Supporting Information for:

Simultaneous, in situ detection of gas-phase carbon disulfide (CS_2) and carbonyl sulfide (OCS) via O_2^+ chemical ionization mass spectrometry

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S1. CS_2 Detection Methods in Literature

Table S1. Existing detection methods of environmental CS_2

Analysis	Sampling	Collection Time	CS_2 LOD	Limitations	References
GC-FPD	In-situ	7 min[1] 10 min[2]	10 ppt[1] < 0.5 ppt[2]		[1–4]
GC-FPD	Adsorption Trap	0.5 – 2 hrs[5,6] 50 min[7] 25-50 min[8]	0.5 µg m^{-2} h^{-1} [5] 16.9 pg[6] 2 pmol S L^{-1} [7,8] 1 ppt[8] 1 pmol L^{-1} [9]		[5–9]
GC-FPD	Tedlar bag	15 min[10] 30 min[11]	0.2 pmol S[12]		[10–13]
GC-FPD	Glass syringe				[14]
GC-FPD	Cryogenic trapping in glass sample trap	0.5- 20 min[15] 20 min[16] 6 min[17] 5 -15 min[18] 20 -50 min[19]	20 ppt[20] 0.5 – 1 ng S/L[16] 3 – 4 ppt[16] 0.1 ng[17] 1 ppt[19]		[15–21]
GC-FPD	Cryogenic trapping in stainless steel bottles				[4]
GC-FPD	Cryogenic trapping in Teflon sample trap	10 – 40 min[22] 6 -10 min[23] 8 – 20 min[24]	< 2 ppt[22] 1.5 ppt[24] < 3 ppt[25]		[14,22–26]
GC-FPD	Cryogenic trapping on a novel sample plate				[14]
GC-FPD	Monel Garrett screen				[14]
GC-FPD	Water headspace in Weiss-type equilibrator	5- 8 min[10] 2 min[3]			[1,3,10]
GC-FPD	Seawater pump	0.5 – 2 hr[7]	2 pmol S L^{-1} [7,8]		[7,8]
GC-MS	Adsorption trap	~30 min[27,28]	0.4 ppt[28]		[27,28]
GC-MS	Stainless steel canisters	1 min[29]	1 pmol L^{-1} [30] 1.5 pM S[31] 0.5 ppt[29,32]		[29–32]
GC-MS	Glass bottles		1.4 pmol L^{-1} [30]		[30]
GC-MS	Cryogenic trapping in Teflon tube				[27]
GC-MS	Submersible pump		1.5 pmol L^{-1} [31]		[31]

GC-MS-IS	Cryogenic trapping in Teflon sample tube		< 3 ppt[25]		[25]
GC-ECD					[33]
GC-ECD	In situ	40 sec[34]	30 fmol[35] 2 ppt[34]		[34,35]
GC-ECD	Cryogenic trapping in Teflon sample tube				[36]
GC-SCD	Silicon lined stainless steel canister		0.1 pg S/s[37]	Nonlinear at high sample volumes and concentrations	[37]
GC-DAD-FID	In situ		60 ng L^{-1} [38]		[38]
PMI-MS in FQ-IF	In situ		26 ppt[39]		[39]
TOF-IMS-PID	In situ		30 ppb[40]		[40]
UV-DOAS	In situ				[41]
DOAS	In situ		2 ppb[42]		[42]
Atomic Absorption (AA)	Activated charcoal sample tubes		7.0 ug[43]		[43]
Colorimetric detection	Liquid samples		0.013 ug mL^{-1} [44]	Presence of sulfides interferes with recovery	[44,45]
Colorimetric detection	Diffusive charcoal samplers				[45]

S2. GC-Vocus Zeros

GC-Vocus zeros can be determined in two ways: 1) a zero air generator overflows the ambient inlet (external zero) and 2) a zero air cylinder is connected directly to the GC system (internal zero). The normalized GC peak areas of CS_2^+ were larger for external zeros compared to internal zeros for both the Azores (13.9 compared to 3.1 normalized counts) and Chicago (53.7 compared to 4.8 normalized counts) when considering GC measurements below the detection limit as 0 ppt in our averaging (**Fig. S1**). Reported counts are normalized by GC trapping volume for comparison across campaigns. The external zeros are likely higher due to limitations of the VOC scrubber in the zero air generator and do not represent a true background. In the Azores, two to four internal zeros were taken each day and applied to paired ambient measurements. In Chicago, an average internal zero value was applied to all ambient measurements. Representative chromatograms of external and internal zeros are shown in **Fig. S2**. While both campaigns utilize the same methodologies, a difference in acquisition times requires the Azores chromatogram to be shifted forward by 50 seconds for accurate comparison. Accuracy of this adjustment is confirmed by the retention time of acetone in both campaigns.

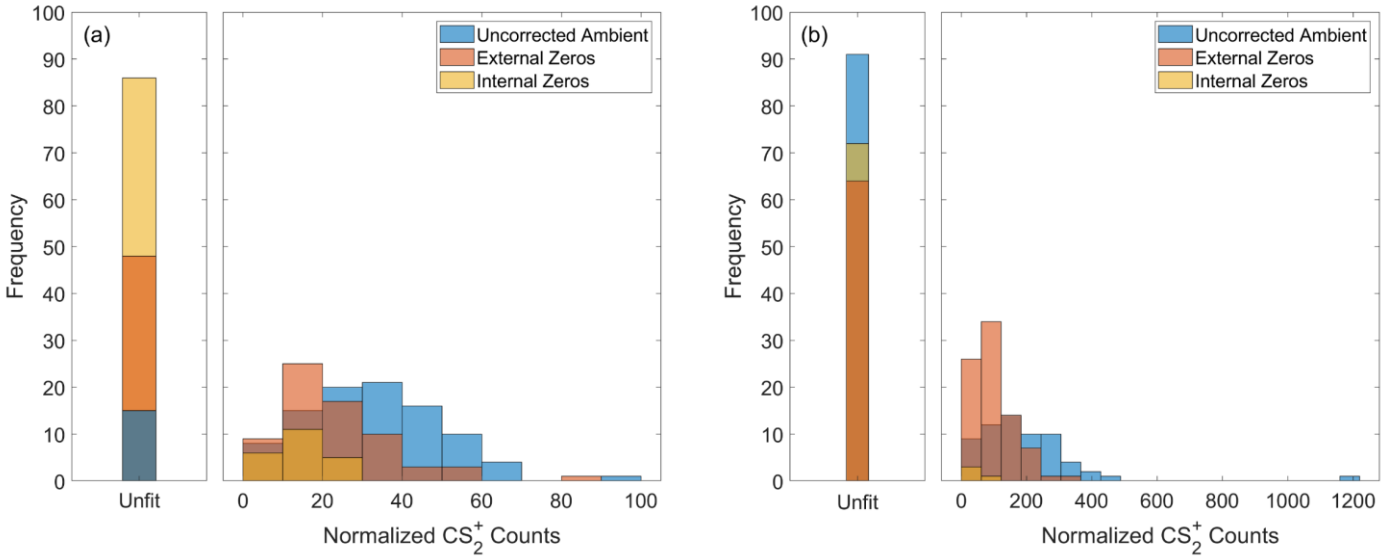

Figure S1. Distribution of ambient, external zero, and internal zero GC signal for carbon disulfide (CS_2^+) from **(a)** AGENA (Graciosa Island, Azores) and **(b)** SMOKIEVOC (Chicago, IL). Counts are normalized to account for varied trapping volumes.

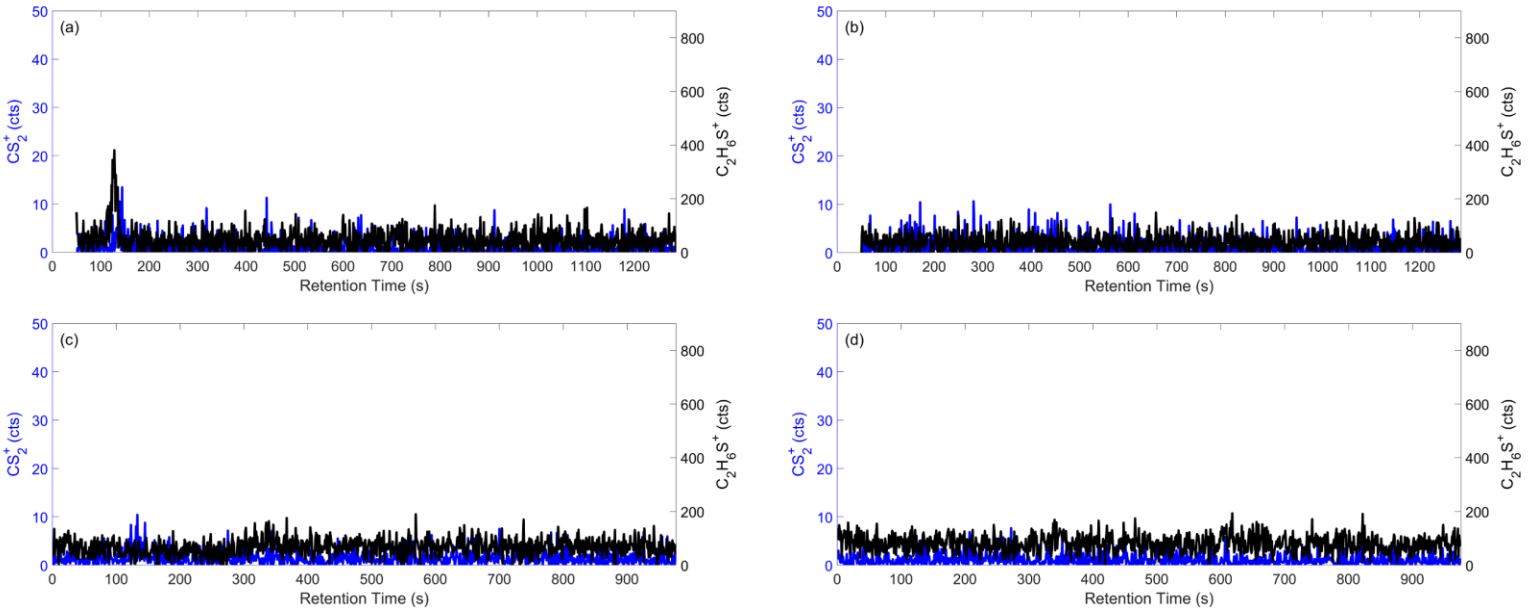

Figure S2. Representative GC chromatograms (5 Hz, 1 second average) of CS_2^+ (blue) and $C_2H_6S^+$ (black) for **(a)** external and **(b)** internal zeros from AGENA (Graciosa Island, Azores) and **(c)** external and **(d)** internal zeros from SMOKIEVOC (Chicago, IL). Trapping volumes are 3 L and 0.5 L respectively.

S3. CS_2^+ GC Spectra

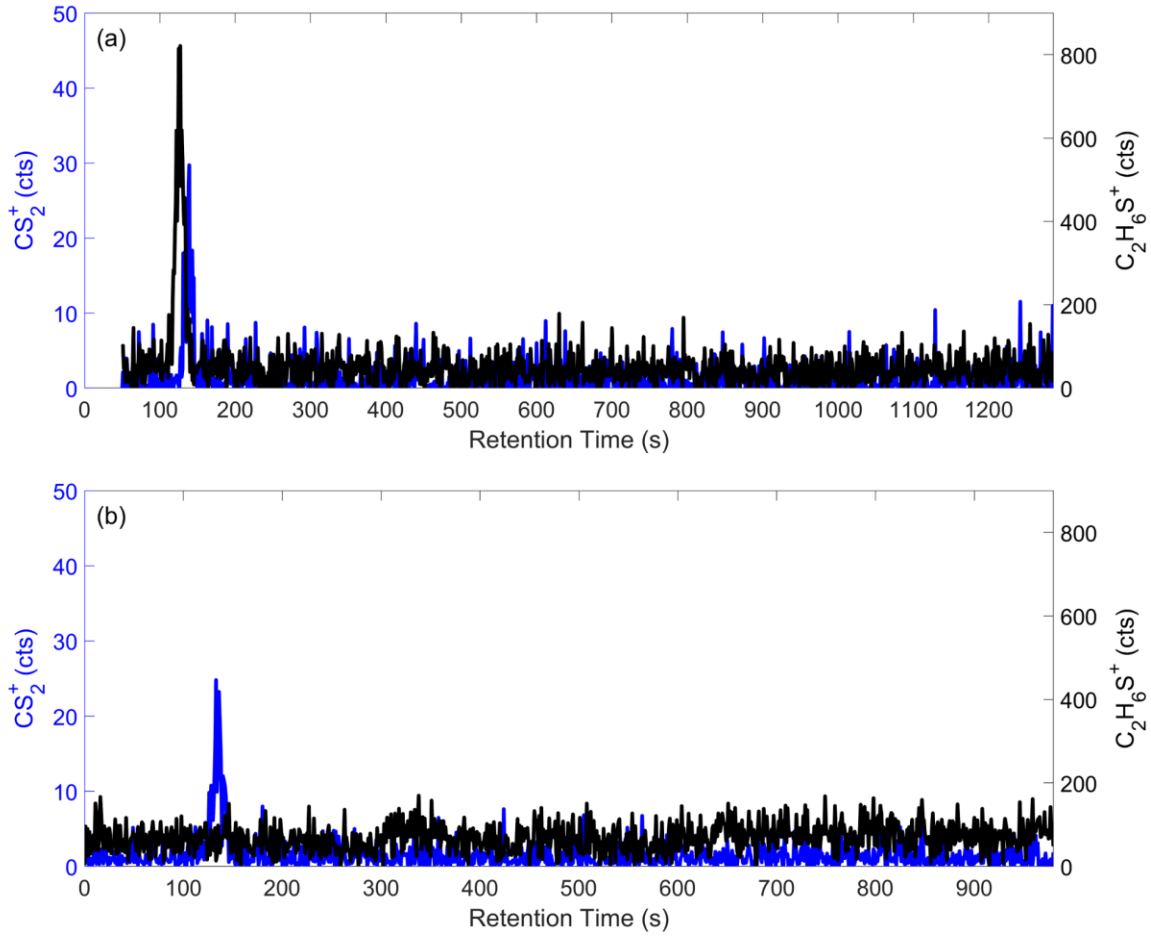

Figure S3. Complete spectra of representative CS_2^+ (blue) and $C_2H_6S^+$ (black) chromatograms taken at 5 Hz (1 second average) for **(a)** AGENA (Graciosa Island, Azores) and **(b)** SMOKIEVOC (Chicago, IL) field campaigns. Trapping volumes are 3 L and 0.5 L respectively.

S4. Correlation between O_2^+ and H_3O^+ Product Ions of Representative Campaign Calibrants

Under PTR ionization, O_2^+ is a residual ion that is present at a signal intensity around 1.5 orders of magnitude below that of $H_5O_2^+$ (37 m/z), a representative peak for H_3O concentration. It experiences some spectral fluctuations due to varied sampling environmental and instrument state, but strong signal correlations between the charge transfer and proton transfer product ions were observed across the campaign for both d3-DMS (R^2 = 0.97) in the Azores and benzene (R^2 = 0.96) in Chicago (**Fig S4**). This highlights the reliability of M^+ product ion production and the robust application of this calibration method.

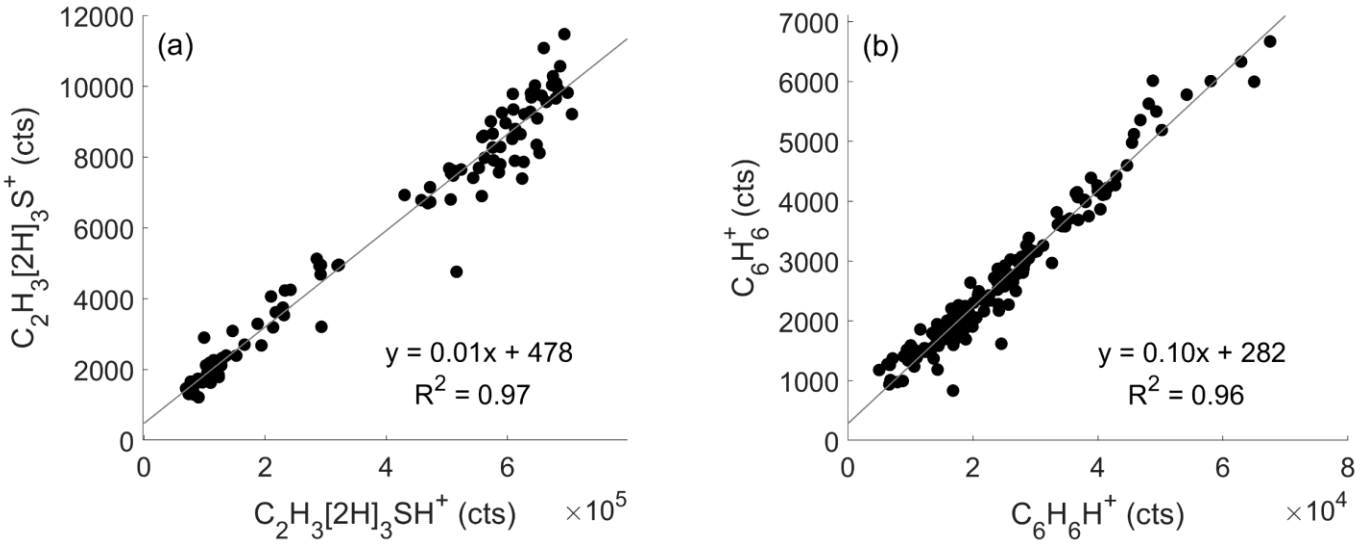

Figure S4. Correlations of the charge transfer product ion versus the proton transfer product ion under PTR ionization conditions for **(a)** d3-DMS ($C_2H_3[2H]_3S$, R^2 = 0.97) in the AGENA field campaign (Graciosa Island, Azores) and **(b)** benzene (C_6H_6, R^2 = 0.96) in the SMOKIEVOC field campaign (Chicago, IL).

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