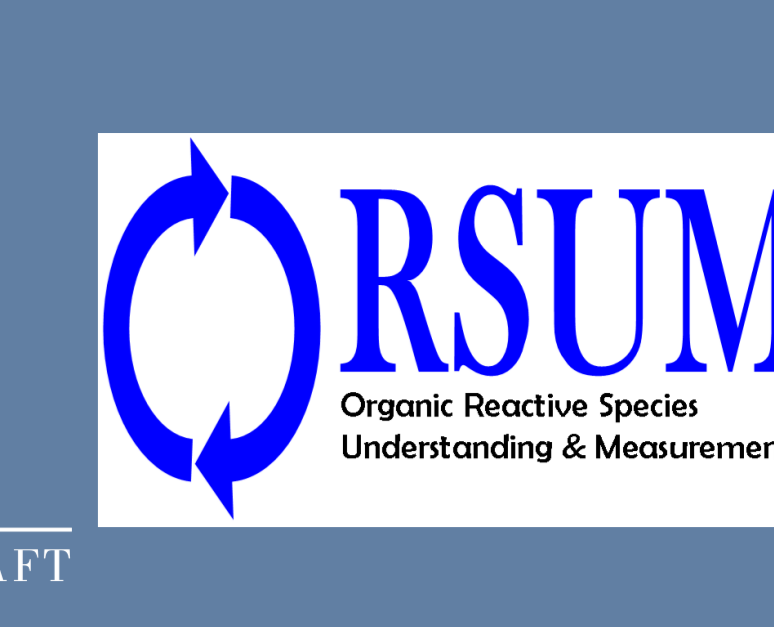
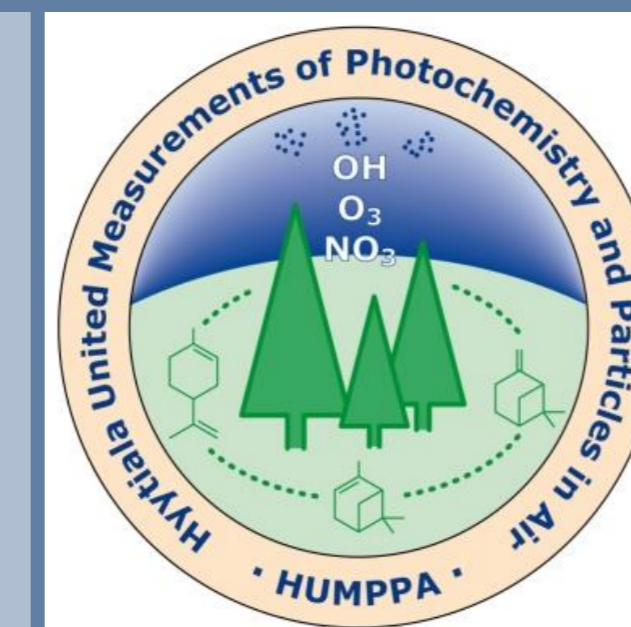


A new method for total OH reactivity measurements using a fast Gas Chromatographic Photo-Ionization Detector (GC-PID)

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History of total OH reactivity instruments

The hydroxyl radical (OH) is the most effective oxidant in the atmosphere. The highly reactive OH is thought to act as cleaning agent, initiating the photochemical removal of chemicals from the atmosphere. The total OH reactivity is the total loss rate of OH due to all atmospheric reactive species. These atmospheric sinks of OH are currently poorly constrained and focus of many intensive field observations. Different techniques have developed to measure total OH reactivity directly. All available techniques are large, complex and expensive.

Pump-and-probe LIF

Artificially high OH is produced by a flash photolysis beam and the OH decay due to OH reactive compounds is detected by Laser induced fluorescence (LIF). Within a time resolution of **30-180 s** the uncertainty is **10-12 %** and the detection limit **1-2 s⁻¹**.

1999 Calpini et al

(2001 Jeanneret et al; 2004 Sadanaga et al; 2010 Lou et al)

Discharge flow tube LIF

High OH levels are generated using a mercury UV lamp, induced with a movable inlet into a flow tube and detected by LIF. Different inlet positions lead to different reaction times of OH with ambient reactive molecules. Within the uncertainty of **16-25 %** the detection limit is **1 s⁻¹** for averaging times of **210 s**.

2001 Kovacs and Brune

(2009 Mao et al)

Comparative Reactivity Method (CRM)

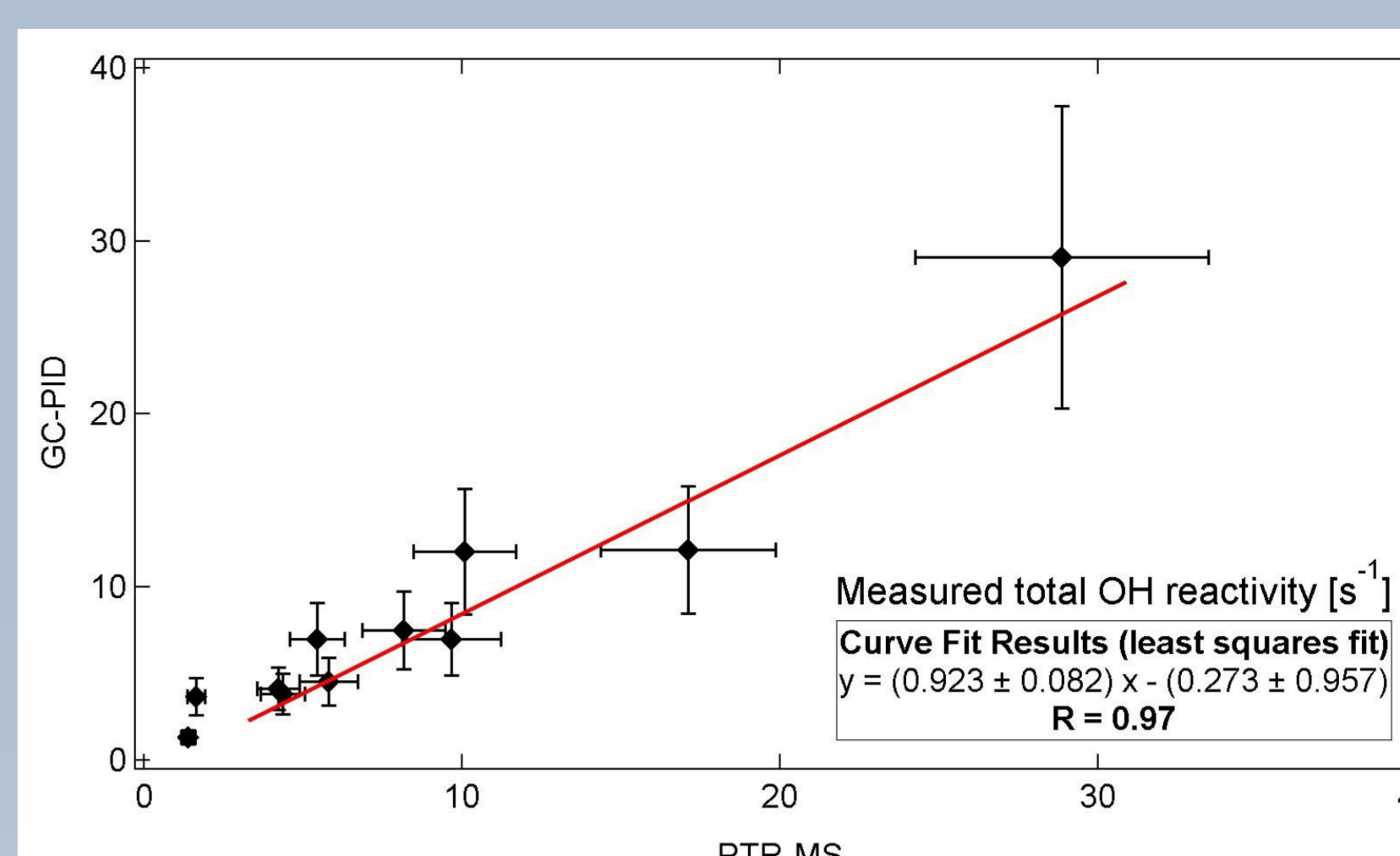
The competitive reaction of a reagent which is not present in ambient air with OH alone and in the presence of atmospheric reactive molecules is monitored using a Proton Transfer Reaction Mass Spectrometer (PTR-MS). The total OH reactivity can be measured down to **3-4 s⁻¹** within the uncertainty of **16-20 %** and a time resolution of **10-60 s**.

2008 Sinha et al

(2012 Sinha et al; 2012 Nölscher et al)

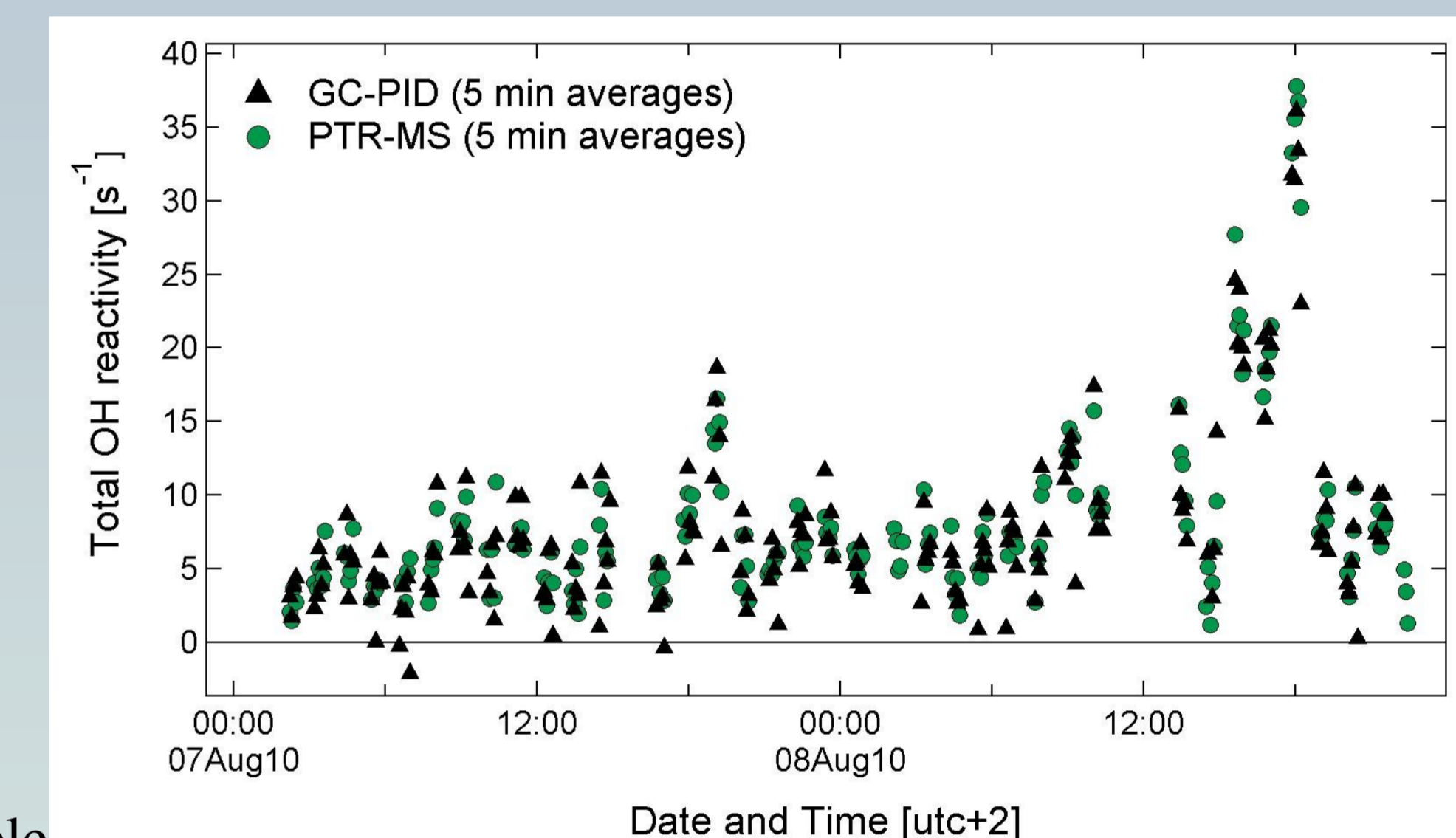
This study presents a small, portable, less power consuming and less expensive alternative method for total OH reactivity measurements.

The HUMPPA-COPEC 2010 field campaign



To verify the reliability of the two detectors for CRM total OH reactivity measurements, standard tests are conducted. Excellent agreement for PTR-MS and GC-PID was found for known propane and propene mixtures in a range of 2-30 s⁻¹. The linear least squares fit and the Pearson R show good correlation.

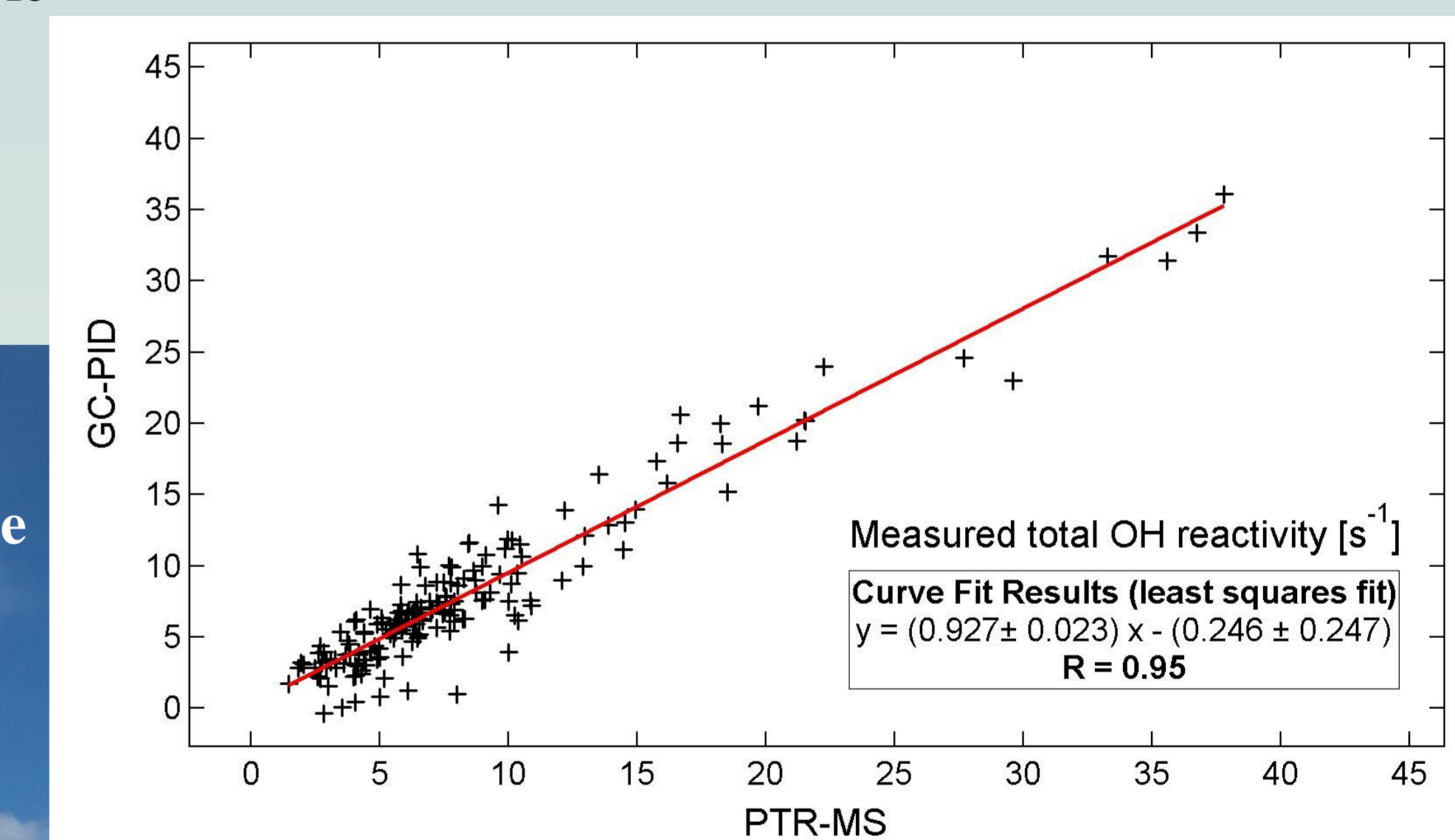
Direct total OH reactivity measurements within the summertime boreal forest canopy during HUMPPA-COPEC 2010 provided the opportunity for first intensive field tests of the GC-PID. Both detectors were operated in parallel for CRM, the data was analyzed and averaged to 5 minutes. PTR-MS (green) and GC-PID (black) show good agreement in a total OH reactivity range from the limit of detection to 40 s⁻¹.



Generally PTR-MS and GC-PID show excellent correlation for the boreal forest field observations.

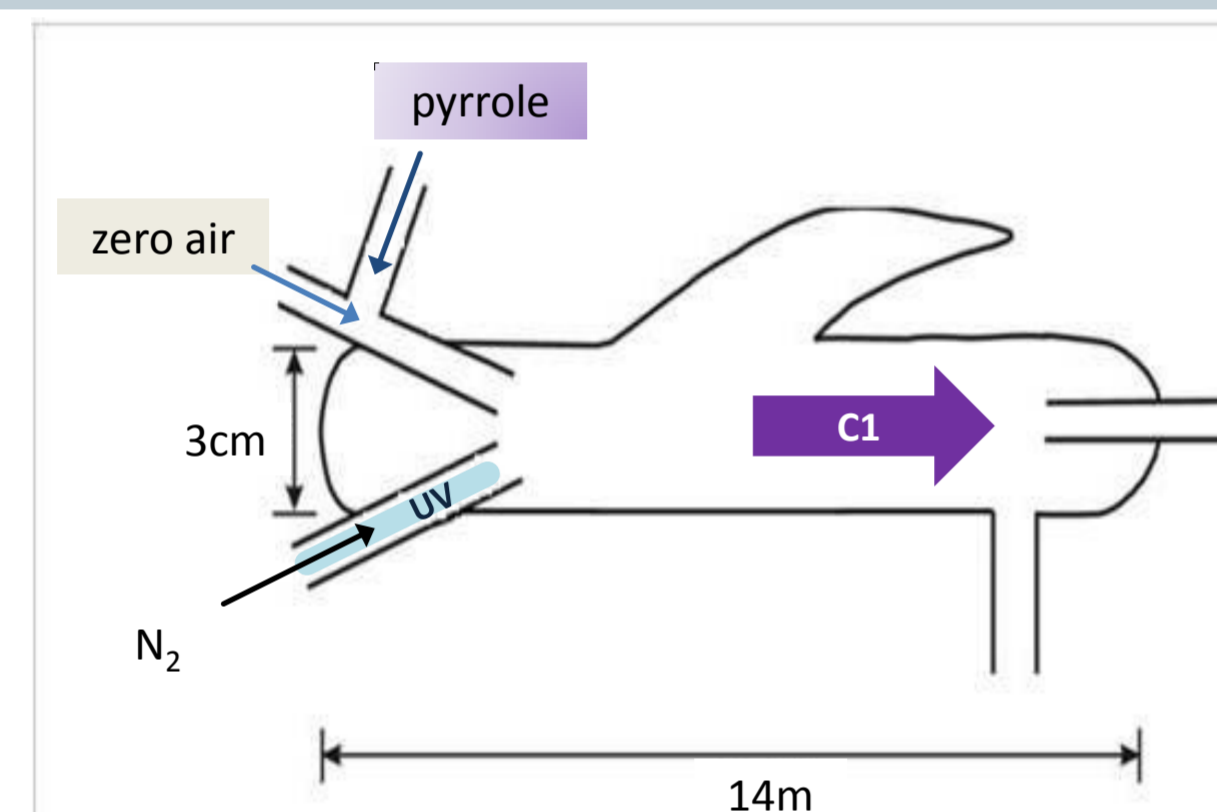
Both instruments were able to detect total OH reactivity using CRM and operated in comparable time resolution, detection limit, and sensitivity.

The new method offers a robust, portable, and less expensive alternative for total OH reactivity measurements in unpolluted environments.

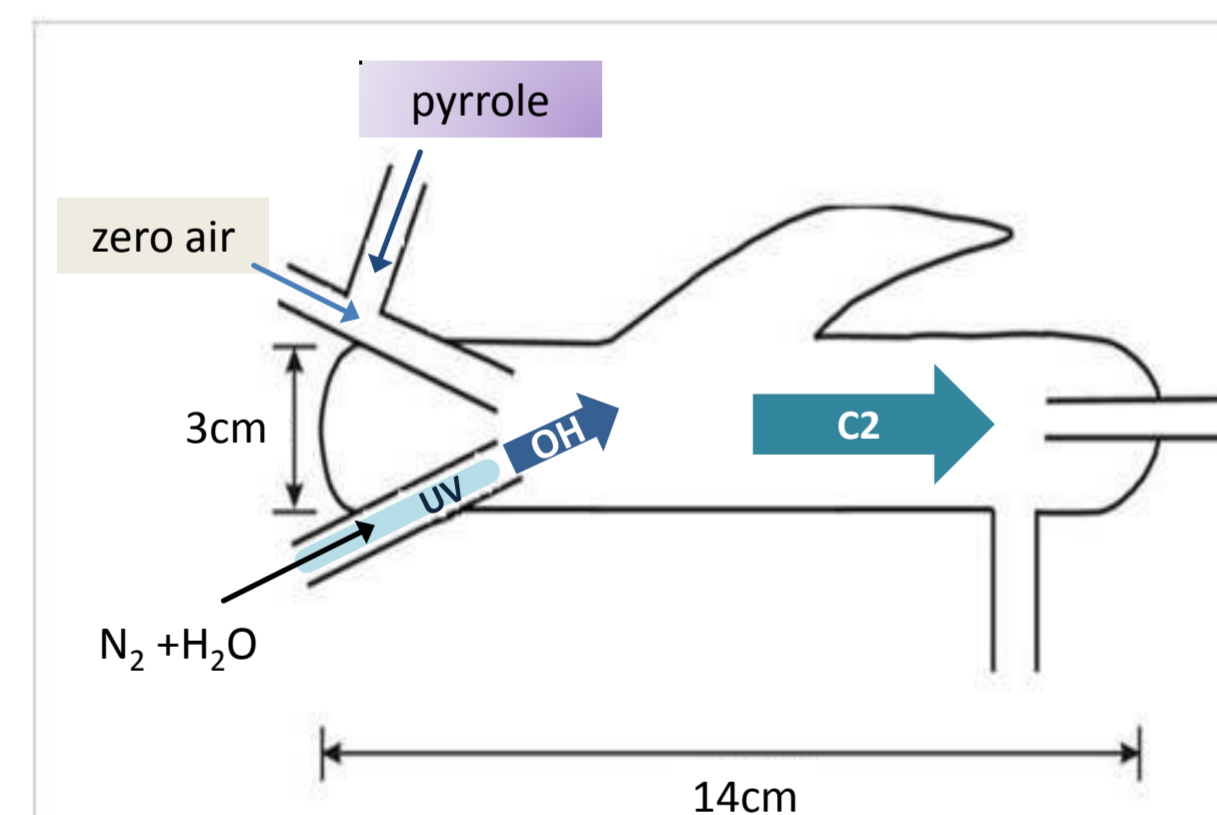


PTR-MS and GC-PID comparison for CRM total OH reactivity measurements

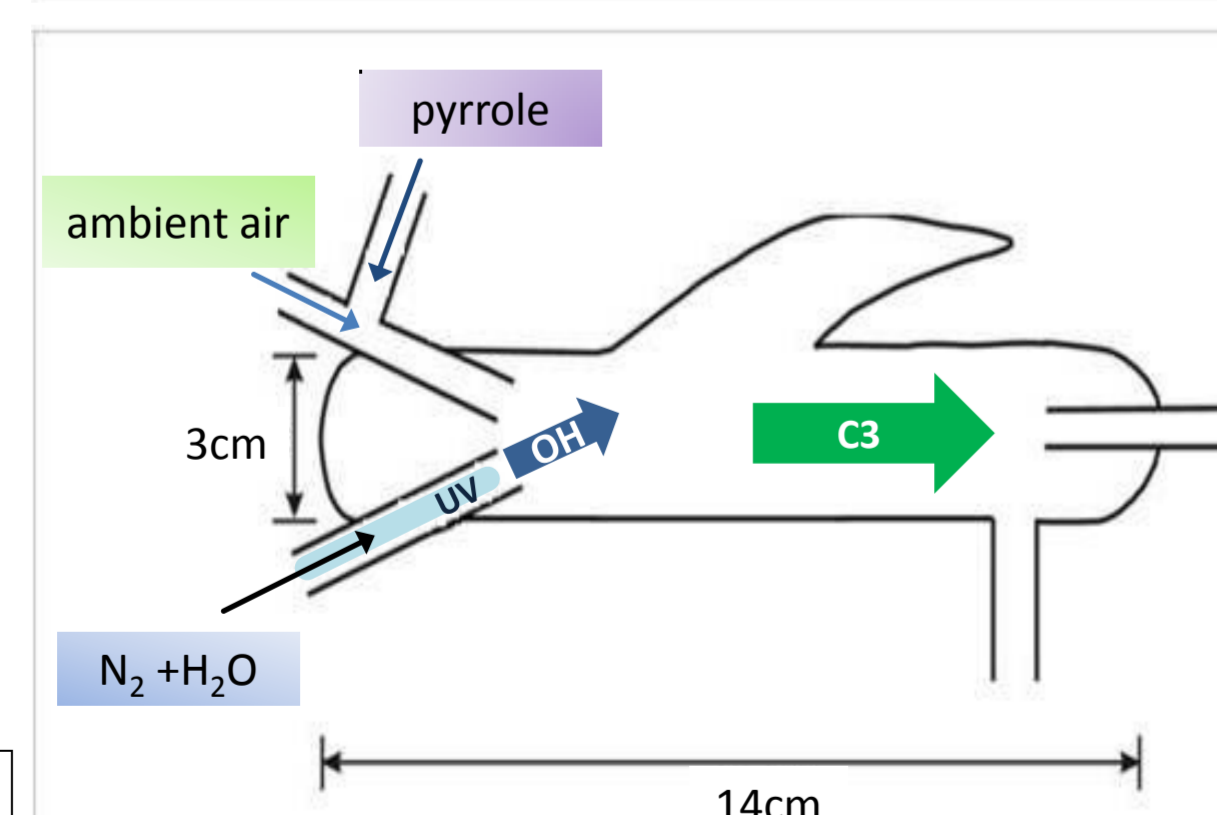
The reactive molecule (pyrrole (C₄H₅N)) is introduced into a Teflon coated glass reactor, diluted with zero air and quantified with a suitable detector - (C1).



Next, OH radicals are generated, enter the glass reactor and react with pyrrole. According to the amount of OH the observed pyrrole signal decreases to a new level - (C2).



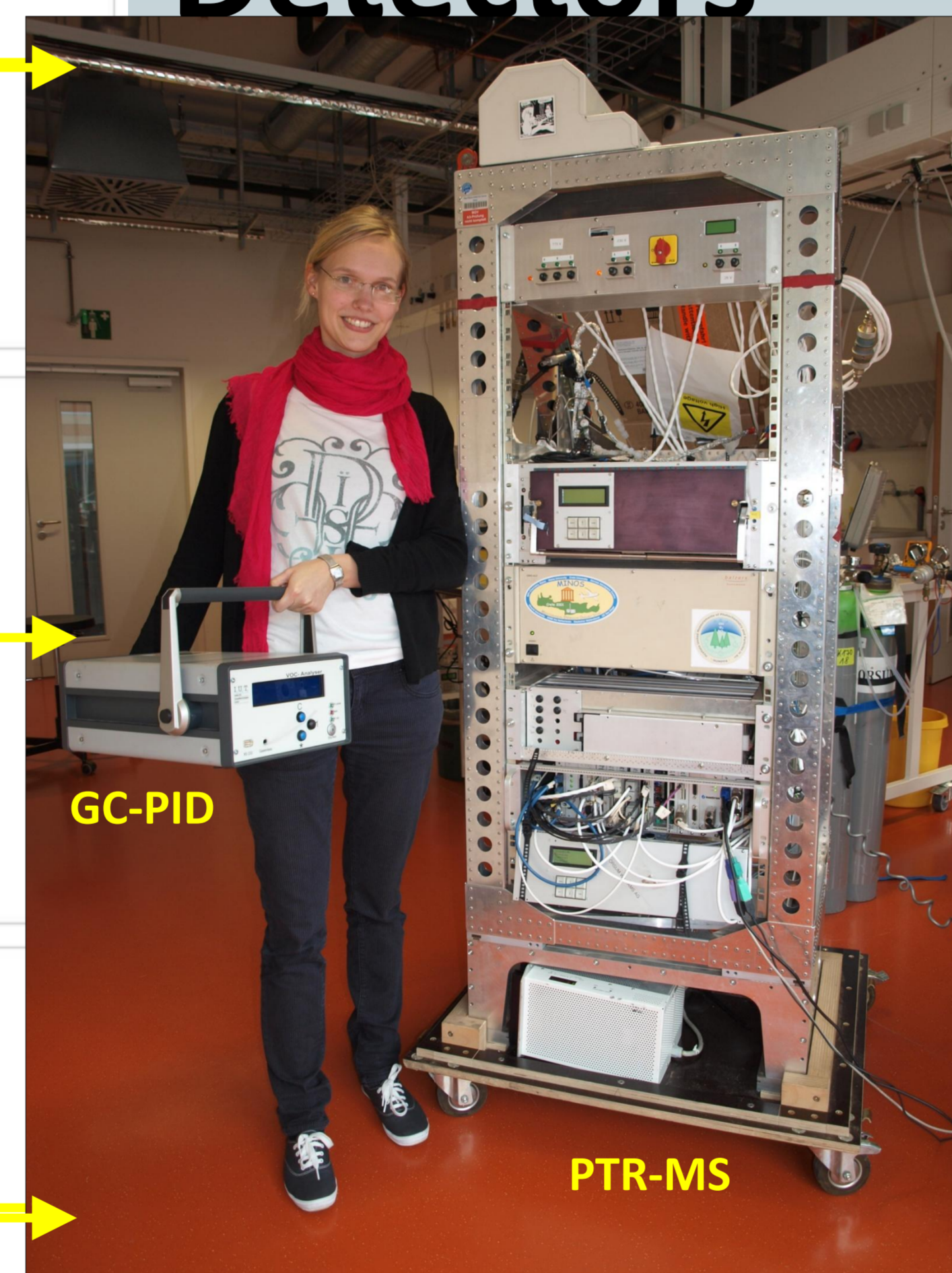
By exchanging the zero air with ambient air, other OH reactive molecules enter the reactor and compete with pyrrole-molecules for OH. The pyrrole signal increases - (C3).



$$\Rightarrow R_{total} = C1 \cdot k_{OH+Pyr} \cdot \frac{C3 - C2}{C1 - C3}$$

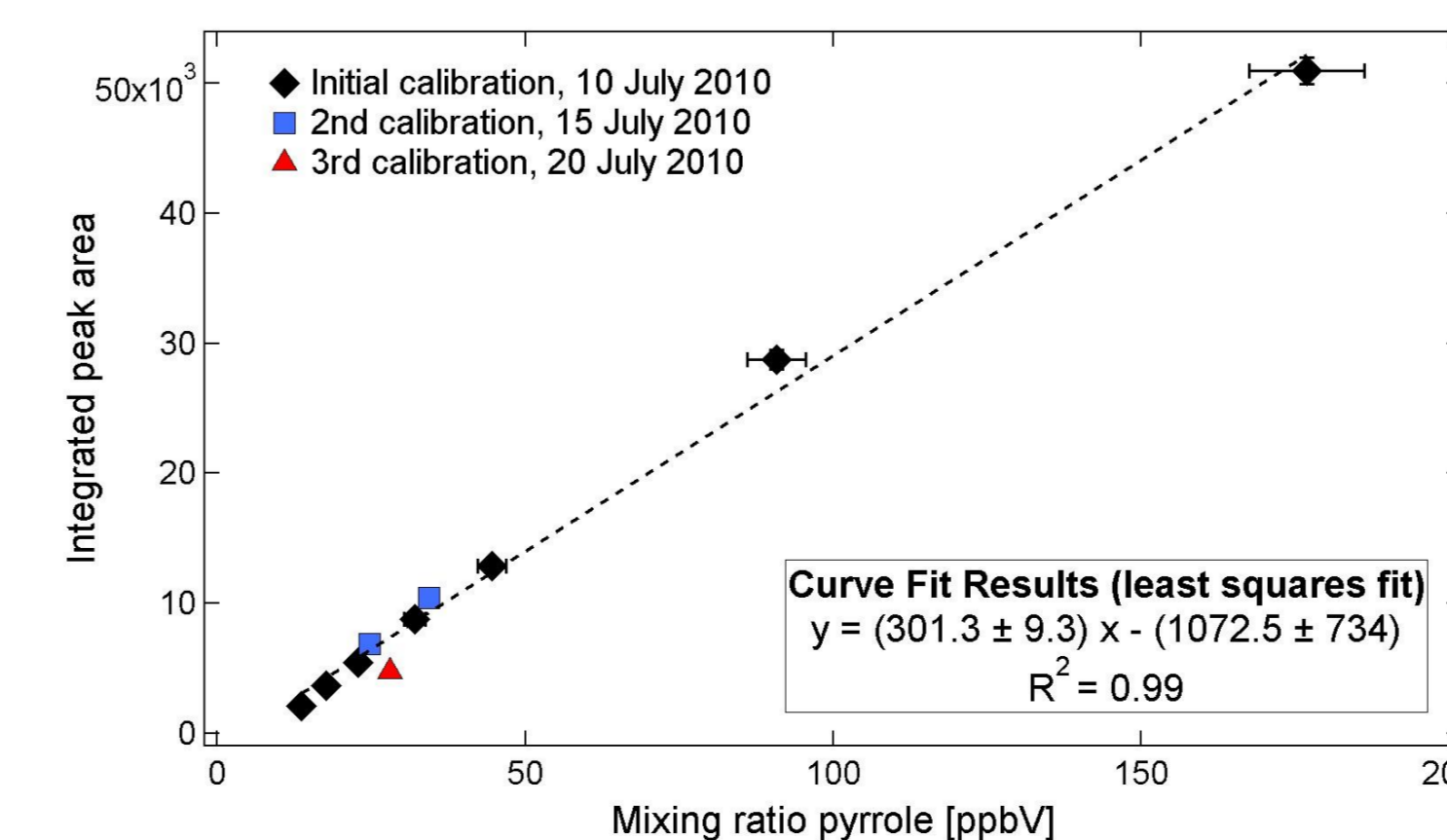
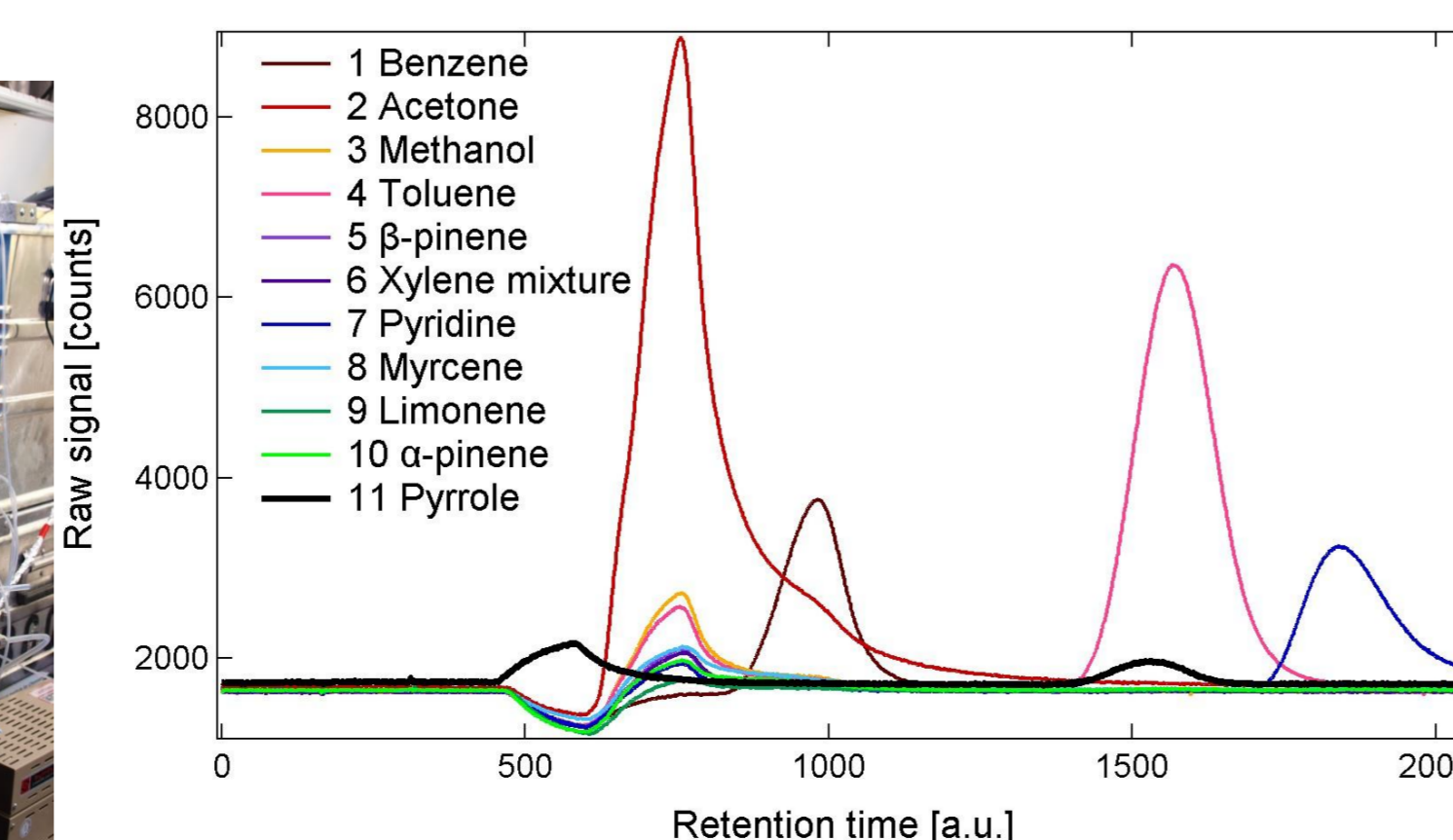
Sinha et al 2008

Detectors



	PTR-MS	GC-PID
Measurement principle	PTR-MS (IONICON) is a fast and precise technique to detect selectively gas molecules with higher proton affinity than water. Proton transfer ionizes the molecules of interest before they are accelerated in a drift tube, separated by a quadrupole mass spectrometer and detected.	The custom-build GC-PID (VOC-Analyzer from Environics-IUT GmbH) generates a chromatogram by drawing an air probe through a short column and ionizing it via UV light before detecting. The concentration of the detected compound can be derived from the integrated peak area.
Size	650 x 1660 x 550 mm	260 x 160 x 400 mm
Weight	150 kg	8 kg
Power	max.. 1500 W	max. 50 W (+internal battery for ca. 12 hrs)
Inlet flow	30-300 sccm	50-250 sccm
Interference/Challenges	humidity changes sensitivity	humidity, toluene interference
Cost	ca. 180 k€	ca. 18 k€
Limit of detection	3-4 s ⁻¹	3-6 s ⁻¹
Uncertainty	16-20 %	25-46 %
Stability	stable over several weeks	decreasing after several weeks
Time resolution - raw	10-60 s	60 -70 s
Time resolution - ave	1-5 min	5-20 min

Pyrrole is detected after 45-55 s retention time (1300-2000 a.u.). Apart from pyrrole many other compounds are in principle detectable by the GC-PID, of which toluene overlaps with the pyrrole retention time window and is therefore a potential interference candidate for ambient observations. Calibrations for pyrrole show good linearity, but decreasing sensitivity with time.



A detailed comparison of the two detection techniques for CRM total OH reactivity measurements is presented in a manuscript which has been submitted to AMT.

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