



# Proton transfer induced analyses for VOC measurements

Nora Zannoni, CNR ISAC

[nora.zannoni@cnr.it](mailto:nora.zannoni@cnr.it)

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3.1: "Fund for the realisation of an integrated system of research and innovation infrastructures"



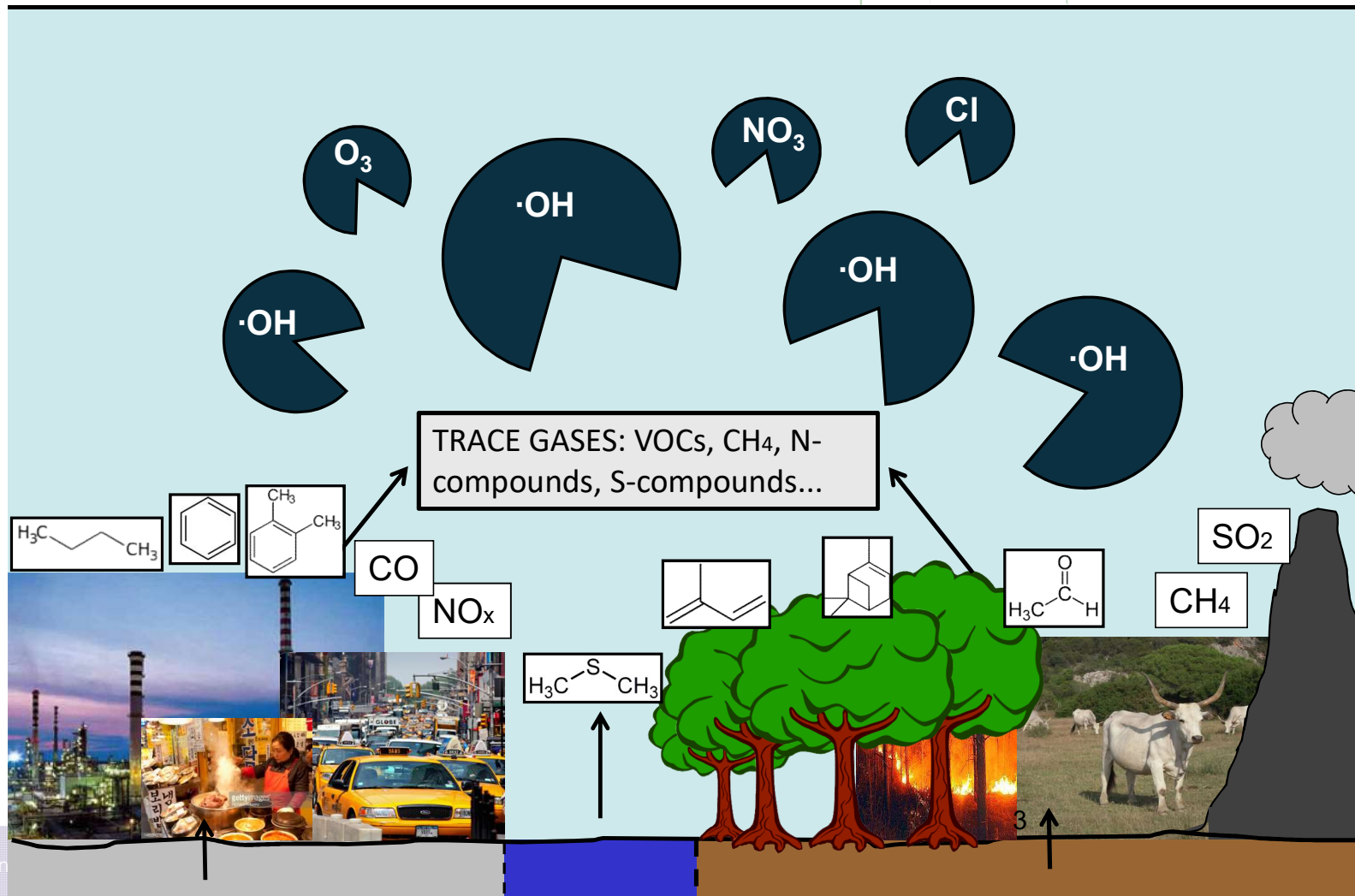
# Reactive trace gases in the troposphere

Gas	% of dry air
Nitrogen, Oxygen, Argon	99.9*
Carbon dioxide CO <sub>2</sub>	420 ppm
Methane CH <sub>4</sub>	1.9 ppm
Ozone O <sub>3</sub>	~0.01 ppm**
Volatile Organic Compounds VOC	~0.005 ppm
Halogenated compounds	~0.002 ppm

< 0.1%  
important

\*1%=10000 ppm \*\*in the troposphere

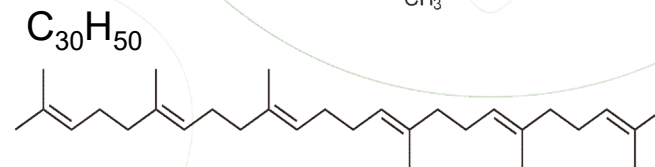
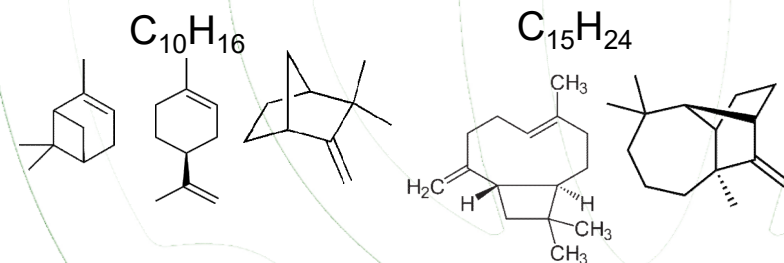
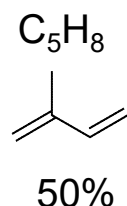
# Sources and sinks



# Volatile Organic Compounds



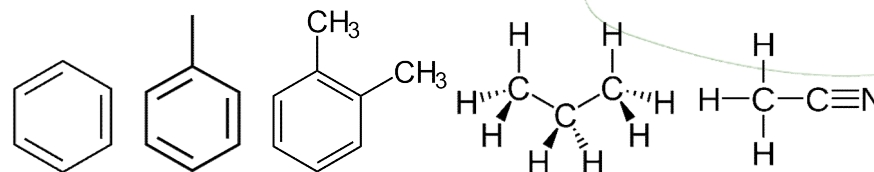
Biogenic VOCs ≈  
90% VOCs ~760  
TgC/y



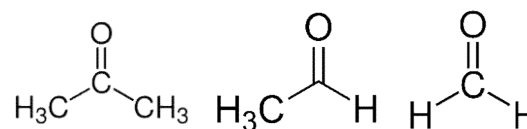
≈  $10^4$ - $10^5$  chemical species

Goldstein and Galbally, ES&T 2007

Anthropogenic VOCs ≈  
10% VOCs

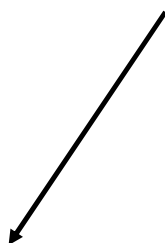


Oxygenated VOCs  
both origins

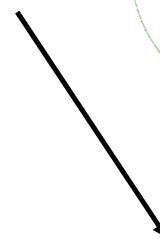


## Challenges for quantifying VOCs

- Low concentrations need sensitive instruments
- Very reactive chemical species prone to artifacts
- Myriad of compounds in air samples (separation)
- Field sampling more challenges



**Bottom up:  
mass spectrometry  
(PTR-MS, GC-MS..)**



**Top down:  
total OH reactivity**

## PTR-MS basic principles

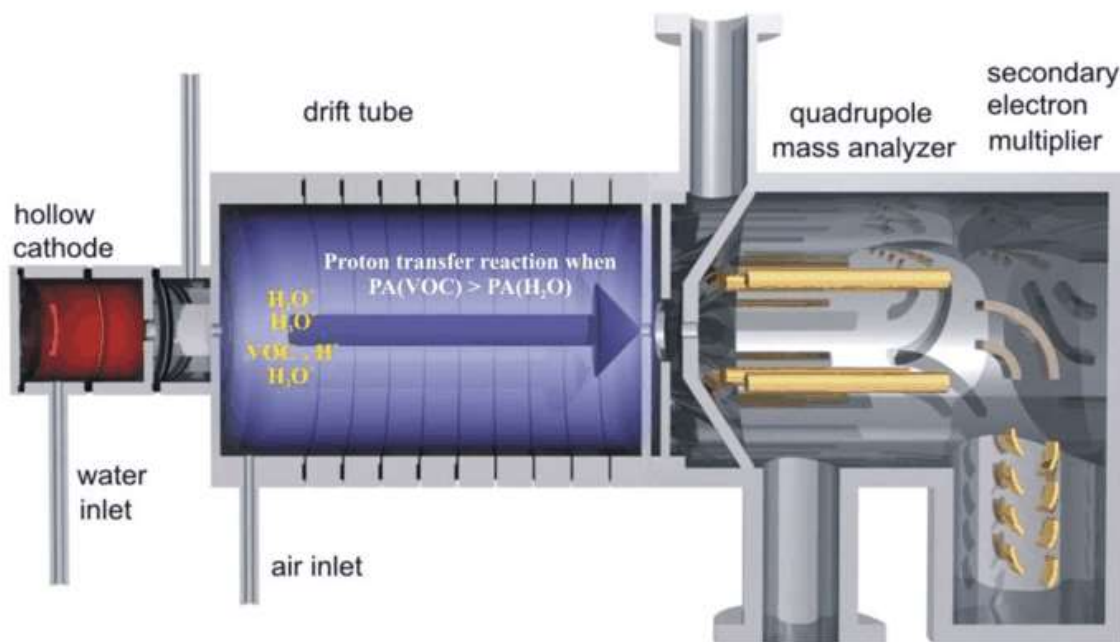
Essentially, PTR is a subset of *Chemical Ionisation*. It was defined and refined by Werner Lindinger in the 1990's, and resulted in the first commercially available instrument (*Ionicon*)

- Aim is to achieve 'Soft' ionisation so as not to fragment the molecule(s) of interest: less fragments = less mass spectral 'noise'.
- In positive ion mode, most frequently used reaction is:



- For this *protonation* reaction to occur, the proton affinity of R must be greater than that of water
- The ionisation probability is almost the same as the collision cross-section, so the aim is to induce sufficient collisions to ensure efficient analyte ionisation

# Proton Transfer Reaction Mass Spectrometry



1. Production of ions hydronium  $\text{H}_3\text{O}^+$
2.  $\text{H}_3\text{O}^+ + \text{R} \rightarrow \text{RH}^+ + \text{H}_2\text{O}$
3. Compounds are differentiated according to their  $m/z$
4. The ion signal is converted into electrical signal

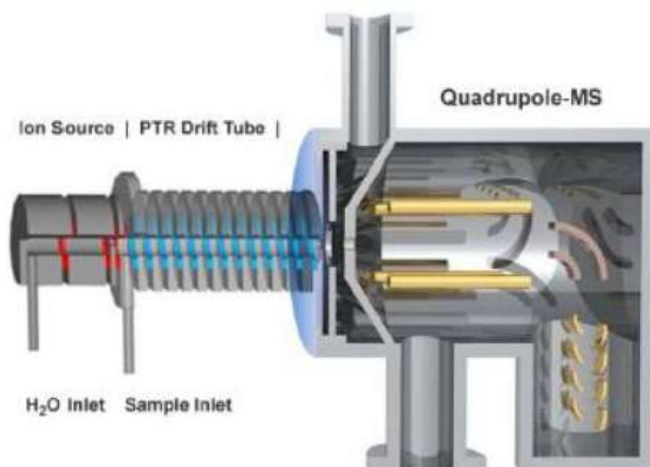
## PTR-MS in sections

- o Ion source: generates a high flux of  $\text{H}_3\text{O}^+$  primary reagent ions, alternative reagent ions ( $\text{NO}^+$ ,  $\text{O}_2^+$ , etc.) are minimized,
- o Reactor: typically set up as a drift tube reactor where trace gases are mainly ionized via collisions with  $\text{H}_3\text{O}^+$  ions. The energetic conditions in the reactor should be well defined and quasi-homogeneous (spatial and temporal) in order to provide well-constrained reaction kinetics,
- o Ion transfer unit: this component is made of regular electrostatic lenses, or more advanced ion optics to increase the efficiency of ion transfer to the mass spectrometer. An ideal ion transfer unit will conserve the collision energetics of the reactor,
- o Mass spectrometer: first models of PTR-MS were incorporating a Quadrupole Mass Spectrometer (QMS) but new models are equipped with Time of Flight Mass Spectrometers (ToFMS). ToFMS exhibit several advantages compared to QMS such as better ion transmissions at high  $m/z$ , the rapid acquisition of the whole mass spectra, and the separation of some isobaric compounds (i.e. species with the same nominal mass but different elemental composition),
- o Inlet: this component is a flow or pressure-controlled system that will carry ambient trace gases from the sampling point to the reactor, ideally without any interaction between the targeted analytes and walls from tubing or other parts. Temperature regulated capillary inlets are usually used to reduce wall effects.

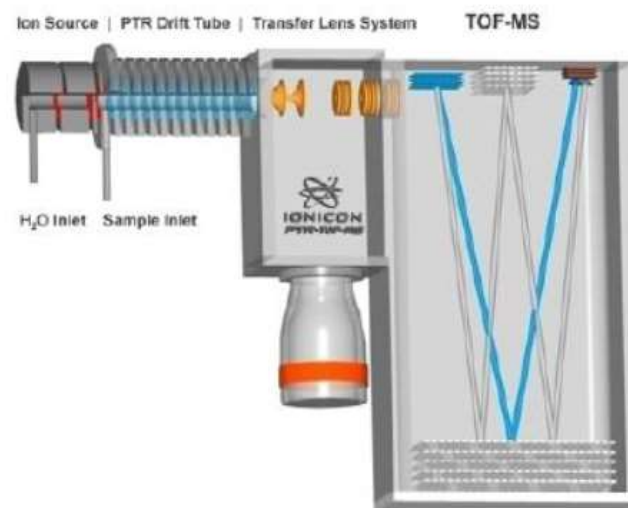
# Commercial PTR-MS

## PTR-MS

### PTR-QMS

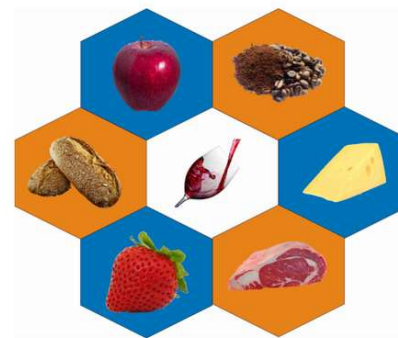


### PTR-TOFMS



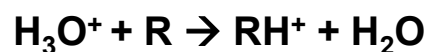
Courtesy of Ionicon Analytik GmbH/[www.PTRMS.com](http://www.PTRMS.com)

# A variety of scientific applications



## Proton affinity

In order to be detected by PTR-MS, an analyte has to exhibit a larger proton affinity than water



Species	Formula	m/z	Proton Affinity (kJ mol <sup>-1</sup> )
Water	H <sub>2</sub> O		691
Methanol	CH <sub>3</sub> OH	33.033	754
Acetonitrile	C <sub>2</sub> H <sub>3</sub> N	42.034	776
Acetaldehyde <sup>a</sup>	C <sub>2</sub> H <sub>4</sub> O	45.033	769
Acetone <sup>b</sup>	C <sub>3</sub> H <sub>6</sub> O	59.049	812
Isoprene <sup>c</sup>	C <sub>5</sub> H <sub>8</sub>	69.070	831
Methyl Ethyl Ketone <sup>d</sup>	C <sub>4</sub> H <sub>8</sub> O	73.065	826
Benzene <sup>e</sup>	C <sub>6</sub> H <sub>6</sub>	79.054	750
Toluene <sup>f</sup>	C <sub>7</sub> H <sub>8</sub>	93.070	784
C8-aromatics	C <sub>8</sub> H <sub>10</sub>	107.086	≈ 790
C9-aromatics	C <sub>9</sub> H <sub>12</sub>	121.101	≈ 790
Monoterpenes	C <sub>10</sub> H <sub>16</sub>	81.070 + 137.132	≈ 780

**a** potential interference from ethanol ionization by O<sub>2</sub><sup>+</sup> if formed in the ion source, **b** small contribution from propanal (<10%), **c** potential interferences from cycloalkanes and higher-carbon aldehydes (urban), 2-methyl-3-buten-2-ol (forest), methylbutanals (forest), 1-penten-3-ol (forest), **d** Methyl ter-butyl ether and butanals (urban, biomass burning), **e** fragmentation from ethylbenzene and benzaldehyde (urban), **f** fragmentation from higher aromatics (urban) and monoterpenes (forest).

Compound	PA (kJ/mol)
Oxygen	421
Nitrogen	493
Carbon Dioxide	541
Sulphur Dioxide	672
<b>Water</b>	<b>691</b>
Hydrogen Sulphide	709
Benzene	750
Methanol	754
Toluene	784
Naphthalene	803
Ethyl Acetate	836
Tri ethyl phosphate	909

Compounds above water in the proton affinity table will not be ionised, whereas compounds below will.

The good news is that most VOCs have higher proton affinities than water and will receive a proton from  $H_3O^+$

Generally, larger molecules have larger proton affinities

## Known issues...

**formaldehyde**, which exhibit a proton affinity ( $713 \text{ kJ mol}^{-1}$ ) that is only slightly higher than that of water, are difficult to quantify accurately due to a significant deprotonation rate that is dependent on humidity, which in turn induce a humidity-dependent PTR-MS response. In addition, formaldehyde measurements at  $m/z$  31.018 could also be biased in some environments by the detection of fragments from protonated methyl hydroperoxide, methanol and ethanol. **Alcohols** are another class of compounds that is difficult to quantify in ambient air by PTR-MS due to protonated analytes undergoing dehydration (loss of  $\text{H}_2\text{O}$ ).

## Primary ions

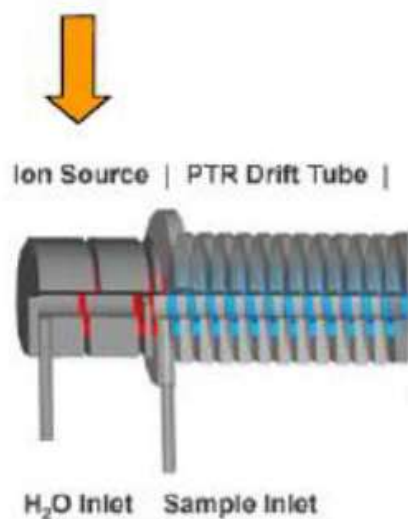
Table 2: Reagent ion quantification

Reagent ion	Main isotope m/z		Less abundant isotope m/z		Isotopic ratio
$\text{H}_3\text{O}^+$	$\text{H}_3^{16}\text{O}^+$	19.018	$\text{H}_3^{18}\text{O}^+$	21.022	487
$\text{H}_3\text{O}^+(\text{H}_2\text{O})$	$\text{H}_3^{16}\text{O}^+(\text{H}_2^{16}\text{O})$	37.029	$\text{H}_5^{17}\text{O}^{16}\text{O}^+$ $\text{DH}_4^{16}\text{O}_2^+$	38.033	645
			$\text{H}_3^{18}\text{O}^+(\text{H}_2^{16}\text{O})$ $\text{H}_3^{16}\text{O}^+(\text{H}_2^{18}\text{O})$	39.033*	242
$\text{O}_2^+$	$^{16}\text{O}_2^+$	31.990	$^{16}\text{O}^{18}\text{O}$	33.994	242
$\text{NO}^+$	$^{14}\text{N}^{16}\text{O}^+$	29.998	$^{14}\text{N}^{18}\text{O}^+$	32.002	487

\* Quantification of  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$  at m/z 39.033 may be prone to interferences from the detection of  $\text{C}_3\text{H}_3^+$  in some environments

# PTR-MS ion source

Hollow cathode ion source:



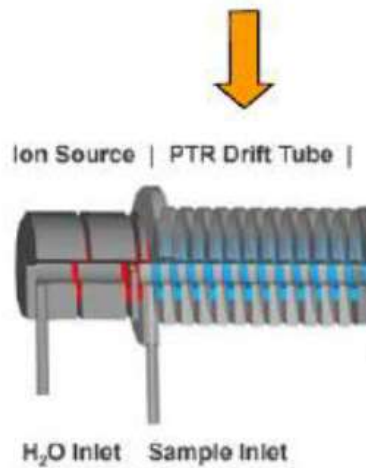
→ production of H<sub>3</sub>O<sup>+</sup>



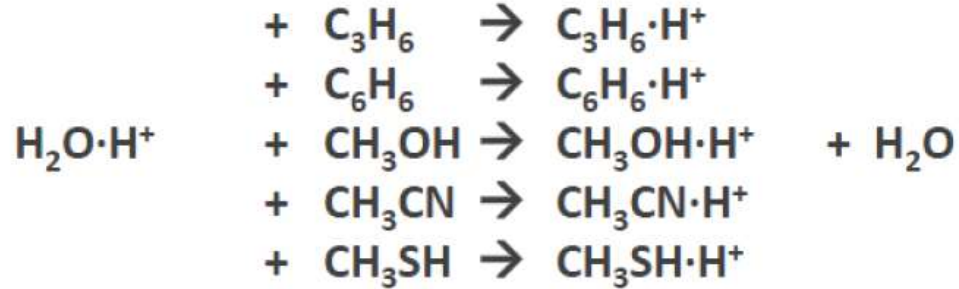
→ H<sub>3</sub>O<sup>+</sup> is injected into the drift tube

# PTR-MS drift tube

→ Collision of  $\text{H}_3\text{O}^+$  with VOCs:

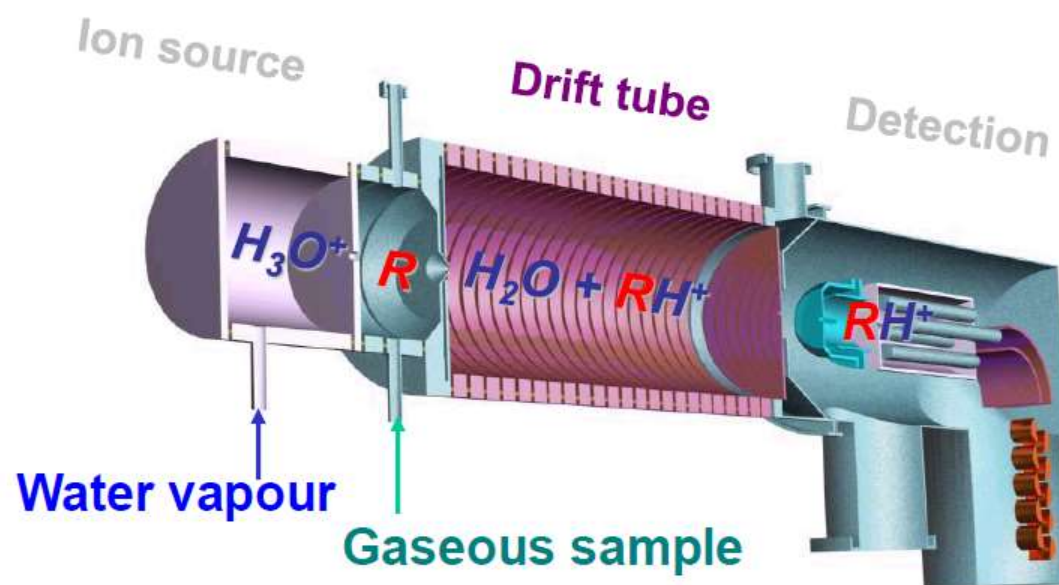
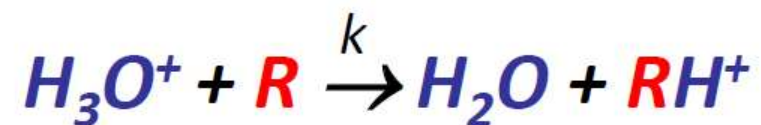


→ Proton transfer reaction (PTR)



Courtesy of Ionicon Analytik GmbH/[www.PTRMS.com](http://www.PTRMS.com)

→ VOC having proton affinity higher than  $H_3O^+$  can be monitored.



## PTR-MS and ACTRIS

The final Standard Operation Protocol (SOP) for VOC measurements (Actris deliverable WP4/D4.9 v.2014/09/30) reports guidelines for online measurements using Gas Chromatography (GC) but only preliminary recommendations were given for Proton Transfer Reaction-Mass Spectrometry (PTR-MS). Document released in April 2025 is a supplement to the SOP mentioned above and as such replaces section 5.2 in the ACTRIS deliverable WP4/D4.9 v.2014/09/30.

- Commercialized instruments equipped with conventional drift tubes (DC electrical field and operating pressure of a few mbar) and Time of Flight Mass Spectrometers (ToFMS). Only remarks for quadrupoles.
- Proton transfer reactions using hydronium ions ( $\text{H}_3\text{O}^+$ ), (other ionization methods using  $\text{NO}^+$ ,  $\text{O}_2^+$ ,  $\text{NH}_4^+$  and other reagent ions are not covered),
- Proper operations in the field: sampling, zeroing, calibrating, extracting and reporting data. Remarks are also provided for the use of PTR-MS on atmospheric simulation chambers.

## Advantages of using PTR-MS

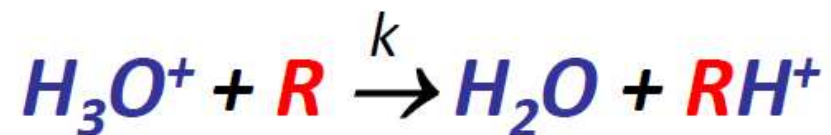
**While compound identification by online gas chromatography remains the standard technique for many purposes, PTR-MS is complementary for these advantages:**

- o Minimize potential losses or the spurious formation of VOCs during the sampling stage since ambient air is directly analyzed (within seconds after sampling) without any preconcentration step,
- o Reduce artifacts due to sample conditioning since PTR-MS does not require sample pretreatment to remove O<sub>3</sub> or water before analysis,
- o Provide fast time resolution (as high as 10 Hz) together with high sensitivity and low limits of detection,
- o Untargeted quantitative analysis is possible.

# Required properties for PTR-MS instruments



- o High ion purity. The sum of all impurities ( $\text{O}_2^+$ ,  $\text{NO}^+$ ,  $\text{NH}_4^+$ , etc.) should be lower than 3% of  $[\text{H}_3\text{O}^+ + \text{H}_3\text{O}^+(\text{H}_2\text{O})]$ ,
- o Negligible chemical processing of the sample gas by radicals/photons from the ion source,
- o The reaction kinetics in the reactor generally comply with the simple kinetics. Limitations and exceptions must be well constrained and explained (e.g. back reaction for formaldehyde). This includes the requirement that  $\text{H}_3\text{O}^+$  must constitute at least 80% of the reagent ions,  $\text{H}_3\text{O}^+ + \text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ , under normal operating conditions,
- o Collision energetics in the reactor must be nearly homogeneous and well constrained. In addition, the electrical field has to be tuned to minimize fragmentation of protonated trace gases (e.g. <30% for isoprene when  $E/N \leq 130 \text{ Td}$ ),
- o Collision energetics in the transfer region must be well constrained. Ion intensities for species produced from endothermic reactions ( $\text{N}_2\text{H}^+$  or  $\text{CO}_2\text{H}^+$ ) in the transfer region should be minimized,
- o Parameters of the mass spectrometer (mass resolution, mass accuracy, transmission, peak shape) must be well constrained,
- o Raw data (mass spectra) must be recorded and accessible to the user.



Assumptions:

- $[RH^+]$  is the only product
- $[H_3O^+] \gg [RH^+]$

Then, from a kinetic analysis:

$$[R] = \frac{1}{kt} \frac{[RH^+]}{[H_3O^+]}$$

$k$ : proton transfer rate coefficient

$t$ : reaction time

## How we get to VOC concentrations

$$VMR = \frac{C_{AH^+} \times IF_{AH^+} \times FF_{AH^+}}{C_{H_3O^+}} \left/ \left( \frac{T_{AH^+}}{T_{H_3O^+}} \times \frac{d \times k}{K_0 \times N_0} \times \frac{N^2}{E} \right) \right.$$

In Eq. 1,  $VMR$  is the volume mixing ratio,  $C_X$  (counts) the total signal detected over the measurement duration for species  $X$  ( $X=AH^+$ ,  $H_3O^+$ ),  $IF_{RH^+}$  an isotopic correction factor (see below),  $FF_{RH^+}$  a correction factor accounting for the potential fragmentation of  $AH^+$  (see section 3b),  $d$  (cm) the length of the reactor,  $E$  (V/cm) the voltage applied to the reactor per unit of length,  $T_X$  the transmission for species  $X$ ,  $k$  ( $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ ) the proton transfer reaction rate constant for the detected VOC,  $N$  ( $\text{molecule cm}^{-3}$ ) the density of molecules in the reactor,  $N_0$  ( $\text{molecule cm}^{-3}$ ) and  $K_0$  ( $\text{cm}^2 \text{V}^{-1} \text{S}^{-1}$ ) the density of molecules and the  $H_3O^+$  ion mobility in air at 1 atm and  $0^\circ\text{C}$ , respectively. It is worth noting that  $C_X$  signals are often reported in units of  $\text{counts s}^{-1}$  in PTR-MS software while these signals are expressed in units of counts for the total duration of a measurement in the following. The latter can be calculated from the signal expressed in  $\text{counts s}^{-1}$  multiplied by the measurement duration in s.

The inclusion of an isotopic correction factor ( $IF_{AH^+}$ ) in Eq. 1 is necessary since  $C_{AH^+}$  is only quantified from the detection of the most abundant isotopes (all carbon atoms being  $^{12}\text{C}$ , oxygen atoms being  $^{16}\text{O}$ , nitrogen atoms being  $^{14}\text{N}$  and hydrogen atoms being  $^1\text{H}$ ).  $C_{AH^+}$  has to be corrected on the basis of the known natural abundance of stable isotopes as illustrated in the example below.

Other parameters required to calculate VMR from measured signals ( $C_{H_3O^+}$ ,  $C_{AH^+}$ ) in Eq.1 are known from the instrument design and operating conditions ( $d$ ,  $N$ ,  $E$ ,  $K_0$ ) or tabulated in the literature ( $k$ ), with the exception of the instrumental mass discrimination ( $T_{AH^+}$ ,  $T_{H_3O^+}$ ), which is referred to as “transmission” in the following. Since the transmission function is instrument dependent, calibrations are needed to quantify it over the  $m/z$  range of interest (including  $T_{AH^+}$ ,  $T_{H_3O^+}$ ). This method is referred to as ‘kinetic approach’ in section 3.b. Recommended reaction rate constants have been published by several authors (for instance Zhao et al.<sup>8</sup> and Cappellin et al.<sup>9</sup>) and are reported in the PTRLibrary database ([tinyurl.com/PTRLibrary](http://tinyurl.com/PTRLibrary))<sup>6</sup>. For unknown compounds the usually recommended value is  $3 \times 10^{-15} \text{ m}^3 \text{ s}^{-1}$  since most proton transfer rate constants range from  $2\text{-}4 \times 10^{-15} \text{ m}^3 \text{ s}^{-1}$ .

## Isotopic correction factor

**Example:** *A measurement of isoprene derived from the ion signal recorded at  $m/z$  69.070 indicates a mixing ratio of 2.5 ppbv.*

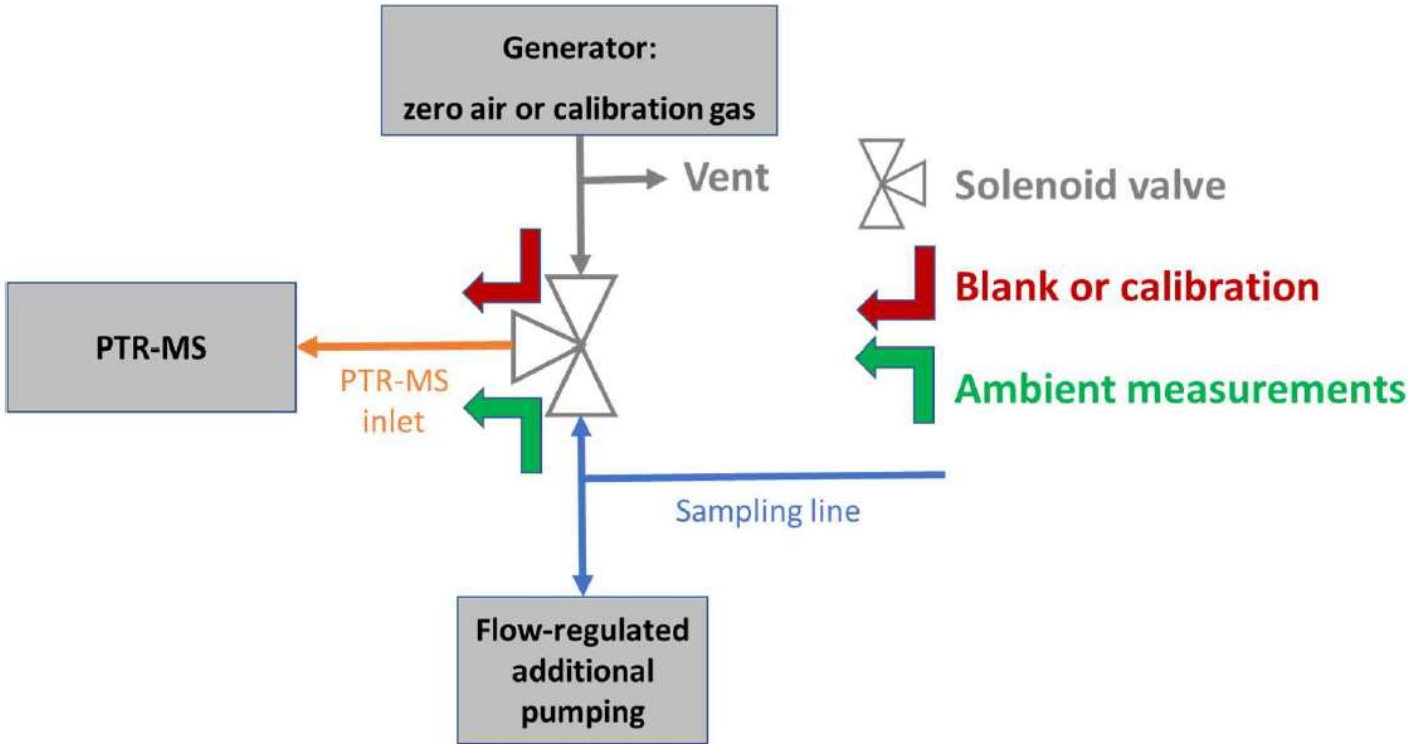
*What is the mixing ratio expected for the sum of all ambient stable isotopes?*

*The detection of isoprene at  $m/z$  69.070 is from its most abundant isotope ( $^{12}\text{C}_5^1\text{H}_8$ ), whose natural abundance is 94.544%. In order to account for the presence of other stable isotopes ( $^{13}\text{C}$ ,  $^2\text{H}$ ), the measured VMR at  $m/z$  69.070 has to be multiplied by a factor of 1.057 (calculated as  $1/0.94544$ ).*

## How we get to VOC concentrations

$$VMR = \frac{c_{AH^+}}{c_{H_3O^+}} \times 10^6 / S_N(AH^+)$$

# Designing a set-up for field measurements



## Quality assurance: zero measurements

PTR-MS is not a zero-background measurement technique due to VOC sorption processes (adsorption/desorption) inside the sampling line and the drift tube, which requires frequent blank measurements to track background signals at all  $m/z$  of interest.

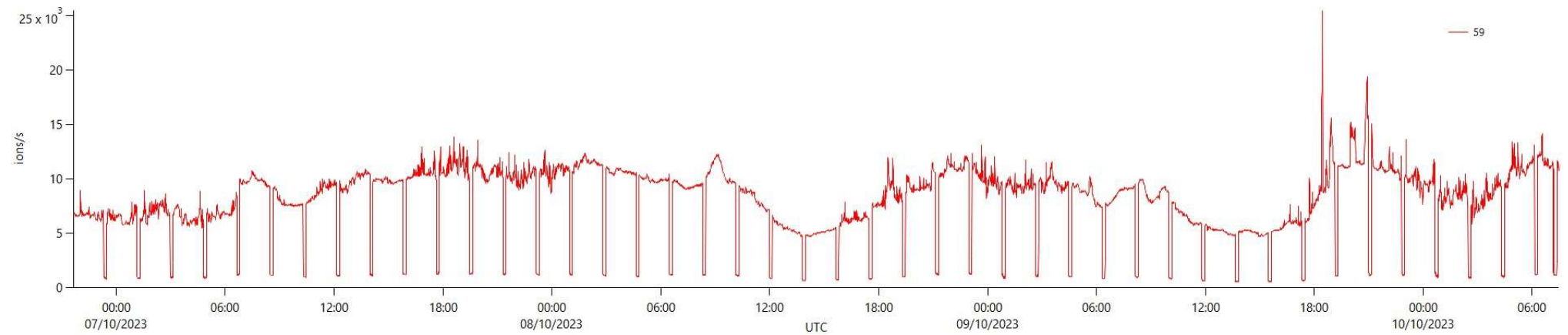
VOC free air can be produced from ambient air using

- (i) a catalyst (Platinum Pt, Palladium Pd) held at a temperature of 350-400°C,
- (ii) a VOC scrubber containing a solid sorbent, or
- (iii) a cylinder of dry zero air (high purity, 5.0) with a humidification system containing high purity water.

When zeroing the instrument, sufficient time should be allowed to allow gas-surface interactions to reach an equilibrium. The duration of the blank will depend on the inlet tubing and other internal materials inside the PTR-MS (temperature regulated PFA and surface treated stainless steel tubes result in quickest response times) and the chemical property of the compounds of interest.

**Example:** cis-pinonic acid for a traditional PTR-MS instrument with Peek inlet capillaries and an instrument optimized for fast equilibration responses (PFA and Sulfinert only, coating of the inner surface of the drift tube to avoid losses of low-volatility species). For the conventional instrument, cis-pinonic acid blank measurements will need to last several tens of minutes to achieve reliable blank values, while for the optimized PTR-MS, this period is reduced to 3-5 min

# Quality assurance: zero measurements



## Example of values to expect for common VOCs

Table 3: Blank values for PTR-ToFMS

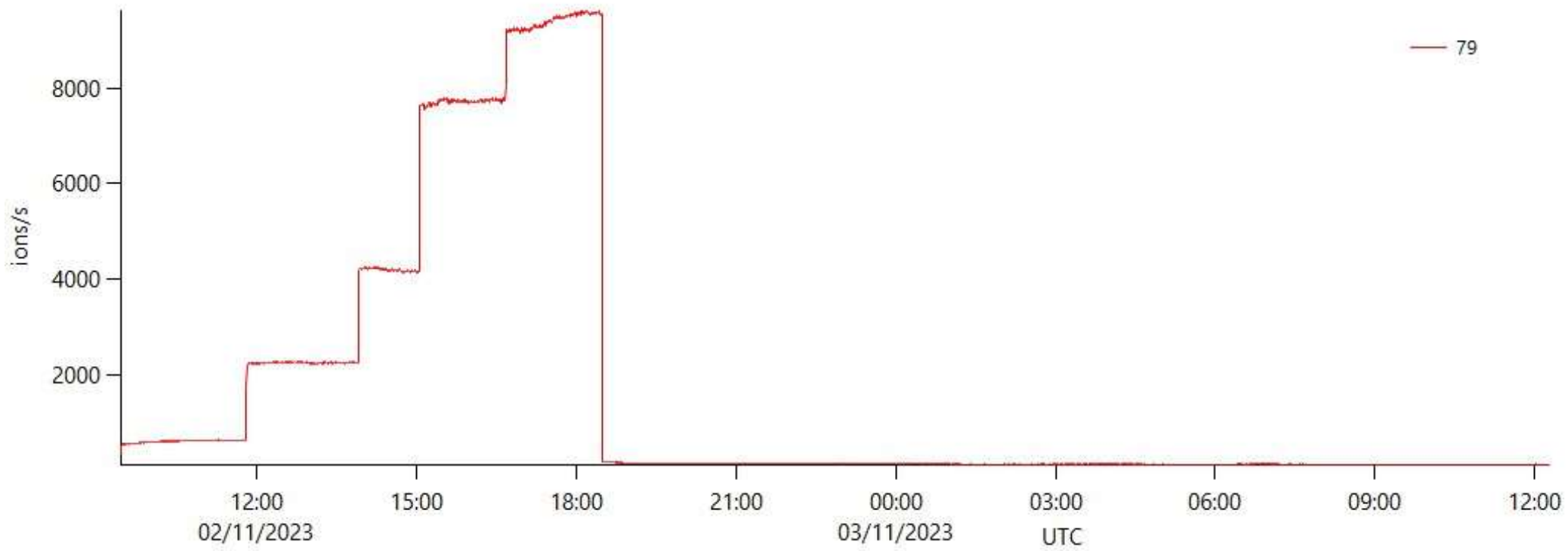
Species	Formula	m/z	Blank values (pptv)*
Methanol	CH <sub>3</sub> OH	33.033	30-90
Acetonitrile	C <sub>2</sub> H <sub>3</sub> N	42.034	30-110
Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O	45.033	40-270
Acetone	C <sub>3</sub> H <sub>6</sub> O	59.049	60-500
Isoprene	C <sub>5</sub> H <sub>8</sub>	69.070	20-70
Methyl Ethyl Ketone	C <sub>4</sub> H <sub>8</sub> O	73.065	10-70
Benzene	C <sub>6</sub> H <sub>6</sub>	79.054	20-80
Toluene	C <sub>7</sub> H <sub>8</sub>	93.070	20-140
C8-aromatics	C <sub>8</sub> H <sub>10</sub>	107.086	10-110
C9-aromatics	C <sub>9</sub> H <sub>12</sub>	121.101	5-200
Monoterpenes	C <sub>10</sub> H <sub>16</sub>	81.070 + 137.132	60-100 + 10-50

# Calibrations

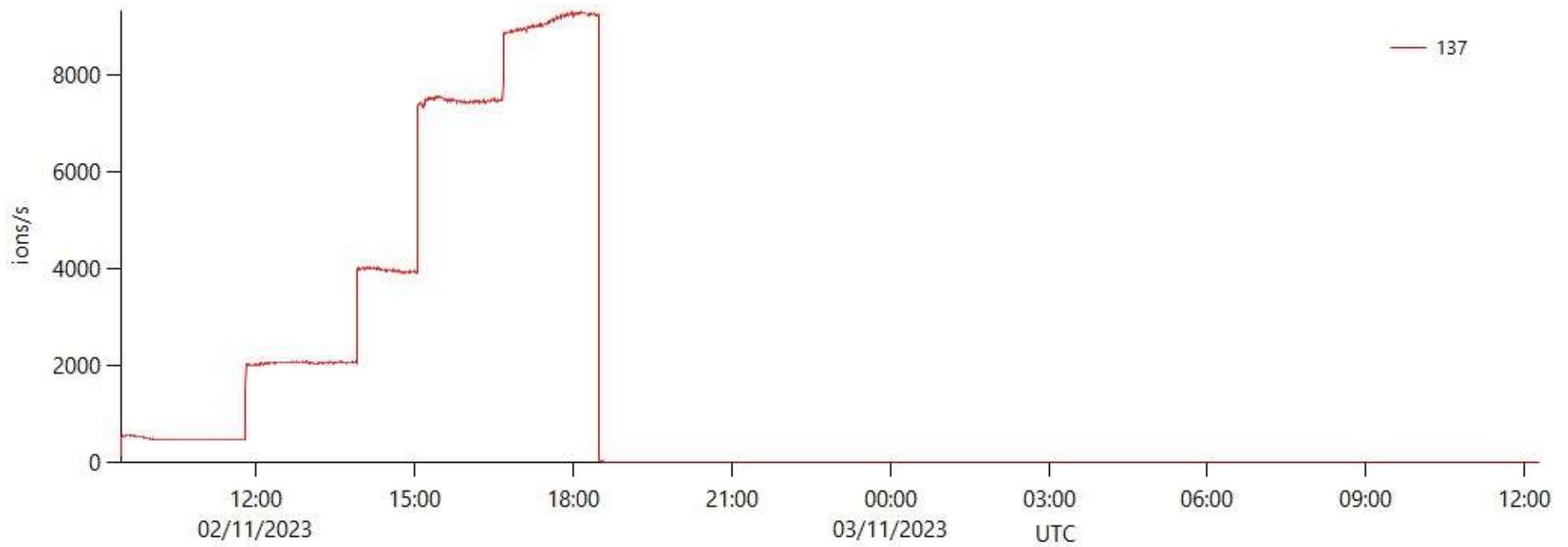
**Calibration Frequency** – Calibrations using either the “kinetic approach” or the “calibration approach” should be performed once a week (including the start and end of the campaign) when the campaign lasts less than two months and twice a month when long term measurements are conducted (> two months). If a significant drift in sensitivity is observed since the installation of the instrument (decrease of more than 20% at the highest  $m/z$ ), re-optimization of the detector high voltage should be considered (Annex 6).

For laboratory experiments such as atmospheric simulation chambers, both the kinetic and calibration approaches can be used at the beginning and/or end of the experiment campaign. Nevertheless, another approach relying on repeated introductions of known amount of the compounds of interest into the atmospheric simulation chamber can also be used. It is however highly recommended to verify the generated concentrations using independent optical instrumentation such as FTIR. Uncertainties associated to these measurements will have to be factored in the calibration accuracy discussed in section 3c.

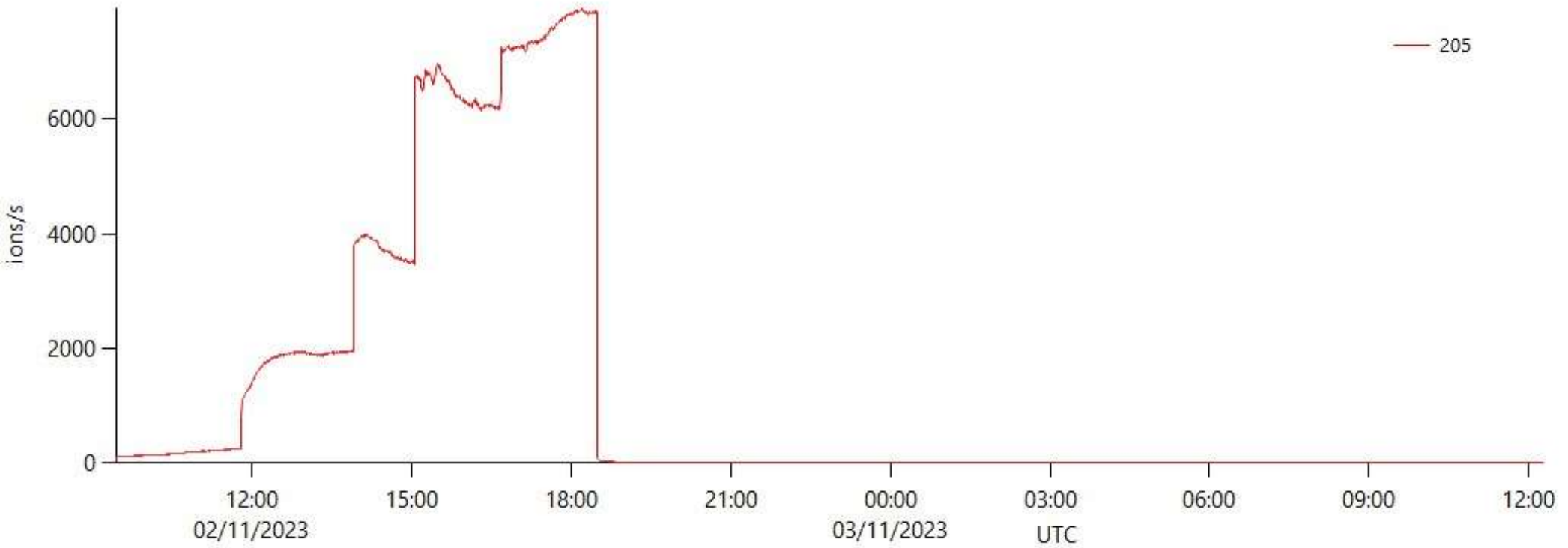
# Calibrations



# Calibrations



# Calibrations



## Material, sampling, heated lines

The **sampling height** has to be carefully chosen to provide an air sample representative of the surrounding area (type of vegetation, orography, soil, water, snow) (ACTRIS deliverable WP4/D4.9 v.2014/09/30). If possible, VOCs should be measured at 2-3 different heights for a significant period of time to determine which inlet height is suitable.

Recommended materials include **coated stainless steel** (Silcosteel or SilcoNert®1000 and Sulfinert or SilcoNert®2000) preferably, or **polymer after a sufficient passivation time before use** (PFA, PTFE). As recommended for other VOC measurement techniques (ACTRIS deliverable WP4/D4.9 v.2014/09/30), untreated stainless steel should not be used. The **sampling line can be slightly heated** to reduce VOC sorption effects. Measurements of compounds exhibiting a good thermal stability such as those reported in Table 1 can be performed with a sampling line heated to 40-50°C. If low-volatility compounds such as **IVOC and SVOC** are targeted, the **temperature can be increased up to 80°C**. It is important to ensure that there is **no cold spot** in the sampling line to avoid condensation of water and the loss of low-volatility or high-solubility VOCs. The latter needs to be carefully considered if the instrument is housed in an air-conditioned unit where the temperature is lower than in ambient air. Typical inner diameters of the sampling lines are in the range 2-12 mm and the length will depend on the measurement height and place. Generally, the sampling line should be as short as possible and the flow rate should be high enough (a few L/min to a few tens of L/min) to reduce the residence time below a few seconds. For this purpose, **additional pumping capabilities are usually required** (see Fig.1) since the drift tube flow rate is usually ranging from a few tens to a few hundreds of mL/min.

# Operating conditions

Table 4: Field operating conditions

Parameter	Range	Comments
Temperature (°C)	50-60 (up to 80 if IVOC & SVOC are targeted)	This temperature should be kept higher than that of the PTRMS-inlet to prevent condensation. Higher temperature: less memory effects and improved response time, less losses of semi-volatile VOCs.
Pressure (mbar)	1-4	Higher pressure reduces the diffusion of sampled air into the ion source in certain PTR-MS models, resulting in lower impurity levels of $O_2^+$ and $NO^+$
E/N (Td)	120-140	A higher E/N reduces the abundance of $H_3O^+(H_2O)$ but increases the fragmentation of protonated VOCs
PTR-MS inlet Sampling flow rate (SCCM)	50-500	A higher flow rate reduces the impact of instrument related contamination on blank signals
Sampling line flow rate	See section 4.a	A higher flow rate reduces the impact of sampling line related contamination on blank signals

# Drift tube

Table 5: Criteria for optimum tuning of the ion source/drift tube

Ion source	
Primary ions purity	$[O_2^+ + NO^+] < 3\%$ of $[H_3O^+ + H_3O^+(H_2O)]$
Primary ions distribution	$[H_3O^+(H_2O)] < 20\%$ of $[H_3O^+ + H_3O^+(H_2O)]$

# PTR-MS applied to atmospheric sciences in Italy



...from December 2022



Ri-URBANS Milan  
Jan 2023-Feb 2024

ALFA rural Po Valley  
Sept-Nov 2023

ECOSYSTER Indoor air  
April-May 2024

EMEP Bologna  
September 2024

ACTRIS Mt. Cimone  
October 2024

# Field campaigns

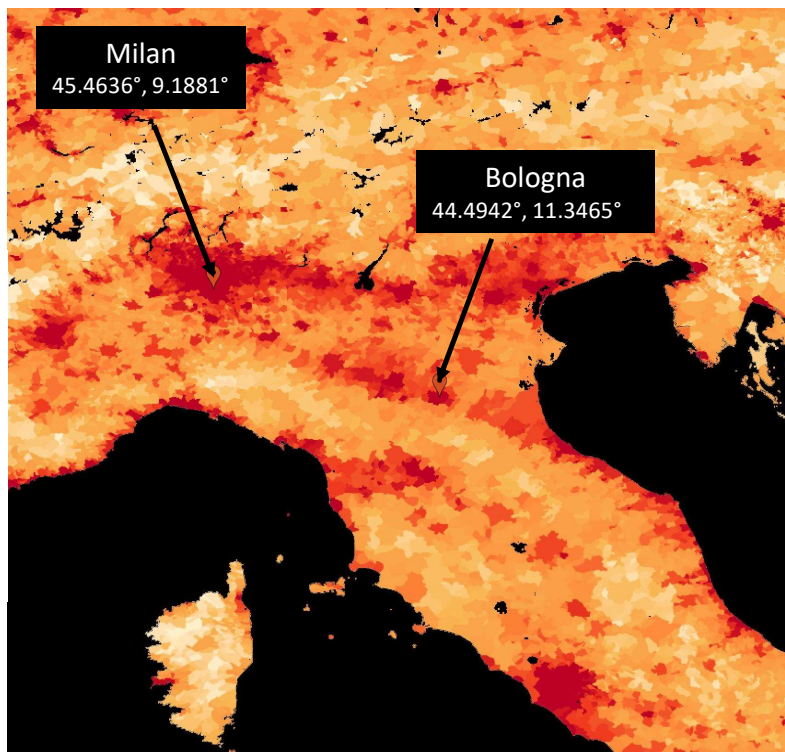


## Milan

Metropolitan area: 3.2 million inhabitants  
Suburban site  
Jan 2023-Feb 2024  
RI-URBANS- ACTRIS (The Aerosol, Clouds and Trace Gases Research Infrastructure)  
Goal: Diel and seasonal variability VOC



Source: Google maps



Source: NASA worldview, population density 2020



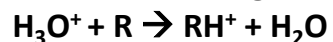
## Bologna

Metropolitan area: 1 million inhabitants  
Suburban site  
September 2024  
EMEP (co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe)  
Goal: VOC concentration in EU



# VOC measurements

Method: Vocus Chemical Ionization Time of Flight Mass Spectrometer 2R, Tofwerk



Time resolution: 1 sec

Mass resolution: 10000

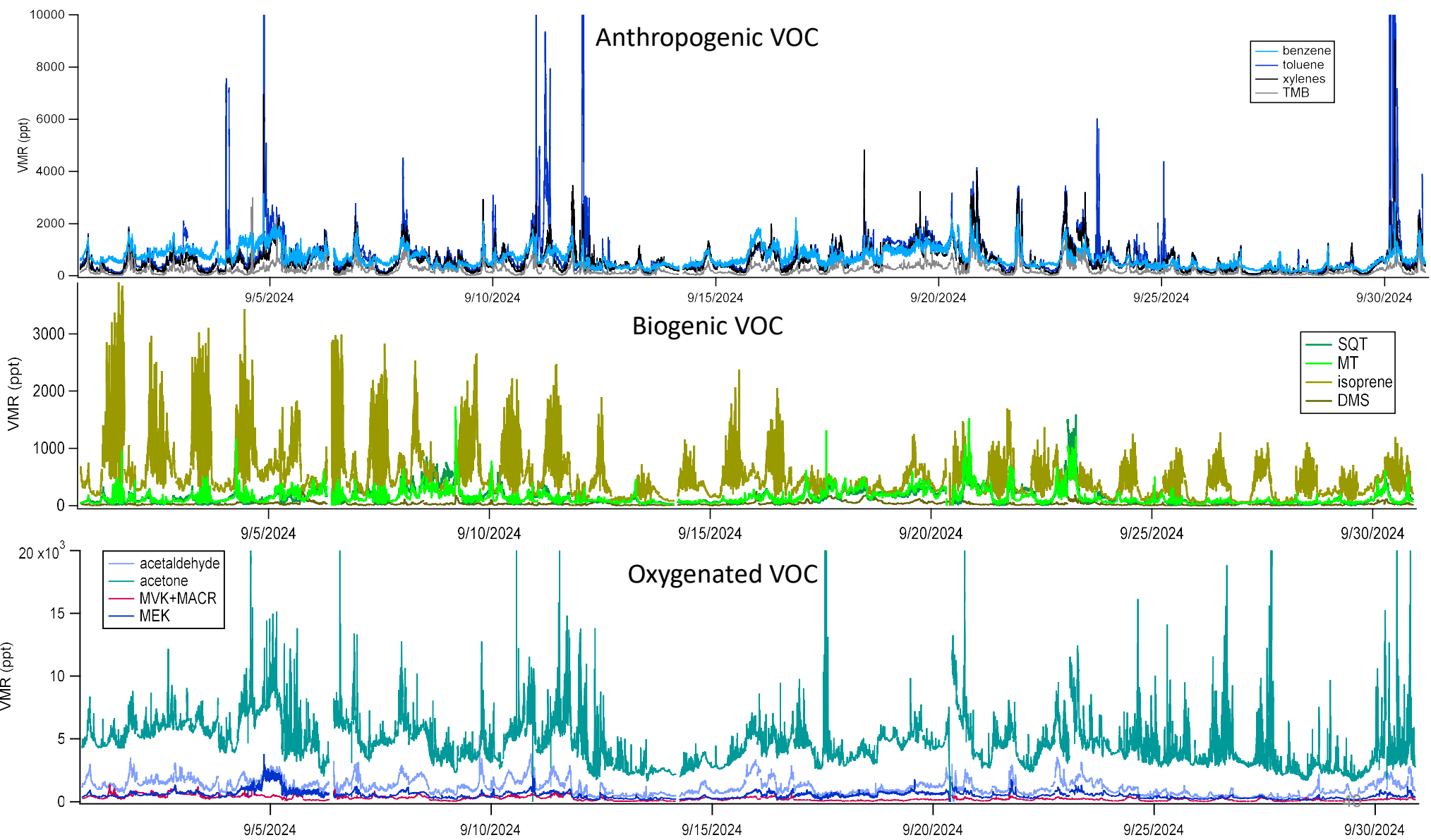
Data analysis performed with Tofware, Aerodyne

Mass accuracy < 5 ppm

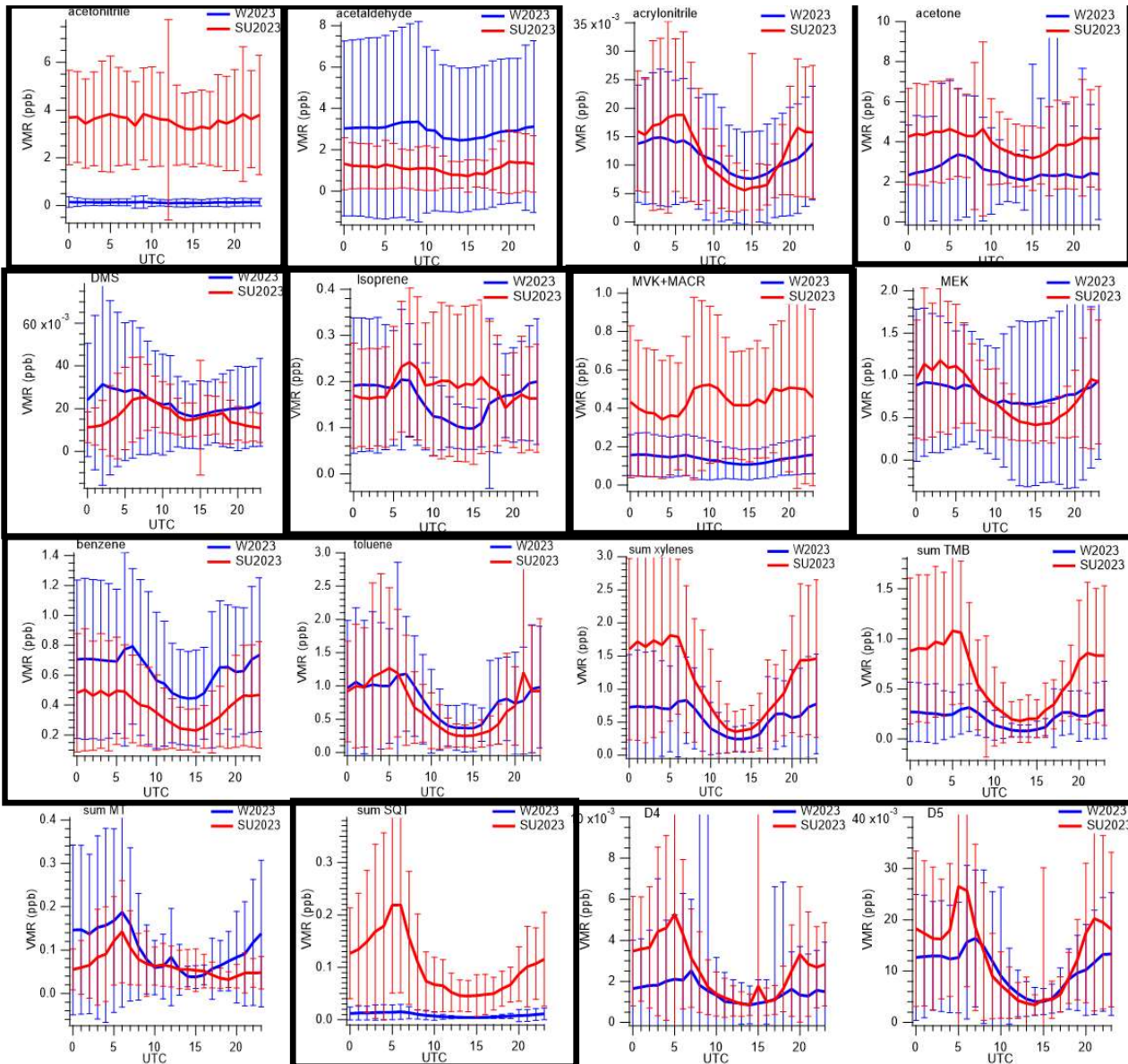
Focus on 16 VOC, unambiguously determined, uncertainty < 20%, LoD ~ ppt:

ID	formula	mass	LoD Mi (ppt)	LoD Bo (ppt)	uncertainty Mi (%)	uncertainty Bo (%)
acetonitrile	C2H4N+	42.033826	12	21	14	8
acetaldehyde	C2H5O+	45.033491	43	181	10	8
acrylonitrile	C3H4N+	54.033826	2	3	12	13
acetone	C3H7O+	59.049141	35	41	11	7
DMS	C2H7S+	63.026298	1	11	11	9
isoprene	C5H9+	69.069877	6	36	12	8
MVK+MACR	C4H7O+	71.049141	8	30	9	8
MEK	C4H9O+	73.064791	6	27	11	8
benzene	C6H7+	79.054227	7	75	11	8
toluene	C7H9+	93.069877	4	15	15	8
xylenes	C8H11+	107.085527	2	6	15	8
TMB	C9H13+	121.101177	1	4	16	9
MT	C10H17+	137.132477	1	3	16	15
SQT	C15H25+	205.195077	3	11	14	9
D4	C8H25O4Si4+	297.082442	2	2	17	17
D5	C10H31O5Si5+	371.101233	1	1	15	9





# Diel and Seasonal Variability in Milan



- W ~ SU concentrations for most VOC except BVOC and acetonitrile
- Similar DP: larger concentration during the night than during the day
- Day/night differences milder for OVOCS
- Morning and evening peaks
- W and SU morning and evening peaks shifted due to time differences and sunlight duration
- Opposite DP for DMS, isoprene, MVK+MACR in summer

## References:

Ellis&Mayhew: Proton Transfer Reaction Mass Spectrometry: Principles and Applications, 2013 Wiley

Ionicon Analytik Gmbh [www.ionicon.com](http://www.ionicon.com)

Measurement Guidelines for VOC Analysis by PTR-MS

Authors: S. Dusanter, R. Holzinger, F. Klein, T. Salameh, M. Jamar

Contributions from M. Müller, C. Amelynck, B. Verreyken, A. Muñoz, I. Ylivinkka



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Mission 4 "Education and Research" - Component 2: "From research to business" - Investment  
3.1: "Fund for the realisation of an integrated system of research and innovation infrastructures"

