



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.

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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 CO₂, 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 N₂ 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 CO₂, H₂O, and CH₄ 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 CO₂, H₂O and CH₄ 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 (CO₂/H₂O or CH₄). 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., ³⁶Ar/³⁸Ar) 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

Table 1
Abbreviations and acronyms.

ATM	Atmospheric analysis region
BG	Background analysis region
G#	Getter with associated number
GC	Gas chromatograph
GCMS	Gas chromatograph-mass spectrometer
GPS	Gas processing system
GSFC	Goddard Space Flight Center
HC#	High-conductance valve with associated number
MN#	Gas manifold with associated number
MSL	Mars Science Laboratory
m/z	Mass-to-charge ratio
NASA	National Aeronautics and Space Administration
PDS	Planetary Data System
PM#	Pressure monitor with associated number
QMS	Quadrupole Mass Spectrometer
SAM	Sample Analysis at Mars
SMS	Sample Manipulation System
SSIT#	Solid Sample Inlet Tube with associated number
TID	Test identifier, uniquely assigned to a single experiment performed by SAM
TLS	Tunable Laser Spectrometer
V##	Valve with associated number
VMR	Volume mixing ratio
WRP#	Wide range pump with associated number

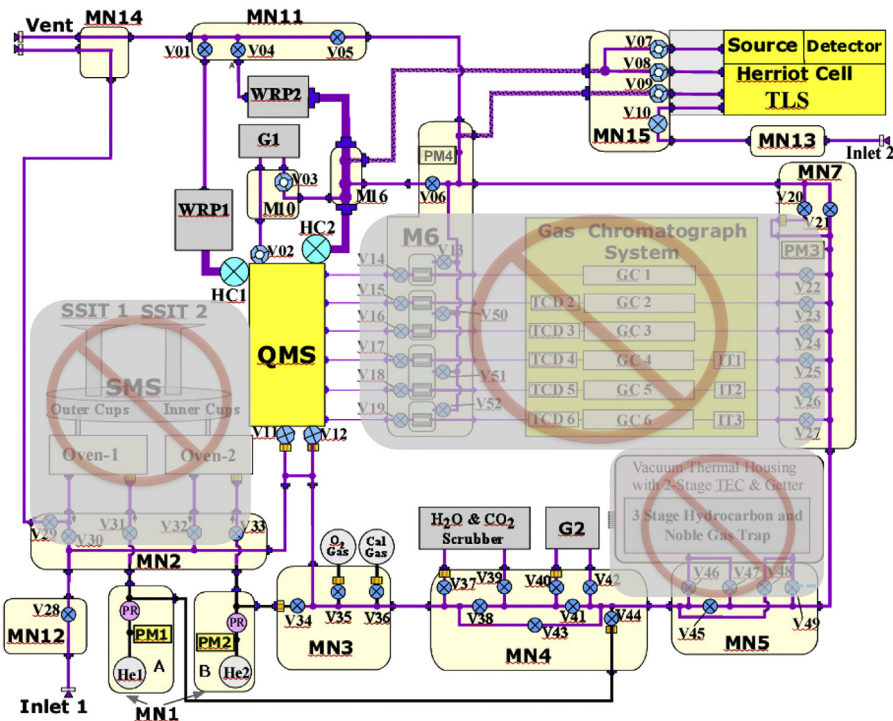


Fig. 1. SAM gas processing system. Portions not relevant to the atmospheric experiments discussed in this paper are covered with gray-shaded boxes. System components include the quadrupole mass spectrometer (QMS), tunable laser spectrometer (TLS), gas chromatograph (GC), gas manifolds (MN#), microvalves (V##), sample manipulation system (SMS), solid sample inlet tubes (SSIT#), wide-range pumps (WRP#), getters (G#), pressure monitors (PM#), and high-conductance valves (HC#).

trap (Mahaffy et al., 2012). These include AS-NG, which involves multiple iterations of atmospheric gas introduction and removal of active gas by scrubbing to enrich the concentration of Ne, Ar, Kr, and Xe for optimal measurements. This scheme also allows greater precision in determination of the nitrogen isotopic composition. The experiment may be performed in various modes, which achieve incrementally greater degrees of enrichment in the targeted species.

In a “dynamic mode” version of the enrichment protocol (AS-DNG), the gas sample in the manifold is exposed to a H₂O and CO₂ scrubber to remove CO₂ and all other chemically active gases (except CH₄), while the QMS is continuously pumped by

WRP1. This allows measurement of atmospheric argon (³⁶Ar/³⁸Ar) and nitrogen (¹⁵N/¹⁴N) isotope ratios that cannot be obtained as precisely through the AS-DIRECT experiment. A “semi-static mode” protocol (AS-SSNG) operates as described for dynamic mode, but adds passive pumping by the getter in the QMS as well as restricted conductance via partial closure of the high-conductance valve at the exit from the QMS. The semi-static experiment scheme achieves greater enrichment in nitrogen and noble gases than the simpler dynamic mode experiment while maintaining safe operating pressures in the QMS. Data from the first execution of these modes on Mars, which employed up to twelve successive cycles of

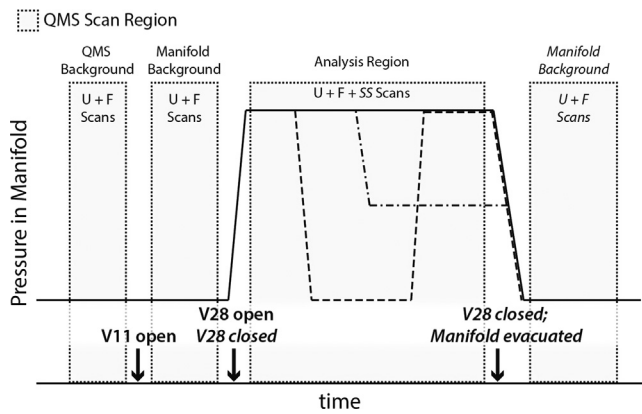


Fig. 2. Example experiment sequence for atmospheric analysis. “U”=Unit, “F”=Fractional, and “SS”=Smart Scans.

atmospheric sample introduction and scrubbing, resulted in a substantial increase in the signal-to-noise ratio for the trace levels of krypton present in the atmosphere.

In the full “static mode” AS-NG experiment, sample enrichment is achieved in two stages. In the first stage, the sample is exposed to the scrubber and getter in the manifold to remove active gases. Krypton and xenon are removed from the sample by trapping on the Carbosieve element of the cooled SAM trap. During this stage, the QMS is pumped as usual with the WRPs to evacuate active gases from the QMS. This sample introduction and scrubbing process is repeated several times, incrementally enriching the sample in noble gases to enable abundances and isotope ratios of the light noble gases to be secured. In the second stage, valves to the WRPs are closed off and the QMS is operated in static mode, where active gases are pumped only by a getter. Krypton and xenon are released from the SAM trap into the now evacuated manifold and are progressively introduced to the QMS at increasing pressure levels. This experiment design is intended to expand the dynamic range sufficiently to measure even the trace ^{124}Xe and ^{126}Xe isotopes.

2.1.1.3. Trace species enrichment. The scrubber not only can be used to remove CO_2 and active gases for noble gas measurements, but also can be heated to release these trapped species back into the gas phase. While the molecular sieve element of the scrubber will remove CO_2 and other gases that adsorb on its surface, another scrubber element contains a magnesium sulfate that will adsorb water by rehydration. Both CO_2 and H_2O can then be released from the scrubber by heating for analysis by either the QMS or the TLS. A separate SAM trap includes a Tenax TA component that can adsorb hydrocarbons and other gases. In the trace species enrichment experiment or AS-ENR, the QMS will search for higher molecular weight atmospheric species that are trapped on the scrubber or the SAM trap more efficiently than CO_2 . These trace species may be analyzed either directly by the QMS or after passing through the GC. The scrubber can also be used to enrich water for more precise D/H measurements by the TLS.

2.1.2. QMS

During a typical SAM atmospheric experiment, gas is introduced through Inlet 1 and fills the manifold. A neutral gas sample is admitted into the ion source of the QMS through a glass capillary associated with V11 and ionized via electron ionization. The resultant ions are focused with a set of electrostatic lenses into the mass analyzer, which consists of four hyperbolic rods. Mass separation is achieved by applying a combination of radio frequency (RF) and static (DC) voltages to opposite pairs of rods.

Ions of the chosen m/z value will successfully traverse through the quadrupole region and be detected by one of the redundant continuous dynode secondary electron multipliers. The QMS also includes a Faraday cup that can provide ion flux information when the electron multiplier is saturated, but its operation is not discussed here because it was not used for analysis of the initial atmospheric experiments on Mars.

QMS experiments are configured by setting parameters that control options such as scan duration and mass range. The QMS scans across the mass range in discrete steps. The details of the QMS scanning mode can be summarized by the following parameters:

2.1.2.1. Mass range. The full mass range of the QMS covers m/z 1.5–535.5. The highest mass at which significant signal is detected in direct atmospheric experiments is generally m/z 46, from heavy CO_2 . QMS scans during atmospheric experiments typically extend to maximum m/z values above those characteristic of the most abundant atmospheric species, to enable long-term characterization of a broader instrument background. The greatest signal-to-noise ratio for atmospheric experiments can be achieved by scanning only over the m/z range of interest for measuring atmospheric species.

2.1.2.2. Integration period. The length of time spent measuring counts at a single m/z value is configurable. However, all QMS experiments have used the default integration period of 17 ms with a 3-ms pause for reconfiguration and to allow voltages to settle before counting at another m/z value. We report data values in units of counts/s, so a single count observed during one integration period is quantized to a value ~ 58 counts/s.

2.1.2.3. Mass interval. Each QMS integration period is spent measuring a discrete m/z value. In a “unit scan,” these values are integers separated by $\Delta m/z=1$ unit. In a “fractional scan,” $\Delta m/z=0.1$ unit. Technically, this parameter is not the same as mass resolution. The effective mass resolution depends on the tuning of the QMS and can be estimated from the data using the full width at half maximum (FWHM) of the mass peaks. Peak widths vary across the QMS mass range. In the m/z range from 20 to 150 (relevant to atmospheric measurements), the FWHM increases from 0.4 at m/z 20 to 0.55 at m/z 60, and then decreases to 0.35 at m/z 150.

2.1.2.4. Bands and smart scans. Nominally, the QMS scans over the designated mass range with steps of the designated mass interval, measuring every step in the range. In SAM’s smart scan mode, a broad “band” of m/z values is scanned, and unit scans are performed in the mass range of each band only if that band contains signal above background that exceeds a specified threshold value. The SAM smart scanning concept was developed and targeted for detection of transient signals encountered during GCMS analysis and has limited value for atmospheric analysis.

2.1.2.5. Vector scans. In vector scan mode, the QMS samples ions only at a pre-selected set of m/z values, maximizing observations for the targeted species of interest.

2.1.2.6. Ionization filament current. Ionization of neutral gases is achieved with an electron impact ion source that utilizes a 97% W, 3% Re wire. The nominal filament emission current is 20 μA , although higher currents up to 200 μA may be utilized in experiments targeting trace atmospheric species. Higher currents produce greater sample ionization, which may be desirable for analysis of trace compounds.

3. Experiment design for atmospheric QMS measurements

QMS atmospheric experiments may utilize various combinations of the options described above. Table 2 summarizes the parameters utilized during the first several atmospheric experiments performed by SAM on Mars. This flexibility allows design of experiments for specific purposes. However, all experiments typically begin with a common initial sequence. First, the gas manifolds are nominally brought to a controlled temperature selected to be in the 25–135 °C range for evacuation of the GPS and QMS by the WRPs. Background spectra of the evacuated instrument are then acquired. The valve between the QMS and gas manifold, V11, controls gas flow into the QMS through a capillary leak, enabling two types of instrument background measurements.

3.1. QMS background

SAM QMS experiments begin with this mode, in which V11 is closed and the QMS conducts scans while isolated from the gas manifold.

3.2. Manifold background

Upon completion of the QMS background, V11 is opened to allow measurement of the background in the gas manifold.

Following the background measurements, atmospheric sample is introduced through V28, which controls the inlet from the martian atmosphere to the gas manifold. For direct atmospheric measurements, the atmosphere is typically analyzed by introducing an atmospheric sample to the gas manifold through V28 with V11 closed, then closing V28 and opening V11 to allow the QMS to measure the atmospheric sample trapped in the gas manifold. A volume expansion within the manifold may also be performed to reduce the sample pressure in the QMS during a portion of the experiment and to facilitate TLS analysis.

4. Instrument calibration

The entire SAM suite was subjected to an extensive pre-launch verification and calibration effort prior to delivery of the instrument to the Jet Propulsion Laboratory. These tests were designed to assess both engineering and science readiness. Most calibration experiments were conducted in an environmental chamber that simulates the range of pressures and temperatures expected on Mars. Tests that specifically addressed QMS functionality included exercise of the nominal direct atmospheric experiment sequence at chamber temperatures of +45 °C, +25 °C, and –20 °C. Additional experiments targeting QMS performance were run with SAM outside the chamber and again following integration with Curiosity to verify full functionality of the SAM suite.

To characterize QMS performance, gases of known composition were introduced through the sample inlet in a manner identical to that used operationally on Mars. The pre-flight calibration process included tuning of the QMS, derivation of corrections for detector nonlinearity effects, establishment of empirical calibration constants for use in determining atmospheric mixing ratios, and tests to validate detection methods for trace gases. These topics are discussed in the following sections. The SAM operations strategy also includes provisions for monitoring changes in QMS performance while on Mars.

4.1. Pre-launch calibration

4.1.1. QMS tuning

QMS tuning refers to the setting of the voltages applied to the quadrupole rods to select the m/z value measured during each integration period. With perfect tuning, fractional scans produce distinct peaks centered at integer m/z values. Separate fixed frequencies are used over three m/z ranges: 1.5–19.5, 19.5–150.5, and 150.5–535.5 (Mahaffy et al., 2012). QMS tuning and temperature compensation algorithms were performed primarily with perfluorotributylamine, $N(CF_3(CF_2)_3)_3$, and perfluorophenanthrene, $C_{14}F_{24}$, which have molecular weights of 671.09 and 642.11 Da, respectively, and fracture extensively upon ionization to produce fragments that access the entire QMS mass range. Tuning in the low-mass range was also facilitated by analysis of a noble gas mixture containing both helium and neon as well as instrument background peaks of water, hydrogen, and methane.

At $m/z < 19.5$, mass peaks have a flat-top shape (Fig. 3), while at higher m/z the shape of the top portion of the peaks is more closely approximated by a Gaussian shape. Over the m/z 19.5–150.5 range, we fit Gaussian profiles to data from the first atmospheric experiment (TID 25008) to determine the centers and widths of each peak as a function of mass to charge ratio (Fig. 4). This analysis shows that QMS tuning after MSL landing is very good, with actual peak centers typically within ± 0.1 of the nominal integer m/z values.

4.1.2. Calibration gas description

SAM instrument calibration involved the use of multiple calibration gases (Table 3). A “Mars mix” was obtained from Praxair to approximate the composition of the atmosphere of Mars as determined by the Viking mass spectrometer (Owen et al., 1977) and consisted by volume of 2.7% N_2 , 1.6% Ar, 1300 ppm O_2 , and 700 ppm CO_2 , with a balance of CO_2 . The isotopic composition of the CO_2 in this gas was measured via injection into a Thermo Scientific Trace Ultra GC-Isolink device coupled to a Thermo Scientific Delta V Plus Isotope Ratio Mass Spectrometer (IRMS). An “equimolar mix” ($\sim 25\%$ each CO_2 , Ar, O_2 , and N_2) calibration gas was prepared on a gas manifold constructed specifically for this purpose. Gas mixing procedures were tested to ensure that isotopic fractionation of CO_2 did not occur during the mixing procedure. Briefly, gas was expanded into the manifold and a 2-L stainless steel cylinder and allowed to equilibrate for 5 min. Valves to the tank were closed, and gas was evacuated from the manifold. Additional gases were introduced and recirculated via pumping to ensure mixing. The total pressure in the cylinder after mixing was ~ 1 bar. All pressures were monitored via a Baratron gauge during the mixing procedure. The equimolar mix was vital to several aspects of QMS calibration, as discussed in subsequent sections, and was also used during Assembly, Test, and Launch Operations (ATLO) calibration at the Jet Propulsion Laboratory.

The gas in the onboard SAM calibration cell, hereafter referred to as the “SAM calibration gas,” is detailed in Table 3. The isotopic compositions of the CO_2 and N_2 used for both the equimolar mix and the SAM calibration gas were measured by dual inlet isotope ratio mass spectrometry on a Thermo Scientific MAT 253 at NASA GSFC. The isotopic composition of the O_2 in the equimolar mix was measured by continuous-flow isotope ratio mass spectrometry at the U.S. Geological Survey in Reston, VA.

4.1.3. Corrections for detector effects

The SAM QMS contains two single-channel electron multiplier detectors (“EM1” and “EM2”), operated in pulse counting mode. Two effects can cause pulse counting systems to detect fewer events than actually occur at high count rates. The first effect is

Table 2
Parameters used during initial QMS atmospheric experiments^a.

	TID 25008 Sol 19	TID 25009 Sol 27	TID 25012 Sol 45	TID 25027 Sol 77	TID 25079 Sol 232	TID 25111 Sol 341
Comments	Primarily an engineering test to demonstrate functionality after landing; some terrestrial contamination	Utilized multiple filament currents and pressures to evaluate detector performance	Utilized 100% and 10% Mars atmospheric pressure to evaluate detector performance	Designed to maximize signal-to-noise for atmospheric measurements; intermediate background scan included	Dynamic mode enrichment experiment using the H ₂ O and CO ₂ scrubber with dynamic pumping	Semi-static mode enrichment experiment using the H ₂ O and CO ₂ scrubber, restricted dynamic pumping and passive pumping
QMS background	fil: 20 μA US: <i>m/z</i> 2–534, duration 120 s FS: <i>m/z</i> 1.5–249.9, duration 240 s	US: <i>m/z</i> 2–534, duration 120 s FS: <i>m/z</i> 1.5–249.9, duration 240 s fil: 20 μA	fil: 20 μA US: <i>m/z</i> 2–150, duration 150 s FS: <i>m/z</i> 1.5–149.9, duration 900 s US: <i>m/z</i> 2–150, duration 150 s	fil: 20 μA US: <i>m/z</i> 2–150, duration 150 s FS: <i>m/z</i> 1.5–149.9, duration 1200 s US: <i>m/z</i> 2–150, duration 150 s	fil: 20 μA US: <i>m/z</i> 2–150, duration 500 s FS: <i>m/z</i> 1.5–149.9, duration 550 s	fil: 20 μA US: <i>m/z</i> 2–150, duration 300 s FS: <i>m/z</i> 1.5–149.9, duration 300 s VS: duration 30 s
Manifold background #1	fil: 20 μA US: <i>m/z</i> 2–534, duration 120 s FS: <i>m/z</i> 1.5–249.9, duration 240 s	US and FS at each filament current fil: 20 μA, 64 μA, 100 μA, 120 μA US: <i>m/z</i> 2–534, duration 120 s FS: <i>m/z</i> 1.5–249.9, duration 240 s	fil: 20 μA US: <i>m/z</i> 2–150, duration 150 s FS: <i>m/z</i> 1.5–149.9, duration 900 s US: <i>m/z</i> 2–150, duration 150 s	fil: 20 μA US: <i>m/z</i> 2–150, duration 150 s FS: <i>m/z</i> 1.5–149.9, duration 1200 s US: <i>m/z</i> 2–150, duration 150 s	fil: 20 μA US: <i>m/z</i> 2–150, duration 1000 s FS: <i>m/z</i> 1.5–149.9, duration 1000 s	fil: 20 μA US: <i>m/z</i> 2–150, duration 300 s FS: <i>m/z</i> 1.5–149.9, duration 300 s VS: duration 30 s
Valve configuration during atmospheric analysis	V11 open V28 open	V11 open V28 open for ATM1; V11 open, V28 closed for ATM2, with volume expansions	V11 open V28 closed	V11 open V28 closed	For scrub 1: scan first with V11 open, then with V12 open For scrubs 2–10: Close V12 and scrubber, open V28 for 30 s, open scrubber, open V12 for QMS scanning	For each scrub cycle: close V12 and scrubber, open V28 for 30 s, open scrubber, open V12 for QMS scanning with HCV partially closed and QMS getter open.
Analysis region #1	fil: 20 μA FS: <i>m/z</i> 1.5–249.9, duration 100 min	P: 7.7 mbar At fil 20 μA SS: <i>m/z</i> 2–534, duration 120 s At fil 20 μA, 70 μA, 142 μA, 190 μA FS: <i>m/z</i> 1.5–249.9, duration 300 s	P: 7.7 mbar fil: 20 μA US: <i>m/z</i> 2–150, duration 150 s FS: <i>m/z</i> 1.5–149.9, duration 900 s SS: <i>m/z</i> 2–150, duration 300 s US: <i>m/z</i> 2–150, duration 150 s	P: 7.7 mbar fil: 20 μA US: <i>m/z</i> 2–150, duration 225 s FS: <i>m/z</i> 1.5–149.9, duration 1800 s SS: <i>m/z</i> 2–150, duration 300 s US: <i>m/z</i> 2–150, duration 225 s	fil: 20 μA Scrub cycles 1–9: US: <i>m/z</i> 2–50, duration 250 s FS: <i>m/z</i> 1.5–49.9, duration 250 s Scrub cycle 10 US: <i>m/z</i> 2–150, duration 500 s FS: <i>m/z</i> 1.5–149.9, duration 500 s	fil: 20 μA Scrub cycles 1–12: US: <i>m/z</i> 2–150, duration 30 s VS: duration 250 s US: <i>m/z</i> 2–150, duration 30 s VS: duration 250 s US: <i>m/z</i> 2–150, duration 30 s
Manifold background #2				fil: 20 μA US: <i>m/z</i> 2–150, duration 150 s FS: <i>m/z</i> 1.5–149.9, duration 1200 s US: <i>m/z</i> 2–150, duration 150 s	fil: 20 μA US: <i>m/z</i> 2–150, duration 1000 s FS: <i>m/z</i> 1.5–149.9, duration 1000 s	fil: 20 μA US: <i>m/z</i> 2–150, duration 300 s. FS: <i>m/z</i> 1.5–149.9, duration 300 s. VS: duration 30 s
Analysis region #2		P: 0.077 mbar At fil 20 μA, 70 μA, 142 μA, 190 μA FS: <i>m/z</i> 1.5–249.9, duration 300 s	P: 0.077 mbar fil: 20 μA US: <i>m/z</i> 2–150, duration 150 s FS: <i>m/z</i> 1.5–149.9, duration 900 s SS: <i>m/z</i> 2–150, duration 300 s US: <i>m/z</i> 2–150, duration 150 s	P: 7.7 mbar fil: 20 μA US: <i>m/z</i> 2–150, duration 225 s FS: <i>m/z</i> 1.5–149.9, duration 1800 s SS: <i>m/z</i> 2–150, duration 300 s US: <i>m/z</i> 2–150, duration 225 s		
Manifold background #3			fil: 20 μA US: <i>m/z</i> 2–150, duration 150 s FS: <i>m/z</i> 1.5–149.9, duration 900 s US: <i>m/z</i> 2–150, duration 150 s	fil: 20 μA US: <i>m/z</i> 2–150, duration 150 s FS: <i>m/z</i> 1.5–149.9, duration 1200 s US: <i>m/z</i> 2–150, duration 150 s		

^a Abbreviations: “US”=unit scan, “FS”=fractional scan, “VS”=vector scan; Sol is martian day number for MSL mission.

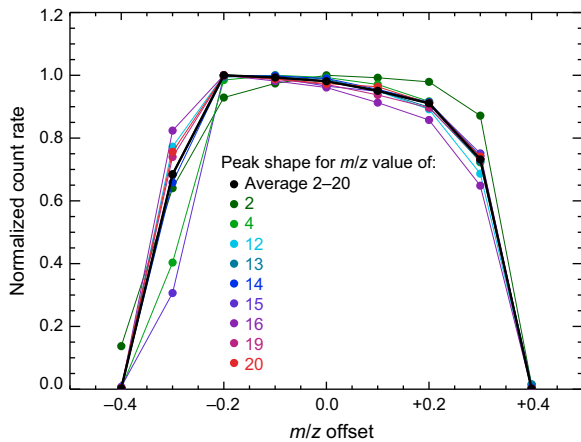


Fig. 3. Average peak shape (black) for the m/z 2–20 range, based on atmospheric data from TID 25008. Also shown (in colored traces, indicated by legend inside left of graph frame) are average peak shapes for the nine m/z values used to construct the average.

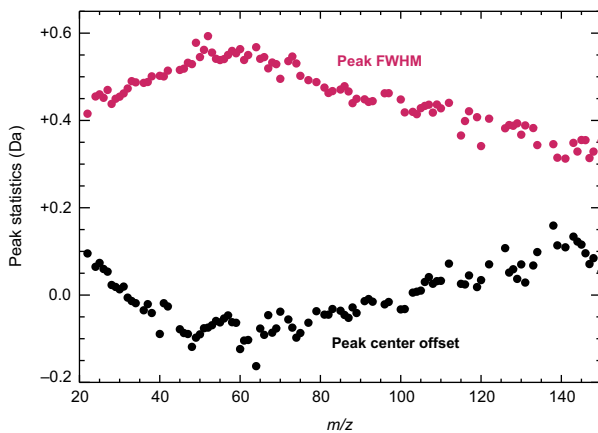


Fig. 4. QMS tuning after MSL landing for the m/z 20–150 range. Peak centers and widths were determined by Gaussian fits to flight data from TID 25008. Peak center offset gives the relative shift of the maximum with respect to the nominal integer m/z value. For example, a maximum at m/z 59.9 is shown as a peak offset of -0.1 Da. Data included for each Gaussian fit span ± 0.4 Da around the nominal integer m/z value.

Table 3
SAM calibration gases.

	Gas mixture components	$\delta^{13}\text{C}$ CO_2	$\delta^{18}\text{O}$ CO_2	$\delta^{15}\text{N}$ N_2	$\delta^{17}\text{O}$ O_2	$\delta^{18}\text{O}$ O_2
SAM Cal Cell ^a	24.32% CO_2 24.1% N_2 24.04% Ar 8.48% ^{131}Xe 15.51% ^{129}Xe 3% Perfluorotributylamine (PFTBA) present in trace amounts: 1-Fluoronaphthalene (1FN) 2,2'-Difluoro-1,1'-biphenyl (DFBP) Perfluorobiphenyl (PFBP)	-42.67^b	$+6.61^b$	0.582 ^b		
Equimolar mix	24.3% CO_2 25.1% N_2 24.8% Ar 25.8% O_2	-42.67^b	$+6.61^b$			
Mars mix (Praxair)	2.7% N_2 1.6% Ar 1300 ppm O_2 700 ppm CO Balance CO_2	-39.16^b	$+0.61^b$	NM	NM	

^a Full details on SAM calibration cell given in Mahaffy et al. (2012).

^b All measurements with 2σ standard deviation below 0.15‰.

known as the “dead time,” the minimum length of time that must separate two events for them to be recorded as two separate pulses (Knoll, 2000). A second effect involves loss of dynode gain at high count rates, which may manifest as an increase in apparent dead time at high count rates (EPA, 2007). Both effects cause the measured signal to diverge from the true signal as count rate increases, leading to erroneously low measurements at high count rates. Accurate quantitative analysis requires a correction to the raw QMS data to account for these phenomena. A standard form for dead time correction for paralyzable detector systems (or extendable dead times) is

$$r = ne^{-nt} \quad (1)$$

where r = observed count rate, n = the true count rate, and τ = the dead time (Knoll, 2000).

The correction for loss of QMS signal with increasing count rate was determined empirically by analyzing gases under nominal operating conditions, based on the assumption that the ratio of two isotopes (or isotopologues) of a given gas should be constant at all count rates. By allowing the “dead time” to grow with count rate according to the relationship

$$\tau = ae^{br}, \quad (2)$$

where a and b are the constants and r = observed count rate, and applying the standard form for dead time correction as described above, a correction was derived for the SAM detector that encompasses effects of both dead time and loss of dynode gain due to the electron multiplier, as well as any minor contributions to the dead time from other components in the system. For simplicity, this is commonly referred to as simply the “dead time correction,” but in this paper it will be called the “detector correction” to emphasize that it encompasses multiple effects.

A preliminary step in the analysis of all QMS data is to apply the detector correction to the raw data based on the current best estimate of the coefficients a and b . For initial experiments performed on Mars, the detector correction coefficients were based on O_2 data acquired during pre-flight calibration using the equimolar gas mix detailed in Table 3. Fig. 5 shows average values for raw (i.e., observed) and corrected data collected at a range of count rates up to detector saturation during this calibration run. The standard assumption for determination of detector corrections applied to the calibration gas implies that the ratio between the

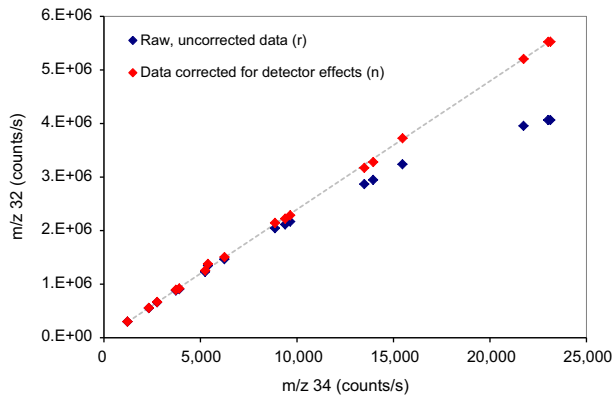


Fig. 5. O_2 calibration data used to derive correction parameters for detector effects, including dead time and gain loss.

Table 4
Detector correction coefficients determined pre-launch.

Detector	Correction coefficients	
	<i>a</i>	<i>b</i>
EM1	2.799e-08	1.969e-08
EM2	5.444e-09	5.189e-07

QMS signal at the O_2 isotopologues m/z 32 and 34 should be constant with count rate (e.g., EPA (2007)). As illustrated in Fig. 5, the ratio for raw, uncorrected data at m/z 32 and 34 decreases with increasing count rate due to the rising disparity between actual and observed signals at m/z 32. The true ratio between these isotopologues was taken as the average value measured at low count rates where detector performance is expected to be linear ($< 5 \times 10^5$ counts/s). The solution for dead time coefficients *a* and *b* was determined by applying Eqs. (1) and (2) to the raw data and iterating until the corrected data followed a linear trend at all count rates up to saturation. This calibration was performed independently for EM1 and EM2, yielding two pre-launch sets of correction coefficients, which are given in Table 4.

4.1.4. Calibration constants for direct atmospheric measurements

To facilitate computation of the VMR of the four main atmospheric constituents on Mars, empirical calibration constants were generated through analysis of the equimolar gas mix containing CO_2 , N_2 , Ar, and O_2 . The calibration constants for these four gases were derived by taking the ratio of a key “marker” fragment of each molecule to ^{40}Ar , allowing computation of relative VMR of atmospheric species by the relationship

$$[X]/[Ar] = F_{Xi/Ar} c_i / c_{40}, \quad (3)$$

where *X* is the atmospheric species, $F_{Xi/Ar}$ 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. A similar relationship was used for measurement of Jupiter’s volatiles by the Galileo Probe Mass Spectrometer, or GPMS (Niemann et al., 1998). The calibration constants were computed from the average ratios of marker fragments over a range of gas manifold pressures from 0.1 to 6.0 mb.

The marker for each species was determined through consideration of expected abundances and potential isobaric interferences from other compounds (Fig. 6). Due to the high concentration of CO_2 in the martian atmosphere, the major molecular ion at m/z 44 saturates the QMS detector under nominal operating conditions of the direct atmospheric experiment. However, the CO_2^+ ion at m/z 22 occurs in a region of the spectrum free of

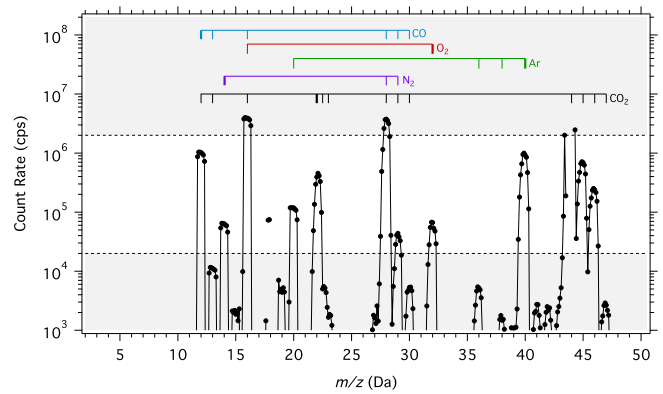


Fig. 6. A typical mass spectrum of Mars Mix in the SAM QMS from ground calibration. The bars show the contributions from the major gas phase species to the mass spectrum at each m/z . Bold vertical dashes indicate the m/z value chosen as the representative ion for each major species in the determination of calibration constants. The white dashed area highlights the region of counts that were considered as ideal for the selection of major ions for each species.

expected interferences and has appropriate signal strength on Mars for accurate atmospheric measurements. The major molecular ion of N_2 at m/z 28 incurs interferences from CO^+ fragments of CO_2 as well as molecular CO^+ ions. The m/z 28 signal also saturates the QMS detector under atmospheric experimental conditions. For these reasons, the signal at m/z 14, which includes contributions from both N_2^+ and N^+ ions, was selected as the marker for N_2 . The contributions of CO^{++} ions at m/z 14 are found to be negligible and are ignored. For O_2 , the major molecular ion at m/z 32 was selected as the marker fragment, since the low abundance of O_2 in the martian atmosphere does not lead to detector saturation.

The final constituent for which a calibration constant was derived was CO, predicted to occur at < 0.1 vol% abundance (Owen et al., 1977). The CO calibration constant was computed from combined results of ground tests performed with the commercially prepared Mars gas mix and the equimolar gas mix. The equimolar mix (with no CO) was used to define a calibration factor for estimating the contribution of CO_2 to m/z 12 based on the observed signal at m/z 22. This factor was then used to correct for CO_2 interference in Mars mix experiments, ultimately yielding a CO calibration constant analogous to those described above for the major atmospheric species. During the first several experiments on Mars, the ratio of observed signal at m/z 22 and 12 suggested that a reduction in instrument background at m/z 12 had occurred since the time of ground calibration. The CO calibration constant was thus modified based on flight data by assuming that the observed difference in the ratio of m/z 22 to 12 in flight data compared to ground test data was solely due to a shift in instrument background at m/z 12 and not to a difference in relative abundance of CO_2 and CO on Mars as compared to the Mars mix tank. This modification allowed rough estimation of an upper limit for the CO abundance from the first several atmospheric experiments on Mars, pending an update to the CO_2 ratio of m/z 22 to 12 which will be obtained upon sampling the onboard calibration gas cell.

The resulting calibration constants are provided in Table 5. Separate sets of constants are provided for use with integrated peak areas derived from fractional scan data and with unit scan data. Both sets of calibration constants were validated prior to launch by applying them to data from several test runs of the SAM AS-DIRECT experiment using the Mars gas mix. The uncertainties for the constants given in the table represent the combined effects of noise in the calibration data, uncertainties due to background subtraction, and the accuracy of the constants in retrieving the correct VMR from the Mars gas mix experiments. A second

Table 5
Calibration constants for VMR determination.

Species	m/z value of marker fragment (i)	$F_{X_i/Ar}^a$ for fractional scan data	$F_{X_i/Ar}^a$ for unit scan data
<i>Empirical calibration constants</i>			
CO ₂	22	160.13 ± 1.31	133.9 ± 0.6
N ₂	14	22.51 ± 0.60	26.6 ± 2.9
O ₂	32	1.45 ± 0.14	1.39 ± 0.19
CO [±]	12	0.512 ± 0.264	0.237 ± 0.122
<i>Calibration factor for estimating CO₂ contribution to m/z 12</i>			
(m22/m12) _{CO₂} ^b		0.434 ± 0.005	0.683 ± 0.010
<i>Constants for estimating molecular ions</i>			
(m44/m22) _{CO₂} ^b		180.04 ± 1.54	146.74 ± 0.59
(m28/m14) _{N₂} ^b		29.28 ± 2.22	35.59 ± 7.13
<i>Relative ionization efficiencies</i>			
Ar/CO ₂		0.899 ± 0.002	0.934 ± 0.007
N ₂ /CO ₂		1.193 ± 0.020	1.263 ± 0.020
O ₂ /CO ₂		0.641 ± 0.004	0.700 ± 0.004

^a See Eq. (3).

^b “m#” = m/z #; m28/m14 ratio assumes $\delta^{15}N = 620\text{‰}$ (see text for details).

method for determining atmospheric VMR involves direct calculation of the ratios of molecular ions for relevant species, after applying corrections for differences in their ionization cross-sections. This method is also necessary for estimation of mixing ratios of trace species for which we have not determined empirical calibration constants either through pre-launch testing with the flight instrument or through experiments using the SAM test bed. Since the major molecular ions of CO₂ and N₂ saturate the QMS detector in direct atmospheric experiments, we derive estimates of CO₂ and N₂ molecular ion abundances from m/z 22 and 14, respectively. Calibration constants for generating these estimates, as well as ratios describing the relative ionization efficiencies for Ar, CO₂, N₂, and O₂ as determined during SAM calibration, are provided in Table 5. These factors represent average values over the range of pressures employed during the calibration experiment. They also may differ slightly from relative ionization cross sections reported in the literature (e.g., Fitch and Sauter, 1983; Nakao, 1975; Rapp and Englander-Golden, 1965) because the QMS produces fewer doubly-charged ions than is typical of commercial mass spectrometers. Results of calculations applying this method to both calibration and flight data are discussed in Section 6. Note that the calibration constant for estimating the signal due to N₂ at m/z 28 from that at m/z 14 was derived from data of the first two semi-static atmospheric enrichment experiments performed on Mars, based on an assumed value of $620 \pm 80\text{‰}$ for $\delta^{15}N$ of atmospheric N₂ (Nier and McElroy, 1977; Owen et al., 1977; Owen, 1992).

4.1.5. Static mass spectrometry for noble gas and trace gas measurements

A limited set of experiments was performed before launch to validate the capability for performing static mass spectrometry to improve precision on measurements of gases and specific isotopologues that occur at low abundance (Mahaffy et al., 2012). These tests were performed with a mixture of the noble gases Ne, Ar, Kr, and Xe at 10 vol% each in a balance of He. Additional experiments will be executed on the SAM test bed at NASA GSFC to optimize plans for noble gas and trace gas measurements prior to their execution on Mars.

4.2. Post-landing calibration

4.2.1. Monitoring detector performance on Mars

The SAM team will monitor QMS detector performance throughout the mission to determine when and if the detector

correction coefficients require updating. Ideally changes to the calibration parameters will be based on results of specialized experiments utilizing the onboard calibration gas. However, as this depletes a SAM consumable resource, it is desirable to also have a method for monitoring detector performance from martian atmospheric data. In principle, this can be accomplished by first identifying a ratio of count rates that is expected to remain constant throughout an experiment. One of the m/z values of this ratio must also have raw count rates that extend into the range where the data become increasingly nonlinear but not yet saturated, $\sim 2 \times 10^6$ – 4×10^6 counts/s.

Two of the atmospheric experiments during the first 90 sols – TID 25009 and 25012 – were used to evaluate the parameters correcting for QMS detector effects. In TID 25009, changes in the filament emission level caused counts at m/z 45 to reach rates as high as 2×10^6 raw counts/sec. Since the ratio of m/z 45 to 46 should remain constant, these data provide a good probe of detector nonlinearity. In TID 25012, diffusion of gas from a “dead volume” in the system caused raw counts at m/z 44 to gradually and continually increase from 2.8×10^6 – 4.3×10^6 raw counts/s in the reduced-pressure sample, coincident with the range best suited to determining detector nonlinearity. Analysis of data from both TID 25009 and TID 25012 determined that best-fit dead time correction parameters from pre-flight data and flight data provide identical corrections within measurement uncertainty.

4.2.2. SAM test bed

The SAM test bed facility is located at NASA GSFC, and has two major components: (1) a vacuum chamber that can replicate the environmental conditions on Mars and (2) a SAM instrument suite inside the vacuum chamber that is virtually identical to the SAM suite on Mars. The chamber can be heated and cooled to simulate the temperature variations encountered on Mars. Also, the pressure and composition of the gas in the chamber can be controlled to duplicate conditions in the martian atmosphere.

The test bed serves two important functions. Before any new script is sent to the rover on Mars, the sequence is first run on the test bed. This ensures that the script correctly performs the desired experiment and that no erroneous commands are sent that could possibly damage SAM or the rover. The second function of the test bed is to assist in the analysis of data acquired on Mars. Various gas mixtures and Mars analogs can be introduced into the test bed SAM in an attempt to duplicate the instrument signal obtained by an experiment performed on Mars. Replicating the instrument response in the test bed raises confidence in the interpretation of data acquired operationally with the flight instrument.

4.2.3. Onboard calibration gas

The SAM calibration gas cell, with volume of 4.76 mL and pressure of 952 mbar, contains SAM calibration gas and is used to monitor the changes in the performance of the instrument over the duration of the mission, as well as to provide a reference gas for QMS and TLS measurements. SAM calibration gas contains an equimolar mix of CO₂, N₂, Ar, and Xe (nominally terrestrial isotopic composition but enriched in ¹²⁹Xe) plus trace quantities of four high molecular weight fluorinated compounds (Table 3).

5. Atmospheric data analysis

5.1. Data acquisition and processing

5.1.1. Flight software and instrument control

SAM flight software (FSW) is embedded in SAM and is designed to operate autonomously over the long durations (many hours) of an experimental sequence. The SAM Command and Data Handling

system contains two nonvolatile memory stores. The first is the 1 MB EEPROM file system, developed to store parameter tables, script files, and other auxiliary data. The other is the 64 MB flash memory array, designed to handle storage and retrieval of telemetry data. Data is written to flash memory during a SAM experimental sequence (which may occur when the MSL rover is powered off), where it can be stored across MSL and SAM power cycles. Telemetry is subsequently transmitted to the rover when the rover's computer transmits a "send telemetry" command to SAM, which is iterated as long as data remains in flash memory.

SAM's commands are written in BASIC with built-in SAM-specific commands. More than 200 commands are built into the SAM BASIC script language. Commands are grouped by subsystem (e.g., QMS, GC, TLS) for organizational purposes. A large library of functions, subroutines, and variables are assembled in a BASIC script library file called "samlib.bas" and reside in SAM's EEPROM file system. All experimental sequences for SAM atmospheric and solid sample analysis are written in BASIC and access these functions. Each experimental sequence has an associated script that has been tested on the SAM test bed at NASA GSFC. Each script is accompanied by a parameter file to allow for flexibility and optimization during operations on Mars.

5.1.2. Data format and archive plan

The SAM telemetry file is constructed from Engineering Data Record (EDR) products generated by the Multi-mission Image Processing Laboratory (MIPL) at JPL. All EDR products and associated data files for a given experiment sequence are collected in a folder labeled with the TID uniquely associated with that experiment sequence. SAM data are made available to the science community through the Geosciences Node of the Planetary Data System (PDS). Python-based tools convert the SAM telemetry for each experiment into a set of ASCII files that can be easily read by a variety of commercial software packages. Data are stored as Reduced Data Record (RDR) products at several processing levels, representing a progression of data corrections and analysis decisions. The SAM archive also includes reference data such as conversion factors used in the progressive processing.

Data for MSL sols 0–89 were released to the public by the PDS on March 20, 2013. SAM data for Release 1 include the first four *AS-DIRECT* experiments shown in Table 2. Data from the first dynamic mode enrichment experiment were included in MSL Release 3 on August 30, 2013.

5.2. Data corrections

This section describes the preliminary corrections that must be applied to the data for quantitative analysis, starting with the application of detector corrections and background subtraction. At each step of the data processing flow, uncertainties are computed and propagated to the next step. The overall data correction process is demonstrated schematically by the block diagram in Fig. 7.

5.2.1. Detector effects

The first step in analyzing any SAM QMS data is to apply the appropriate corrections for the detector dead time and other effects, as discussed in Section 4. This is particularly important for quantitative analysis, such as calculation of isotope ratios and VMR. The corrections are applied to the raw data that is extracted from the telemetry file. Note that data that have been corrected for detector effects are provided in Level 1B RDRs of the SAM data archive at the PDS.

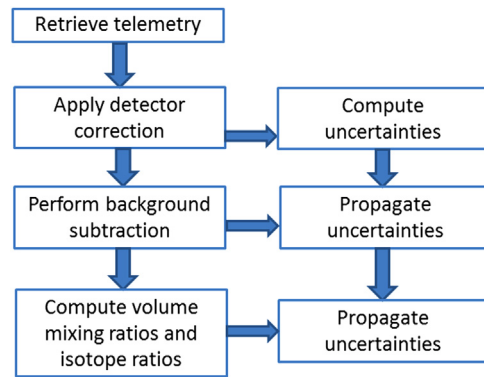


Fig. 7. Schematic representation of the data correction and quantitative analysis process.

5.2.2. Background subtraction

The second step in analyzing SAM QMS data involves determination of instrument background signals at the relevant m/z values and subtracting the background from the data. This is non-trivial, as the background may change throughout a given experiment at each m/z value. Furthermore, this behavior is different for direct atmospheric and enrichment experiments, due to additional sinks for active species in the latter case. Careful estimation of the background must be made for each analysis region based on conditions prevailing at that time.

Residual gas detected during the background measurement intervals of a SAM experiment are attributed to a number of sources. When the QMS is isolated from the manifold, residual background gases may be released by outgassing from surfaces such as lens elements, which increase in temperature as energy is dissipated from the hot filament. Since the pumps are turned off after every experiment, the decay of background gases depends on how long the WRP is utilized before the atmospheric gases are introduced to the QMS. The major background signal to date has been water, with significant levels of hydrogen, methane, and C2–C4 hydrocarbon gases producing additional signal in the first few decades of mass. Since the compression ratio of the WRP is approximately 5×10^8 , the major martian atmospheric gases are also detected. Execution of solid sample evolved gas experiments may also cause an increase in background signal of gases such as HCl that more strongly interact with surfaces. Once the valve to the evacuated manifold is open, residual gases from this source may enter the QMS through the capillary leaks. These gases may include residual gases from previous solid EGA experiments or even helium that permeates the valve seats leading from the helium tanks used in EGA and GCMS experiments.

Fig. 8 shows data for Ar from the fourth atmospheric experiment, TID 25027, annotated to indicate the sequence of background (BG) and atmospheric analysis (ATM) regions. This figure illustrates several key points regarding background levels during direct atmospheric experiments:

- In the first manifold background region (BG1), SAM measured the composition of gas in the evacuated manifold prior to the first ingestion of martian atmosphere. The signal for most m/z values dropped steadily as background species were pumped out by WRP1.
- The signal at m/z 39 – which represents a hydrocarbon contaminant within the instrument that is not present in the martian atmosphere – decayed exponentially throughout the experiment. This behavior reflected a gradual decrease in density, approaching equilibrium between production of background species within SAM and loss by pumping with WRP1.

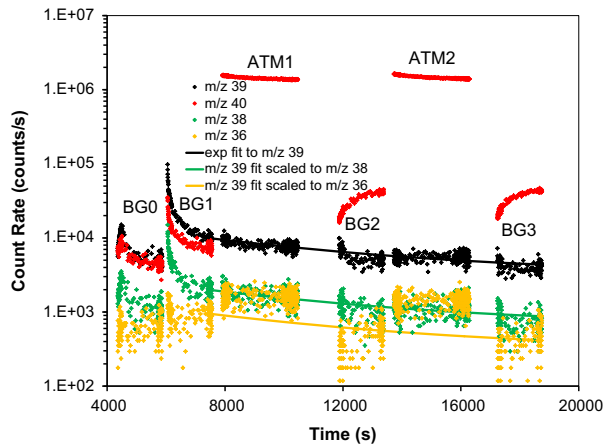


Fig. 8. Background and atmospheric analysis regions of TID 25027.

- The signal at all m/z decreased exponentially during the sample analysis regions (ATM1 and ATM2) due to gradual decrease in pressure through continuous operation of WRP1 with the atmospheric inlet valve (V28) closed. This is especially obvious in the high signal-to-noise trace of m/z 40 in the figure.
- Behavior in BG2 and BG3 was particularly interesting. Each of these two background measurements followed 1500 s of evacuation of the GPS manifolds by WRP2. However, the pump-down did not achieve a perfect vacuum across the entire GPS. In these segments, counts at m/z 40 and 36 from Ar increased as residual Mars atmospheric gas diffused from a dead volume within SAM back into the manifold. The primary dead volume in this case is believed to be gas trapped between the valve seat of V12 and the associated capillary leak. At the other m/z values shown in the figure, the same increase was not observed, since their background signals were dominated by gases produced inside the QMS rather than residual atmospheric sample retained in the manifold.
- Background behavior at m/z 36 (particularly in BG1) differed from that of the other species shown, indicating the presence of a different background species than that observed at m/z 38 and 39.

The simplest background correction consists of subtracting a constant value for each relevant m/z value, taken as an average signal during the final portion of the preceding background region, prior to introduction of atmospheric gas. In this experiment, the end of the BG1 region is most relevant for analysis of the first ingestion of Mars atmosphere (ATM1), while the end of the BG2 region provides appropriate background measurements for the second atmospheric analysis (ATM2). This type of background subtraction is typically performed for rapid preliminary analysis of experimental data.

More sophisticated treatment of the background aims to model evolution of the background signal over time while the atmospheric gas is measured. One approach is to use a background tracer, such as m/z 39 in Fig. 8, to model the time-dependent behavior of other actively produced background species. A smoothed m/z 39 trace can be scaled to the background levels of other m/z to characterize the change in baseline instrument background throughout the experiment. However, modeling of residual background species, such as m/z 40 in the BG2 and BG3 regions, requires independent characterization. This involves assessing the contributions due to residual gas upon introduction of the atmospheric sample and appropriate modeling of the resultant mixture during the atmospheric analysis segments. The contribution of

background subtraction to uncertainty in atmospheric measurements is discussed in Section 5.4.4.

5.3. Quantitative analysis

As discussed in Section 2.1.2, the step between m/z values during QMS scans is parameterized for each experiment, typically employing a combination of unit scans and fractional scans. Each scanning mode has advantages and disadvantages. Unit scans allow faster coverage of a given m/z range, which is especially important for samples in which the composition is expected to change over time, such as evolution of volatiles from solid samples (beyond the scope of this paper). However, slight differences in tuning at different m/z values can affect the accuracy of ratios computed from unit scan data. Fractional scan data are processed by first computing the peak area, defined as the sum of counts within a given range of m/z values. Averages and ratios are then calculated from the peak areas. Fractional scans mitigate issues caused by slight tuning differences between m/z values, but they require significantly more time to cover a given m/z range, thus lengthening the duration of the experiment and increasing the time interval between measurements of each m/z value. Analysis of both unit scan and fractional scan data involves computing average or smoothed values over the time range of interest. Since unit scans consist of data at integer m/z values, the values acquired at the integer m/z steps during fractional scanning may be combined with data acquired during an adjacent period of unit scanning to increase the sample population included in the average.

Table 5 gives calibration constants for computation of VMR of the five most abundant atmospheric gases. Sets of constants are provided for analysis of both fractional scan data and unit scan data. Volume mixing ratios for the major atmospheric constituents are computed from average values of data at m/z 22 (CO_2), 40 (Ar), 14 (N_2), 32 (O_2), and 12 (CO) by applying the constants in Table 5.

5.4. Measurement accuracy and sources of uncertainty

5.4.1. Detector corrections

5.4.1.1. Corrections derived from pre-flight calibration data. Corrections for dead time and other detector effects, as discussed above, are derived by assuming that the ratio of two isotopes (or isotopologues) of a gas must remain constant throughout the operable range of the detector. Implicit are the further assumptions that the two-component form of the detector correction function given in Eqs. (1) and (2) accurately accounts for detector nonlinearity, that the data are of sufficient quality to characterize the nonlinearity as a function of counting rate, and that no isotopic fractionation occurs that would cause the diagnostic isotope ratio to change throughout the calibration experiment.

The uncertainty in the nominal pre-flight detector correction is then driven by the uncertainty in the determination of the diagnostic isotope ratio, i.e. the slope of the array defining linear detector response. For the correction parameters derived from pre-launch calibration data, the uncertainty in the slope of the oxygen isotopologues at m/z 32 and 34 is approximately 0.4% due to noise in the data. Based on this uncertainty in slope, an estimate of the resulting worst-case uncertainties in the true count rate as a function of the observed count rate was derived

$$\text{err} = (-2.09 \times 10^{-22})r^4 + (1.37 \times 10^{-15})r^3 - (7.41 \times 10^{-10})r^2 + (6.78 \times 10^{-4})r \quad (4)$$

where err = the estimated uncertainty in true (i.e., corrected) count rate and r = the observed count rate. For observed count rates

within the viable operating range, this relationship predicts uncertainties of up to $\sim 0.5\%$ as the detector approaches saturation. This is comparable to the statistical noise in a single integration period for data at the highest count rates.

5.4.1.2. Corrections derived from flight data. Deriving detector correction functions from flight data offers a way to monitor detector performance over time. If the correction parameters are derived from calibration experiments using the onboard calibration gas, for which the isotopic composition is known to high precision, the uncertainty will be similar to that described above for the correction function derived from pre-flight data. The difference between the correction function determined from flight data during the first 90 sols and that determined from pre-flight calibration data provides a measure of the detector performance during this time period. The correction functions defined from data of TID 25009 and 25012 were identical to the pre-flight function within the uncertainties described below, indicating no need for a change in parameters.

Uncertainties in a given detector correction function derived from martian atmospheric data are larger than those computed from pre-flight calibration data or the onboard calibration gas due to greater uncertainty in the diagnostic isotope ratio. Considering the ratio of m/z 44 and 45 used to calculate correction parameters from TID 25012 data, the CO_2 in the low-pressure portion of the experiment was highly depleted in ^{13}C compared to the martian atmosphere. For this reason, the martian atmospheric composition as measured by the TLS could not be used to define the ratio describing linearity. The target ratio between m/z 44 and 45 was determined at low count rates, where the data are minimally affected by detector effects.

The uncertainty in detector corrections determined in this manner is dominated by uncertainty in the diagnostic slope due to potential fractionation of the CO_2 as the pressure gradually increased. The ratio of m/z 45 and 46, which occur at relatively low count rates compared to m/z 44, was used to characterize the change in CO_2 isotopic composition in the low-pressure region of TID 25012. Results showed that this ratio changed by 1.87% during the period of low-pressure measurements. This value was then applied to define an error envelope around the solution for the detector correction function computed from data at m/z 44 and 45, yielding a relationship estimating worst-case errors for the detector correction function derived from TID 25012:

$$\text{err} = (1.677 \times 10^{-15})r^3 + (2.397 \times 10^{-10})r^2 + (2.064 \times 10^{-3})r \quad (5)$$

where err = the estimated uncertainty in true (i.e., corrected) count rate and r = the observed count rate. This relationship predicts

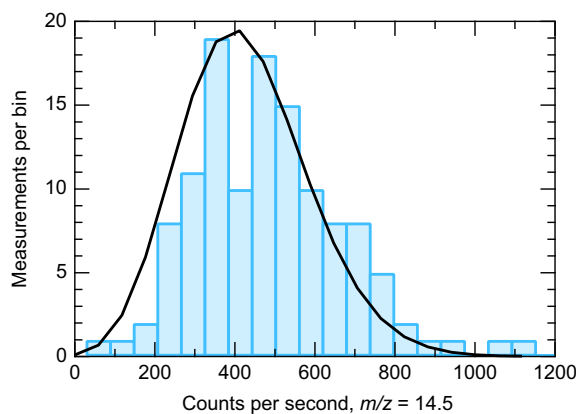


Fig. 9. Histogram of count rates, compared to Poisson distribution with a mean of 7.2 counts/integration period (equivalent to 426 counts/s). Data include 122 atmospheric sample measurements from TID 25027.

uncertainties $< 1\%$ at observed count rates below 2×10^6 counts/s, rising to $\sim 2.45\%$ at count rates approaching saturation.

5.4.2. Noise

At very low count rates where the dead time has minimal effect, the detector behavior is fully linear, but statistical noise can be significant. This is particularly important for minor species and ion fragments that are observed at count rates < 1000 counts/s. In these cases, count rates are observed to follow a Poisson distribution, as expected for counting statistics (Fig. 9).

For quantities measured by taking the mean of many observations, we estimate statistical noise by the standard error of the mean, defined as the standard deviation of the measurements divided by the square root of the number of measurements (Bevington and Robinson, 2002). One method employed to reduce uncertainty from these effects is to discard data with deviations greater than a defined threshold value, typically taken as twice the standard deviation (2σ) of the total population, with respect to the mean. For quantities derived from non-constant signal levels, we fit simple functional forms to the time-variable behavior (see below) and estimate statistical noise by dividing the standard deviation of the residuals from the fit by the square root of the number of measurements. In both cases, the number of measurements is much larger than the degrees of freedom of the functional form. The standard error of the mean quantifies the random error or precision associated with the measurements (e.g., Skoog et al., 1998).

5.4.3. Time-varying count rates

Many of the SAM QMS data are time-variable. Background signal levels are often if not usually variable over the typical background scanning duration of an *AS-DIRECT* experiment sequence, although in some cases the signal level is too low or the background measurement duration is too brief to characterize the variability. In the last two direct atmospheric experiments discussed here (TID 25012 and 25027), signal levels of the full-pressure sample decreased with time as the sample trapped in the gas manifold was gradually pumped out through the QMS. In TID 25012, the signal level during the reduced-pressure portion of the experiment increased with time due to gradual diffusion of a gas pocket out of a small “dead volume”. The same dead volume diffusion effect is seen in the BG2 and BG3 regions in TID 25027 (Fig. 8).

To reduce the uncertainty associated with these effects, a simple functional form, such as a line or exponential, may be fit to the data, and then values generated from the fit are used to calculate count ratios. The remaining uncertainty due to time-variation is assumed to be captured in the error estimate described above for statistical noise. For calculation of isotope ratios in particular, it may be preferable to compute the instantaneous isotope ratio for each scan, then compute a mean value from the ratios. Instantaneous ratios with variations greater than a given threshold away from the mean may be discarded, as described in the previous section. The effects of time-varying signal may also be mitigated by incorporating time-varying background subtraction into the data processing, as discussed in the next section.

5.4.4. Background subtraction

As discussed above, background levels in the SAM QMS vary from mass to mass and from run to run. Additionally, background levels are usually different in each of the separate background measurements within a single experiment. This is an inherent challenge with mass spectrometry in general that is not unique to the SAM QMS. In fact, the flexibility afforded by SAM’s numerous control parameters enables us to better characterize background uncertainties by improving experiment designs in response to observed instrument behavior.

Subtraction of a constant background is particularly appropriate when sufficient time has elapsed during background scanning for the signal to stabilize or when the background level is very low (i.e., a few thousands of counts/s). In the latter case, a more complex functional form cannot be statistically justified. In other cases, the background signal appears to consist of a weak transient component and a much larger constant component. In these cases, we determine the constant background correction using an average of data outside the region most affected by the transient signal, and assume that the standard error of the mean accurately represents the background uncertainty. Since the uncertainty in the final result combines the statistical uncertainties from both the sample and the background measurements, signal-to-noise ratio is improved when we have the same number of background and sample measurements. TID 25027 was the first QMS experiment to achieve background/sample parity (Fig. 8).

Ideally, background measurements would be acquired after sufficient evacuation had been performed by the WRP to stabilize the QMS signal at a steady-state minimum level. Given the operational resource limitations constraining SAM experiment execution, however, background scan durations may not allow sufficient time for the signal to stabilize, leading to uncertainties in our knowledge of the background gas contributing to atmospheric measurements. In some cases, modeling of the background at a particular m/z value is best accomplished by using a tracer m/z most relevant to the expected behavior of the species of interest.

For each m/z value in each experiment, the best practice for estimating variable background uncertainty is as follows. We subjectively determine the best functional form of the background correction, and use that choice to determine a nominal background correction. The background corrections tested typically consist of a constant background or a decaying exponential, depending on the characteristics of the experiment. It may also be informative to model the background based on more than one tracer m/z , to examine potential differences in behavior for active and inert species. The difference between results obtained by applying these various forms then represents the largest contribution to uncertainty in the background. In many cases, this component will dwarf other sources of uncertainty and will dominate the uncertainty reported in the final result. An example of two different background models for TID 25027 is shown in Fig. 10.

5.4.5. Calibration constants

For VMR, the final source of error is the uncertainty in the calibration constant. As discussed above, calibration constants were determined before MSL landing, using pre-flight calibration data. Stated uncertainties include contributions from sample statistical noise, background statistical noise, and uncertainty in the true composition of the calibration gas mixtures. Due to the difference in method of execution of the calibration and flight experiments, the contributions of background uncertainties above those arising from statistical noise are minimal in the calibration experiments.

Additional uncertainty in the validity of the calibration constants for computing VMR was determined by applying the ratios to data from multiple calibration experiments using a commercially prepared gas tank of martian atmospheric composition. The accuracy and variability of results obtained with this approach dominate the uncertainties in the calibration constants cited in Table 5.

6. Results for atmospheric experiments on Mars

As discussed in Section 3, SAM performed four experiments that directly sampled the martian atmosphere with the QMS

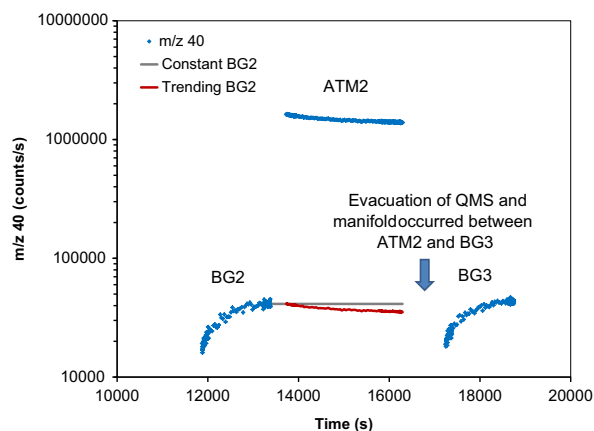


Fig. 10. Example of background uncertainty. Two possible background models for the second atmospheric sample measurement at m/z 40 from TID 25027 are shown. The gray line illustrates a constant background correction taken as the average of the last portion of the preceding manifold background region, while the red line models the background signal dropping proportionally with the ATM2 signal due to gradual pressure loss. Accumulation of more atmospheric data, and improvements in experiment design, will lead to better knowledge of the appropriate background correction and a corresponding reduction in the background uncertainty.

during Curiosity's first 90 sols on Mars. The reader is referred to other publications for the chemical and isotopic composition of the martian atmosphere as retrieved from atmospheric experiments to date (Atreya et al., 2013; Mahaffy et al., 2013; Webster et al., 2013; Wong et al., 2013). Here we discuss differences in atmospheric volume mixing ratios obtained by SAM and Viking.

The VMR for the martian atmosphere determined by SAM (Mahaffy et al., 2013) are broadly similar to those reported for Viking (Owen et al., 1977), but there are also significant differences, particularly for N_2 and ^{40}Ar . Two separate instruments on the Viking landers measured the composition of the martian atmosphere: the Gas Chromatograph Mass Spectrometer (GCMS), which sampled the atmosphere directly with its mass spectrometer (Owen et al., 1977), and the Gas Exchange Experiment (GEX), which determined atmospheric composition by analyzing headspace gases in the GEX test cell with a gas chromatograph (Oyama and Berdahl, 1977). The Viking instruments produced similar results for Mars' atmospheric composition, with VMR of $2.7 \pm 0.5\%$ N_2 and $1.6 \pm 0.3\%$ Ar reported for GCMS (Owen et al., 1977) and $2.3 \pm 0.3\%$ N_2 and $1.6 \pm 0.3\%$ Ar reported for GEX (Oyama and Berdahl, 1977). These compositions yield $^{40}Ar/^{14}N$ ratios of 0.30 ± 0.08 for GCMS and 0.34 ± 0.08 for GEX. A third instrument, the aeroshell-mounted neutral mass spectrometer, measured Ar and N_2 during descent to ~ 125 km altitude, just into the well-mixed layer of the atmosphere (Nier and McElroy, 1977). The data were noisy due to spacecraft motion but showed that $N_2 > Ar$ at the top of the homopause. In contrast to Viking measurements, SAM experiments during the first 90 sols found the atmosphere to comprise $1.89 \pm 0.03\%$ N_2 and $1.93 \pm 0.01\%$ ^{40}Ar , giving $^{40}Ar/^{14}N$ of 0.51 ± 0.01 (Mahaffy et al., 2013).

The Viking GEX gas chromatograph used a Poropak Q column and a thermal conductivity detector and was calibrated with an internal gas supply of Kr (Oyama et al., 1976). Thus the GEX measurement was independent of the corrections used in the mass spectrometers. The difference between SAM and Viking mass spectrometer results could be due to different instrument characteristics or to the manner in which the data were analyzed. We have found no information, either in published literature or in technical reports, describing the analytical methods that were used to compute the martian atmospheric composition from Viking GCMS data.

The SAM empirical calibration constants, however, have been subjected to intense scrutiny to validate the analytical approach and the $^{40}\text{Ar}/^{14}\text{N}$ measured by SAM on Mars. Several tests have been performed in this regard. The first test examined the effects of the differences in isotopic composition of the calibration gas and the martian atmosphere on the computation of VMR. The empirical calibration constants were derived from the major isotopes or isotopologues of CO_2 , N_2 , Ar, and O_2 , with the assumption that contributions from minor isotopes would not significantly alter the resulting VMR. Since all of these gases, especially N_2 and Ar, are enriched in heavy isotopes in the atmosphere of Mars compared to that of Earth, a test was performed in which the calibration constants and VMR calculations were modified according to the measured isotopic compositions of the calibration gases and the martian atmosphere. As expected, changes to the resulting martian atmosphere VMR were negligible compared to those obtained with the original calibration constants, revealing differences only in the third significant digit.

A second test addressed the potential effects of the N_2 fragmentation pattern on VMR calculations. The marker m/z fragments for the other three major atmospheric constituents are representative of the main molecular ions – i.e., m/z 32 is the major isotopologue of O_2 , m/z 40 is the major isotope of Ar, and m/z 22 contains doubly-charged ions of the major CO_2 isotopologue at m/z 44. In the case of N_2 , however, we are quantifying molecular abundance on the basis of both doubly-charged molecular ions and atomic nitrogen ions at m/z 14. While the calibration constant for N_2 can be modified to use only the doubly-charged molecular ions at m/z 14, the same scale factor must be applied to the m/z 14 signal observed in martian atmospheric data when applying the modified calibration constant, so there is no net change in final N_2 VMR.

A third test examined the possibility of errors in preparation of the equimolar mix calibration gas that may have skewed the resulting VMR. This test involved derivation of a completely independent set of empirical calibration constants from data acquired with the Mars gas mix, which was commercially prepared with VMR matching that of the martian atmosphere as obtained with the Viking GCMS (Owen et al., 1977). The new calibration constants were prepared in the same manner as those derived from the equimolar mix, based on the measured signal at the marker m/z values and the known composition of the Mars gas mix. Application of these constants to data acquired on Mars produced VMR very similar to those obtained with the original calibration constants, again retrieving $^{40}\text{Ar}/^{14}\text{N}$ of 0.5.

A fourth test sought to compare results for VMR determined via the empirical calibration constants with those computed from the

ratios of molecular ions of each major atmospheric species. As discussed previously, molecular ion abundances for CO_2 and N_2 were estimated from the signals at m/z 22 and 14. Subsequent application of corrections for relative ionization efficiencies of CO_2 , N_2 , Ar, and O_2 determined for the QMS (Table 5) correctly retrieved the composition of the Mars mix calibration gas and also produced results in accord with those of the empirical calibration constants for experiments performed on Mars.

Fig. 11 illustrates the ratio of $^{40}\text{Ar}/^{14}\text{N}$ obtained for several Mars gas mix calibration experiments via SAM's empirical calibration constants. The actual argon-to-nitrogen ratio of the gas is labeled "Mars Mix Calibration Gas" on the figure, with gray shaded area depicting the uncertainty in composition as reported by the manufacturer. The $^{40}\text{Ar}/^{14}\text{N}$ reported for Viking GCMS (Owen et al., 1977) and GEX (Oyama and Berdahl, 1977) investigations are included for reference, as well as the $^{40}\text{Ar}/^{14}\text{N}$ ratio determined by SAM during atmospheric analyses during the first 90 sols on Mars (Mahaffy et al., 2013). The close agreement between $^{40}\text{Ar}/^{14}\text{N}$ obtained for Mars mix calibration experiments and the actual composition of the Mars mix gas, which was well-characterized through independent analysis by the manufacturer, suggests that the method of retrieving atmospheric mixing ratios with the calibration constants described in this work is sound and provides evidence that Mars' atmospheric composition as measured by SAM is distinct from that determined by Viking. The tests of the calibration constants discussed above provide additional support for the integrity of these constants and the validity of the VMR reported by Mahaffy et al. (2013). Intensive effort is currently underway to explore this surprising discovery and its potential implications for martian atmospheric and climate processes.

7. Future plans

The SAM direct atmospheric experiments described here will nominally be repeated at regular intervals throughout Curiosity's mission on Mars to investigate potential seasonal and sporadic changes in atmospheric composition, including major and minor species abundances and isotope ratios. Routine sampling of the atmosphere will enable temporal characterization of trace species abundance, vital to the search for evidence of volcanic activity in Curiosity's vicinity or elsewhere on Mars. Execution of the experiments at different times of day will also allow characterization of diurnal variations in atmospheric composition and isotope ratios.

The method given in Section 4.1.4 for determining the atmospheric composition with calibration constants is focused solely on obtaining the most accurate possible estimate of the relative

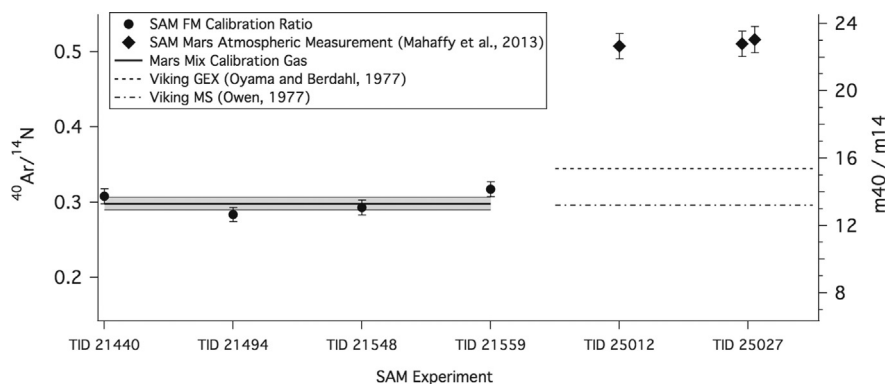


Fig. 11. $^{40}\text{Ar}/^{14}\text{N}$ obtained from Mars gas mix calibration experiments and from experiments performed on Mars by processing the data with SAM's empirical calibration constants. Secondary y-axis emphasizes that a change in relative abundance of Ar and N_2 is seen even in the observed ratio of counts/s at m/z 14 and 40, prior to application of calibration constants. The shaded area represents the uncertainty in the Mars mix calibration gas reported by the manufacturer. Viking results are also shown for reference.

concentrations of the five most abundant constituents. While the simplified enrichment experiment protocols may be used to monitor argon and nitrogen isotopic composition and potentially krypton abundance, future experiments incorporating the full-scale enrichment procedure are needed for precise measurements of the abundances and isotopic compositions of the noble gases and other trace species.

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