

Chemical ionisation quadrupole mass spectrometer with an electrical discharge ion source for atmospheric trace gas measurement

Philipp G. Eger¹, Frank Helleis¹, Gerhard Schuster¹, Gavin J. Phillips^{1,2}, Jos Lelieveld¹ and John N. Crowley¹

5 ¹Atmospheric Chemistry Department, Max-Planck-Institut für Chemie, 55128 Mainz, Germany

²Department of Natural Sciences, University of Chester, CH2 4NU, UK

Correspondence to: John N. Crowley (john.crowley@mpic.de)

Supplement

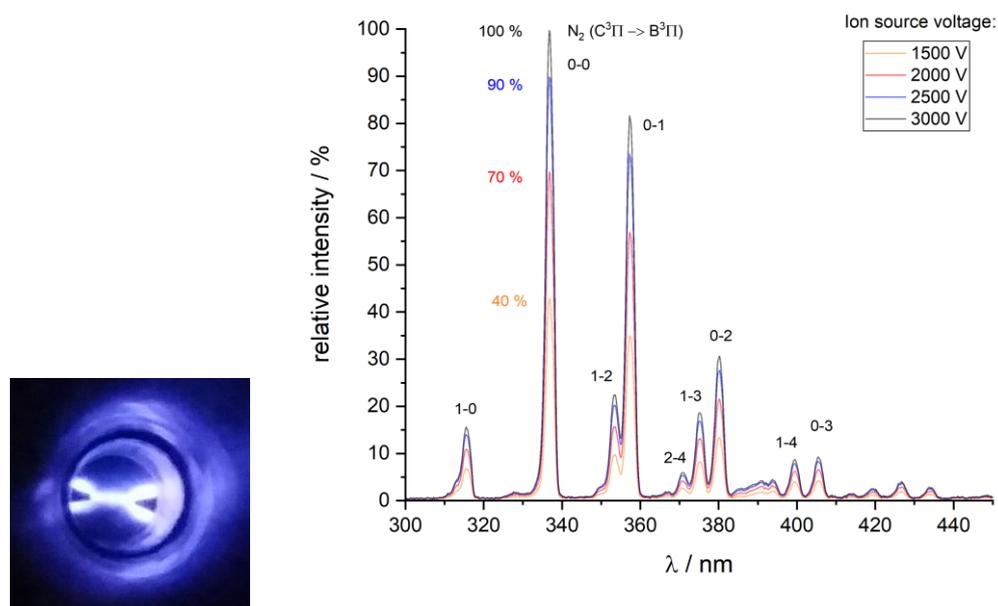


Figure S1. Photo: N₂ emission observed between and around the pointed tungsten tips of the electrodes of the RF discharge source. Right: The emission spectrum was recorded with an Ocean-Optics USB-4000 spectrometer with optical fibre at various high-voltages. The strongest features (not fully resolved using the low-resolution ($\Delta\lambda \approx 1.5$ nm) spectrograph) can be assigned to transitions from the ground vibrational level of the electronically excited N₂ (C³Π_u) state to the B³Π_g state.

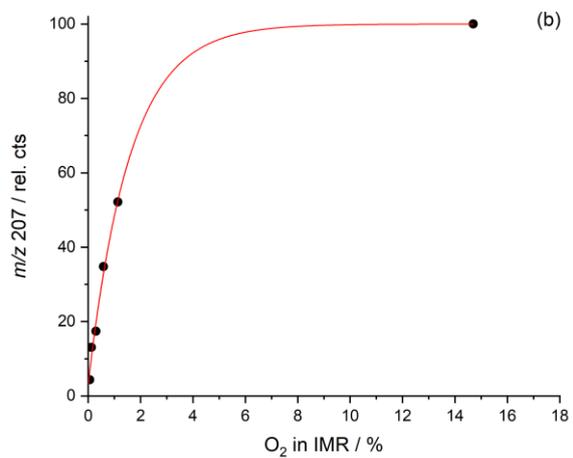
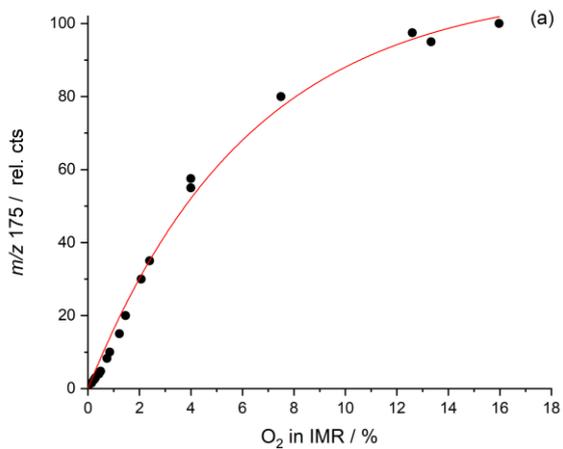


Figure S2. (a): Dependence of IO_3^- signal (m/z 175) on the fractional pressure of O_2 in the IMR when adding 800 sccm N_2 / CH_3I through the RF discharge region. (b): Signal at m/z 207 (ISO_3^-) for a constant amount of SO_2 over the same range of O_2 partial pressures.

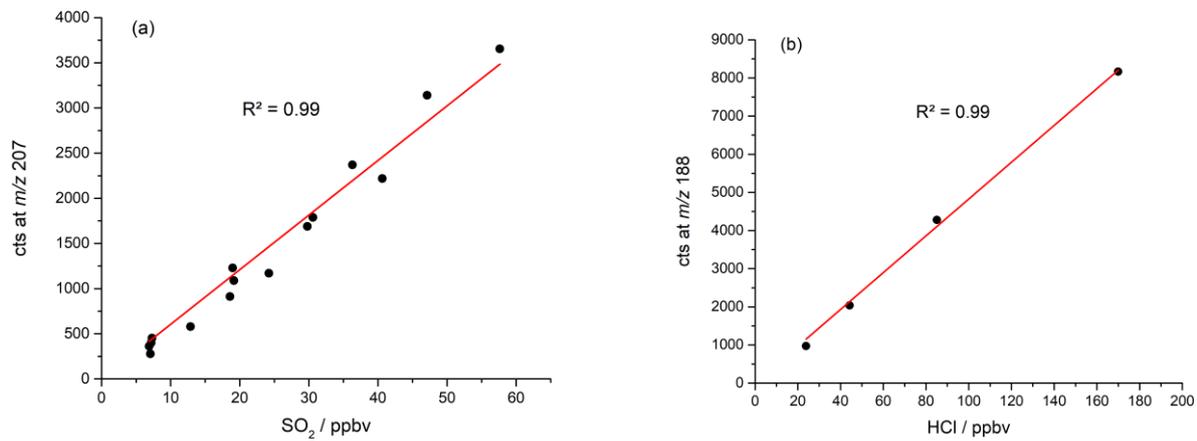


Figure S3. (a) Linear dependence of count rate at m/z 207 (ISO₃⁻) on the SO₂ mixing ratio of the sample measured. (b) Linear dependence of count rate at m/z 188 (I(CN)Cl⁻) on the HCl mixing ratio.

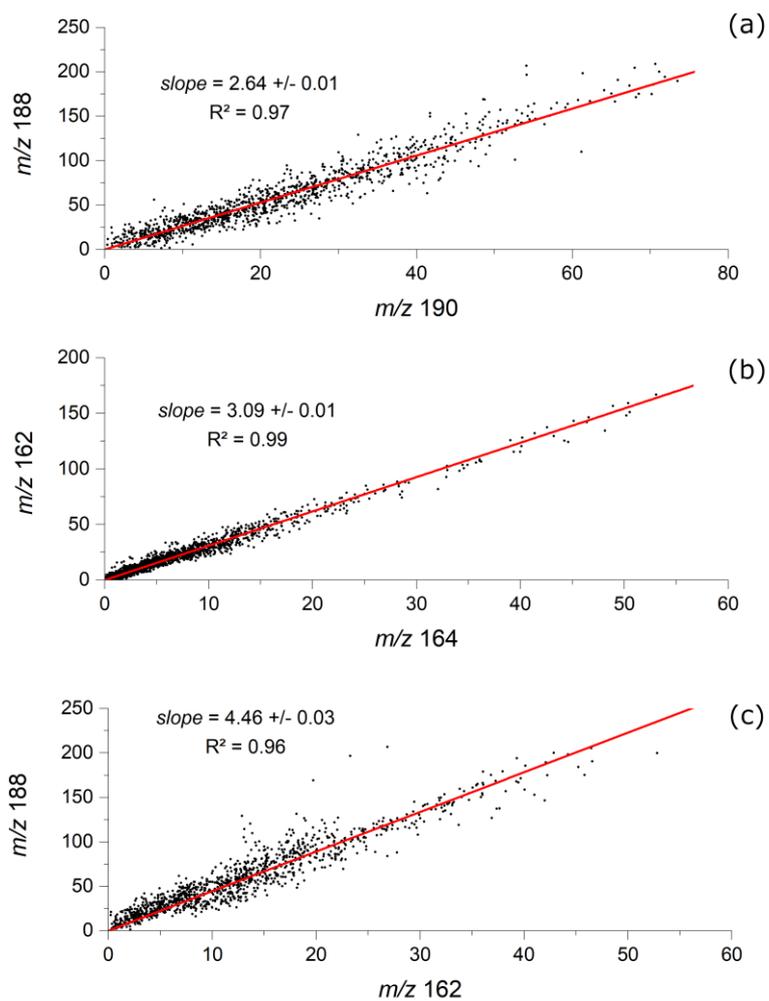
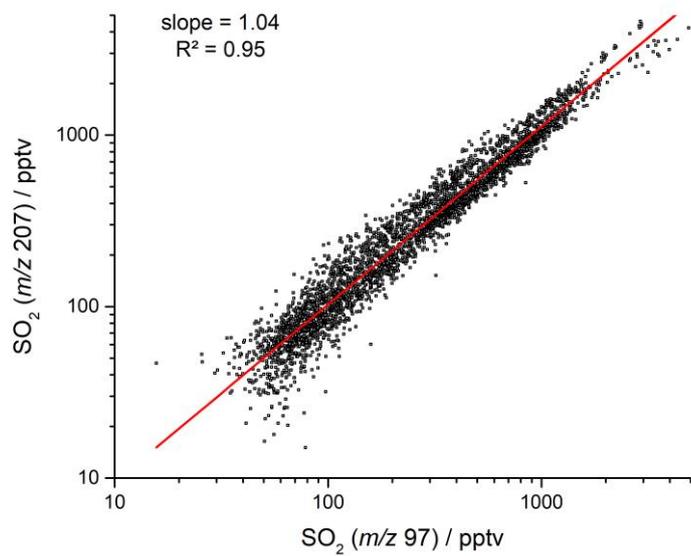


Figure S4. (a) and (b): Correlation of ion signals at m/z 162 versus m/z 164 (ICl^-) and m/z 188 versus m/z 190 (I(CN)Cl^-) during CYPHEX. The expected slope resulting from the isotopic abundance of ^{35}Cl to ^{37}Cl is 3.13. (c) Signal at m/z 188 versus m/z 162. The linear correlation indicates that both ions are from the same trace gas, HCl.



5 **Figure S5:** Correlation between the CI-QMS measurement of SO₂ at *m/z* 207 (ISO₃⁻) vs. *m/z* 97 (HSO₄⁻) during NOTOMO.

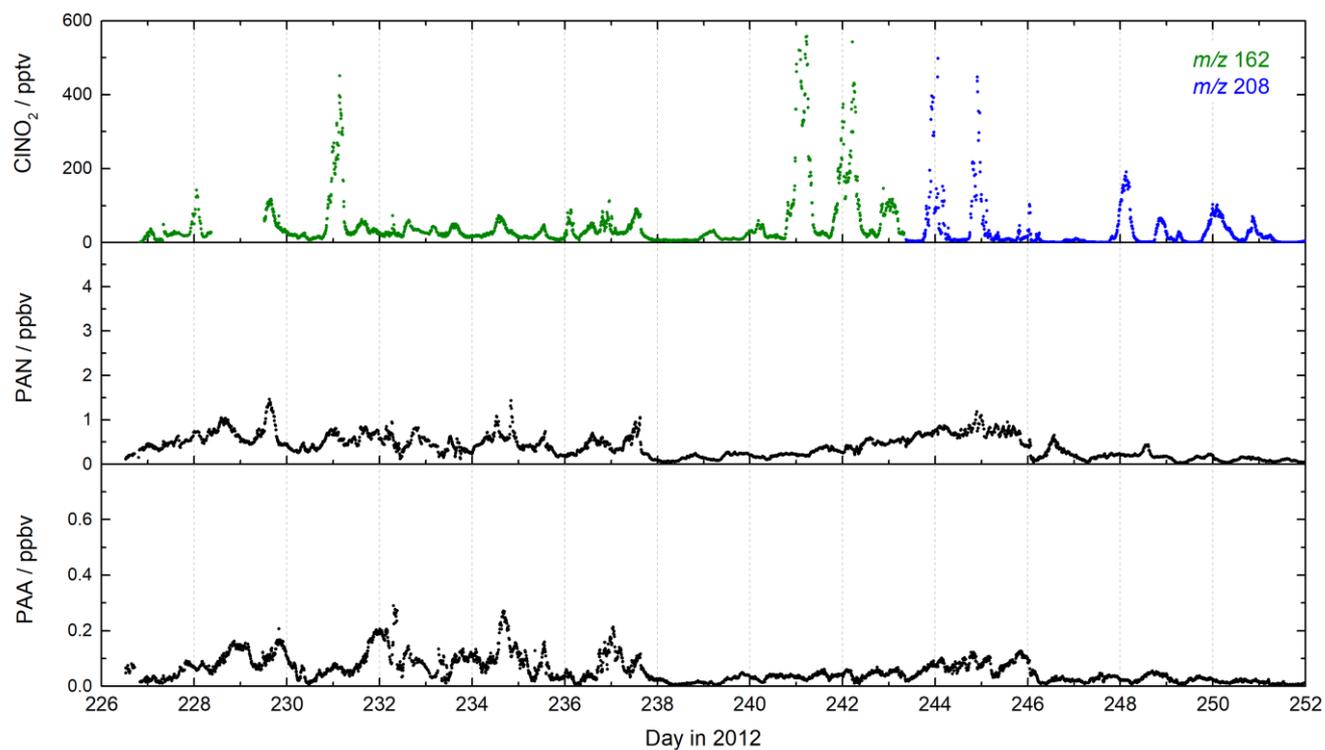


Figure S6: Measurements of ClNO₂, PAN and PAA using CI-QMS with a ²¹⁰Po-ionisation source during the PARADE campaign, which took place at the same location and similar time of year as the NOTOMO campaign in which the RF discharge was deployed. The ClNO₂ data during PARADE has been reported by Phillips et al. (2012).