CALIBRATION OF THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT SUITE FOR THE 2011 MARS SCIENCE LABORATORY.

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Introduction: The Sample Analysis at Mars (SAM) suite of instruments on 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]. The mission of SAM and the other MSL investigations is to quantitatively assess habitability through a series of chemical and geological measurements [2]. Environmental testing of the flight unit of the suite is nearly complete with delivery to the Jet Propulsion Laboratory for integration into the MSL Rover (now named Curiosity) scheduled for 2010. The mission launch delay of two years has enabled additional pre-delivery calibrations to be carried out that complement the *in situ* calibrations that will take place periodically over the course of the 2 year mission on the surface of Mars. Here we describe the variety of SAM calibration experiments performed on the flight instrument.

The SAM Instrument Suite: SAM's instruments are a Quadrupole Mass Spectrometer (QMS), a 6-column Gas Chromatograph (GC), and a 2-channel Tunable Laser Spectrometer (TLS). 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 obtains precise isotope ratios for C, H, and O in carbon dioxide and water and measures trace levels of methane and its carbon 13 isotope. The solid phase materials are sampled by transporting sieved materials delivered from the MSL sample acquisition and processing system to one of 61 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 extact and transform polar molecules such as amino acids, nucleobases, and carboxylic acids into compounds that are sufficiently volatile to transmit through the GC columns. Four 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 Calibration Configuration: The SAM Flight Model (FM) is calibrated in the same chamber (Figure 1) that was developed specifically for SAM environmental testing.

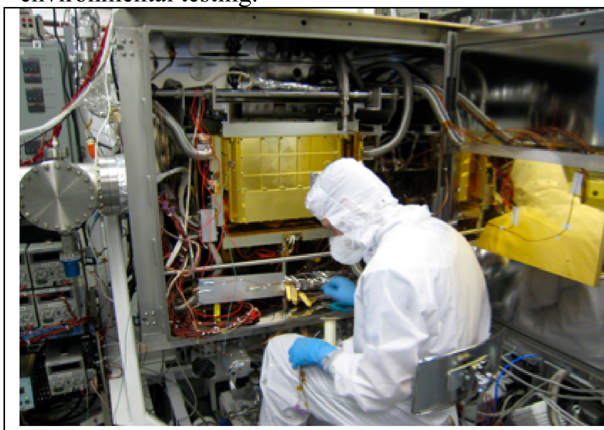

Figure 1. The SAM calibration and test chamber enables the instrument suite to operate with gas composition and pressure identical to that which will be encountered on Mars. The thermal interface of SAM to MSL is realistically simulated with independently temperature controlled surfaces surrounding SAM and a thermal sink designed to be identical to that provided by the thermal control system of the rover.

Independent gas manifold lines were plumbed through chamber wall vacuum feedthroughs to both the SAM gas inlets and vents to enable introduction of calibration gases and pumping independent of the chamber environment.

Calibration Gases for GCMS: Two sets of calibration gases were used in the SAM suite level calibration. The first set of gases consisted of a mixture of butane, pentane, hexane, and benzene in helium that had previously been used to calibrate the GC columns. With an injection loop in the manifold external to the chamber nano-molar levels of these light hydrocarbons could be introduced into the gas stream and onto SAM traps for subsequent GCMS analysis. For calibration using heavier hydrocarbons we have selected a set of fully fluorinated hydrocarbons that can easily be interpreted as terrestrial in the event that any traces of these are detected during analysis of Mars rocks by SAM. Figure 2 shows data from the SAM FM using a mixture of 4 of these fluorocarbons that are loaded into a

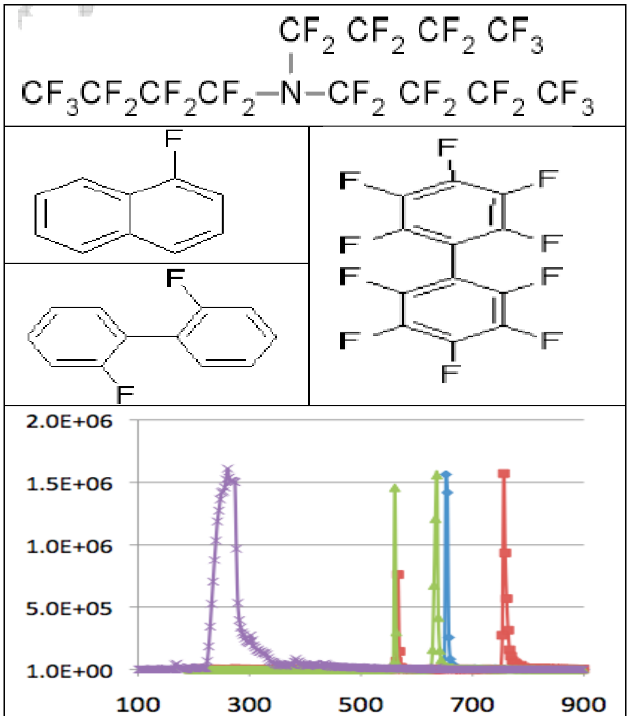

Figure 2. Counts/sec times scale factor (S) vs. time (sec) for GCMS of calibration compounds. Compounds from shortest to longest elution times are perfluorotributylamine (S=1, m/z=119, purple), 1-fluoronaphthalene (S=2.7, m/z=147, green), perfluorobiphenyl (S=82, m/z=334, blue), and 2,2'-difluoro-1,1'-biphenyl (S=43, m/z=190, red) with the signal at ~600 sec due to an unknown background compound.

calibration cell that can also be utilized for *in situ* calibrations during the landed mission. This identical calibration experiment can be carried out *in situ* on Mars to verify that the sub ppb measurement sensitivity for evolved organic compounds is met.

Calibration for Direct QMS Atmospheric Measurements: The response of the QMS to atmospheric gases likely to be found on Mars was obtained by introduceing either pure gases or mixtures of gases over a range of relevant pressures into the SAM manifold. In addition to the fluorocarbons listed in Figure 2, the calibration gas cell includes N_2, CO_2, Ar, and a Xe mix that is heavily spiked with ^{129}X to insure that there would be no danger of mistaking this gas for martian xenon if a leak were to develop in the microvalve seat separating the gas from the inlet manifold

Calibration for Evolved Gas Analysis of Solid Samples: A mixture of calcium carbonate ($CaCO_3$), the ferrous sulfate heptahydrate melanterite ($FeSO_4•7H_2O$), and inert fused silica which in a subset of cases was doped with a fluorocarbon was utilized for solid sample calibration. In these experiments, miniature cups containing milligram amounts of the solid calibrants were lowered into several of the SAM quartz cups and operated in an identical manner as if a powered rock sample had been delivered to that cup through a samle inlets. The evolved gas was continuously monitored by the mass spectrometer as the sample cell was heated from ambient to ~1000 C and H_2O, SO_2, and CO_2 sequentially evolved from the inorganic minerals. Fluorocarbons released from the sample during pyrolysis were trapped for subsequent GCMS analysis and evolved CO_2 sent to the TLS for analysis of carbon and oxygen isotope ratios.

TLS Calibration: The TLS is calibrated for both absolute gas abundances and for isotope ratio measurements using certified gas mixtures whose isotopic ratios have been determined using two independent IRMS analyses to precisions well below the TLS measurement requirements. Calibration has been made over a wide range of temperatures (-44 to +50 C) and pressures (0-100 mbar) during thermal-vacuum testing at both JPL and at GSFC within the SAM suite. Results are consistent with calculations using the HITRAN line list constrained by the Herriott cell path length, laser line width, and measured cell temperature and pressure. In addition, TLS carries an on-board reference gas cell containing certified isotopic standard for carbon dioxide, that will be cross-checked with the QMS during suite testing. Both TLS channels contain strong water lines that will be used for additional cross-checking. In addition to calibration with water isotopic standards, the water isotope channel always includes carbon dioxide spectral lines for absolute water abundance scaling.

Organic Check Material: An organic check material that will touch the entire sample processing chain including the rotory percussive drill on the sample arm is planned. Its implementation as presently designed includes hermetic encapsulation of each sample, held at vacuum to maintain cleanliness. This experiment will minimize the possibility of a false positive detection of organic molecules on Mars. The pure amorphous silica of the type that was utilized in the SAM calibration experiments is highly porous and will be doped homogeneously with fluorocarbons and sampled by the MSL drill and rock powdering system before delivery into the SAM inlets and ovens for GCMS analysis. The doping level is presently intended to deliver several nanomoles of fluorocarbon during each OCM calibration sequence on Mars.

References: [1] Mahaffy, P.R., Space Sci. Rev. 135, 255 (2008). [2] Mahaffy, P.R. (2009) Geochem. News, 121.

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