A versatile Chemical Ionization Mass Spectrometer for Stratospheric Research

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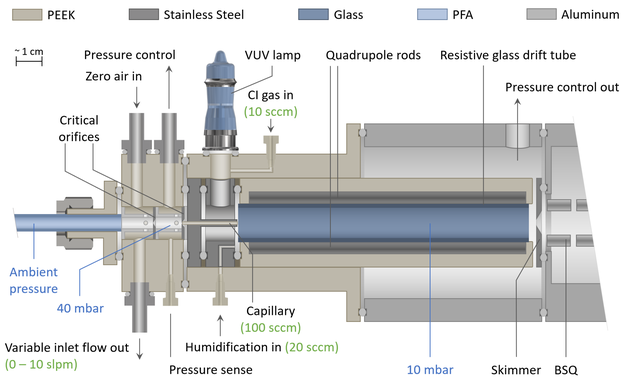
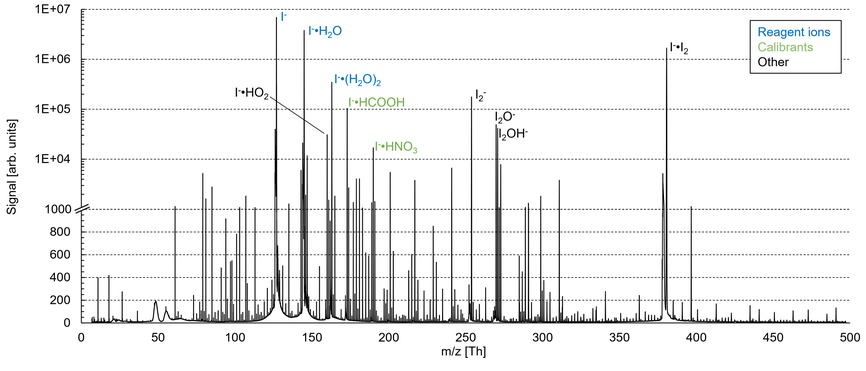
Instrument description

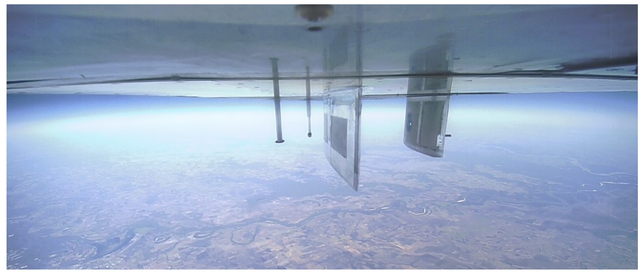
- Based on a Vocus CI-TOF (Aerodyne Research Inc.): The ion-molecule-reactor (IMR) consists of a resistive glass drift tube surrounded by a focusing quadrupole ion guide. The drift tube voltage gradient provides as a constant electric field along its axis and allows for controlling the reagent ion cluster distribution.
- A new ion source replaces the original Vocus glow discharge ion source. Two VUV lamps produce photons, which photo-ionize molecules with ionization energies below 10.6 eV.
- The choice of gases supplied to the ion source determines the reagent ion produced, e.g., methyl iodide (CH_3I) in nitrogen for producing iodide anions (I^-).

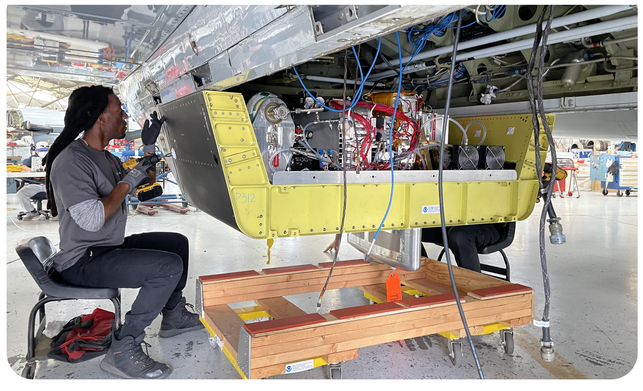


- For operation in the stratosphere onboard a high-altitude research aircraft, a two-stage pressure controlled inlet is used: Sample air enters through two consecutive critical orifices; the pressure between the two orifices is kept constant at approx. 40 mbar at altitudes between 3 and 20 km.
- Pure water vapor is directly supplied to the drift tube through a dedicated port to reduce the dependency of sensitivities due to changes in ambient humidity.
- Fully automated start-up on the ground and operation at temperatures down to 190K and ambient pressures as low as 50 mbar.

Iodide Mass Spectrum







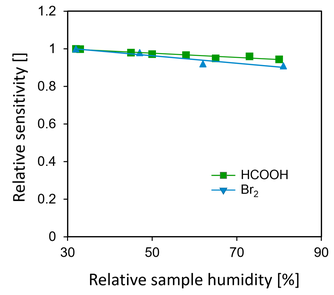
Sensitivities & Limits of Detection

- Sensitivities of up to 70 cps ppt^{-1} are achieved (for nitric acid).

Sensitivities and detection limits (for a sample interval of 10s, 3 standard deviations) for formic acid, nitric acid, bromine, chlorine and chlorine nitrite in iodide mode.

Species	Chemical formula	Sensitivity (cps/ppt)	Background (cps)	Background	Limit of detection 10 s, 3σ, (ppt)
Formic acid	HCOOH	23	$7.9 \cdot 10^5$	34 ppb	51
Nitric acid	HNO_3	76	$5.9 \cdot 10^4$	780 ppt	4.3
Bromine	Br_2	35	220	6 ppt	0.6
Chlorine	Cl_2	8.9	18	2 ppt	0.7
nitryl chloride	$ClNO_2$	9	72	8 ppt	1.3

- Humidity dependency of sensitivities – Added pure water vapor reduces ambient sample humidity dependency:



Versatility

- VUV lamps ionize molecules with an ionization energy < 10.6 eV
- The choice of CI gas determines reagent ion species:
  - Methyl iodide (CH_3I) → I^-
  - Ammonia (NH_3) → NH_4^+
  - Benzene (C_6H_6) → $C_6H_6^+$
- Benzene cations for select biogenic organics (e.g., DMS, Isoprene, Monoterpenes)