

## Special Paper

# Mitigation of the Impact of Terrestrial Contamination on Organic Measurements from the Mars Science Laboratory

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### Abstract

The objective of the 2009 Mars Science Laboratory (MSL), which is planned to follow the Mars Exploration Rovers and the Phoenix lander to the surface of Mars, is to explore and assess quantitatively a site on Mars as a potential habitat for present or past life. Specific goals include an assessment of the past or present biological potential of the target environment and a characterization of its geology and geochemistry. Included in the 10 investigations of the MSL rover is the Sample Analysis at Mars (SAM) instrument suite, which is designed to obtain trace organic measurements, measure water and other volatiles, and measure several light isotopes with experiment sequences designed for both atmospheric and solid-phase samples. SAM integrates a gas chromatograph, a mass spectrometer, and a tunable laser spectrometer supported by sample manipulation tools both within and external to the suite. The sub-part-per-billion sensitivity of the suite for trace species, particularly organic molecules, along with a mobile platform that will contain many kilograms of organic materials, presents a considerable challenge due to the potential for terrestrial contamination to mask the signal of martian organics. We describe the effort presently underway to understand and mitigate, wherever possible within the resource constraints of the mission, terrestrial contamination in MSL and SAM measurements. Key Words: Mars—Organics—Instrumentation—Contamination—*In situ* measurements. Astrobiology 8, xxx-xxx.

### 1. Introduction

MORE THAN THIRTY YEARS AFTER the Viking mission (Biemann *et al.*, 1977), NASA will continue the search for organic matter on the surface of Mars with the Mars Science Laboratory (MSL) planned for launch in 2009. MSL is the follow-up of the Mars Exploration Rovers (MER) (Squyres *et al.*, 2004a, 2004b) that continue to explore the surface of Mars. The MSL payload mass is more than 8 times that of MER and is comprised, in part, by the chemical analytical instruments SAM and CheMin. SAM is the Sample Analysis at Mars instrument package that will be searching for organic material, light isotopes, water, and other volatiles. CheMin will provide mineralogical identification by powder X-ray diffraction/X-ray fluorescence. These instruments are crucial in the context of astrobiology in that they will shed light on

the current geochemical and organic chemical environment on Mars. Both instruments use ground rock and soil samples that are injected into the system for analysis. For this type of instrumentation, (terrestrial) contamination is one of the major concerns because it is very difficult, often impossible, to discriminate between contamination and actual sample. A very basic definition of contamination in this framework is all material that is not of martian origin. Each instrument has its own level of acceptable contamination, depending on its sensitivity and target chemicals. SAM is the instrument most prone to be affected by contamination because of its high sensitivity and the species of interest, organic material (see Section 4). The high astrobiological relevance of measurements made by SAM requires very good contamination control. To mitigate the effect of terrestrial contamination on key MSL organic measurements, an

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organic contamination control plan was initiated prior to MSL payload selection and is presently being iterated and implemented. Here, we describe this plan to create a better understanding of the efforts involved in keeping a mission contamination free.

## 2. The Mars Science Laboratory

The scientific objective of MSL is to explore and assess quantitatively a local region on Mars' surface as a potential habitat for past or present life. To reach this objective, 4 main goals have been defined. The instruments on MSL will assess the biological potential of at least 1 target environment; characterize the geology and geochemistry of the landing region at all appropriate spatial scales; investigate planetary processes relevant to past habitability, including the role of water; and characterize the broad spectrum of surface radiation, including background galactic cosmic radiation, solar energetic particle events, and secondary neutrons (Vasavada *et al.*, 2006).

New landing techniques will be used to deliver the MSL rover directly onto the martian surface within a 20 km bounded diameter landing ellipse (Lockwood, 2006). Figure 1 gives an overview of the MSL entry, descent, and landing sequence. An entirely new aspect of the entry, descent, and landing scenario is that when the descent vehicle is several meters above the surface, MSL will gently be tethered down; and when its wheels make contact, the tether will be severed, which will cause the descent propulsion system to fly off and land away from the vicinity of the rover. It is anticipated that contamination from propulsion products can be mitigated by traversing away from the landing site to mini-

mize the impact on MSL volatile measurements prior to ingestion of martian gases or solids into SAM and CheMin (JPL, 2007a).

The instrument suite of MSL is comprised of 3 suites of instruments: chemical, imaging, and radiation detection. Figure 2 shows the MSL rover with the location of the different instruments.

The instruments include the

- Alpha Particle X-ray Spectrometer (APXS) [an improved version of the APXS is described in Gellert *et al.* (2006)] to measure the elemental abundance of rocks and soil;
- CheMin, the X-ray diffraction/X-ray fluorescence instrument to identify and quantify minerals in complex natural samples (Blake *et al.*, 2007);
- Sample Analysis at Mars (SAM) (Mahaffy, 2007) to analyze pyrolyzed solid samples and atmospheric gas samples by gas chromatography, mass spectrometry, and tunable laser spectrometry;
- ChemCam, a unique instrument to analyze targets up to several meters away from the rover by laser-induced breakdown spectroscopy (Wiens *et al.*, 2005);
- Mars Hand Lens Imager (MAHLI) (Edgett *et al.*, 2005), to provide high-resolution, microscopic color images of rocks, soil, frost, and ice;
- Mars Descent Imager (MARDI) (Malin *et al.*, 2005), to produce high-resolution color video imagery of the descent and landing phase, provide geological context information, and determine the actual landing site of the rover;
- MastCam, to provide multi-spectral (visible to near-infrared) stereo imaging as well as compressed high-definition video (Malin *et al.*, 2005);

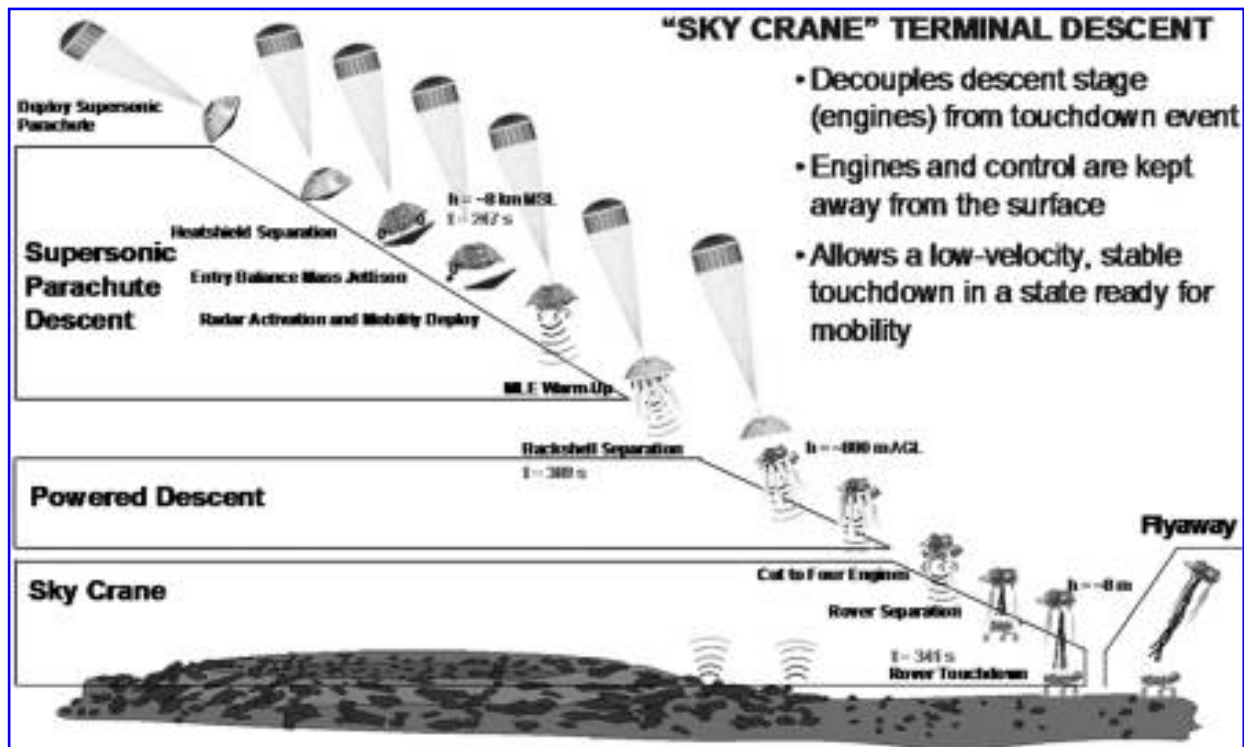


FIG. 1. The atmospheric entry, descent, and landing sequence of MSL (JPL, 2007b).

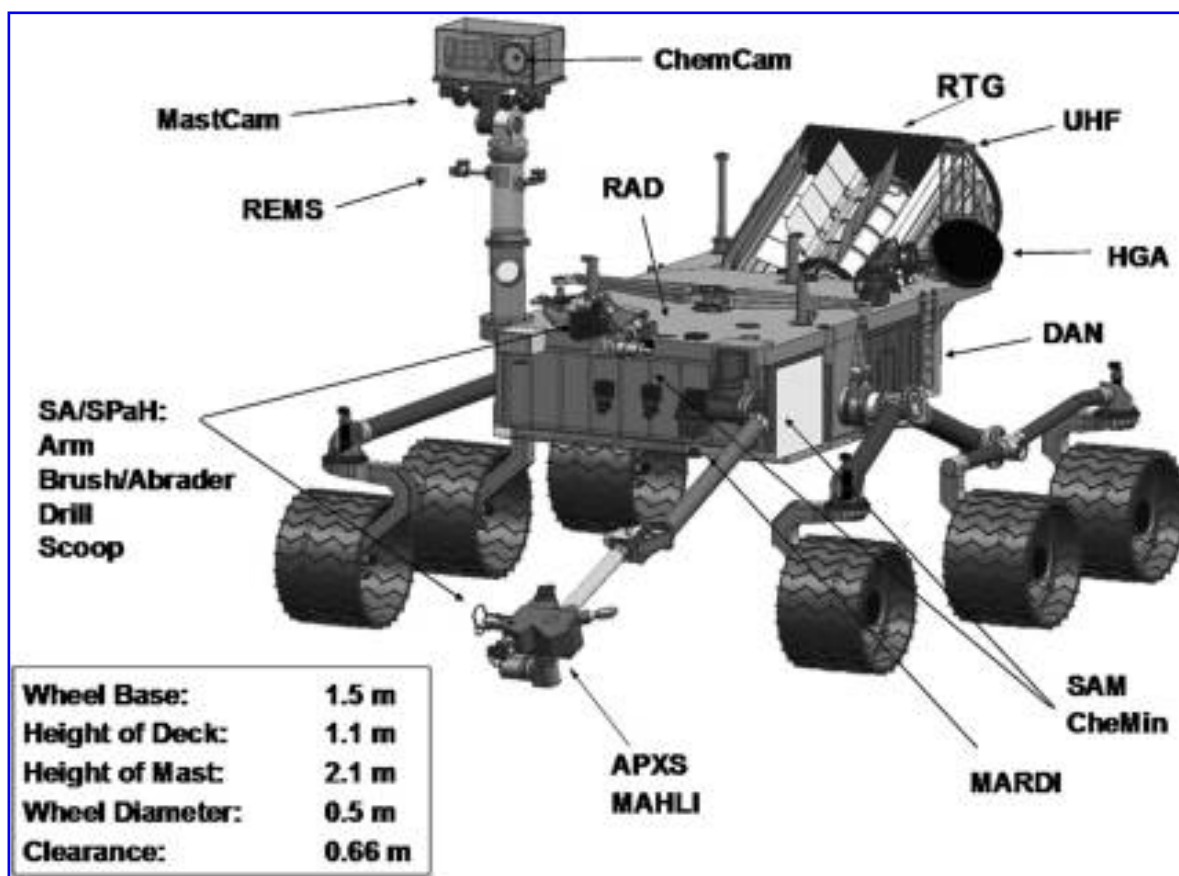


FIG. 2. A schematic overview of the Mars Science Laboratory rover. Legend (clockwise starting at ChemCam): ChemCam, camera with laser-induced breakdown spectroscopy; RAD, Radiation Assessment Detector; RTG: Radioisotope Thermoelectric Generator; UHF: Ultra-High Frequency; HGA: High-Gain Antenna; DAN, Dynamic Albedo of Neutrons; SAM, Sample Analysis at Mars; CheMin, X-ray diffraction / X-ray fluorescence instrument; MARDI, Mars Descent Imager; APXS, Alpha Particle X-ray Spectrometer; MAHLI, Mars Hand Lens Imager; SA/SPaH, Sample Acquisition and Sample Processing and Handling tool; REMS, Rover Environmental Monitoring Station; MastCam, Mast Camera.

- Radiation Assessment Detector (RAD) (Hassler *et al.*, 2006; Wimmer-Schweingruber, 2006), to measure high-energy neutrons, protons, gamma rays, alpha particles, and heavy ions (up to Fe);
- Dynamic Albedo of Neutrons instrument (DAN) (Mitrofanov *et al.*, 2005), to detect backscattered neutrons in order to measure hydrogen in water ice; and
- Rover Environmental Monitoring Station (REMS) (Gómez-Elvira *et al.*, 2008), to measure the meteorological and UV-radiation environments.

The MSL rover design team is developing a power system based on a radioisotope thermoelectric generator (RTG) that continuously generates electricity to charge the MSL battery.

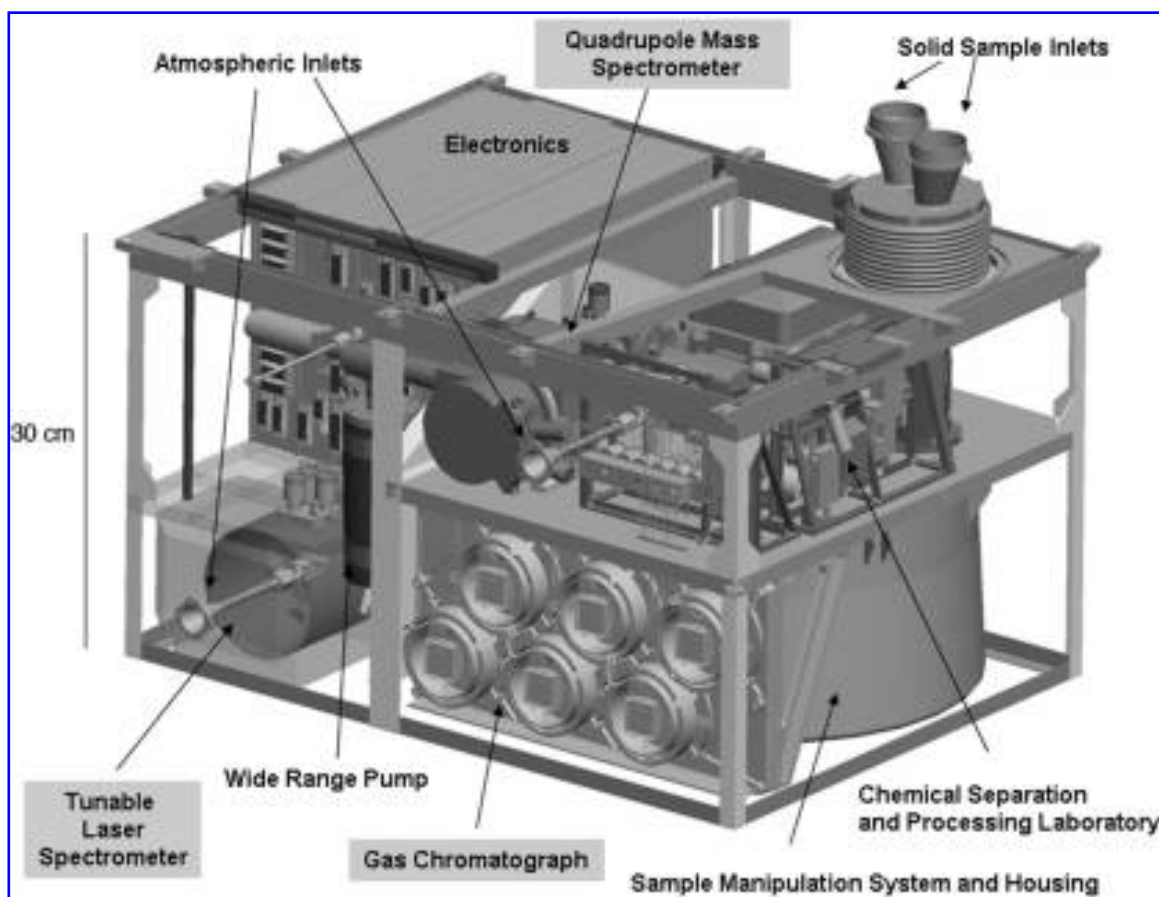
The thermal state of the MSL rover over the course of its 2-year mission is an important parameter in understanding terrestrial volatile transport. The fundamental task of the SAM instrument suite is to analyze gases that are directly sampled from the atmosphere or extracted from soil samples by pyrolysis. To assure valid data interpretation, it is crucial to understand both the thermal state and the thermal history of the rover, and the thermal environment of the rover's location. If terrestrial volatiles present on the rover on the surface of Mars are not well characterized, it will be impossible

to distinguish between terrestrial contamination and martian volatiles.

### 3. Sample Analysis at Mars

The Sample Analysis at Mars instrument suite is designed to measure volatiles and isotopes of light elements and noble gases. It will sample both the atmosphere and volatiles extracted from solid-phase materials. SAM will investigate sources and destruction paths for carbon compounds and search for organic compounds of biotic and prebiotic relevance, including methane. It will also measure the chemical state of other light elements that are important for life as we know it on Earth, and it will measure atmosphere-surface exchange processes. SAM will also investigate the martian atmosphere and provide isotopic measurements of noble gases and light elements to help constrain models of atmospheric loss. Figure 3 shows the SAM instrument suite components (Mahaffy, 2007).

SAM consists of 3 complementary analytical instruments: a quadrupole mass spectrometer (QMS), a gas chromatograph (GC), and a tunable laser spectrometer (TLS). The QMS analyzes the atmospheric gases and the gases thermally evolved from solid samples and is the primary detector for



**FIG. 3.** The Sample Analysis at Mars instrument suite illustrating the placement of instruments and major subsystems. The solid sample will be delivered to the Solid Sample Inlets and transported to the Sample Manipulation System. There the sample will be pyrolyzed, either directly or after derivatization. The gaseous sample will then be transported to the Chemical Separation and Processing Laboratory, and from there it will be injected into the Gas Chromatograph, the Quadrupole Mass Spectrometer, and the Tunable Laser Spectrometer. Direct atmospheric sampling is enabled by the Atmospheric Inlets.

the GC. The GC separates complex mixtures into molecular components for QMS and can perform stand-alone analysis. The TLS measures precise H, C, and O isotope ratios of 2 targeted species:  $\text{CH}_4$  and  $\text{CO}_2$ . It also measures the mixing ratio of  $\text{CH}_4$  in atmospheric gas.

The rover's sample acquisition, processing, and handling system (SA/SPaH) will deliver soil and rock samples through the solid sample inlet tubes (SSIT) to one of the sample cups of the Sample Manipulation System, which will position and seal the cup in the pyrolysis oven of the chemical separation and processing laboratory (CSPL). In the CSPL, the sample will either be chemically derivatized after solvent extraction or directly pyrolyzed. The evolved gases will then be transported into the GC, the QMS, or the TLS. To enhance the detection sensitivity and isotopic precision, the gases can be separated and enriched in the CSPL prior to transportation to one of the instruments. Separate inlet tubes provide a path for entry of atmospheric gases. A complex network of tubing, manifolds, high-conductance valves, and vacuum pumps distributes atmospheric and evolved solid-sample gases to the various instruments.

SAM is designed to operate during the entire MSL surface mission. Consumables such as the GC carrier gas are suffi-

cient for more than 80 separate analyses over the nominal mission, and a large subset of SAM science operations can be continued after these consumables are exhausted.

#### 4. Organic Contamination

The TLS and GCMS instruments in the SAM suite will be able to detect methane and other organic molecules with sub-parts-per-billion sensitivity in many cases. This high sensitivity demands that contaminant background levels be very low. Table 1 provides target levels for background contamination in the atmospheric samples and the solid samples, respectively. These levels are so low that the project has to be prepared for the possibility of potential self-contamination.

The SAM sensitivity requirements demand considerable attention toward all organic and certain non-organic molecular or particulate terrestrial contaminants. Cross-contamination of organic material between the different samples is also of concern. Contamination control is essential for several areas of terrestrial geochemical research; and lessons learned from ocean floor research, for example, can be useful for space mission planning (Grosjean and Logan, 2007).

TABLE 1. MAXIMUM AMOUNT OF CONTAMINATION IN NANOGRAMS (NG) THAT CAN BE TRANSFERRED TO ORGANIC AND MOLECULAR ANALYSIS EXPERIMENTS PRIOR TO THEIR DELIVERY TO THE INSTRUMENTS (ADAPTED FROM MAHAFFY *ET AL.* 2003)

	<i>ng/g sample</i>	<i>Notes</i>
Benzene or aromatic hydrocarbons	8	MSL may deliver grams of the sample to the processing system. The nominal volume of sample provided to SAM is 0.05 cubic centimeters.
Carbonyl- and hydroxyl-containing compounds	10	
Amino acids	1	
Amines or amides	2	
Non-aromatic hydrocarbons	8	
DNA	1	
Total reduced carbon	40	

Assumptions: State of organic cleanliness can be assessed by analyzing specific representative molecules.

While it is impossible to eliminate the possibility of contamination, even the task of minimizing it necessitates the reduction of all potential terrestrial sources to very low levels as well as the development of accurate models for prediction of transport mechanisms. To analyze this problem, NASA commissioned an Organic Contamination Science Steering Group, which identified 4 primary areas of focus prior to the announcement of opportunity for the MSL mission. These strategies were developed to provide direction for the engineering and operations teams responsible for the design, fabrication, assembly, and operations of Mars landed systems and the science teams responsible for analysis of the data from Mars (Mahaffy *et al.*, 2003). Some of these strategies were also employed during the Viking mission (Flory *et al.*, 1974). The strategies include the following:

- (1) Identify and quantify the contaminants of most concern with regard to their possible adverse impact on the goals of each lander mission.
- (2) Understand methods of quantifying residual contamination and its abundance and transport during all stages of lander development and operation.
- (3) Suggest possible contamination-mitigation options.
- (4) Examine the use of controls and facility-provided standards to be analyzed by lander instruments after arrival at Mars.

Even with the best efforts at mitigation, some residual contamination is likely to be observed by sensitive instruments

on the surface of Mars. The use of controls will then be important for achieving definitive scientific conclusions, as will the characterization of terrestrial organic material transported to Mars that might credibly mix with atmospheric or solid-phase martian samples.

Table 2 illustrates a range of molecular classes and compounds that would be of considerable importance for the MSL investigation, the source of which could be indigenous to Mars or Earth.

## 5. Sources of Contamination and Mitigation

Each sufficiently volatile organic material that becomes part of the rover or the MSL aeroshell, by way of design or flight-hardware processing or environment, is a potential source of organic molecules. These molecules can be in the form of gases (outgassing from molecules within the bulk material or molecular films on the surface of the material), films (deposition and condensation of gaseous molecules or contact transfer of contaminants), or particles. The goal in designing and building MSL is to minimize the overall quantity of these contaminants and to know when they might be present as possible contaminants.

To assure that the quantity of contaminants arriving at the sensitive inlets are within acceptable standards, the program relies on (1) identification of potential sources through rigorous review of drawings and processes, (2) predictions of contaminant levels at sensitive surfaces, (3) elimination or

TABLE 2. CONTAMINANTS OF CONCERN FOR MARS LANDED MISSIONS (MAHAFFY *ET AL.* 2003)

<i>Molecular class</i>	<i>Examples</i>
C, H aromatics	Benzene, toluene, higher mw <sup>†</sup> aromatics, polycyclic aromatic hydrocarbons
S, N, O heterocyclic aromatics	Furan, pyridine, pyrimidine, benzothiophene
Carboxylic acids and their salts	Alkyl and aromatic acids, fatty acids
Non-aromatic hydrocarbons	Alkanes, alkenes ( <i>i.e.</i> , isoprenoids such as pristane, pytane)
Nitrogen-containing compounds	Amino acids, amines, amides, purines, pyrimidines, porphyrins
Alcohols	Methanol, higher mw linear and branched-chain alcohols
Carbonyl	Esters, ketones, aldehydes, and their mw distributions
Sulfonic, phosphonic acids	Methanesulfonic acid
Lipids and derivatives	HC chains, fatty acids, fats, phospholipids, hopanes, steranes
Sugars and derivatives	Glucose
Proteins	Polar and non-polar
Nucleic acids, nucleotides	DNA fragment

<sup>†</sup>, mw, molecular weight.

reduction of sources (through cleaning, bake-out,<sup>a</sup> pyrolysis,<sup>b</sup> material substitutions, directed venting, filters, molecular absorbers, etc.), and (4) addition of design elements to prevent transport (barriers, seals, relocating components, directed venting, etc.).

Drawing reviews are used to evaluate the contamination potential of materials used in an assembly as well as the contamination potential of the fabrication environment and materials and the processes used during fabrication. Once identified, high-risk materials are either eliminated through alternate material selection or the risk is mitigated through process improvements, additional cleaning, bake-out of volatiles, and reduction in the quantity of material used. This is not an easy process, as many materials have heritage on previous Mars missions that were not as contamination sensitive. Changes to materials or processes can trigger costly requalification tests of components. Where this becomes an overriding concern, an effort is made to contain or redirect the contaminants or reallocate the contamination budget. To be successful, this process must be a collaborative and iterative effort between the contamination-control engineers and the subsystem developers, especially in the case of parts with no prior flight heritage. A series of training seminars and workshops on how to design for contamination mitigation are presently used to facilitate this crucial design review process.

One of the most challenging aspects of the MSL mission is predicting contamination transport with confidence. While modeling of mass transport in a vacuum for the cruise phase of the mission is readily understood and some work has been done with particle redistribution models, there is little work on transport in the reduced pressure and winds of the martian environment. These transport analyses are complicated by the very small quantity of materials that is acceptable at the sensitive surfaces. A diffusion model has been developed that is discussed in detail in Section 6. An interesting result of this model is demonstration of the effectiveness of buoyancy around the hot RTG in sweeping molecules produced or vented in this vicinity up and away from the rover and ground. Initial studies have shown that, by taking advantage of this effect and carefully locating vents, the initial outgassing rate requirements could be an order of magnitude higher than would otherwise be permissible.

One goal of the contamination control plan is to have *a priori* knowledge of the materials used, especially those that occupy large areas of the GCMS data space and produce multiple chromatographic and mass spectral peaks (discussed in more detail in Section 7). To achieve this, a materials testing program has been put into place. GCMS data is collected for organic-releasing materials used on the exterior of the rover and for materials used in large quantities in the interior of the rover. Assembled parts of the instruments or the rover will be tested when material sampling cannot be obtained. The data obtained will ultimately be compared to flight data to facilitate identification of terrestrial contaminants within a SAM measurement. Identification of the source may permit the elimination or reduction of its effect through changes

to the mission operations plan (changing temperatures, orientation with respect to wind, time of sampling, etc.). Additionally, samples of materials are kept and stored in an archive for testing during the mission should the need for future testing arise.

The flight hardware is being processed in a similar way as it was for other contamination-sensitive missions, which includes the use of class 10,000 or better clean rooms (10,000 particles per m<sup>-3</sup>) that are monitored for both particulate and airborne molecular contaminants and require full gowning protocols. What will distinguish this mission from others, however, will be the use of monitored bake-outs, during which emissions, emission rates, and the composition of all the outgassed materials are measured with FTIR and GCMS. Previous missions have used timed, unmonitored bake-outs, and in most other aerospace testing, higher-weight volatiles were measured. Also, the contamination control plan described here will include an emphasis on keeping the most critical surfaces exceptionally clean by avoiding any contact with organics that could transfer even minor amounts of non-volatile residue. Unnecessary introduction of DNA contaminants will likewise be avoided, as planetary protection wipes or bake-outs will not eliminate all traces of this contaminant. The techniques required to remove all chemical traces of an organism's presence (DNA, cell wall, or other cellular components, for example) are usually not compatible with aerospace materials or electronics. For example, though heating the equipment to 450–550°C in air would destroy virtually all organic contaminants, the necessary organic compounds needed to make the rover work would also be destroyed. Thus, baking the rover to destroy organics is not an option, and any contaminants introduced during integration and testing will remain. An expanded personnel training program with a focus on the importance of avoiding contact transfer of contaminants through proper gloving protocols and cleaning of tools and ground support equipment will be implemented and required of all personnel that enter the clean rooms. To meet the extraordinary low contamination levels on the surfaces of the instruments that will have contact with martian gas or solid rock samples, the program will employ extended high-temperature bake-outs.

The instrument itself will verify that the contamination goals for the most-sensitive surfaces (*i.e.*, those in contact with sample gas or solid matter) have been met. Other contamination requirements will be verified with standard techniques: particle and molecular witness plates,<sup>c</sup> particle monitors, residual gas analyses, cryogenic quartz crystal monitors, thermally controlled quartz crystal monitors, visual inspections, tape lifts, etc. The methods unique to MSL are (1) the GCMS characterization of materials and assemblies, (2) the more extensive characterization of species generated during bake-out and thermal vacuum testing, and (3) the use of cold cathode gauges in a special setup to track partial pressures generated by outgassed species. Lastly, significant effort is being put into the development of a robust calibration/verification system that utilizes blanks to assess and determine background contaminants accumulated during

<sup>a</sup>Bake-out: release of contaminants from a surface by heating in a vacuum.

<sup>b</sup>Pyrolysis: decomposition of contaminants through heating.

<sup>c</sup>Witness plates: plates that have experienced the same environmental and biological conditions as the instrument throughout the assembly and testing phase.

each phase of the mission (see Section 8). This data will be used to interpret results.

## 6. Molecular Contaminant Transport through the Martian Atmosphere

One of the considerations with regard to the SAM sample inlets is contamination transport through the atmosphere. Two processes play a role in contamination transport: the martian wind and the updraft created by the buoyancy from the RTG heating the martian atmosphere. Although the martian atmosphere is  $\sim 100$  times less dense than that of Earth, it is still sufficiently dense that the collisional mean free path for contaminant molecules is much smaller than typical rover dimensions (Knudsen number  $\ll 1$ ). For typical conditions on Mars—a pressure of 6.6 mbar and a temperature of 240 K—the molecular density is about  $2 \times 10^{23} \text{ m}^{-3}$ , and the collision mean free path is on the order of  $10^{-5}$  meters. Therefore, fluid equations are appropriate to describe contaminant transport, not free molecular flow.

Martian wind velocities, as measured by Viking 2 (Murphy *et al.*, 1990), range from  $1 \text{ m s}^{-1}$  to about  $20 \text{ m s}^{-1}$  with updraft velocities reaching more than  $0.5 \text{ m s}^{-1}$ . To calculate contaminant transport, the approach, assuming the velocity of the martian wind as a boundary condition, is to first solve for the wind velocity field in the vicinity of the rover. The code solves in 3 dimensions the mass and momentum conservation equations, treating the atmosphere as a slow-speed incompressible fluid. This flow field, with the addition of molecular diffusion, is then used to model the transport of rover-generated contaminants. The MSL rover geometry is modeled as a collection of cubes with an edge length of 0.1 meters, as shown in Fig. 4.

To estimate the updraft velocity and buoyancy, we use the following relations

$$v \approx \sqrt{2g \left( \frac{\Delta T}{T_0} \right) h} \quad (1)$$

$$\Delta T^{3/2} = \frac{P}{A_{\text{RTG}} \rho_0 C_p} \sqrt{\frac{T_0}{2gh}} \quad (2)$$

where  $A_{\text{RTG}}$  is the RTG cross-sectional area,  $v$  is the updraft velocity,  $C_p$  is the heat capacity of the atmosphere at con-

stant pressure,  $\Delta T$  is the change in atmospheric temperature due to local heating by the RTG,  $h$  is the height of the RTG,  $g$  is the gravitational acceleration,  $P$  is the atmospheric pressure,  $\rho$  is the mean atmospheric density, and  $T_0$  is the nominal ambient atmospheric temperature.

For the model calculations for Mars, we have assumed:

$$\rho = 0.024 \text{ kg m}^{-3}$$

$$T_0 = 240 \text{ K}$$

$$P = 660 \text{ Pa}$$

$$g = 3.7 \text{ m s}^{-2}$$

$$A_{\text{RTG}} = 0.56 \text{ m}^2$$

$$h = 0.6 \text{ m}$$

$$C_p = 791 \text{ J kg}^{-1} \text{ K}^{-1}$$

The resultant updraft velocity is approximately  $0.8 \text{ m s}^{-1}$ , and the change in temperature is approximately 35 K.

The martian wind-flow field is integrated in time to a steady state using an artificial compressibility algorithm (Ramshaw and Mousseau, 1990), to which a Boussinesq approximation buoyancy force was added.

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} = -\frac{1}{\rho_0} \nabla p + \nu_0 \nabla^2 \mathbf{u} - \mathbf{g} \frac{\Delta T}{T_0} \quad (3)$$

In Eq. 3,  $\mathbf{u}$  is the wind velocity,  $\rho_0$  is the ambient density,  $\nu_0$  is the bulk viscosity, and  $\Delta T$  is the local heating due to the rover RTG. Incompressibility is satisfied when an artificial pressure,  $p$ , reaches steady state.

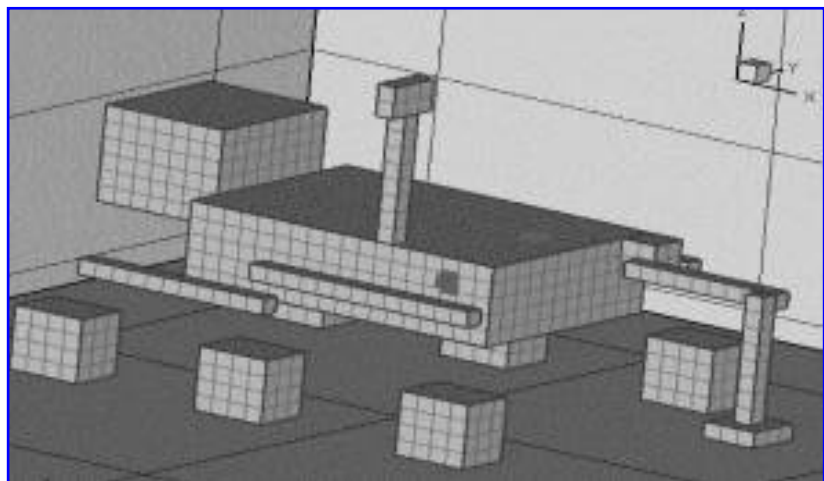
$$\frac{\partial p}{\partial t} = -\rho_0 a^2 \nabla \cdot \mathbf{u} \quad (4)$$

In Eq. 4,  $a$  is an artificial sound speed. The differencing scheme is first-order explicit in time and first-order upwind in space.

Contaminant densities,  $n$ , are calculated with a first-order advection-diffusion scheme

$$\frac{\partial n}{\partial t} + \nabla \cdot (n\mathbf{u}) = \nabla \cdot (D\nabla n) \quad (5)$$

where  $\mathbf{u}$  is from the martian wind-flow field from the previous calculation and  $D$  is the diffusion coefficient. Conta-



**FIG. 4.** Geometrical model of the MSL rover used for contamination transport analysis. SAM's atmospheric inlet is located on the side of the model, the soil sample port on the top deck.

minant fluxes are specified from rover surfaces. Since the problem is linear in contaminant densities, contributions from different rover surfaces can be calculated separately and added together.

The diffusion coefficients are calculated from the published diffusion coefficients for trace materials in CO<sub>2</sub> (Karaiskakis and Gavril, 2004). For example, the diffusion coefficients in CO<sub>2</sub> at 240 K when scaled with temperature and pressure range from 0.0007 to 0.002 m<sup>2</sup> s<sup>-1</sup>. The H<sub>2</sub>O-CO<sub>2</sub> diffusion coefficient in the martian atmosphere was calculated from the published data as follows:

$$D_{(T=393.8K,p=1000\text{ mbar})} = 0.297\text{ cm}^2\text{ s}^{-1} = 2.97 \times 10^{-5}\text{ m}^2\text{ s}^{-1}$$

$$p_{\text{Mars}} \approx 6.6\text{ mbar}$$

$$T_{\text{Mars}} \approx 240\text{ K}$$

$$D \sim \frac{T^{3/2}}{p}$$

$$D_{(T=240K,p=\text{mbar})} = 2.12 \times 10^{-3}\text{ m}^2\text{ s}^{-1}$$

The accuracy of the code algorithms was validated by comparison with the analytical solution of the advection diffusion equation in cylindrical geometry for a circle of radius  $R_0$  emitting a flux of  $F_{\text{tot}}$ . A typical result is shown in Fig. 5.

$$\begin{aligned} \frac{\partial n}{\partial t} + \mathbf{u} \cdot \nabla n &= D \nabla^2 n \\ \mathbf{u} &= (0,0,u_z) \\ z &= u_z t \\ n(r,z) &= \frac{F_{\text{tot}}}{\pi u_z \left( 4D \frac{z}{u_z} + R_0^2 \right)} \exp\left( -\frac{r^2}{4D \frac{z}{u_z} + R_0^2} \right) \end{aligned} \quad (6)$$

where  $\mathbf{u}$  is the wind velocity as defined previously,  $z$  is the  $z$  component of the wind,  $r$  is the radial distance from the  $z$ -axis, and  $t$  is time.

The expression above is useful for estimating the contamination from distant sources, such as the MSL parachute.

Results of an example transport calculation in the vicinity of the rover are shown in Fig. 6. In the example, a flux of

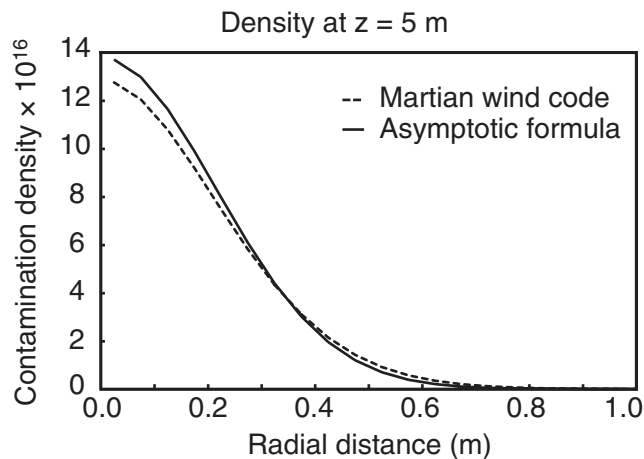


FIG. 5. Code-calculated atmospheric contamination density compared with an analytical formula as a function of radius at an axial distance of 5 meters from the source.

water molecules coming out of the electronics' bay vent (in this example, located in the optimal position near the RTG) is carried by a martian wind traveling at 1 m s<sup>-1</sup> and blowing toward the SAM atmospheric inlet. Calculations were run with several different wind velocities, and this velocity predicted the highest concentration of the contaminant at the SAM atmospheric inlet. The contaminant concentration for most other wind conditions was much lower.

The calculations show that 0.01 g hr<sup>-1</sup> water vapor, much larger than expected, coming out of the electronics' bay would result in a 0.2 ppm concentration at the atmospheric inlet and still satisfy SAM's requirement of less than 2 % of the expected ambient concentration. The figure shows surfaces of 100 ppb, 10 ppb, and 1 ppb density for a contaminant escaping from a vent (not shown), located at the right rear of the rover body. The calculated concentration at the atmospheric inlet drops dramatically with wind direction, since advection dominates over diffusion in the martian atmosphere.

## 7. GCMS Analyses of Volatile Emissions from Polymeric Species in MSL and SAM

### 7.1. Polymer emission testing

There has been a significant amount of testing of the semi- and non-volatile residue from polymeric materials in the aerospace community since the time of the Viking mission (Campbell *et al.*, 1975, 2006; NASA, 1990). These tests were primarily focused on changes in the mechanical and electrical properties of the base material (Fishman *et al.*, 1966) and resulted in the development of the micro-VCM test (volatile condensable material) (ASTM E-595). This test provides a single-point determination of the material loss over time under vacuum, by baking the material at 125°C for 24 hours. Most spaceflight systems are only concerned with molecular contamination that condenses on critical surfaces. However, in the case of sensitive spectroscopic systems searching for trace organics, molecular contamination will result in background signals that obscure the presence of the environmental molecular species. Standard testing of polymer outgassing is inadequate for applications of polymers in spaceflight instrumentation such as high-intensity laser and mass spectrometry. For these applications, the total volatile emission of the polymeric materials must be analyzed (Cannham, 2005).

### 7.2. Testing requirements

On SAM, the most contamination-sensitive instruments are the QMS and the GC. To get the most reliable results, a new testing method has been developed that is representative of the response of SAM. Cure state, polymer geometry, operating temperature, and processing can drastically affect the emissions from polymers. Because the cure state can affect the total molecular weight and the material composition due to loss of semivolatiles, the total thermal history is a critical parameter. In this method, significant effort is being made to evaluate the polymeric materials in a geometry similar to the geometry of the instrument.

The SAM instrument will retrieve its gaseous samples through oven pyrolysis and direct atmospheric sampling. These samples can be selectively preconcentrated to lower

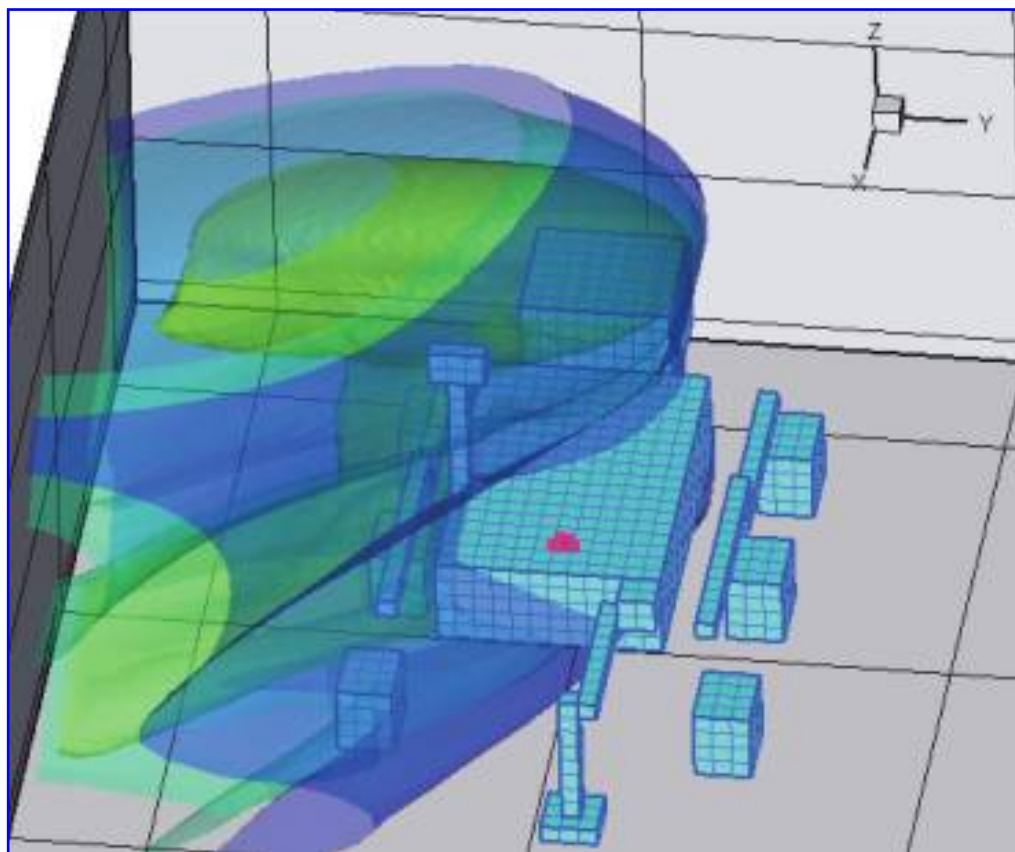


FIG. 6. Results of an example calculation showing surfaces of 100 ppb, 10 ppb, and 1 ppb density for a contaminant emanating from a vent (not shown), located at the right rear of the rover body. The outermost contour corresponds to 1 ppb, the innermost contour to 100 ppb.

the detection limit by sorbent trapping and thermal desorption. The preconcentration will be carried out on porous polymer sorbents and carbon molecular sieves. Short-path thermal desorption GCMS provides concentration, separation, and detection capabilities similar to the techniques that will be used by SAM and will therefore be used as a detection technique.

### 7.3. Polymer emission testing protocol

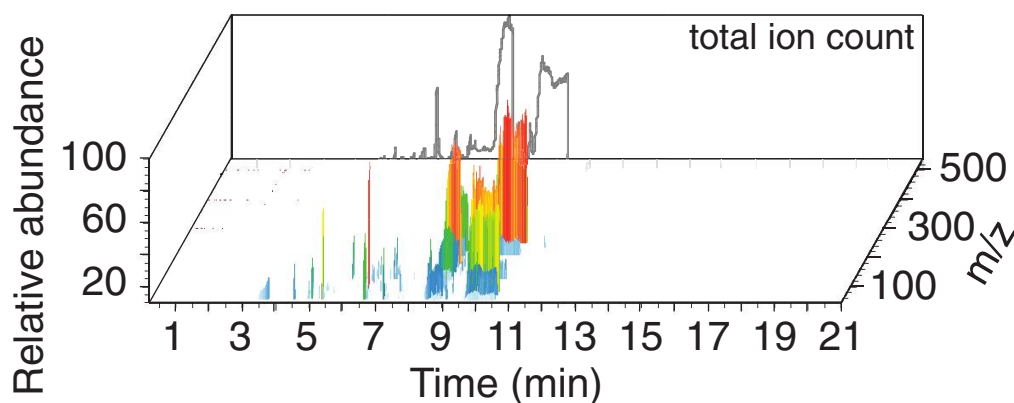
As the sample processing is critical to the characteristics of the polymer, the polymer samples were processed as they will be on the spacecraft. The geometry of the sample should also be representative of the in-use geometry to assure similar material transport. The samples were loaded into glass tubes encased in a temperature-controlled heater block. Nitrogen was used to deplete the concentration of the emissions over the sample, which prevented a decrease in the rate of emission due to a significant partial pressure of contaminant being established over the sample, and was flowed over the samples at a rate of  $10 \text{ ml min}^{-1}$ . The nitrogen with the emitted species then flowed into a thermal desorption tube containing 300 mg of 0.5 mm glass beads and 50 mg of Tenax TA<sup>®</sup>.

The thermal desorption process was carried out by way of a Scientific Instrument Services AutoDesorb<sup>®</sup> 2000 system with a micro cryotrap. Before use, the thermal desorption

tubes were conditioned for 8 hours at  $350^\circ\text{C}$  with a nitrogen flow of  $40 \text{ ml min}^{-1}$ . A blank thermal desorption tube was analyzed with each set of samples to verify the efficacy of the cleaning process. The needles attached to the tubes were conditioned for at least 2 hours at  $350^\circ\text{C}$  before use. The emissions from the polymers were collected over 24-hour intervals for a minimum of 3 days. These samples were analyzed immediately after the sample collection to minimize any potential effects of long-term storage of the emissions on the adsorbent. The GC column used was an SGE HT5  $0.22 \text{ mm} \times 25 \text{ m} \times 0.25$  micron polyimide-coated silica column. A quadrupole mass filter unit, with a 15 KV conversion dynode—a Finnigan SSQ 7000—was used as mass spectrometer. This allowed for either positive or negative ions to be detected with similar efficiency by an electron multiplier. The detection was carried out by pulse counting with the electron multiplier. Electron impact mass spectra were collected between 45 and  $650 \text{ amu s}^{-1}$  at one scan per 0.3 s.

### 7.4. Representative results

Figure 7 shows an example of results obtained from a representative SAM polymer analysis. The GCMS data are matched against a spectral library to provide the composition of the volatile compounds released from this material. The pyrolysis GCMS data can be represented by a chromatogram that shows the sum of all of the ion currents as a



**FIG. 7.** A 3-dimensional representation of GCMS data, showing the relative abundance of a compound in the time-mass domain. The GC measures the retention time in minutes (plotted on the  $x$ -axis) of a compound on the chromatographic column, resulting in a total ion count chromatogram. This is the 2-dimensional plot in the background. To distinguish between different compounds with the same retention time, the QMS measures the mass-to-charge ratio of the compounds (plotted on the  $z$ -axis).

function of the retention time in the GC column. The total ion count trace in Fig. 7 shows such a chromatogram. GC and GCMS methods are optimally carried out with conditions selected such that there are no background peaks interfering significantly with the analytes of interest.

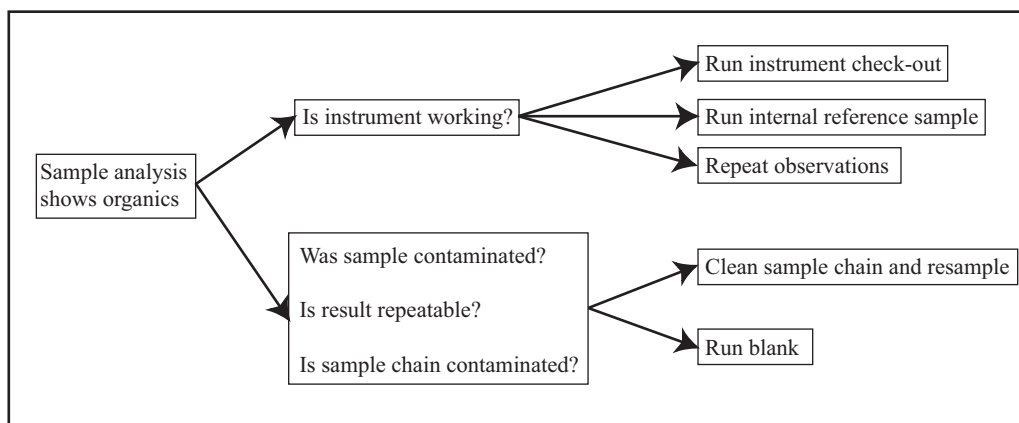
However, in the case of the SAM instrument, with its objective to cover a broad spectrum of martian organic compounds, there may be background contamination peaks occurring within the data sets. Primary contaminants that could impact the SAM science investigation are those materials specified in Table 2, given that these include prime measurement target compounds that occupy this GCMS data space. The compounds from a single polymer used on MSL have physical and chemical properties that could cover the wide data space shown in Fig. 7. To detect the target analytes, these must either not overlap significantly with the contaminants or must have a much higher abundance than those released from terrestrial contaminants. With identification of the contaminant emission from the materials in the 3-dimensional space of elution time and compound ion fragment intensity patterns, the potential impact of these mate-

rials on the corresponding scientific data space can be determined.

## 8. Operational Mitigation

The SAM investigation has internal calibrants, both solid and gas, for the preparation of a baseline against which to compare data obtained from martian samples. This calibration baseline does not yield information with regard to potential contaminants that might be associated with parts of the sample chain that are external to SAM. Such sites of potential contamination include the drill and other parts of the sample-acquisition hardware that will contact samples before they are introduced to SAM's solid-sample inlet tubes.

Prior to first use, the MSL sample acquisition and delivery system is to be cleaned by repeatedly acquiring martian sample with a powdering drill, ingesting sample into the distribution system, and dumping it onto the ground. To test whether this cleaning operation has been successful, the MSL mission will fly well-characterized calibrants housed on the rover exterior that can be acquired and processed in the same



**FIG. 8.** A scenario decision tree for deployment of the external calibrant upon a detection of organic molecules on Mars by SAM.

manner as a martian sample. This calibrant material is an inorganic, non-crystalline refractory material with a simple chemical composition, such as a SiO<sub>2</sub> ceramic. The material will be suffused with a low concentration of a fluorinated hydrocarbon, which is unlikely to be found on Mars but is volatile enough to be released upon pyrolysis into the GC and QMS of the SAM instrument suite. This fluorinated polycyclic aromatic hydrocarbon compound is a single isomer and has not been found in natural terrestrial or interstellar organics (kerogens). Even in the event of fluorination of the same base polycyclic organic hydrocarbon, multiple isomers would be formed and allow detection of the interference. The GCMS analysis of this calibration compound results in one single sharp gas chromatographic peak with a mass spectrum that consists of less than 5 mass-to-charge peaks exceeding 10% of the base peak, which results in an extremely small obscuration of the SAM GCMS data space. This allows the material to function as both a calibrant and as a blank, providing both the assurance that sample has been delivered to SAM and an organic baseline against which SAM can recognize contaminants in the chain of sample handling from acquisition to delivery. Figure 8 shows a scenario decision tree for the deployment of the external calibrant upon a detection of organic molecules on Mars by SAM.

The use of carrier gas blanks and both interior and exterior calibrants affords SAM a robust method of distinguishing between contaminant signatures and the true discovery in martian rock and regolith of organic molecules that were not transported there by the MSL mission.

## 9. Conclusions

Implementation of rigorous contamination control procedures is essential for a mission such as MSL with its focus on the detection and identification of organic compounds that might be found in the atmosphere or preserved in rocks or soils. A first step in implementation of such a program is a detailed transport analysis to understand how terrestrial volatiles might make their way into the analysis chain. Characterization of organic materials that the MSL rover brings to Mars and careful use of blanks and standards will also be essential to evaluate the robustness of organic detections at Mars. We have described the present plan and initial steps taken to mitigate the impact of terrestrial contamination on the MSL science investigation of organic compounds. This project demands a rigorous adherence to contamination control throughout the remainder of MSL development. Project funding and schedule constraints continue to be a challenge that, at times, impedes the plan's full implementation. The goal is to focus resources on the most critical components to assure that they meet requirements. Recently, the sophisticated and complex Sample Manipulation System achieved outgassing rates that were lower than those for the most sensitive far-ultraviolet optics and particle surface cleanliness levels similar to those required for scatter-sensitive optics.

## Abbreviations

APXS, Alpha Particle X-ray Spectrometer; CheMin, X-ray diffraction/X-ray fluorescence instrument to identify and quantify minerals in complex natural samples; CSPL, chemical separation and processing laboratory; DAN, Dynamic

Albedo of Neutrons instrument; GC, gas chromatograph; GCMS, gas chromatograph and mass spectrometer; MAHLI, Mars Hand Lens Imager; MARDI, Mars Descent Imager; MER, the Mars Exploration Rovers; MSL, Mars Science Laboratory; QMS, quadrupole mass spectrometer; RAD, Radiation Assessment Detector; REMS, Rover Environmental Monitoring Station; RTG, radioisotope thermoelectric generator; SAM, Sample Analysis at Mars; SA/SPaH, Sample Acquisition and Sample Processing and Handling tool; SSIT, solid-sample inlet tubes; TLS, tunable laser spectrometer.

## References

- Biemann, K., Oró, J., Toulmin, P., III, Orgel, L.E., Nier, A.O., Anderson, D.M., Simmonds, P.G., Flory, D., Diaz, A.V., Rushneck, D.R., Biller, J.E., and Lafleur, A.L. (1977) The search for organic substances and inorganic volatile compounds in the surface of Mars. *J. Geophys. Res.* 82:4641–4658.
- Blake, D.F., Sarrazin, P., Bish, D.L., Chipera, S.J., Vaniman, D.T., Ming, D., Morris, D., and Yen, A. (2007) CheMin: a definitive mineralogy instrument on the Mars Science Laboratory (MSL '09) rover [abstract 3320]. In *7<sup>th</sup> International Conference on Mars Abstracts*, Lunar and Planetary Institute, Houston.
- Campbell, W.A., Marriott, R.S., and Park, J.J. (1975) *Outgassing Data for Spacecraft Materials*, NASA TN D-8008, NASA Goddard Space Flight Center, Greenbelt, MD.
- Campbell, W.A., Marriott, R.S., and Park, J.J. (2006) *Outgassing Data for Selecting Spacecraft Materials*, NASA Goddard Space Flight Center Materials Engineering Branch, Greenbelt, MD. Available online at <http://outgassing.nasa.gov>.
- Canham, J.S. (2005) Short path thermal desorption GC/MS for screening of molecular contamination in laser systems. In *36<sup>th</sup> Annual Boulder Damage Symposium on Optical Materials for High Power Lasers. Laser-Induced Damage in Optical Materials: 2004*, edited by G.J. Exarhos, A.H. Guenther, N. Kaiser, K.L. Lewis, M.J. Soileau, and C.J. Stolz, *Proceedings of the SPIE* 5647:427–438.
- Edgett, K.S., Bell, J.F., III, Herkenhoff, K.E., Heydari, E., Kah, L.C., Minitti, M.E., Olson, T.S., Rowland, S.K., Schieber, J., Sullivan, R.J., Yingst, R.A., Ravine, M.A., Caplinger, M.A., and Maki, J.N. (2005) The Mars Hand Lens Imager (MAHLI) for the 2009 Mars Science Laboratory [abstract 1170]. In *36<sup>th</sup> Lunar and Planetary Science Conference Abstracts*, Lunar and Planetary Institute, Houston.
- Fishman, N., Muraca, R.F., Thomas, H.G., and Whittick, J.S. (1966) Polymers for spacecraft hardware materials specifications and engineering information. *Monthly Technical Progress Report No. 21, February 10 to March 9, 1966*, NASA Technical Report Server Accession Number 66N24972, Document ID 19660015683, Report Number NASA-CR-74688, 1964, NASA, Washington, DC.
- Flory, D.A., Oró, J., and Fennessey, P.V. (1974) Organic contamination problems in the Viking molecular analysis experiment. *Orig. Life Evol. Biosph.* 5:443–455.
- Gellert, R., Rieder, R., Brückner, J., Clark, B.C., Dreibus, G., Klingelhöfer, G., Lugmair, G., Ming, D.W., Wänke, H., Yen, A., Zipfel, J., and Squyres, S.W. (2006) Alpha Particle X-Ray Spectrometer (APXS): results from Gusev Crater and calibration report. *J. Geophys. Res.* 111, doi:10.1029/2005JE002555.
- Gómez-Elvira, J., and the REMS Team. (2008) Environmental monitoring instrument for Mars exploration [abstract 1647]. In *39<sup>th</sup> Lunar and Planetary Science Conference Abstracts*, Lunar and Planetary Institute, Houston.
- Grosjean, E. and Logan, G.A. (2007) Incorporation of organic contaminants into geochemical samples and an assessment of

- potential sources: examples from Geoscience Australia's marine survey S282. *Org. Geochem.* 38:853–869.
- Hassler, D.M., Wimmer-Schweingruber, R.F., Beaujean, R., Böttcher, S., Burmeister, S., Cucinotta, F., Müller-Mellin, R., Posner, A., Rafkin, S., Reitz, G., and the RAD Team. (2006) The Radiation Assessment Detector (RAD) on the Mars Science Laboratory (MSL) [abstract 02720]. In *36<sup>th</sup> COSPAR Scientific Assembly Abstracts*, Committee on Space Research, Paris.
- JPL. (2007a) Mission timeline: entry, descent, and landing. *Mars Science Laboratory: The Mission*, Jet Propulsion Laboratory, Pasadena, CA. Available online at [http://marsprogram.jpl.nasa.gov/msl/mission/tl\\_edl.html](http://marsprogram.jpl.nasa.gov/msl/mission/tl_edl.html) (accessed April 8, 2007).
- JPL. (2007b) *NASA's 2009 Mars Science Laboratory*, Jet Propulsion Laboratory, Pasadena, CA. Available online at [http://webgis.wr.usgs.gov/msl/docs/MSL\\_overview\\_LS.pdf](http://webgis.wr.usgs.gov/msl/docs/MSL_overview_LS.pdf) (accessed April 8, 2007).
- Karaiskakis, G. and Gavril, D. (2004) Determination of diffusion coefficients by gas chromatography. *J. Chromatogr. A* 1037: 147–189.
- Lockwood, M.K. (2006) Mars Science Laboratory: the next generation of Mars landers. *J. Spacecr. Rockets* 43:257.
- Mahaffy, P.R. (2007) Exploration of the habitability of Mars: development of analytical protocols for measurement of organic carbon on the 2009 Mars Science Laboratory. *Space Sci. Rev.* doi:10.1007/s11214-007-9223-1.
- Mahaffy, P.R., Beaty, D., Anderson, M., Aveni, G., Bada, J., Clemett, S., Des Marais, D., Douglas, S., Dworkin, J., Kern, R., Papanastassiou, D., Palluconi, F., Simmonds, J., Steele, A., Waite, H., and Zent, A. (2003) Science priorities related to the organic contamination of martian landers [unpublished white paper]. *MEPAG Topical Analysis Reports*, Mars Exploration Program Analysis Group. Available online at <http://mepag.jpl.nasa.gov/reports/index.html>.
- Malin, M.C., Bell, J.F., Cameron, J., Dietrich, W.E., Edgett, K.S., Hallet, B., Herkenhoff, K.E., Lemmon, M.T., Parker, T.J., Sullivan, R.J., Sumner, D.Y., Thomas, P.C., Wohl, E.E., Ravine, M.A., Caplinger, M.A., and Maki, J.N. (2005) The Mast cameras and Mars Descent Imager (MARDI) for the 2009 Mars Science Laboratory [abstract 1214]. In *36<sup>th</sup> Lunar and Planetary Science Conference Abstracts*, Lunar and Planetary Institute, Houston.
- Mitrofanov, I.G., Litvak, M.L., Kozyrev, A.S., Mokrousov, M.I., Sanin, A.B., and Tretyakov, V. (2005) Dynamic Albedo of Neutrons (DAN): active nuclear experiment onboard NASA Mars Science Laboratory [abstract 1635]. In *36<sup>th</sup> Lunar and Planetary Science Conference Abstracts*, Lunar and Planetary Institute, Houston.
- Murphy, J.R., Leovy, C.B., and Tillman, J.E. (1990) Observations of the martian surface winds at the Viking Lander 1 site. *J. Geophys. Res.* 95:14,555–14,576.
- NASA. (1990) *Outgassing Data for Selecting Spacecraft Materials*, Reference Publication 1124 Revision 2, NASA, Washington, DC.
- Ramshaw, J.D. and Mousseau, V.A. (1990) Accelerated artificial compressibility method for steady-state incompressible flow calculations. *Computers & Fluids* 18:361–367.
- Squyres, S.W., Arvidson, R.E., Bell, J.F., III, Brückner, J., Cabrol, N.A., Calvin, W., Carr, M.H., Christensen, P.R., Clark, B.C., Crumpler, L., Des Marais, D.J., d'Uston, C., Economou, T., Farmer, J., Farrand, W., Folkner, W., Golombek, M., Gorevan, S., Grant, J.A., Greeley, R., Grotzinger, J., Haskin, L., Herkenhoff, K.E., Hviid, S., Johnson, J., Klingelhöfer, G., Knoll, A.H., Landis, G., Lemmon, M., Li, R., Madsen, M.B., Malin, M.C., McLennan, S.M., McSween, H.Y., Ming, D.W., Moersch, J., Morris, R.V., Parker, T., Rice, J.W., Jr., Richter, L., Rieder, R., Sims, M., Smith, M., Smith, P., Soderblom, L.A., Sullivan, R., Wänke, H., Wdowiak, T., Wolff, M., and Yen, A. (2004a) The Spirit rover's Athena science investigation at Gusev Crater, Mars. *Science* 305:794–799.
- Squyres, S.W., Arvidson, R.E., Bell, J.F., III, Brückner, J., Cabrol, N.A., Calvin, W., Carr, M.H., Christensen, P.R., Clark, B.C., Crumpler, L., Des Marais, D.J., d'Uston, C., Economou, T., Farmer, J., Farrand, W., Folkner, W., Golombek, M., Gorevan, S., Grant, J.A., Greeley, R., Grotzinger, J., Haskin, L., Herkenhoff, K.E., Hviid, S., Johnson, J., Klingelhöfer, G., Knoll, A.H., Landis, G., Lemmon, M., Li, R., Madsen, M.B., Malin, M.C., McLennan, S.M., McSween, H.Y., Ming, D.W., Moersch, J., Morris, R.V., Parker, T., Rice, J.W., Jr., Richter, L., Rieder, R., Sims, M., Smith, M., Smith, P., Soderblom, L.A., Sullivan, R., Wänke, H., Wdowiak, T., Wolff, M., and Yen, A. (2004b) The Opportunity rover's Athena science investigation at Meridiani Planum, Mars. *Science* 306:1698–1703.
- Vasavada, A.R. and the MSL Science Team. (2006) NASA's 2009 Mars Science Laboratory: an update [abstract 1940]. In *37<sup>th</sup> Lunar and Planetary Science Conference Abstracts*, Lunar and Planetary Institute, Houston.
- Wiens, R., Maurice, S., Bridges, N., Clark, B., Cremers, D., Herkenhoff, K., Kirkland, L., Mangold, N., Manhés, G., Mauchien, P., McKay, C., Newsom, H., Poitrasson, F., Sautter, V., d'Uston, C., Vaniman, D., and Shipp, S. (2005) ChemCam science objectives for the Mars Science Laboratory (MSL) rover [abstract 1580]. In *36<sup>th</sup> Lunar and Planetary Science Conference Abstracts*, Lunar and Planetary Institute, Houston.
- Wimmer-Schweingruber, R.F., Beaujean, R., Böhm, E., Böttcher, S., Burmeister, S., Herbst, K., Kortmann, O., Martin, C., Müller-Mellin, R., Seimetz, L., Kolbe, S., Reitz, G., Hassler, D., Andrews, J., Bullock, M., Grinspoon, D., Epperly, M., Posner, A., Rafkin, S., Smith, K., Cucinotta, F., and Cleghorn, T. (2006) The Mars Science Laboratory (MSL) Radiation Assessment Detector (RAD). *Third European Space Weather Week*, Brussels. Available online at <http://sidc.oma.be/esww3/presentations/Session7/Wimmer.pdf> (accessed April 28, 2008).

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