

Sensitivity of the TEGA mass spectrometer

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The sensitivity determination of the TEGA mass spectrometer served two purposes 1) Track the mass spectrometer health and ability to detect evolved gases on each channel throughout the mission and 2) Utilize sensitivity as a calibration to enable quantification of evolved gases detected by TEGA. Sensitivity was determined when gas was sampled through the atmospheric valve (Sols 9-16, 141) and through the sample valve (all sols) (Figures 1 - 3). The TEGA mass spectrometer measured CO₂ from the martian atmosphere before each analysis which served to measure sensitivity. The constant martian atmospheric CO₂ concentration (95.3%) provided TEGA with an ideal calibrant (CO₂) in which to gauge mass spectrometer health and quantify evolved gases. TEGA sensitivity was determined on channels 3 and 4 as these channels examined masses 44 (¹²CO₂) and 45 (¹³CO₂). Channel 1 and 2 sensitivities were not reported as these channels did not detect masses 44 and 45. The channel 2 data was also of low quality because the channel 2 electron multiplier (CEM) degraded significantly early in the mission and most masses were not collected beyond sol 25. Sensitivity degradation on channel 1 (1-4 Da) was not characterized because there was no sufficient independent measurement in which to link sensitivity. Furthermore, the primary purpose of channel 1 was to assess the D/H ratio of water so the mass ratios were the focus of the measurement rather than the absolute abundance.

The sensitivity (CO₂ cps/mbar) was determined by subtracting the average instrument background CO₂ (m/z 44 and m/z 45) (CO_{2BG}) counts within the mass spectrometer from the average counts of the CO₂ in the atmosphere (CO_{2ATM}) (Figure 1) and the dividing that value by the mbar of CO₂ in the Martian atmosphere (pCO₂ = total Martian atmospheric pressure * 0.953). Total Martian atmospheric pressure was measured daily by the Phoenix Meteorological Station.

$$\text{CO}_2\text{ sensitivity} = (\text{CO}_{2\text{ATM}} - \text{CO}_{2\text{BG}})/\text{pCO}_2 \quad [1]$$

All TEGA runs analyzed the martian atmosphere as a calibration point. The background counts of CO₂ within the mass spectrometer were determined before atmospheric sampling. This was accomplished by taking the average of multiple mass 44 (and 45) measurements before the sample or atmospheric valves were opened. These counts were collected in the bracketed portion marked BG in Figures 1b and 2. The CO₂ counts of the martian atmosphere were determined by averaging the CO₂ counts collected in the bracketed region marked SV or AV in Figures 1b and 2. The red arrow in Figure 1b indicated where the sample valve to the mass spectrometer was opened while the end of the bracketed SV time indicated where the sample valve closed. For dedicated atmospheric analyses (sols 9 - 16, 141), sensitivity data was collected through sample valve first that was then closed, which was followed by sensitivity data collected through atmospheric valve (Figure 2). For soil sample analyses, sensitivity data was collected solely through the sample valve. Following the opening of the sample (or atmospheric) valve, the CO₂ counts increased and then stabilized representing the CO₂ counts at martian atmospheric pressure. The martian atmosphere was present in the case of the sample valve because the martian atmosphere had leaked into the TEGA plumbing through the sample exhaust frit (EF) (Figure 3). Between analyses, the martian atmosphere leaked into the TEGA plumbing through

the exhaust frit (EF), allowing it to be sampled at the beginning of each analysis but before carrier gas purged the martian atmosphere from the TEGA instrument.

Mass 44 sensitivity was not determined for the first 4 atmospheric analyses (sols 9 to 16) because the mass 44 count rate was too high using the atmosphere inlet and high emission current to permit analysis (Tables 1 and 2). However, mass 45 count rate was in range and these results were provided (Figure 4, Tables 1 and 2).

The sensitivity of the TEGA mass spectrometer on channel 3 initially decreased, hitting a minimum on sol 70, but then increased for the most part until it stopped working on sol 92 (Figures 4 and 5). The channel 3 sensitivity decreased until sol 70 but then increased, but not to sensitivity levels from the beginning of the mission. One issue that may have caused sensitivity loss was that the channel electron multipliers (CEM) were believed to have degraded over time. Ultimately, channel 3 stopped working after sol 92. The degradation and ultimate loss of channels 2 and 3 was not fully understood but could have been due to the reaction of carbon-bearing compounds (including CO and CO₂) with the CEM material, beginning in pre-mission testing and continued when analyzing the martian atmosphere.

The sensitivity of channel 4 was stable for all the CO₂ measurements through the atmospheric valve (Figure 4a). However, despite filament operation at the same emission current (~290 mA) the sensitivity decreased when CO₂ was measured through the sample valve (Figure 4b). This suggested that gas conductivity issues associated with the plumbing may have contributed to the decreased sensitivity. Evolved CO₂ detected through sample valve (filament emission current, ~89 mA) (Figure 5) experienced the lowest sensitivity on sol 70 but gradually increased back to values at the beginning of the mission. On sol 90 and for all sols including and after sol 129, the channel 4 sensitivity increased ~20X relative to sensitivities earlier in the mission. The higher sensitivity for later sols was not likely attributed to improved sensitivity of channel 4, but was instead attributed to improved evolved gas conductivity through sample frit (SF) and other plumbing constrictions (e.g., puncture valves) to the mass spectrometer (Figure 5). It was unclear why the evolved gas conductivity improved for the later sols of the mission.

Relative ionization cross-sections can be used to convert other detected gases (e.g., O₂, water) counts to CO₂ counts thus permitting quantification using CO₂ sensitivity values (e.g., Archer et al., 2014). Other detected gases (e.g., water or O₂) were not quantified using atmospheric calibrations because the levels were too low and never significantly above background levels to be useful for abundance determinations (Sutter et al., 2024). The relative ionization cross section value (X_{gas}) used to convert water or O₂ counts to CO₂ counts can be found in (Nakao, 1975) where:

$$\text{TEGA CO}_2 \text{ counts} = X_{\text{CO}_2}/X_{\text{O}_2 \text{ or H}_2\text{O}} \times \text{TEGA O}_2 \text{ or H}_2\text{O counts} \quad [2]$$

Differences between mass spectrometer systems and how they were tuned can lead to different ionization efficiencies (Archer et al., 2014) where typical cross section variations in the literature are ~20%. (Archer et al., 2014). This error should be incorporated into TEGA abundance determinations of other gases.

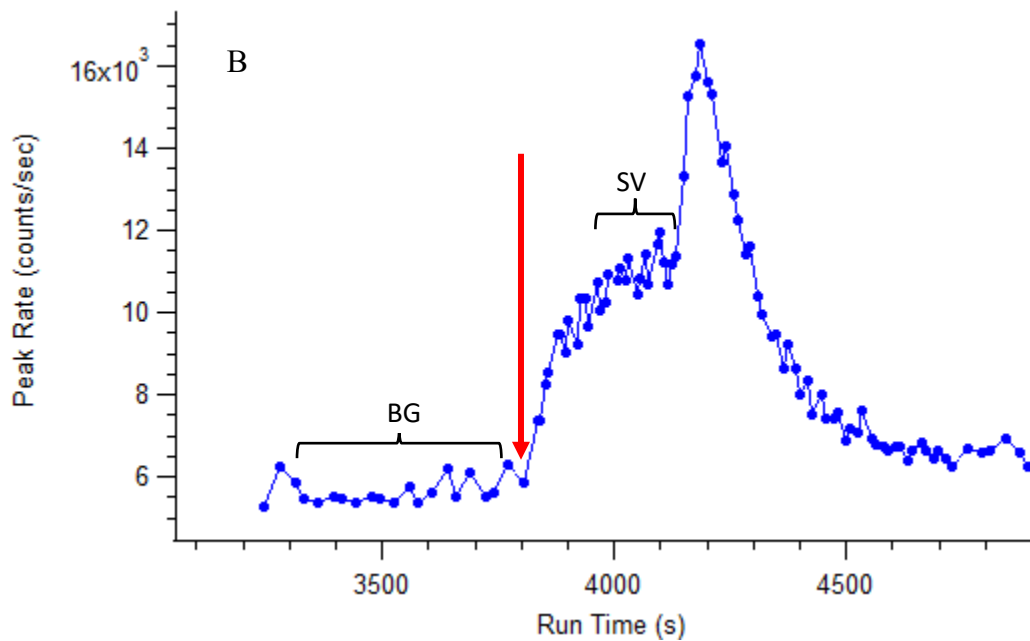
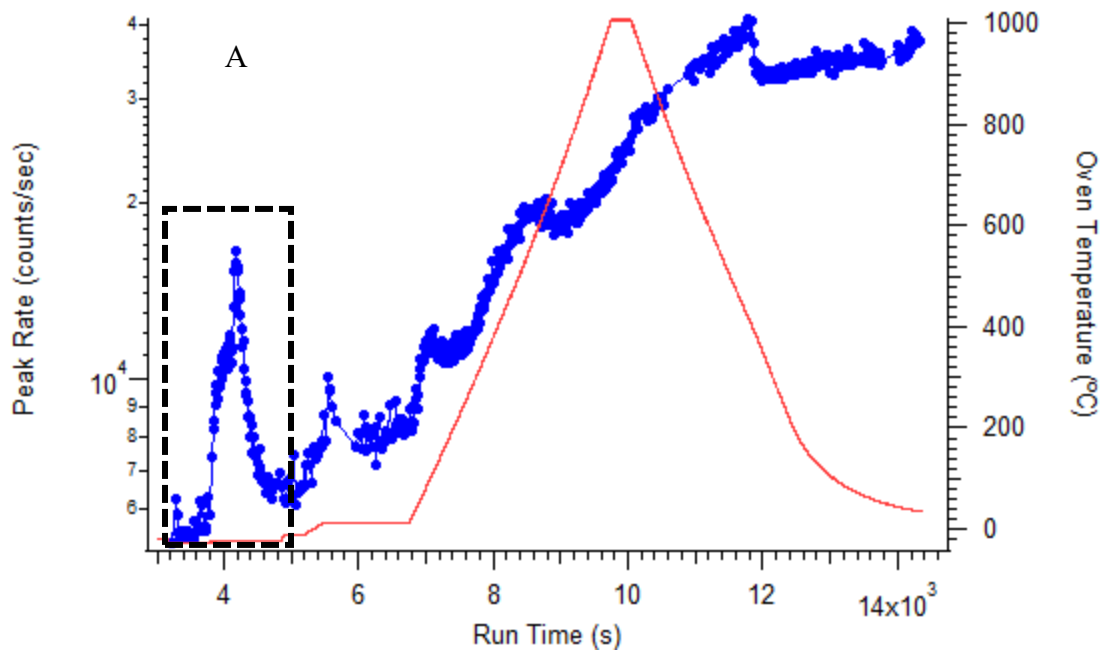


Figure 1 a) Channel 4 mass 44 versus time and oven temperature versus time for sol 22 high temperature heating of the Baby Bear sample. b) Dashed box in a) demonstrating where mass spectrometer background (BG) and atmospheric CO₂ data were collected through the sample valve (SV) for sensitivity calculations. Red arrow marks opening of the sampling valve

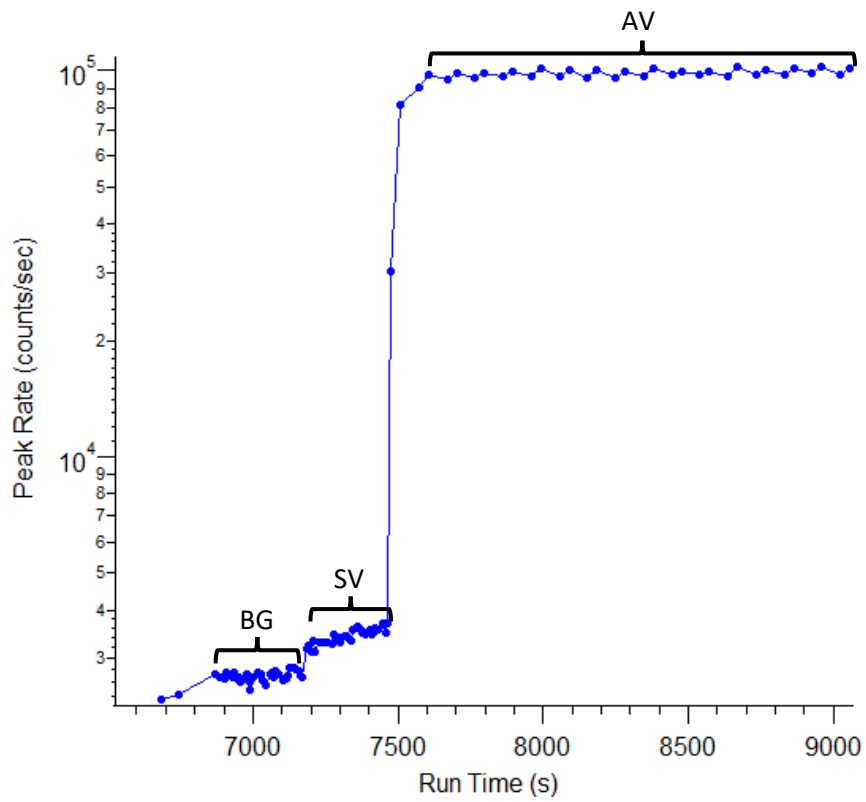


Figure 2. Sol 11 atmospheric analysis demonstrating where mass 45 background (BG) and mass 45 was measured through the sample (SV) and atmospheric (AV) valves respectively.

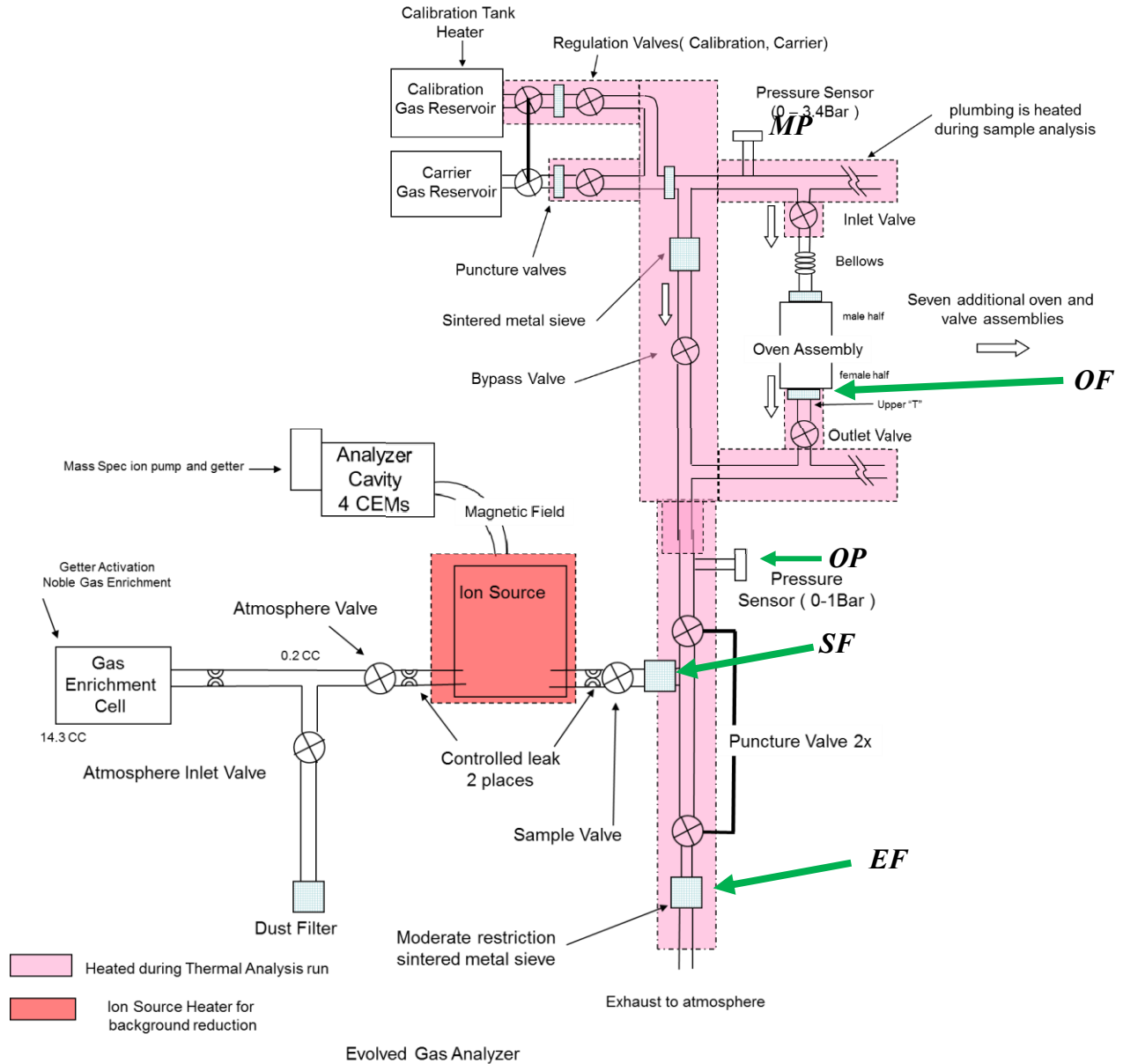


Figure 3. Schematic of the TEGA instrument indicating relative positions of valves, frits, pressure sensors, ovens, and mass spectrometer. Abbreviations, oven outlet frit (*OF*), manifold pressure sensor (*MP*), outlet pressure sensor (*OP*), sample frit (*SF*), exhaust frit (*EF*). Heavy red dashed line encloses mass spectrometer. (Sutter et al., 2024)

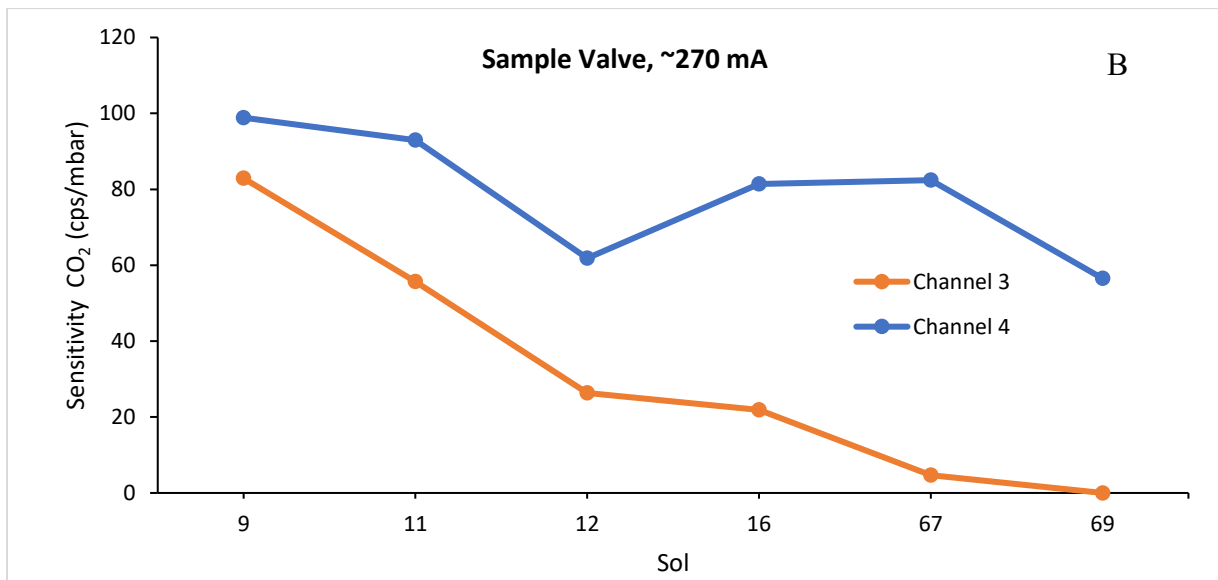
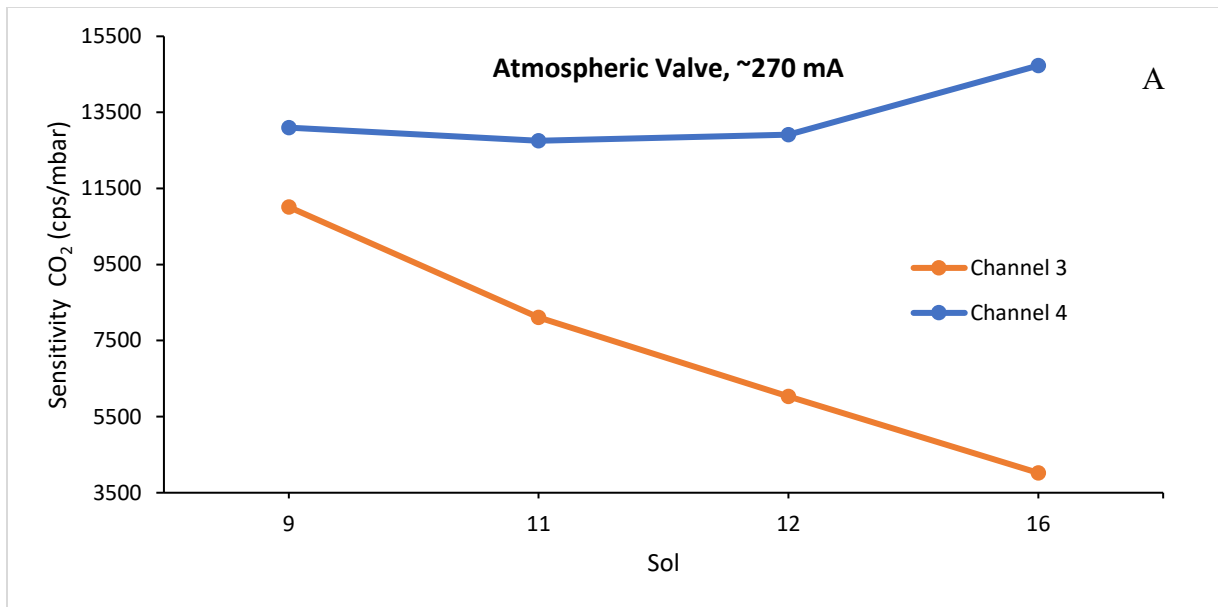


Figure 4 TEGA mass spectrometer sensitivity for mass 45 analyzed at ~270 mA emission current on channels 3 and 4 sampled through the a) atmosphere valve and b) sample valve.

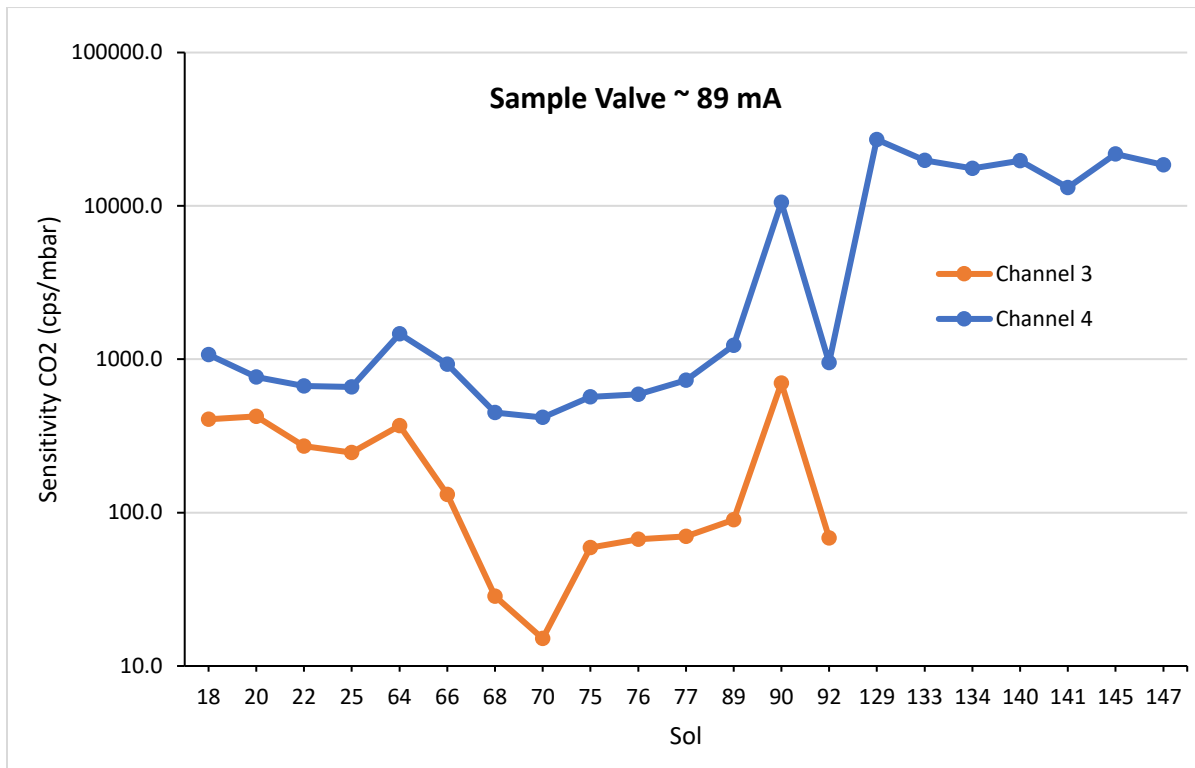


Figure 5. TEGA mass spectrometer sensitivity for mass 44 analyzed at ~89 mA emission current.

Table 1. Channel 3 sensitivity for Mars atmospheric mass 45 and 44 detected through atmospheric and sample valves. Standard deviation of mean values (SD). Sols 9-16 analyses separately collected atmosphere first through sample valve and then the atmospheric valve.

Sol	Emission Current	Mars ATM	Mars ATM pCO ₂	m/z 45	SD	m/z 44	SD
	mA	mbar		cps CO ₂ /mbar pCO ₂			
ATMOSPHERIC VALVE							
9	269.53	8.48	8.08	11012.94	214.60	-	-
11	270.53	8.47	8.07	8111.07	151.31	-	-
12	266.66	8.40	8.00	6030.55	106.87	-	-
16	269.31	8.41	8.02	4021.20	94.33	-	-
SAMPLE VALVE							
9	267.56	8.48	8.08	82.90	11.90	-	-
11	268.56	8.47	8.07	55.66	10.49	-	-
12	265.89	8.40	8.00	26.39	7.38	-	-
16	267.10	8.41	8.02	21.89	11.25	-	-
18	89.18	8.37	7.99	5.09	1.62	405.49	63.19
20	88.11	8.33	7.94	1.17	1.46	423.41	124.91
22	87.69	8.31	7.92	2.42	1.41	271.11	32.87
25	88.43	8.32	7.93	3.16	1.64	246.22	43.84
64	88.92	7.87	7.50	4.16	0.81	368.69	28.79
66	89.36	7.84	7.48	-	-	131.51	9.72
67	265.53	7.83	7.46	4.71	1.84	450.38	84.41
68	88.80	7.82	7.45	-	-	28.54	7.68
69	265.00	7.83	7.46	-	-	147.75	22.18
70	87.80	7.82	7.45	-	-	15.10	5.89
75	89.60	7.78	7.41	0.44	0.26	59.11	10.52
76	89.60	7.75	7.38	-	-	66.91	11.60
77	89.20	7.73	7.37	-	-	70.01	10.56
89	90.60	7.63	7.28	1.05	0.57	89.67	13.36
90	88.20	7.64	7.28	-	-	700.58	21.26
92	88.60	7.62	7.26	-	-	68.34	14.30

Table 2. Channel 4 sensitivity for Mars atmospheric mass 45 and 44 detected through atmospheric and sample valves. Standard deviation of mean values (SD). Sols 9-16, 141 analyses separately collected atmosphere first through sample valve and then the atmospheric valve.

Sol	Emission Current	Mars ATM	Mars ATM pCO ₂	m/z 45	SD	m/z 44	SD
	mA	mbar		cps CO ₂ /mbar CO ₂			
ATMOSPHERIC VALVE							
9	269.53	8.48	8.08	13100.30	252.79	-	-
11	270.53	8.47	8.07	12754.27	513.21	-	-
12	266.66	8.40	8.00	12915.81	196.20	-	-
16	269.31	8.41	8.02	14730.57	404.57	-	-
141	88.00	7.31	6.97	2117.07	21.91	165604.55	19547.66
SAMPLE VALVE							
9	267.56	8.48	8.08	98.87	15.98	-	-
11	268.56	8.47	8.07	92.97	17.97	-	-
12	265.89	8.40	8.00	61.83	11.10	-	-
16	267.10	8.41	8.02	81.43	19.29	-	-
141	88.00	7.31	6.97	293.66	11.33	13142.69	502.85
18	89.18	8.37	7.99	15.52	3.40	1073.22	119.96
20	88.11	8.33	7.94	9.20	2.03	765.98	47.47
22	87.69	8.31	7.92	8.04	2.56	668.59	77.73
25	88.43	8.32	7.93	8.52	3.15	660.87	83.90
64	88.92	7.87	7.50	16.95	2.31	1467.50	128.09
66	89.36	7.84	7.48	-	-	926.11	45.46
67	265.53	7.83	7.46	82.43	7.01	6715.26	259.68
68	88.80	7.82	7.45	-	-	448.79	32.47
69	265.00	7.83	7.46	56.53	6.70	4784.97	208.18
70	87.80	7.82	7.45	-	-	417.19	37.65
75	89.60	7.78	7.41	6.75	1.16	567.78	54.56
76	89.60	7.75	7.38	-	-	590.26	56.44
77	89.20	7.73	7.37	-	-	729.62	64.67
89	90.60	7.63	7.28	14.66	3.01	1231.36	114.20
90	88.20	7.64	7.28	-	-	10536.67	177.90
92	88.60	7.62	7.26	-	-	952.29	97.84
129	88.60	7.33	6.99	-	-	27087.10	450.49
133	89.40	7.27	6.93	-	-	19840.04	408.71
134	88.40	7.33	6.98	-	-	17595.84	501.73
140	88.60	7.26	6.92	-	-	19733.14	374.98
145	88.40	7.35	7.00	-	-	21828.36	533.97
147	88.20	7.37	7.02	-	-	18468.38	485.82

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