



Supplement of

Challenges associated with the sampling and analysis of organosulfur compounds in air using real-time PTR-ToF-MS and off-line GC-FID

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1. Mixing ratios measurements using PTR-MS parameters:

The PTR-MS records in real time the intensity of protonated ions $[M+H]^+$ as a function of time. Ultimately, mixing ratio (M_{ppb} in ppb) from the PTR-MS measurements can be determined from the following equation:

$$M_{ppb} = \frac{10^9}{k} \cdot \frac{22400 \cdot \mu_0 \cdot U_{drift}}{N_A \cdot l^2} \cdot \frac{T_{drift}^2 [K]}{T_0^2 [K]} \cdot \frac{p_0^2 [mbar]}{p_{drift}^2 [mbar]} \cdot \frac{TR_{H_3O^+}}{H_3O^+} \cdot \sum_i \frac{C_i^+ \cdot I_{ab}}{TR_{C_i^+}} \quad (1)$$

with C_{ppb} , the concentration of the $[M+H]^+$ ion generated in the ion drift source; k , the reaction rate constant ($\text{cm}^3 \text{s}^{-1}$) between a target molecule and protonated water reagent (H_3O^+) forms by the hollow cathode; μ_0 , the reduced ion mobility ($= 2.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$); U_{drift} the total voltage of the drift tube ($= 600 \text{ V}$); N_A the Avogadro number ($= 6.023 \times 10^{23} \text{ molecules mole}^{-1}$); l , the length of the reaction chamber ($= 9.3 \text{ cm}$); T_{drift} ($= 60^\circ\text{C} = 333 \text{ K}$) and T_0 (273.15 K), the drift temperature and the temperature at standard condition respectively; p_{drift} ($2.11\text{-}2.15 \text{ mbar}$) and p_0 (1013.25 mbar) the drift pressure and the pressure at standard condition respectively; C^+ and H_3O^+ the signal measured for the $[M+H]^+$ ion and the H_3O^+ ion (taken at m/z 21; typical count rate were $\sim 2 \times 10^6 \text{ s}^{-1}$), respectively; $TR_{C_i^+}$ and $TR_{\text{H}_3\text{O}^+}$ the transmission efficiency of the ion of interest and the H_3O^+ ion (m/z 21) respectively; and I_{ab} , the isotopic abundance of the ion of interest.

2. Dynamic injection system.

A dynamic solution injection system was used to calibrate the two analytical methods for dimethyl trisulfide (DMTS). The system was first validated using dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) standards by comparing the data obtained with the certified gas cylinder. The dynamic solution injection method was adapted from Jardine et al. (Jardine *et al.*, 2010). Briefly, a standard solution of the OSC pure standard was prepared each day in cyclohexane (Fluka, Spectranalyzed grade) with concentrations of about $1\text{-}3 \times 10^{-5} \text{ mol ml}^{-1}$. These solutions were then injected using a syringe pump (Pump systems Inc., model NE-

1000) at a flow rate of $0.5 \mu\text{L min}^{-1}$ into an empty, septum-sealed 20-mL scintillator glass vial. A controlled stream of dry synthetic air was flowing in and out of the vial at a constant flow rate set by a mass flow controller (Alicat), allowing the OSC standard to vaporize entirely. The outflow of the system was directed to the inlet of the PTR-ToF-MS without further dilution. From this system, the fluctuations of the syringe pump were visible, and we chose to average over several cycles to get the value of the signal intensity for a given concentration during calibration. Concentrations in the range of 0-200 ppb were generated, with an accuracy of ~ 4 to 10% (2 standard deviations). No metal connector or tubing was used in this system.

Figure S1. Dynamic injection system

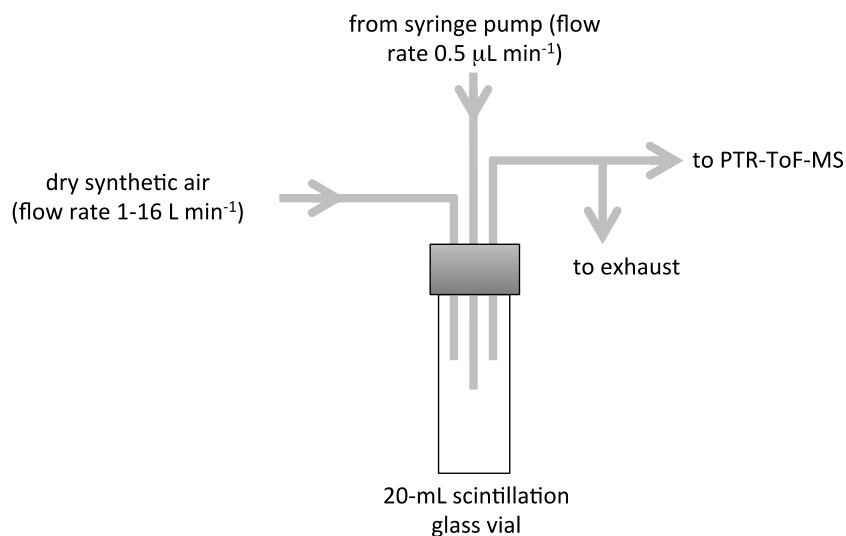


Figure S2. High-resolution mass spectra for each individual OSC fragments:

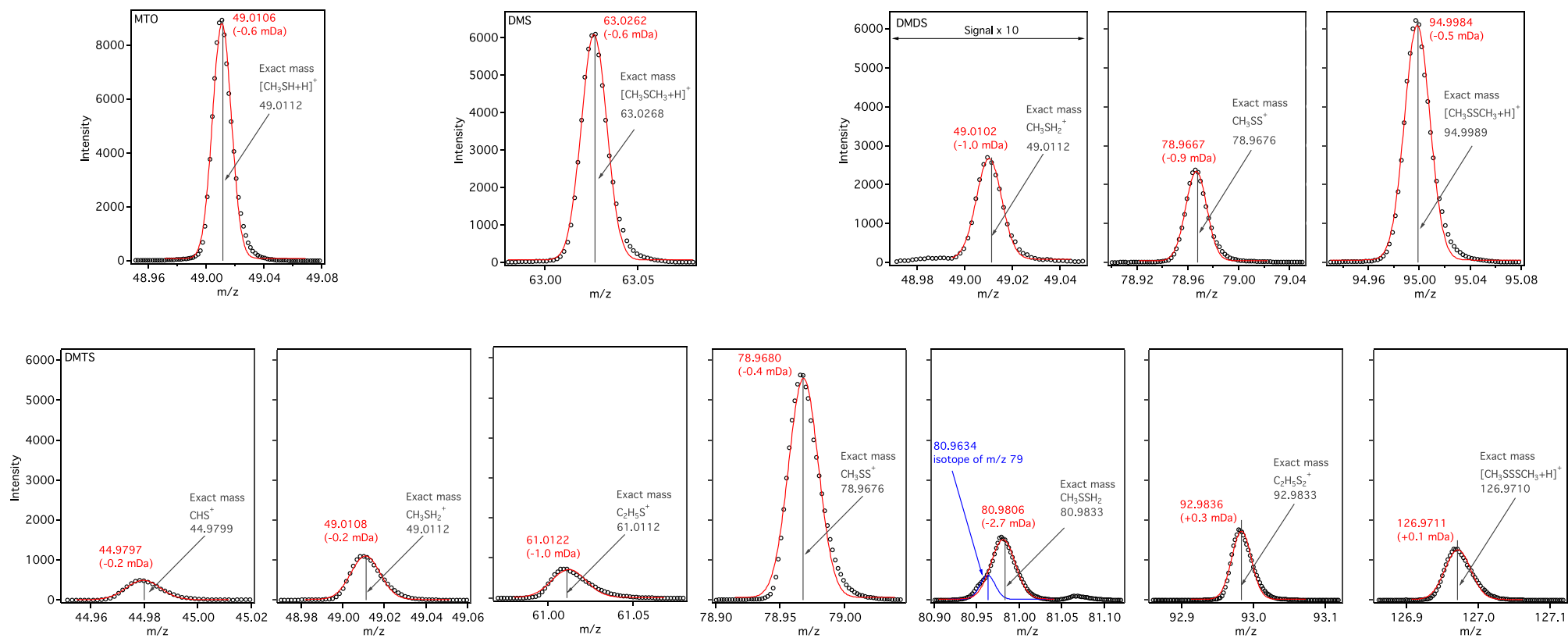


Figure S3. Fragmentation ratio observed for DMDS as a function of the electric field strength (E/N) values. Adapted from Schuhfried et al. (Schuhfried *et al.*, 2013)

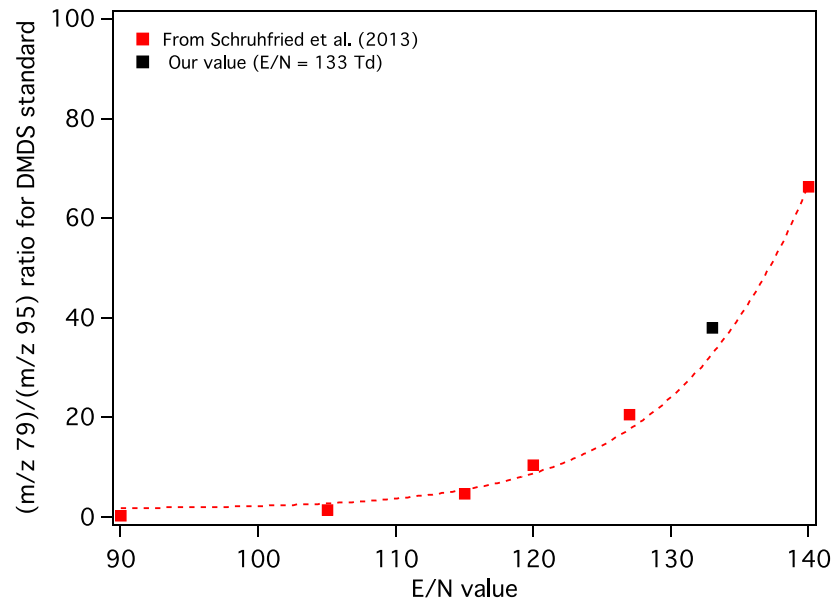


Figure S4. High-resolution mass spectra for DMTS nominal mass m/z 96:

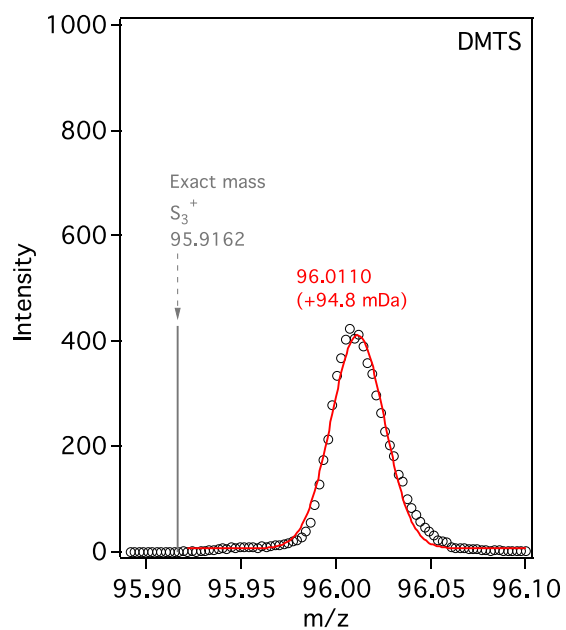


Figure S5. Calibration curves for DMS, DMDS, DMTS and MTO. The hydronium ion signal intensity was $2.4\text{-}2.9 \times 10^6$ counts per second for these measurements

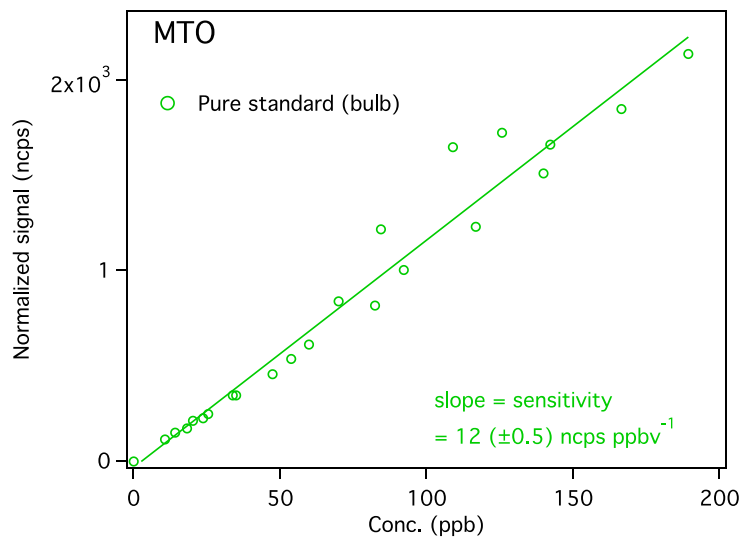
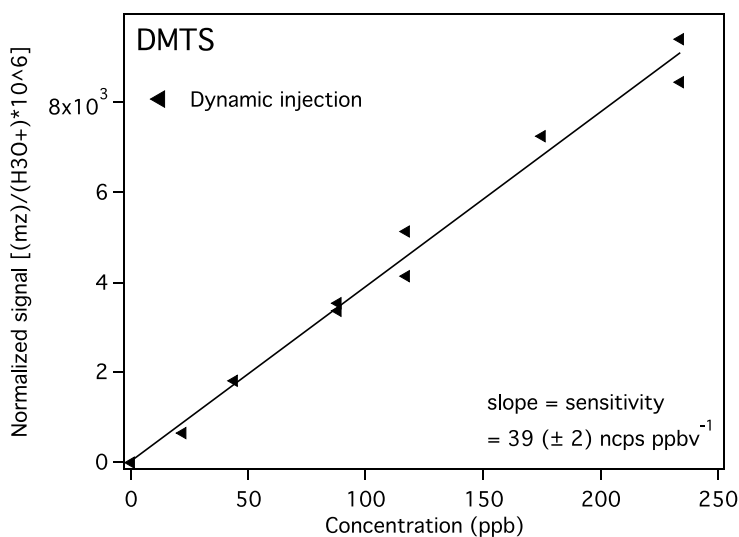
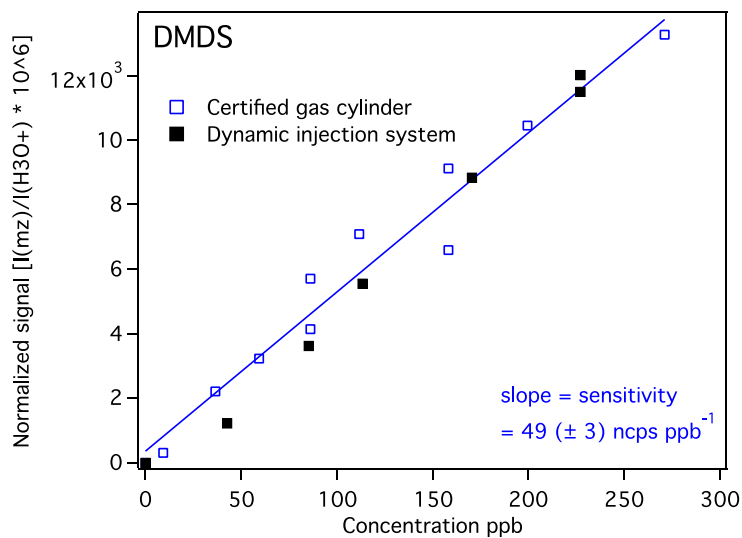
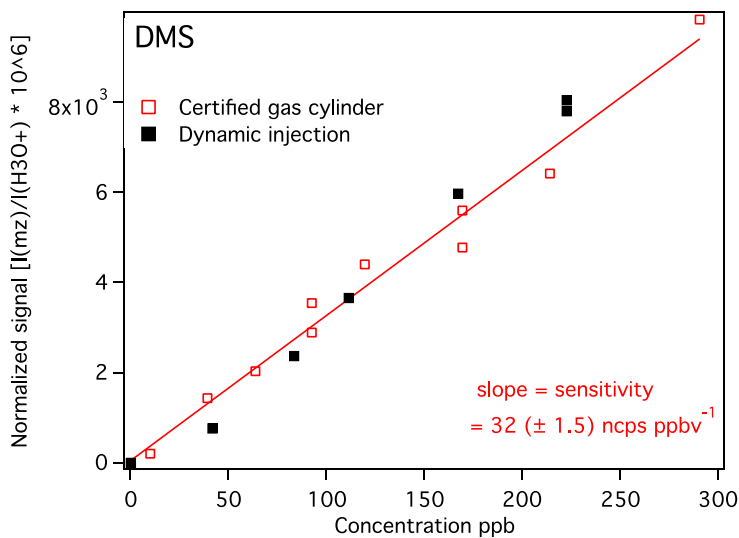


Figure S6. PTR-MS signal intensity profile acquired from a certified gas cylinder containing 4.03 ppm MTO standard in nitrogen. (a) Normalized signal intensity for mass m/z 49 - Loss of MTO on different surfaces including 20-cm long tubing made of stainless steel (ss), copper (Cu) or glass (all the connections were PTFE tubing and connectors). (b) The mixture was stored overnight in the regulator prior measurement to test the reactivity of CH_3SH on metal surface.

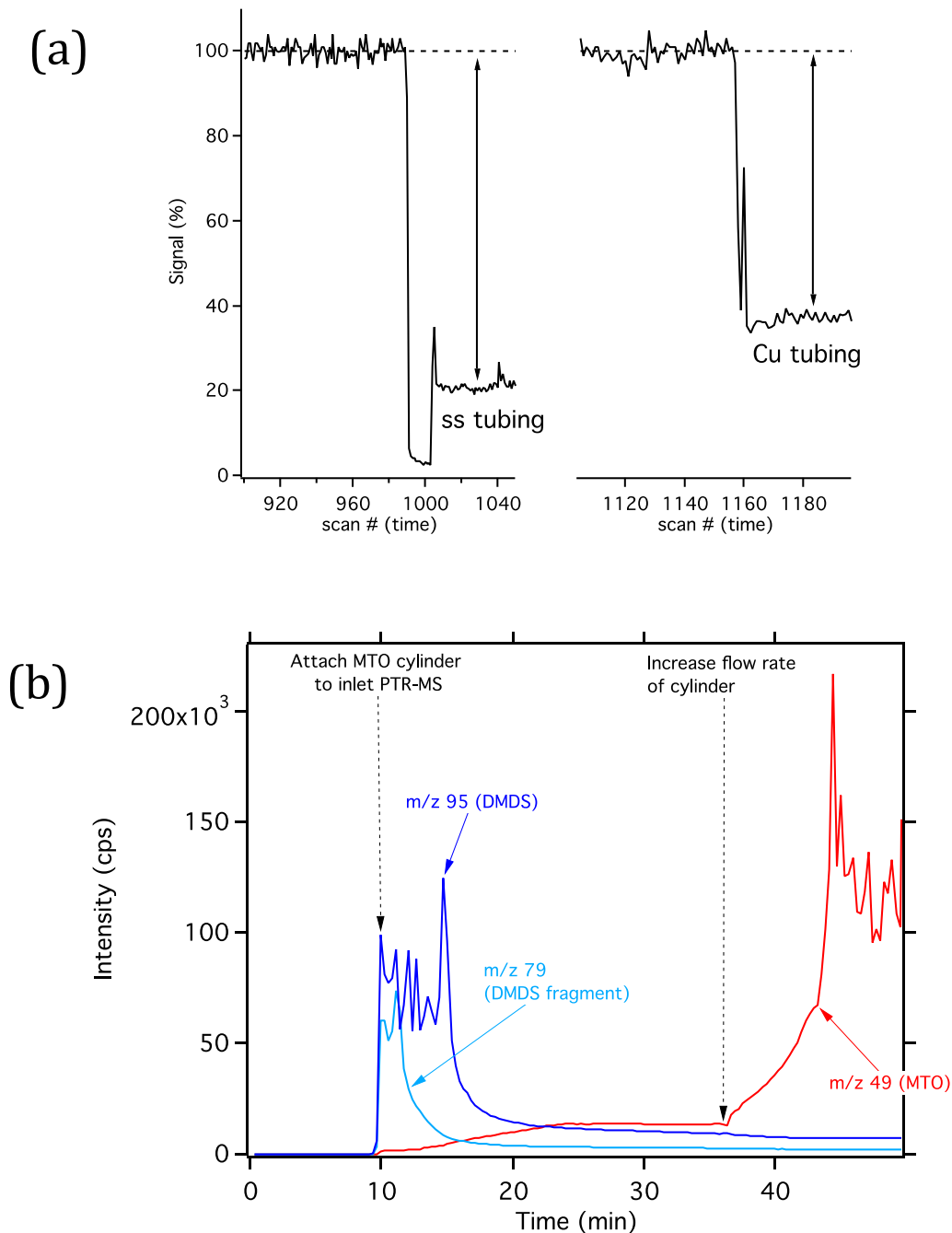
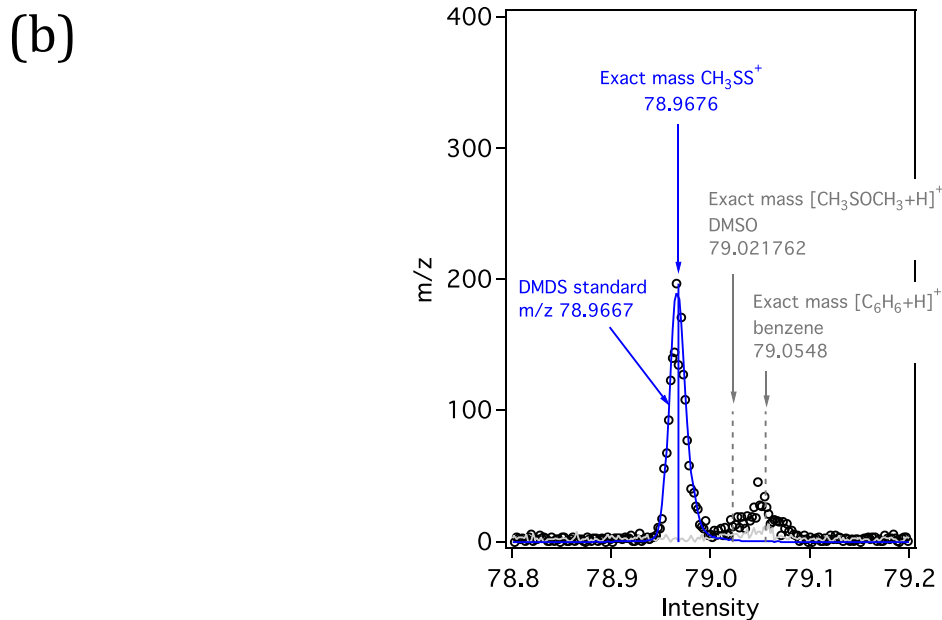
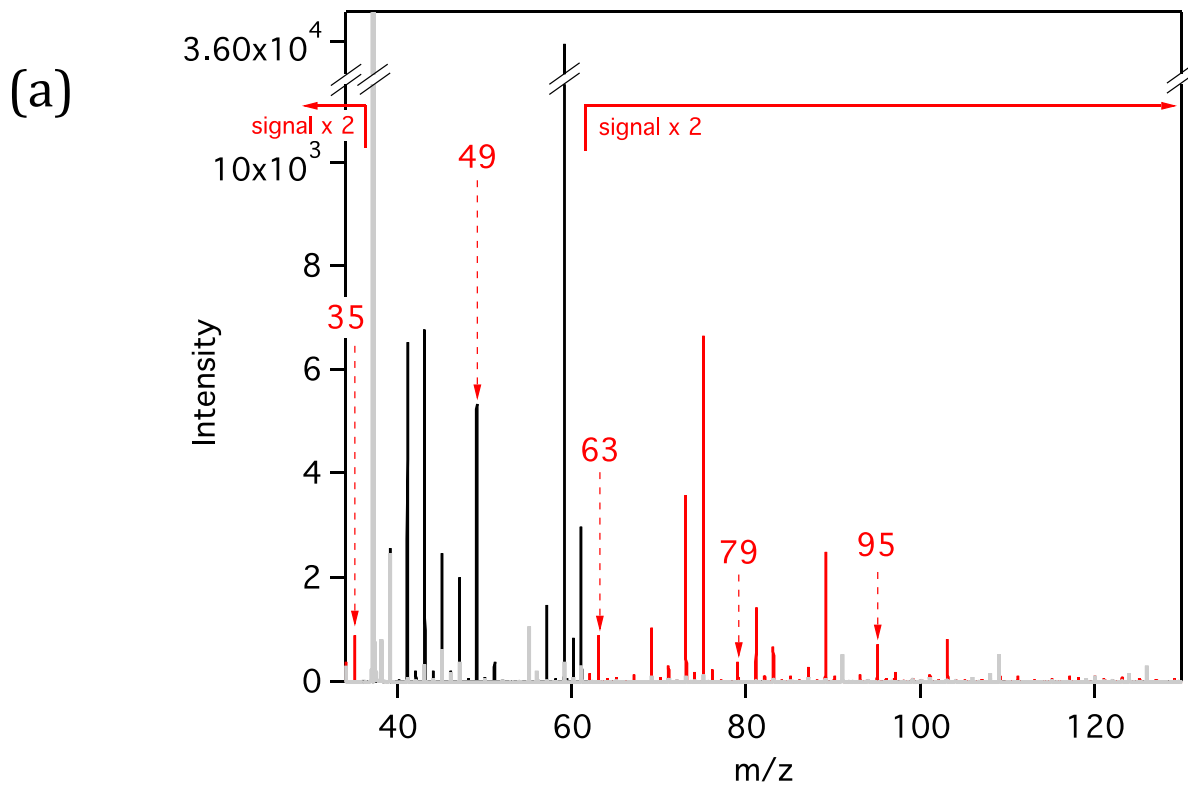


Figure S7. Representative PTR-MS mass spectrum from a bin sample. The red signal corresponds to the MS spectra intensity multiply by 2; the grey signal corresponds to a background MS spectra.



REFERENCES

- Jardine, K. J., Henderson, W. M., Huxman, T. E., and Abrell, L.: Dynamic Solution Injection: a new method for preparing pptv-ppbv standard atmospheres of volatile organic compounds, *Atmos Meas Tech*, 3, 1569-1576, 2010.
- Schuhfried, E., Probst, M., Limtrakul, J., Wannakao, S., Aprea, E., Cappellin, L., Mark, T. D., Gasperi, F., and Biasioli, F.: Sulfides: Chemical ionization induced fragmentation studied with proton transfer reaction mass spectrometry and density functional calculations, *J. Mass Spectrom.*, 48, 367-378, 2013.