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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: CO₂ 0.957(±0.016), N₂ 0.0203(±0.0003), Ar 0.0207(±0.0002), O₂ 1.73(±0.06) × 10⁻³, CO 7.49(±0.026) × 10⁻⁴.

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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 CO₂, N₂ and noble gases (Franz et al., 2014). The precision required for meaningful measurements of isotope ratios and of VMR for the minor atmospheric species O₂ 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 CO₂ 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 CO_2^+ and CO_2^{++} ions, suggesting an increase in production of 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 CO_2 , which interfere with measurements of O_2 VMR. This contribution was quantified to allow subtraction of these CO_2 fragments from the mass spectrum, ensuring improved accuracy in computed 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 μA . 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 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 CO_2 , Ar, O_2 , and N_2 . The calibration constants for these four gases were derived from the ratio of a key “marker” fragment of each molecule to ^{40}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 CO_2 isotopic measurements were informed by independent analysis of the isotopic composition of 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 CO_2 abundances. This m/z value comprises 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 CO_2^+ ions at m/z 22 in Mars data has been observed to deviate from the behavior of CO_2^+ ions at m/z 45 and 46, suggesting an increase in the production of

CO_2^+ ions with pressure. This phenomenon was investigated by a series of experiments on the SAM breadboard that were designed to simulate SAM atmospheric experiments on Mars. A 9-foot piece of 0.25-inch diameter copper tubing was coiled to produce a gas reservoir with volume approximately 10 times that of the breadboard gas manifold. The coil was installed between the breadboard QMS and a Mars mix gas cylinder with pressure regulator. The isotopic composition of the CO_2 in this gas mixture was measured by injection into a Thermo Scientific Trace Ultra GC-Isolink device coupled to a Thermo Scientific Delta V Plus Isotope Ratio Mass Spectrometer (IRMS). For each experiment, the coil and manifold were evacuated, then a valve between them was closed and background spectra were collected for 5 min with the QMS open to the manifold through the glass capillary. With pressure controlled by the regulator, Mars mix gas was introduced into the coil and allowed to equilibrate for 2–3 min to minimize isotopic fractionation. The coil was then isolated from the gas cylinder and opened to the breadboard manifold for 30 s to simulate introduction of martian atmospheric gas into SAM's manifold. The coil was isolated from the manifold once again and gas was allowed to equilibrate in the manifold and through the capillary leak into the QMS for 2–3 min prior to analysis. Mass spectra were subsequently collected for 10 min in each experiment.

Experiments were performed at reservoir pressures of 5.5–10 mb, encompassing the range of atmospheric pressures observed at the martian surface by Curiosity (Harri et al., 2014). The difference in spectra obtained at the pressure endpoints is illustrated in Fig. 1, where the proportional increase in signal at m/z 22 and 45 from 5.5 to 10 mb is indicated by the red-shaded boxes overlying the spectra. The excess ions at m/z 22 were characterized through changes in the ratio of m/z 22 and 45 with pressure, as shown in Fig. 2 (a). In the absence of instrument effects, this ratio should maintain a constant value at all pressures, dictated by the isotopic composition of the CO_2 . The observed growth in the ratio of m/z 22 and 45 is not interpreted as an isotopic fractionation because the ratio between m/z 45 and 46 does not exhibit the same behavior, instead maintaining an approximately constant value across this range of pressures. The correction for m/z 22 was derived from the multiplicative factor required to drive the observed m/z 22 to 45 ratio to the correct value at each pressure. The most precise corrections were obtained with a correction factor

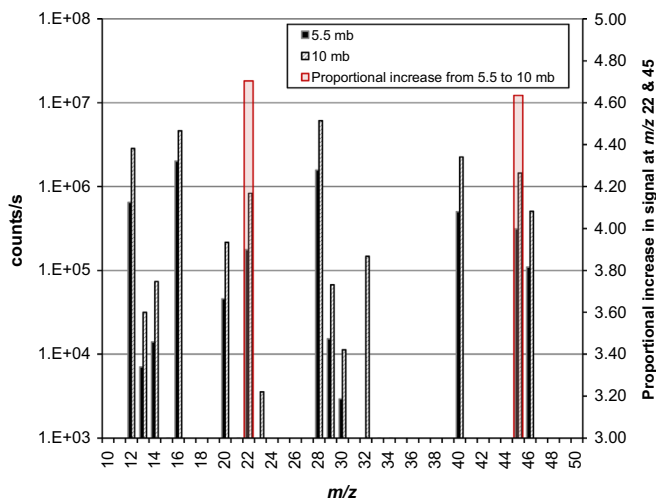


Fig. 1. Spectra from calibration experiments with the SAM breadboard QMS at 5.5 and 10 mb. Red boxes overlying the spectra illustrate the disproportionate increase with pressure of ions observed at m/z 22 compared to m/z 45. Note that there is no signal at m/z 44, the major isotopologue of CO_2 , due to detector saturation. Some m/z shown reflect contributions from other components in the Mars mix gas. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

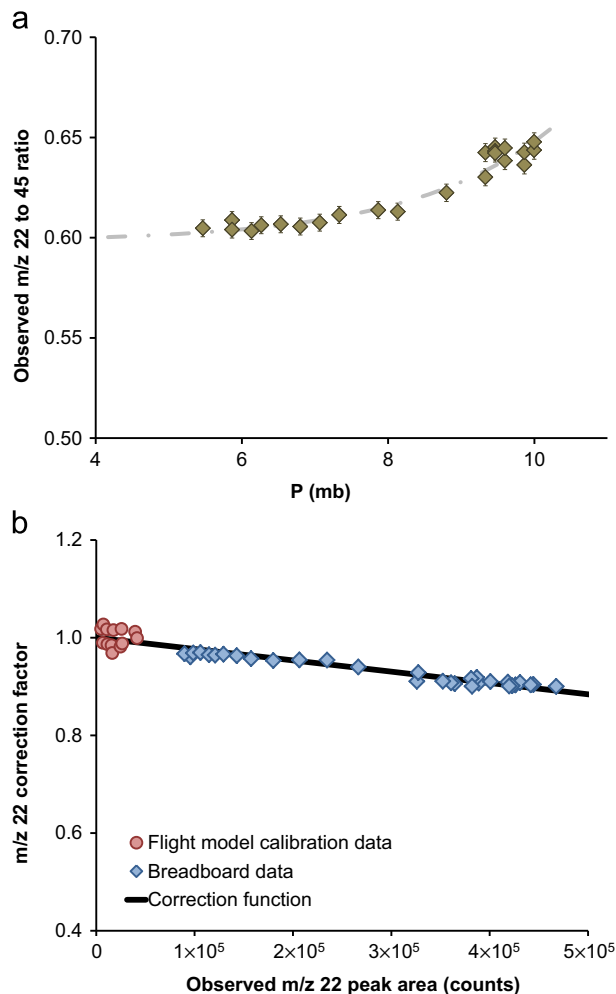


Fig. 2. (a) Illustration of growth in the ratio between m/z 22 and 45 with pressure in breadboard experiments, suggesting an increase in production of CO_2^+ ions in the QMS source. This effect is not interpreted as an isotopic fractionation because the ratio between m/z 45 and 46 remained approximately constant with pressure. (b) Correction function derived from combined flight model and breadboard data. Data shown reflect fractional scan peak areas. Error bars reflect effects of statistical noise and dead time correction for the observed signal, propagated through calculations of background subtraction and isotope ratios. Error bars in (b) are smaller than the symbols.

derived as a function of the observed m/z 22 signal. Because the martian atmosphere is comprised of approximately 96% CO_2 , the observed m/z 22 signal provides an accurate representation of the increase in molecules responsible for the pressure effect on ionization. Application of a similar correction to gas of significantly different composition would require appropriate parameterization for that gas. In addition, dependence of the correction on the observed m/z 22 signal underscores the importance of monitoring detector gain throughout the instrument lifetime and modifying operating parameters, if necessary, to maintain stable performance characteristics. Over more than one Mars year of operation, the detector health has been monitored on a regular basis and the pulse height distribution shows minimal change in detector performance to date.

For the SAM atmospheric correction, data from breadboard experiments were combined with data from flight model calibration, as illustrated in Fig. 2(b), yielding a linear relationship between the correction factor and the observed m/z 22 signal:

$$F_{22} = a \times m22_{\text{obs}} + b \quad (2)$$

$$m22_{\text{corr}} = F_{22} \times m22_{\text{obs}} \quad (3)$$

Table 1Coefficients for m/z 22 correction function and correction factor for estimation of m/z 32 fragments from CO_2 .

Scan mode	m/z 22 correction coefficients		m/z 32 correction factor
	a	b	c
Fractional scan	$-2.321 \times 10^{-7} \pm 1.094 \times 10^{-8}$	1.000 ± 0.003	$4.558 \times 10^{-4} \pm 7.104 \times 10^{-6}$
Unit scan	$-5.467 \times 10^{-8} \pm 1.030 \times 10^{-8}$	1.001 ± 0.005	$4.292 \times 10^{-4} \pm 3.344 \times 10^{-5}$

where $m22_{\text{obs}}$ is the observed signal at m/z 22 and $m22_{\text{corr}}$ is m/z 22 signal after correction. The coefficients of the fit are provided in Table 1 for both fractional scan and unit scan data. The signal for fractional scan data is parameterized as integrated peak area (counts) and the signal for unit scan data is counts/s observed at the integer m/z . For fractional scan data of experiments at Mars ambient pressure, the correction typically reduces the observed integrated counts at m/z 22 by 5–8%.

3.2.3. m/z 32 correction

Experiments performed with pure CO_2 using the SAM test bed have revealed a small but measurable contribution at m/z 32 from combination of oxygen fragments produced during the ionization process. Since the martian atmosphere is dominated by CO_2 , however, the abundance of these fragments observed on Mars is significant compared to the abundance of O_2^+ ions, and the CO_2 contribution to m/z 32 must be removed from the mass spectrum to obtain accurate measurements of O_2 VMR. The correction factor was determined from the ratio of the major CO_2 isotopologue at m/z 44 to m/z 32 for pure CO_2 and is provided in Table 1. The correction is applied as follows:

$$m32_{\text{corr}} = m32_{\text{obs}} - c \times m44_{\text{obs}} \quad (4)$$

where $m32_{\text{obs}}$ is the observed signal at m/z 32 and $m32_{\text{corr}}$ is the corrected signal. As described in the preceding section, the signal for fractional scan data is parameterized as integrated peak area (counts), while unit scan data are counts/s at the integer m/z . During processing of Mars data, the adjustment at m/z 32 is typically applied to an estimate of m/z 44 based on the observed signal at m/z 22, which requires pre-application of the m/z 22 correction given in Section 3.2.2. Care must be taken to ensure that CO_2 in the QMS background contributing excess fragments at m/z 32 is addressed during data processing. When this correction is incorporated into processing of fractional scan data for experiments at Mars ambient pressure, the integrated counts observed at m/z 32 are typically reduced by 30–50 percent.

3.2.4. Assessment of possible artifacts at m/z 14

The marker fragment used to compute N_2 VMR is m/z 14, comprised of approximately 40% N^+ ions and 60% N_2^+ ions (Wong et al., 2013). There is also a minor contribution from CO^{++} ions generated from CO and CO_2 in the martian atmosphere, but their abundance compared to ions at m/z 14 sourced from nitrogen is negligible. Given the relationship observed between CO_2^+ ion production and pressure as discussed in Section 3.2.2, we investigated whether a similar increase in production of N_2^+ ions occurs at elevated pressure. Calibration performed with pure nitrogen gas on the SAM test bed indicated no such effect on N_2^+ production. Furthermore, the partial pressures of N_2 during the determination of calibration constants on the flight model bounded the partial pressures observed on Mars, which was not the case for CO_2 (Fig. 2(b)).

Table 2

Calibration constants for VMR determination.

Empirical calibration constants			
Species or ratio	m/z value of marker fragment (i)	$F_{\text{X}_i/\text{Ar}^+}$ for fractional scan data	$F_{\text{X}_i/\text{Ar}^+}$ for unit scan data
CO_2	22	161.3 ± 3.3	135.3 ± 2.8
N_2	14	22.10 ± 0.45	26.51 ± 0.67
O_2	32	1.453 ± 0.013	1.337 ± 0.017
CO	12	0.3303 ± 0.0179	0.6006 ± 0.0561
$(m22/m12)_{\text{CO}_2}$ ^b		0.4305 ± 0.0079	0.5686 ± 0.0087
$(m44/m22)_{\text{CO}_2}$ ^c		183.59 ± 2.83	145.88 ± 1.17

^a See Eq. (1).

^b Calibration factor for estimating signal at m/z 12 due to CO_2 .

^c Constant for estimating the molecular ion CO_2^+ at m/z 44 from the signal at m/z 22 due to CO_2^+ ions. This factor applies to pressure-corrected m/z 22 data.

3.2.5. Refined calibration constants

The corrections described in Sections 3.2.1 through 3.2.3 were incorporated into a revised set of calibration constants for calculation of VMR from SAM data. In addition to the effects on CO_2 and O_2 VMR due to adjustments in the signals at m/z 22 and 32, the signal at m/z 22 is used directly in the computation of CO abundances. Since the relevant calibration factor was derived from pre-launch experiments designed to simulate atmospheric analyses on Mars, the introduction of m/z 22 correction also requires an update to the CO calibration factor. The procedure for deriving the CO calibration factor, including compensation for changes evident in the QMS background on Mars compared to pre-launch calibration, was discussed in detail by Franz et al. (2014). The same procedure was repeated after application of the m/z 22 correction to both flight data and data from Mars mix calibration experiments. The resulting revised CO calibration factor incorporated data for experiments performed over an entire martian year, lending greater confidence to the resulting background-shifted baseline for m/z 12 compared to m/z 22.

Refined calibration constants for the five most abundant gases in the martian atmosphere are provided in Table 2. The table gives updated calibration factors for estimating molecular ions at m/z 44 based on observed CO_2^+ ions at m/z 22, incorporating the correction for pressure effects at m/z 22. Additional corrections for the average m/z 22 peak widening since calibration are factored into specific calibration constants that utilize m/z 22, including those for CO_2 and CO as well as the constant for estimating CO_2 contributions at m/z 32 that affect calculations of O_2 abundance, given in Table 1.

4. Application of refined calibration coefficients to Mars data

To assess the impact of the corrections defined in Section 3 on volume mixing ratios, the corrections were applied to data acquired during SAM atmospheric experiments on sols 45 and 77 (at solar longitudes of 175° and 193° , respectively). Results are given in Table 3, with previously reported VMR provided for comparison (Mahaffy et al., 2013). The most significant change seen between the two data sets is a decrease in the CO_2 VMR due

Table 3

Effects of applying refined calibration constants to VMR calculations for data acquired on MSL sols 45 and 77 (at solar longitudes of 175° and 193°, respectively).

Species	VMR reported previously (Mahaffy et al., 2013)	VMR after application of refined calibration constants ^a
CO ₂	0.960(±0.007)	0.957(±0.016)
N ₂	0.0189(±0.0003)	0.0203(±0.0003)
Ar	0.0193(±0.0003)	0.0207(±0.0002)
O ₂	1.45(±0.09) × 10 ⁻³	1.73(±0.06) × 10 ⁻³
CO	< 1.0 × 10 ⁻³	7.49(±0.026) × 10 ⁻⁴

^a Weighted mean and associated uncertainty for each compound.

to the downward adjustment of m/z 22 signal, which produces a concomitant increase in VMR of other atmospheric species. For N₂ and Ar, this is evident as small increases in each VMR outside the previously estimated uncertainties, although the revised ⁴⁰Ar/¹⁴N ratio of 0.51 ± 0.01 is identical within uncertainty to that reported previously. The increase in O₂ VMR due to the reduction in m/z 22 signal, although offset by the reduction in m/z 32 signal due to CO₂ fragments, is also enhanced by improved modeling of the QMS background compared to the earlier analysis.

The availability of data over a complete martian year allows a more robust estimate of the shift in baseline ratio of m/z 12 to 22 for CO₂, which is required for computation of CO abundance, than was possible shortly after landing on Mars (Mahaffy et al., 2013). As discussed by Franz et al. (2014), this shift in baseline is interpreted to reflect a gradual reduction in instrument background at m/z 12 during calibration and initial operation on Mars. The CO calibration constant was derived from a gas mixture containing 700 ppm CO, which corresponds to the average annual CO abundance measured from orbit with the Compact Reconnaissance Imaging Spectrometer (CRISM) on the Mars Reconnaissance Orbiter (MRO) spacecraft (Smith et al., 2009). The shift in m/z 12–22 from reduction in instrument background was estimated by comparing the average ratio of m/z 12–22 for the calibration Mars mix gas to the average ratio observed by SAM on Mars, which can now be taken to represent an average annual value. The additional confidence inspired by the expanded data set now allows estimation of precise CO VMR for individual SAM experiments, rather than simply an upper limit as initially reported (Mahaffy et al., 2013).

The final differences evident in the refined calibration constants provided in Table 2 and the revised VMR presented in Table 3 are changes in the estimated measurement uncertainties. Effects of statistical noise and detector dead time correction, propagated through subsequent calculations of background subtraction and isotope ratios, are included in uncertainty estimates for results of both calibration and flight data (Franz et al., 2014). The original calibration constants reported in Franz et al. also incorporated the variations in VMR computed for several Mars mix experiments into the uncertainties in the constants (Franz et al., 2014). Repeated measurements of VMR throughout the nominal mission have revealed variations in CO₂, O₂, and CO that are smaller than the variations obtained in the Mars mix calibration experiments. Since those calibration experiments were focused more on engineering validation than on obtaining optimal

scientific data, the variations in resulting VMR were eliminated from the uncertainties estimated for the refined calibration constants provided in Table 2. However, the refined constants do reflect the addition of uncertainties due to the variation in average QMS tuning throughout the martian year, and the revised VMR presented in Table 3 also incorporate propagation of uncertainties due to application of the m/z 22 and 32 corrections, as described in Section 3.

The SAM team will continue to monitor QMS performance carefully throughout the extended mission. In addition, SAM carries a calibration gas cell containing an equimolar mix of CO₂, N₂, Ar, and Xe (nominally terrestrial isotopic composition but enriched in ¹²⁹Xe) and trace quantities of four high molecular weight fluorinated compounds, as described by Franz et al. (2014). If a need is indicated by experiments using the calibration cell on Mars or by routine monitoring of QMS performance during nominal atmospheric experiments, the calibration constants will be updated again in future contributions.

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