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# Reevaluated martian atmospheric mixing ratios from the mass spectrometer on the Curiosity rover

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## ABSTRACT

The Sample Analysis at Mars (SAM) instrument suite of the Mars Science Laboratory (MSL) Curiosity rover is a miniature geochemical laboratory designed to analyze martian atmospheric gases as well as volatiles released by pyrolysis of solid surface materials (Mahaffy et al., 2012). SAM began sampling the martian atmosphere to measure its chemical and isotopic composition shortly after Curiosity landed in Mars' Gale Crater in August 2012 (Mahaffy et al., 2013). Analytical methods and constants required for atmospheric measurements with SAM's quadrupole mass spectrometer (QMS) were provided in a previous contribution (Franz et al., 2014). Review of results obtained through application of these constants to repeated analyses over a full martian year and supporting studies with laboratory instruments offer new insights into QMS performance that allow refinement of the calibration constants and critical reassessment of their estimated uncertainties. This report describes the findings of these studies, provides updated calibration constants for atmospheric analyses with the SAM QMS, and compares volume mixing ratios for the martian atmosphere retrieved with the revised constants to those initially reported (Mahaffy et al., 2013). Sufficient confidence is enabled by the extended data set to support calculation of precise abundances for CO rather than an upper limit. Reanalysis of data acquired on mission sols 45 and 77 (at solar longitudes of 175° and 193°, respectively) with the revised constants leads to the following average volume mixing ratios: CO<sub>2</sub> 0.957(±0.016), N<sub>2</sub> 0.0203(±0.0003), Ar 0.0207(±0.0002), O<sub>2</sub> 1.73(±0.06) × 10<sup>-3</sup>, CO 7.49(±0.026) × 10<sup>-4</sup>.

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## 1. Introduction

The Sample Analysis at Mars (SAM) instrument suite was designed to perform *in situ* measurements of the martian atmosphere, including determination of its chemical and isotopic composition, with unprecedented precision (Mahaffy et al., 2012; Webster and Mahaffy, 2011). The design of SAM's quadrupole mass spectrometer (QMS) builds upon a lineage of successful flight instruments fabricated at NASA Goddard Space Flight Center (GSFC) that have operated in a variety of extraterrestrial environments (Niemann et al., 2002; Niemann et al., 1980a; Niemann et al., 1992; Niemann et al., 1979; Niemann et al., 1980b). The SAM QMS allows determination of volume mixing ratios (VMR) for the

most abundant atmospheric species on Mars via application of empirical calibration constants as well as isotope ratios of CO<sub>2</sub>, N<sub>2</sub> and noble gases (Franz et al., 2014). The precision required for meaningful measurements of isotope ratios and of VMR for the minor atmospheric species O<sub>2</sub> and CO may only be achieved through meticulous characterization and removal of instrument artifacts and estimation of associated measurement uncertainties.

The work described in this paper was motivated by observations acquired with the SAM flight instrument on Mars and with engineering models (SAM breadboard and test bed) located at GSFC and described below. Comparison of VMR obtained by SAM throughout the martian year has revealed cyclical variations that appear to correlate with seasonal pressure changes observed by environmental monitoring instruments (Harri et al., 2014; Hess et al., 1977). The variations observed by SAM, particularly in CO<sub>2</sub> abundance, are much smaller than the estimated measurement uncertainties, prompting reevaluation of the error sources folded into the calibration constants. In addition, the relationship between counts and pressure has been

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observed to vary disproportionately between  $\text{CO}_2^+$  and  $\text{CO}_2^{++}$  ions, suggesting an increase in production of  $\text{CO}_2^+$  ions with pressure. This behavior was reproduced in experiments on the SAM breadboard, enabling development of a correction algorithm to mitigate the effect. Finally, experiments with the SAM test bed have revealed a minor contribution from ionization fragments of  $\text{CO}_2$ , which interfere with measurements of  $\text{O}_2$  VMR. This contribution was quantified to allow subtraction of these  $\text{CO}_2$  fragments from the mass spectrum, ensuring improved accuracy in computed  $\text{O}_2$  abundances.

## 2. Instrument description

The SAM instrument suite and operational modes for atmospheric analyses are described in detail elsewhere (Franz et al., 2014; Mahaffy et al., 2012). Briefly, SAM's components are connected by a series of gas manifolds, with two turbomolecular pumps and numerous valves controlling flow through the system. Atmospheric gas is typically ingested into an evacuated manifold that is subsequently isolated from the martian environment before analysis. Gas flows from the manifold through a glass capillary into the QMS ion source, where it is ionized by electron impact ionization utilizing a W/3%Re wire, with nominal filament emission current of 20  $\mu\text{A}$ . The mass analyzer consists of four hyperbolic rods to which a combination of radio frequency (RF) and static (DC) voltages are applied to achieve mass separation. Selected ions of a given mass/charge ( $m/z$ ) ratio traverse through the quadrupole region and are ultimately detected by one of the redundant continuous dynode secondary electron multipliers. For experiments designed to study the major atmospheric species, the QMS typically scans  $m/z$  values from 1.5 to 149.9 in steps of 0.1, although the highest  $m/z$  relevant to major atmospheric species is 46, from isotopically heavy  $\text{CO}_2$ . The integration period for measuring counts at a single  $m/z$  value is configurable, but all QMS experiments to date have used the default integration period of 17 ms with a 3-ms pause for reconfiguration between  $m/z$  values.

The SAM breadboard and test bed include quadrupole mass spectrometers fabricated at GSFC to the same design as the flight model and controlled with identical electronics and flight software, rendering these instruments high-fidelity facsimiles of SAM. The breadboard employs the SAM prototype QMS in a laboratory setting that allows flexibility in plumbing configuration for a range of experiments supporting both atmospheric and solid sample analyses. The test bed comprises a replica of SAM, including all instrument and gas processing system components. The test bed is housed in an environmental chamber that simulates martian ambient conditions. For the studies described here, both instruments utilized operating parameters analogous to those of atmospheric experiments on Mars.

## 3. QMS calibration

### 3.1. Pre-launch calibration

Before SAM was delivered to the Jet Propulsion Laboratory for integration with Curiosity, pre-launch calibration was performed on all suite components. This effort included QMS tuning, derivation of detector correction functions, and determination of empirical calibration constants for VMR measurements (Franz et al., 2014). QMS tuning is designed to produce peaks centered near the integer  $m/z$  value that are sharp enough to minimize cross-talk between adjacent unit and half-unit channels and to minimize variations in peak width across the mass range of the instrument while maintaining the highest possible sensitivity. Differences in tuning across the mass range and between regions of different RF

frequency produce differences in number of ions detected for the same absolute abundance, even when differences in ionization efficiency for chemical species are considered. The calibration process is designed to account for these differences. For atmospheric VMR calculations, these corrections were made by deriving empirical calibration constants based on measurements of gas mixtures of known chemical composition. These included a “Mars mix” with composition approximating that of the martian atmosphere as determined by the Viking mass spectrometer and an “equimolar mix” containing  $\sim 25\%$  each of  $\text{CO}_2$ , Ar,  $\text{O}_2$ , and  $\text{N}_2$ . The calibration constants for these four gases were derived from the ratio of a key “marker” fragment of each molecule to  $^{40}\text{Ar}$ , from which relative VMR of atmospheric species are then computed by the relationship

$$[X]/[\text{Ar}] = F_{X_i/\text{Ar}} \cdot c_i/c_{40}, \quad (1)$$

where  $X$  is the atmospheric species,  $F_{X_i/\text{Ar}}$  is the calibration constant for that species at the ion fragment  $i$ , and  $c_i$  and  $c_{40}$  are the counts at  $m/z$   $i$  and 40, respectively. The calibration constant for CO was defined through combined data of experiments with the equimolar mix and Mars mix (Franz et al., 2014).

Relevant constants for  $\text{CO}_2$  isotopic measurements were informed by independent analysis of the isotopic composition of  $\text{CO}_2$  in the equimolar mix by dual inlet isotope ratio mass spectrometry on a Thermo Scientific MAT 253 at GSFC (Franz et al., 2014).

### 3.2. Calibration refinement

The SAM team has carefully monitored QMS performance throughout the nominal operational mission of one Mars year. This effort has indicated some minor changes in QMS parameters since pre-launch calibration and two sources of instrument artifacts that must be addressed for optimal accuracy in processed data. The required corrections are discussed in Sections 3.2.1 through 3.2.4 and revised calibration coefficients are provided in Section 3.2.5. Results of applying these corrections to data acquired during SAM's initial experiments on Mars are discussed in Section 4. Note that throughout the paper, references to “observed” QMS signal imply data that have been corrected for dead time and background, as appropriate.

#### 3.2.1. QMS tuning

The most significant change in QMS performance on Mars compared to pre-flight calibration is observed at  $m/z$  22, the marker fragment used in calculation of  $\text{CO}_2$  abundances. This  $m/z$  value comprises  $\text{CO}_2^+$  ions and serves as a proxy for the major isotopologue at  $m/z$  44, which saturates the QMS detector at pressures encountered during martian atmospheric measurements. Slight widening of the  $m/z$  22 peak has increased the average peak area by approximately 3.6% compared to calibration. This widening is believed to reflect effects of ambient temperature on the gain of the RF circuit, which are mitigated by a temperature compensation algorithm integral to the flight software. Changes in peak area have also been observed for the other marker fragments used in VMR calculations, but less than 2% on average. These changes have been incorporated into updated fractional scan calibration constants. Similarly, changes to the average relative peak center values on Mars are reflected in updated unit scan calibration constants.

#### 3.2.2. $m/z$ 22 correction

In addition to the change in peak width described above, the pressure-normalized signal from  $\text{CO}_2^+$  ions at  $m/z$  22 in Mars data has been observed to deviate from the behavior of  $\text{CO}_2^+$  ions at  $m/z$  45 and 46, suggesting an increase in the production of

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