

INITIAL EXPERIMENTS WITH THE SAMPLE ANALYSIS AT MARS ONBOARD CALIBRATION GAS CELL. H. B. Franz^{1,2}, M. G. Trainer¹, C. A. Malespin^{1,3}, P. R. Mahaffy¹, P. G. Conrad¹, J. L. Eigenbrode¹, G. Flesch⁴, H. L. K. Manning⁵, E. Raaen¹, C. R. Webster⁴, M. H. Wong⁶, and the MSL Science Team. ¹NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771, Heather.B.Franz@nasa.gov, ²University of Maryland, Baltimore, MD 21228, ³Universities Space Research Association, Houston, TX 77058, ⁴Jet Propulsion Laboratory, Pasadena, CA 91009, ⁵Concordia College, Moorhead, MN 56562, ⁶University of Michigan, Ann Arbor, MI 48109

Introduction: The Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) “Curiosity” rover was designed to measure the chemical and isotopic composition of martian volatile compounds *in situ* with unprecedented precision [1-2]. The SAM suite can sample both atmospheric gas and gas released through thermal processing of solid materials with its three instruments: a quadrupole mass spectrometer (QMS), a tunable laser spectrometer (TLS), and a gas chromatograph (GC). Chemical composition is determined with the QMS, while both the QMS and TLS are utilized for isotopic measurements. The TLS is designed specifically to measure the abundances and isotope ratios of carbon, oxygen, and hydrogen in CH₄, CO₂, and H₂O at high precision. Isotope ratios of other compounds must be determined with the QMS, which can scan continuously over *m/z* values of 1.5 to 535.5. CO₂ isotope ratios may also be determined from QMS data to complement the high-precision measurements performed with the TLS. The GC separates and concentrates trace species, particularly organic compounds present in solid samples, for detection and quantification in conjunction with QMS analysis.

SAM carries calibration materials to provide a mechanism for linking observations acquired on Mars with “ground truth” data acquired before launch. These materials include both calibration gas and solid calibrants used to validate atmospheric measurements, pyrolysis oven temperature models, GC detection of organic compounds, and analysis of CO₂ released by heating of calcium carbonate. Here we describe QMS results from the first experiments performed on Mars with the SAM onboard calibration gas cell.

Pre-flight Calibration: Prior to integration with Curiosity, the SAM suite was subjected to a rigorous series of experiments designed to test functionality and to produce calibration constants necessary for quantitative analyses on Mars. Pre-flight calibration to support atmospheric measurements utilized various gas mixes. An equimolar mixture comprising CO₂, N₂, Ar and O₂ in proportions of ~25% each was prepared at NASA Goddard Space Flight Center (GSFC). This “EQ mix” tank and a commercially prepared “Mars mix” tank with contents approximating the martian atmospheric composition as determined by Viking [3] were used to establish empirical calibration constants required to

calculate volume mixing ratios (VMR) of the top five atmospheric gases: CO₂, N₂, Ar, O₂, and CO [4-5]. These gas mixes were also used for calibration of CO₂ isotopic analyses by both QMS and TLS. Ground truth for CO₂ isotopes was provided through independent measurements with commercial mass spectrometers at NASA GSFC [4]. A noble gas mix containing ~10% each Ne, Ar, Kr and Xe in balance of He was used to determine mass fractionation corrections for Kr and Xe isotope ratios [6].

Calibration Gas Cell: The SAM calibration cell contains approximately equimolar proportions of CO₂, N₂, Ar, and Xe enriched in the ¹²⁹Xe isotope, with trace amounts of four fluorinated hydrocarbons (F-HCs) to ensure detection of organic compounds by the GC (Table 1). The calibration cell was exercised several times during pre-flight testing, allowing derivation of corrections for isobaric interferences at masses corresponding to Xe isotopes due to the F-HCs [7].

Table 1. Calibration gas cell contents
(Data from [1])

Compound*	Molecular weight	100 °C MR
CO ₂	44	24.32%
N ₂	28	24.10%
Ar	40	24.04%
Xe _T	131	8.48%
¹²⁹ Xe	129	15.51%
PFTBA	671	3.00%
1-FN	146.161	0.54%
DFBP	190.189	0.016%
PFBP	334.112	0.0078%

*Xe_T = Xenon of near-terrestrial isotopic composition;

PFTBA = perfluorotributylamine;

1-FN = 1-Fluoronaphthalene;

DFBP = 2,2'-Difluoro-1,1'-biphenyl;

PFBP = Perfluorobiphenyl.

Experimental Methods: The calibration cell has been utilized on Mars twice to date, in July and December 2015. Prior to measuring the calibration gas in each experiment, the gas manifold and transfer lines were heated and evacuated, and background measurements were obtained. Calibration gas was then intro-

duced into the manifold through a 0.02-second “squirt,” producing an initial pressure of approximately 6 mb. During the first experiment, the TLS was also evacuated at the beginning of the run, and calibration gas was introduced to the TLS upon the initial squirt and held there for analysis following completion of QMS operations. In the second experiment, both the evacuation and loading of the TLS were delayed until after completion of analysis by the QMS. In both cases, a portion of the manifold was evacuated by the SAM turbopump, followed by a volume expansion that reduced the calibration gas pressure in the manifold to ~3 mb before beginning QMS measurements.

Successive volume expansions were performed in each experiment, allowing QMS analyses at multiple pressures. Calibration gas was leaked from the manifold into the ion source of the QMS through a capillary tube. The QMS scanned continually through a pre-selected set of m/z values relevant to the compounds present in the calibration cell [4,7].

Data Reduction: QMS data acquired during the calibration experiments were processed by first applying corrections to account for detector dead time, pressure and background effects, as discussed at length in [4-5]. VMR and isotope ratios were then computed from integrated fractional scan peak areas at each $m/z \pm 0.4$, averaged over multiple scans. VMR were determined from marker fragments at m/z 22, 14, 40 and 132 for CO₂, N₂, Ar, and Xe, respectively. CO₂ isotope ratios were calculated from m/z 22, 45 and 46, while Xe isotope ratios were calculated from m/z 124, 126, 128-132, 134 and 136 after correction for interferences by F-HCs.

Results: Results of both calibration gas experiments performed on Mars suggest introduction of additional atmospheric gas to the manifold during volume expansions, which complicates efforts to model the instrument background, particularly at the lowest calibration gas pressures. This behavior is evident in VMR calculations showing the presence of excess CO₂ as well as in CO₂ isotope ratios. Values of $\delta^{13}\text{C}$ computed from QMS data matched the known composition of the calibration gas at the highest pressure in each experiment, but drifted to heavier compositions at lower pressures, consistent with addition of isotopically enriched atmospheric CO₂ [8-9] during the volume expansions.

Xe measurements successfully retrieved the expected enrichment in ¹²⁹Xe compared to terrestrial isotopic composition. We will present updated results of this ongoing analysis at the conference.

References: [1] Mahaffy et al. (2012) *Space Sci. Rev.* 170. [2] Webster (2005) *Appl. Opt.* 44. [3] Owen et al. (1977) *J. Geophys. Res.* 82. [4] Franz et al., *Planet. Space Sci.* 96. [5] Franz et al., *Planet. Space Sci.* 109-110. [6] Conrad et al., *Nature Geosci.*, submitted. [7] Franz et al, in prep. [8] Webster et al. (2013) *Science* 341. [9] Mahaffy et al. (2013) *Science* 341.