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Analytical techniques for retrieval of atmospheric composition with the quadrupole mass spectrometer of the Sample Analysis at Mars instrument suite on Mars Science Laboratory

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ABSTRACT

The Sample Analysis at Mars (SAM) instrument suite is the largest scientific payload on the Mars Science Laboratory (MSL) Curiosity rover, which landed in Mars' Gale Crater in August 2012. As a miniature geochemical laboratory, SAM is well-equipped to address multiple aspects of MSL's primary science goal, characterizing the potential past or present habitability of Gale Crater. Atmospheric measurements support this goal through compositional investigations relevant to martian climate evolution. SAM instruments include a quadrupole mass spectrometer, a tunable laser spectrometer, and a gas chromatograph that are used to analyze martian atmospheric gases as well as volatiles released by pyrolysis of solid surface materials (Mahaffy et al., 2012). This report presents analytical methods for retrieving the chemical and isotopic composition of Mars' atmosphere from measurements obtained with SAM's quadrupole mass spectrometer. It provides empirical calibration constants for computing volume mixing ratios of the most abundant atmospheric species and analytical functions to correct for instrument artifacts and to characterize measurement uncertainties. Finally, we discuss differences in volume mixing ratios of the martian atmosphere as determined by SAM (Mahaffy et al., 2013) and Viking (Owen et al., 1977; Oyama and Berdahl, 1977) from an analytical perspective. Although the focus of this paper is atmospheric observations, much of the material concerning corrections for instrumental effects also applies to reduction of data acquired with SAM from analysis of solid samples.

1. Introduction

The Sample Analysis at Mars (SAM) instrument suite was designed to assess Mars' inventory of volatiles in both atmospheric and solid reservoirs (Mahaffy et al., 2012). Measurements of the atmospheric chemical and isotopic composition seek to characterize the current martian surface environment and to constrain models of climatic evolution. Our current knowledge of the abundances of atmospheric constituents and their isotopic compositions are based on (1) data gathered by previous landed and orbital missions, particularly Viking, Phoenix, and Mars Reconnaissance Orbiter, e.g., Hoffman et al. (2008), Nier et al. (1976a, 1976b), Niles et al. (2010), Owen et al. (1977), Oyama and Berdahl (1977), Smith et al. (2009), (2) spectroscopic remote sensing, e.g., Encrenaz et al. (2012), Hartogh et al. (2010), Krasnopolsky et al. (2007), and (3) analysis of martian meteorites, e.g., Becker and Pepin (1984), Bogard and Johnson (1983), Watson et al. (1994). In situ measurements of the

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martian atmosphere have been acquired with instruments of the Viking and Phoenix missions. The Viking compositional measurements most analogous to those of SAM were performed with the mass spectrometers on both landers (Anderson et al., 1972; Nier et al., 1976b; Owen et al., 1977; Rushneck et al., 1978). These were double-focusing magnetic sector instruments that operated in the mass range of 12–215 Da (Rushneck et al., 1978). Martian atmospheric gas could be sampled either directly into the ion source or scrubbed first for removal of CO and CO_2, enriching the sample in trace gases (Owen et al., 1977). The Viking landers also generated independent measurements of atmospheric composition by analyzing headspace gas with the gas chromatograph of the Gas Exchange Experiment (GEx) (Oyama and Berdahl, 1977) Viking results are discussed in more depth in Section 6. The Evolved Gas Analyzer of the Phoenix lander was also a magnetic sector instrument that utilized four different trajectories through the mass analyzer to cover separate mass ranges between 0.7 and 140 Da (Hoffman et al., 2008). Like the Viking instruments, it was capable of sampling atmospheric gas directly into the ion source or enriching the sample in noble gas species first (Hoffman et al., 2008).

SAM is equipped to perform in situ measurements of the martian atmosphere with unprecedented precision. The tools and techniques developed to accomplish this task were built on the foundation laid by these previous studies, exploiting our current knowledge of Mars to focus and refine SAM investigations. This refinement includes gas handling components to optimize isotopic analysis of atmospheric species, particularly N_2 as well as Ar and other noble gases with isotopes of low abundance; to detect species present at trace levels, including organic compounds; and to measure the abundance and isotopic composition of CO_2, H_2O, and CH_4 at high precision with the SAM tunable laser spectrometer (Webster and Mahaffy, 2011).

This paper focuses on the analytical techniques utilized to obtain chemical and isotopic composition values from SAM's quadrupole mass spectrometer measurements. We discuss the determination of empirical calibration constants for retrieval of volume mixing ratios (VMR) for the most abundant atmospheric species. We also demonstrate the development of analytical functions to correct for instrument artifacts and to characterize measurement uncertainties. Brief descriptions of the SAM instrument and the measurement techniques are given first to offer insight into data retrieval methods. The reader is referred to papers by Mahaffy and Webster for detailed descriptions of SAM and the TLS (Mahaffy et al., 2012; Webster, 2005; Webster and Mahaffy, 2011). For convenience, Table 1 defines the most common abbreviations and acronyms used in this paper.

2. Instrument description

The SAM suite is comprised of three primary instruments: a quadrupole mass spectrometer (QMS), a tunable laser spectrometer (TLS) and a six-column gas chromatograph (GC). The QMS and the TLS are the primary instruments used to analyze atmospheric samples. The TLS specifically targets CO_2, H_2O and CH_4 and determines their abundances and the isotopic ratios of their atomic constituents to very high precision (Webster, 2005; Webster and Mahaffy, 2011). The QMS can survey mass/charge (m/z) values from 1.5 to 535.5 in steps of 0.1 and is the only instrument on MSL capable of measuring the VMR of atmospheric species and the isotopic ratios of nitrogen and the noble gases. The QMS, TLS, and GC are coupled with a gas processing system (GPS) and a sample manipulation system (SMS), the latter of which is used for analyzing solid samples.

2.1. Instrument components

2.1.1. Gas processing system

Fig. 1 illustrates how SAM's components are connected with numerous valves and a series of gas manifolds, allowing samples to be analyzed by any or all of the three instruments. The GPS consists of two turbomolecular pumps (Wide Range Pumps, WRP1 and WRP2, developed by collaboration between Creare, Inc., and engineers at NASA Goddard Space Flight Center (GSFC)), two gas inlets, a system of valves and manifolds, gas scrubbers, a getter and a hydrocarbon trap. The WRPs evacuate the QMS, the TLS and the gas manifolds. Their pumping speed of 3 L/s represents a major technological advancement over the sputter ion pumps used for the Viking (Rushneck et al., 1978) and Phoenix (Hoffman et al., 2008) mass spectrometers, which achieved effective pumping speeds of 500 cc/s and 1 L/s, respectively. This allows the SAM QMS to achieve a dynamic range of $\sim 10^9$ (Mahaffy et al., 2012), compared to 10^6–10^7 for Viking (Owen et al., 1977) and $\sim 10^7$ for Phoenix (Hoffman et al., 2008). Atmospheric gas may be introduced into SAM through two inlets. Inlet 1 (controlled by valve 28, or V28) allows for an ingested sample of atmospheric gas to be manipulated, separated, and/or enriched before being directed to any of the three instruments for analysis. Inlet 2 (V10) brings atmospheric gas directly and only to the TLS. The scrubbers and getter are used for separating and enriching atmospheric trace species to enable improved sensitivity and accuracy in composition and isotopic measurements.

Like a terrestrial laboratory, the SAM instrument suite has many configurable options that allow a range of experiment strategies to be employed on Mars. An important facet of SAM's analytical flexibility is the range of gas handling modes that may be employed. The three primary gas handling modes for atmospheric measurements are as follows.

2.1.1.1. Direct atmospheric. Direct analysis of the martian atmosphere by the QMS and TLS is the most frequent atmospheric measurement expected to be made by SAM. This experimental sequence, an example of which is illustrated in Fig. 2, is designated *AS-DIRECT*. In this sampling mode, the sample is simply ingested martian atmospheric gas. Experiments employing QMS direct atmospheric sampling may or may not include TLS measurements. TLS measurements are made in “batch mode” in which gas in the Herriot cell of the TLS is isolated from the manifold and may require volume expansions to achieve different pressures according to the target analyte (CO_2/H_2O or CH_4). Separate sequences can be run for *AS-DIRECT-QMS* and *AS-DIRECT-TLS* measurements when the duration of running both QMS and TLS experiments is undesirable due to MSL resource or operational constraints. The duration of each of these experiments can run 4–8 h per instrument with extended integration time for either QMS or TLS, which results in greatly improved measurement precision. In addition, trace gas and isotopic analysis (e.g., $^{36}Ar/^{38}Ar$) may benefit not only from longer integration times but also from additional background scans and measurements at multiple pressures. Because of the structure of the flight software, parameter files governing variables such as number of scans and pressure can be readily modified to optimize atmospheric experiments following an initial survey using the nominal *AS-DIRECT* experiment with QMS and TLS.

2.1.1.2. Noble gas enrichment. Despite the wide dynamic range of the SAM QMS in the *AS-DIRECT* mode, a further extension of this range is necessary to improve counting statistics and to more accurately subtract the instrument background signal for measurements of minor isotopes of noble gases. SAM can perform additional atmospheric experiments requiring specialized gas processing using its scrubbers, getter, and hydrocarbon/noble gas