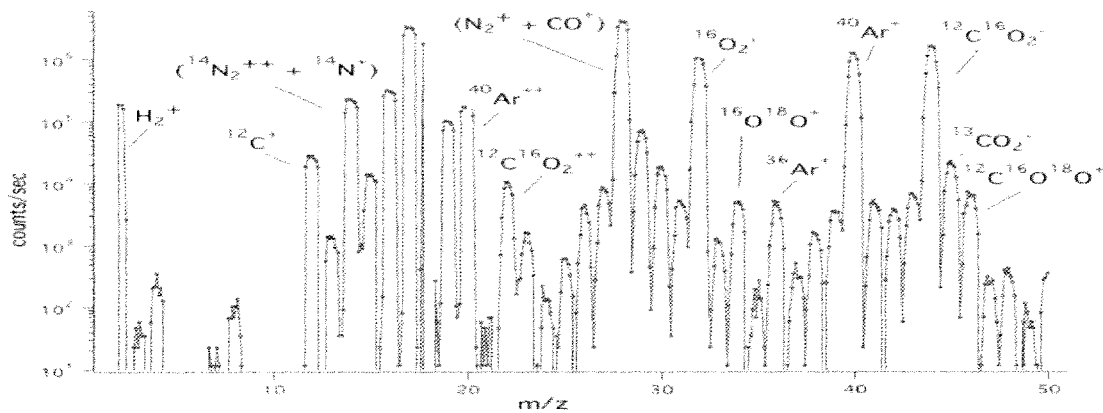


Figure 2. In this calibration experiment approximately equal parts of CO<sub>2</sub>, Ar, N<sub>2</sub>, and O<sub>2</sub> were introduced into the QMS through its flow restrictor capillary leak and the QMS m/z values were scanned in 0.1 Da increments. Several of the relevant ions and their isotopes are labeled. The raw data are shown. A significant detector dead time correction is necessary to accurately calculate mixing and isotope ratios. At the 20 μAmp emission level selected for this scan the m/z = 18 peak of water is saturated. Longer pump times and a QMS bake reduce the water background signal in the instrument.

SAM environmental testing. This chamber generates the range of temperatures and pressures expected at Mars and utilizes a 4-component Mars gas mix. Gas manifold lines are introduced through the chamber wall to enable separate introduction of calibration gases and to provide exhaust-pumping lines. A subset of calibration runs was carried out with SAM out of the chamber. Although many calibration runs were carried out with a mixture of gases in the predicted Martian composition, the spectrum shown in Figure 2 utilizes approximately equal volumes of these 4 gases to establish the instrument response. Figure 3 illustrates the extent of the dead time correction to the counts needed as detector approaches saturation.

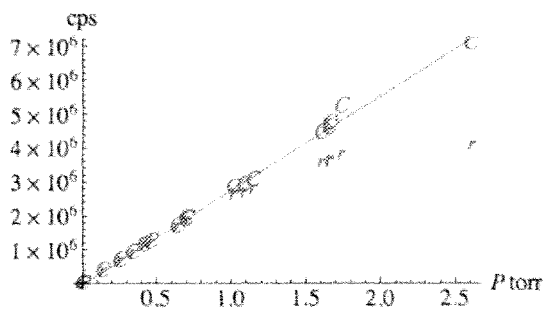


Figure 3. The detector dead time correction established during calibration is shown for m/z = 40 at a variety of manifold pressures. “C” designates the corrected counts, “r” the raw data, and “cps” counts/second.

**Calibration Constants for Direct Atmospheric Measurements:** Doubly charged ions or fragments can also provide a suitable reference signal when a parent ion is saturated (Figure 4). The calibration exercise described has established a set of calibration constants

to enable rapid conversion of such ratios secured from SAM on Mars into atmospheric volume mixing ratios. δ<sup>13</sup>C of the calibration gas has been independently determined in our laboratory and independent calibration of the other isotope ratios in these gases is planned.

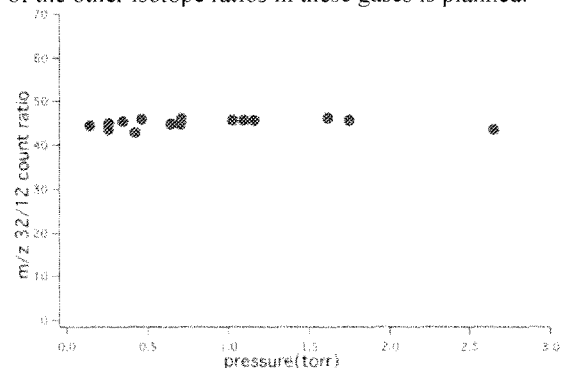


Figure 4. Use of the C<sup>+</sup> fragment signal from CO<sub>2</sub> as a reference enables mixing ratios to be secured even when the parent CO<sub>2</sub><sup>+</sup> signal is saturated. The standard deviation in this case of the ratio of the dead time corrected O<sub>2</sub><sup>+</sup> to C<sup>+</sup> signal is ~2%.

**References:** [1] Mahaffy, P.R., *Space Sci. Rev.* **135**, 255 (2008). [2] Mahaffy, P.R. (2009) *Geochem. News*, **121**. [3] Grotzinger, J., *Nature Geoscience* **2**, 231, (2009). [4] Mahaffy, P. R., et al., (2010) *Lunar and Planetary Institute Science Conference Abstracts*, 41, 2130. [5] Webster, C. R., Mahaffy, P. R., *Planet. Space Sci.* (2010), doi:10.1016/j.pss.2010.08.021

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