



Performance comparison of the VOCUS PTR-TOF 2R with other VOC analyzers

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contents

Introduction

What is CI-MS ?

VOCUS a new kind of PTR-TOF

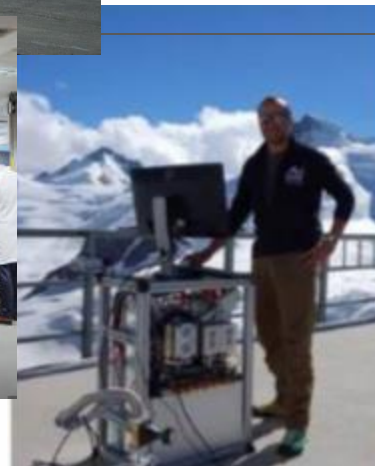
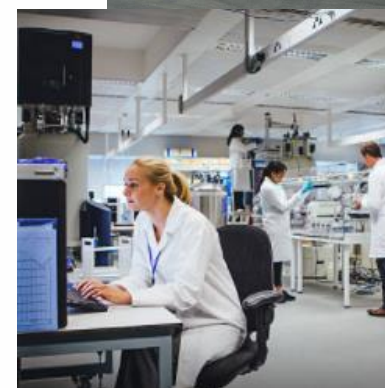
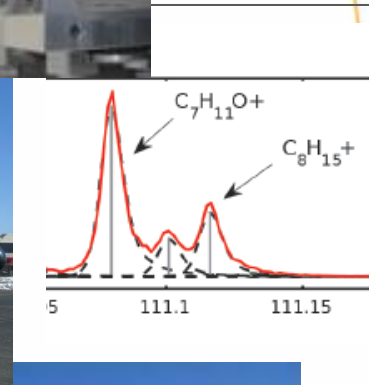
Comparison with
environmental analyzer

Conclusion

Tofwerk is a global provider of TOF technology

Intro

- CHEMLYS is a company specialised in gas analysis, based in Lyon, representing TOFWERK in France.
- TOFWERK is a global provider of TOF with over **400** mass spectrometers delivered and supported around the world
- Family of end-user products and custom designs for OEM and research
- Broad range of designs, collaborations, and applications
- Expertise in field-deployable instrumentation
 - Uniquely bring laboratory performance to mobile platforms and difficult environments
 - Demands robust and reliable instruments



Fight against air pollution is ongoing!

Intro

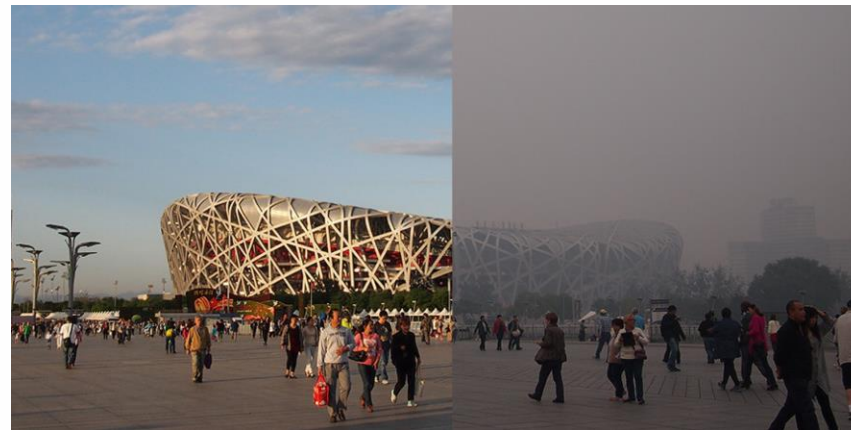


ATMOSPHERIC CHEMISTRY

Volatile chemical products emerging as largest petrochemical source of urban organic emissions

Brian C. McDonald,^{1,2*} Joost A. de Gouw,^{1,2} Jessica B. Gilman,² Shantanu H. Jathar,³

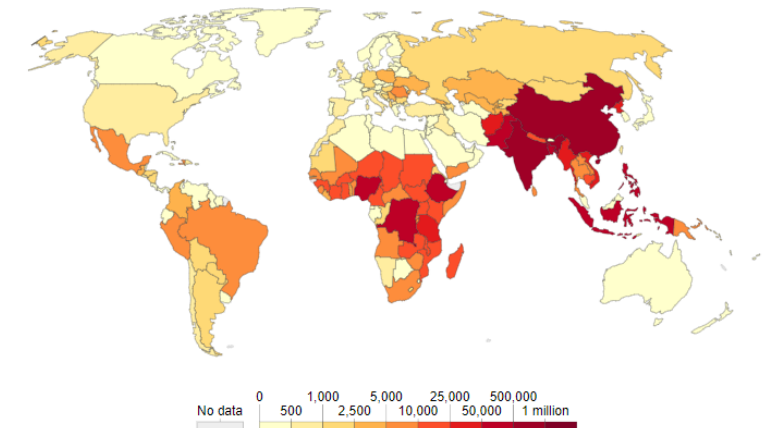
- Ambient air, both outdoor and indoor, contains thousands of VOCs
- The VOCs pattern is **evolving**! (Un-expected) wider range of compounds need to be identified and quantified. Often **retrospective** analysis is important.
- Require **sub part-per-billion (ppbv)** detection limits in seconds for common VOC, pptv and lower LOD for more oxidized trace VOC which contribute to aerosol formation and growth



McDonald et al., Science 359, 760 – 764 (2018)

Absolute number of deaths from household air pollution, 2016
Annual number of premature deaths attributed to illness as a result of household air pollution from the use of solid fuels for cooking and heating.

OurWorld
in Data



Source: Institute of Health Metrics and Evaluation (IHME)

Chemical analysis by mass spectrometry

Intro

- Mass spectrometry measures the **mass-to-charge ratio** (m/Q) of gas-phase ions
- Analysis of ions by mass spectrometry enables **identification** and **quantification**
- Neutral molecules must be converted to ions, which requires a controlled **ionization** step to charge them in a quantitative manner
- Proton Transfer Reaction (**PTR**) is one such chemical ionization method that ionizes many classes of compounds



Types of CI

CI

Type	Acronym	Reaction
Proton Transfer Ionization	PTR	$M + H_3O^+ \rightarrow MH^+ + H_2O$
Charge Exchange Chemical Ionization (positive and negative)	CECI	$M + R^+ \rightarrow M^+ + R$
		$M + R^- \rightarrow M^- + R$
Ion Adduct Chemical Ionization	IACI	$M + I^- \rightarrow MI^-$
Anion Abstraction Chemical Ionization	AACI	$M + R^+ \rightarrow (M-A)^+ + RA$

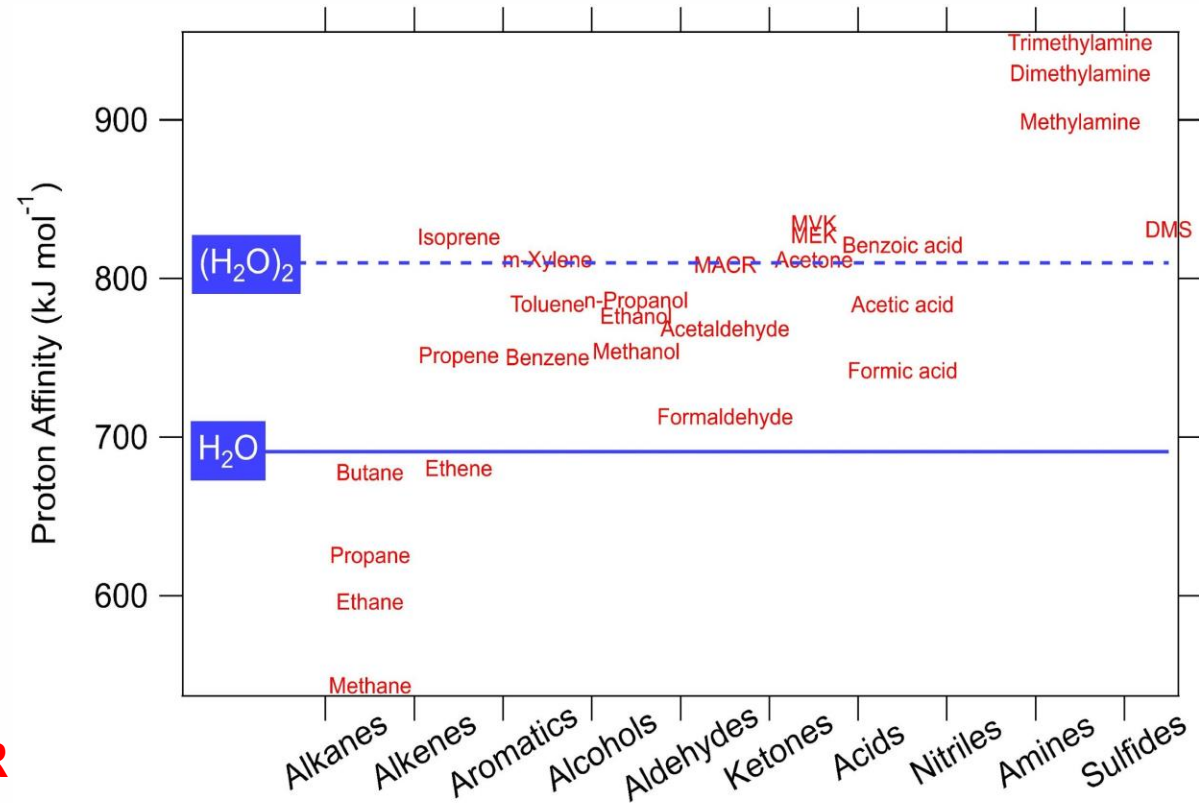
- There are multiple different types of chemical ionization reaction available
- In this talk we focus on **PTR**

PTR ionization: the chemical reaction



- **Chemical Ionization occurs** if M has higher proton affinity than reagent ion [H_3O^+ or $(\text{H}_2\text{O})\text{H}_3\text{O}^+$]
- **Exothermic and fast for**
 - Most alkenes
 - Aromatics
 - Most functional groups

Most VOCs are detectable with PTR



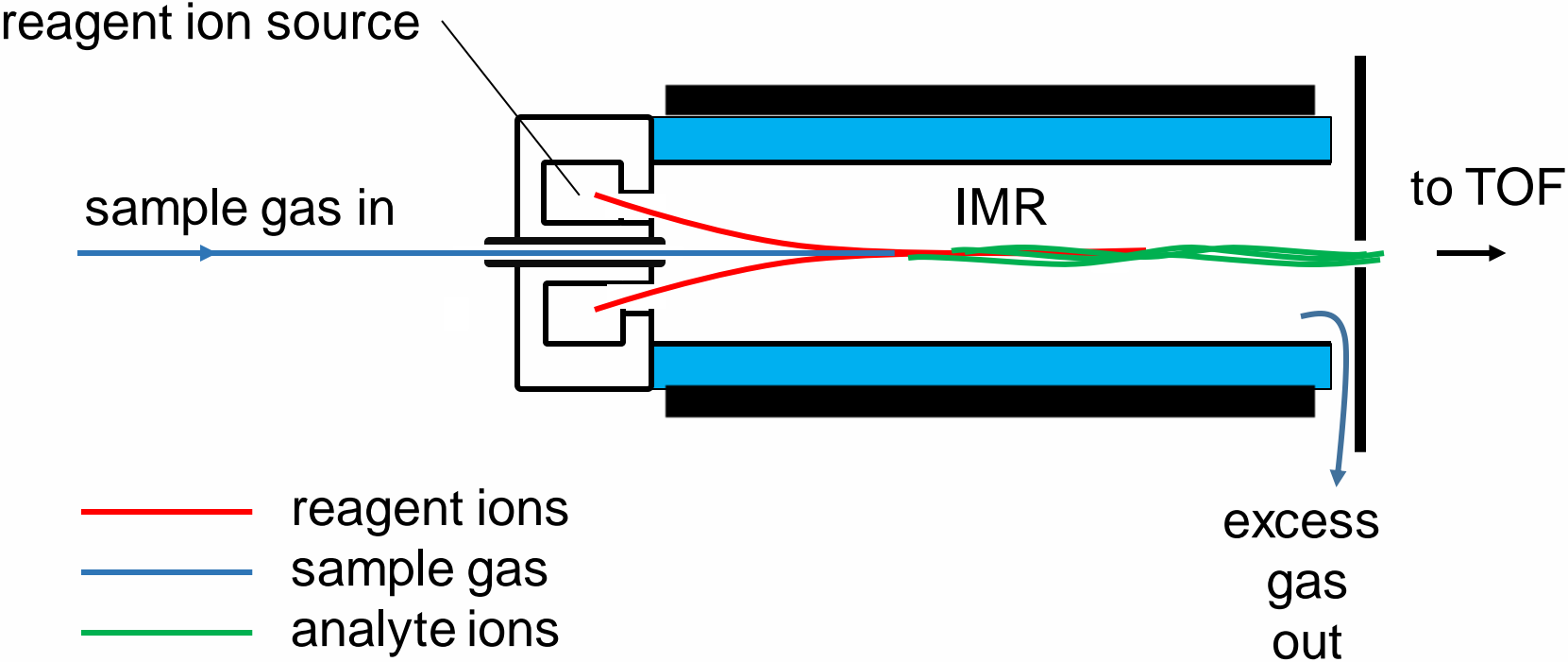
CI

Proton transfer occurs

No Reaction

Sample continuously mixing with reagent ions

IMR



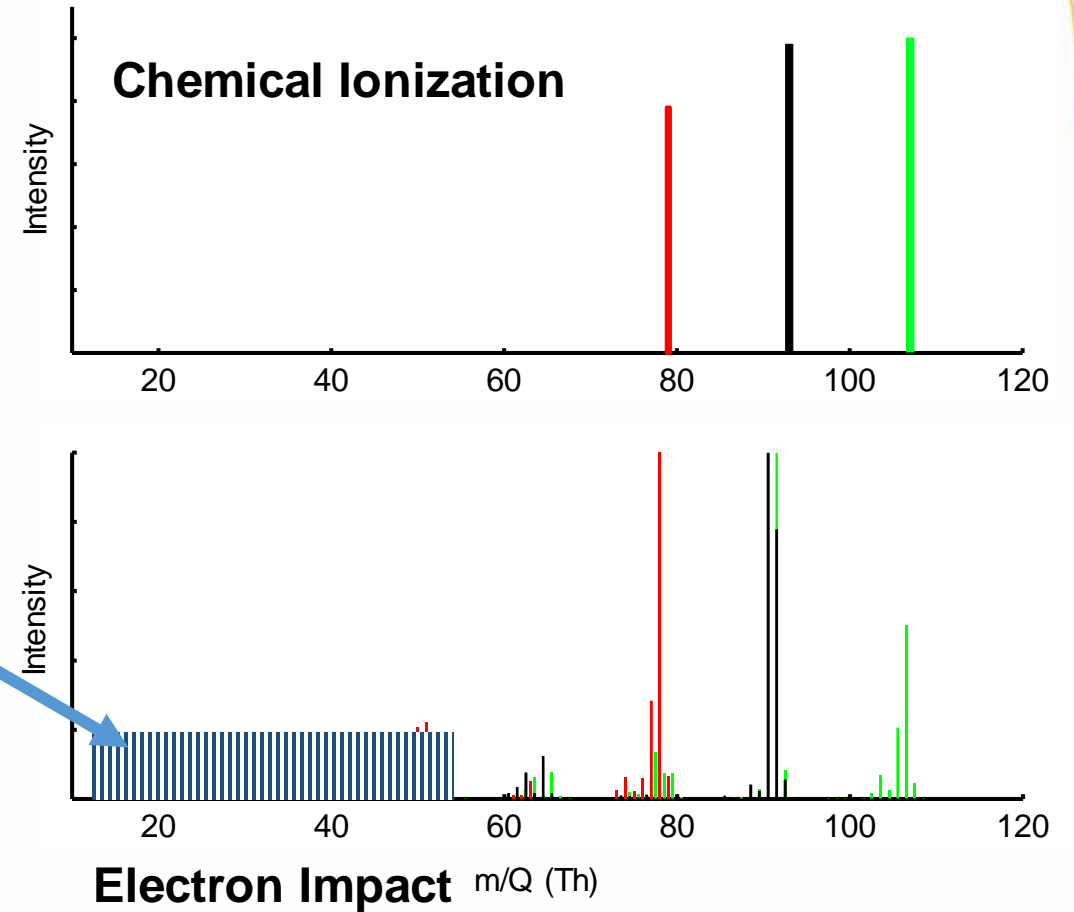
CI: selective ionization

CI

PTX in N₂:

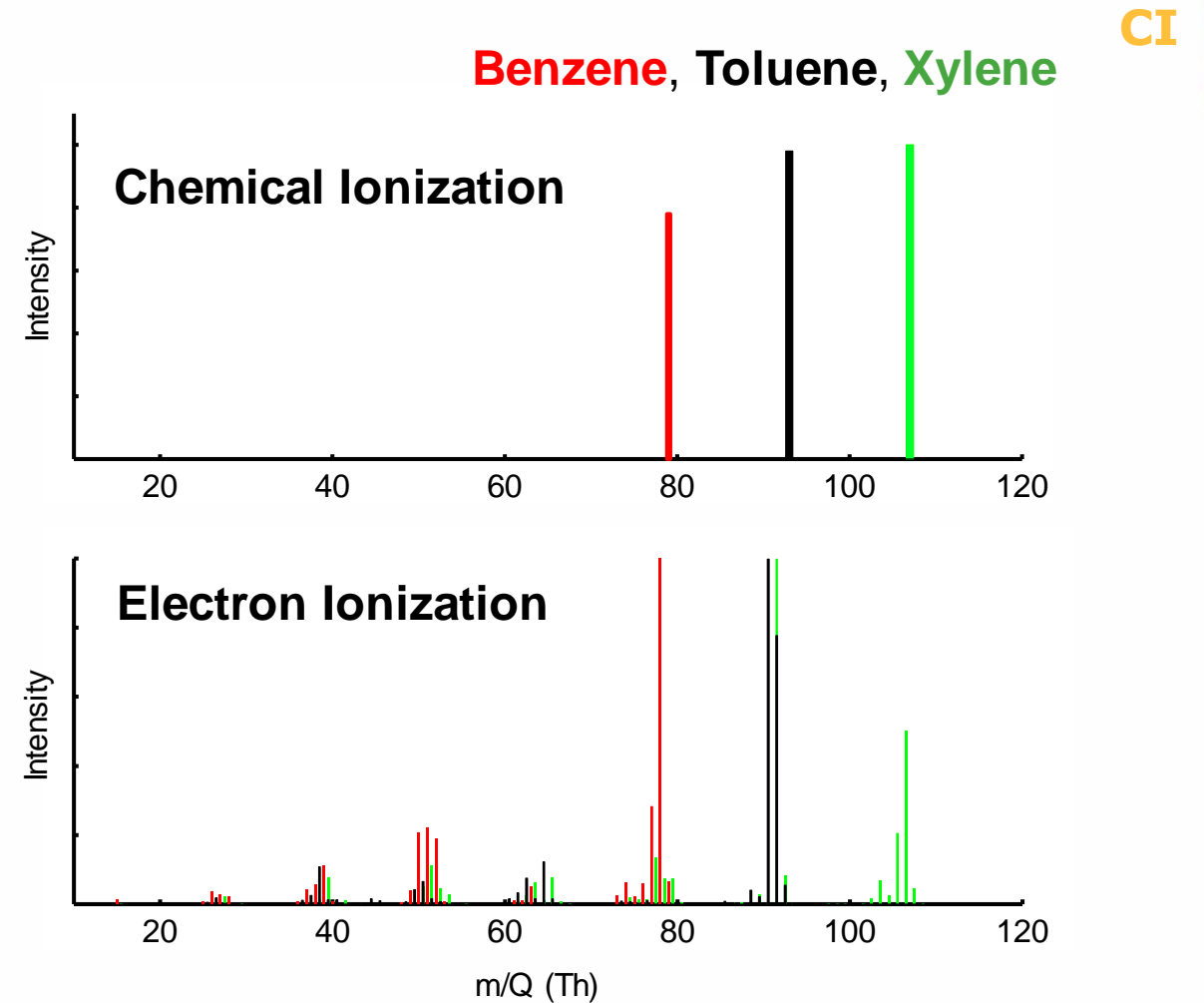
- PTR ionizes only **Benzene**, **Toluene**, and **Xylene**
- Abundant Air gases like **N₂**, **O₂**, **Ar**, **CO₂**, **CO** are **not** ionized
- Much fewer ions:
 - No **saturation** effects
 - Much fewer **interferences**
 - Much less **background**
 - Much less Coulomb repulsion

→ **Selective Ionization = concentration**



CI: soft ionization

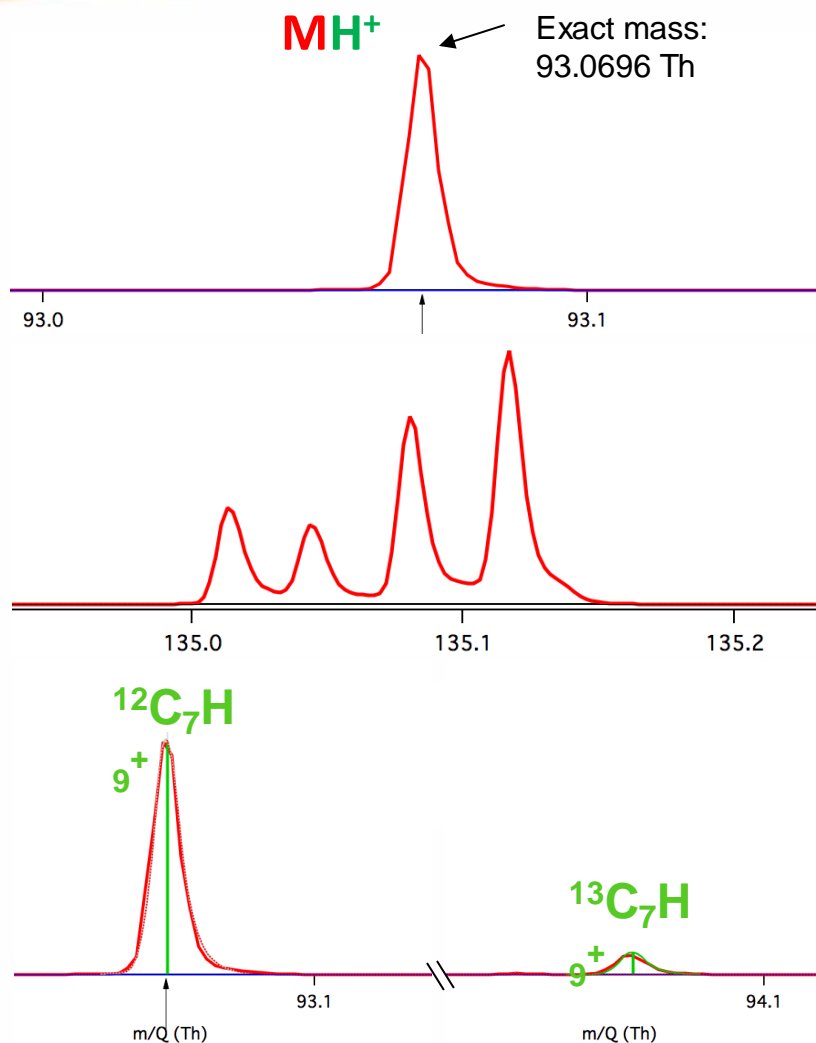
- CI is **soft**
- Fewer **fragments**
- Fewer **interferences**
- always **molecular ion**
- simplifies **identification**
- Mass spectra are **easily interpretable**
- Often no **chromatography** necessary



→ soft ionization allows for separation and identification in a mass analyzer

Robust Identification with CI-MS

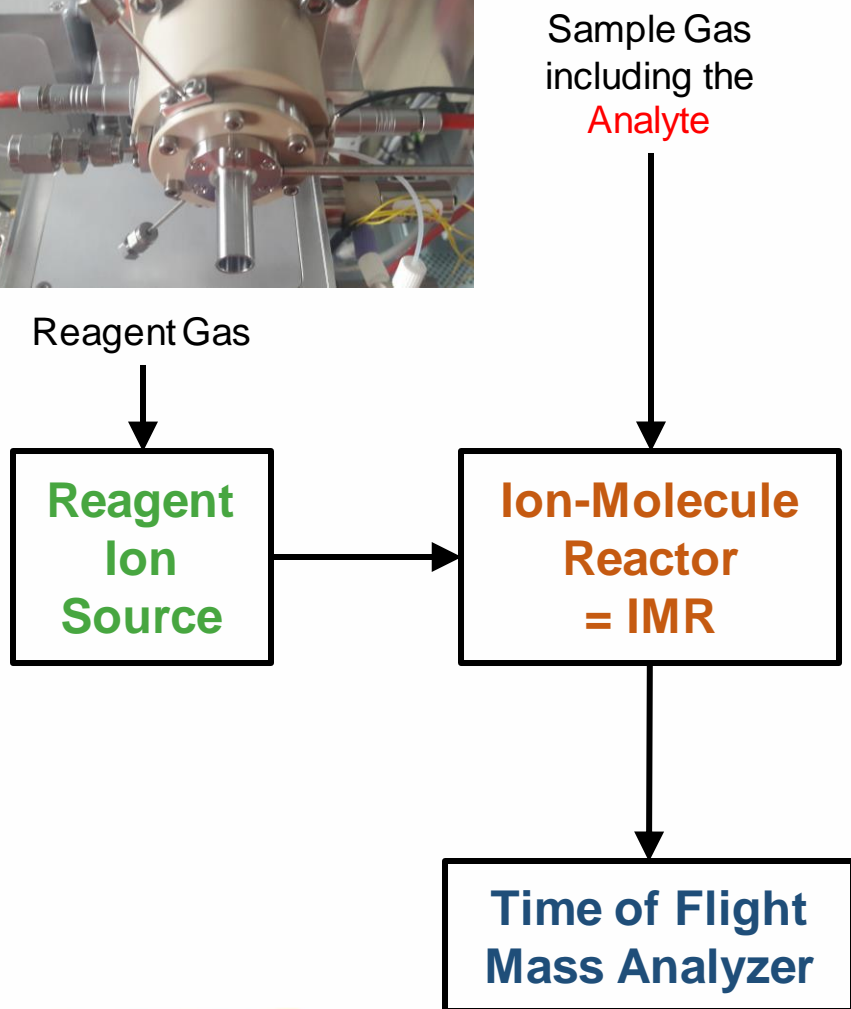
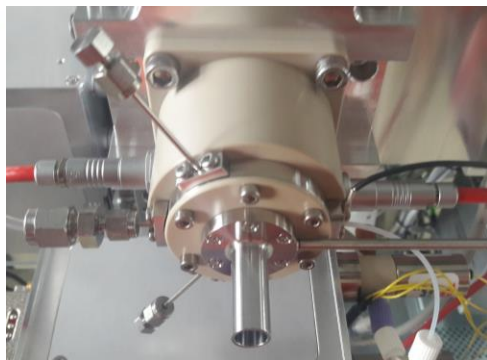
CI



- **Molecular Ion:** is always present
- **Mass accuracy:** A reported exact mass accurate within 0.0003 Th allows molecular formula calculation and identification.
- **High Resolution:** Separates interferences (isobars)
- **Isotopic distribution:** Confirmation of the molecular assignment by matching isotopic distributions.
- **Fragments:** Confirmation of the molecular assignment by CID can be used in PTR-MS, but is often not necessary

Vocus Development Goals

Vocus



TOFWERK applications required better performance in terms of **sensitivity** and **separation power**

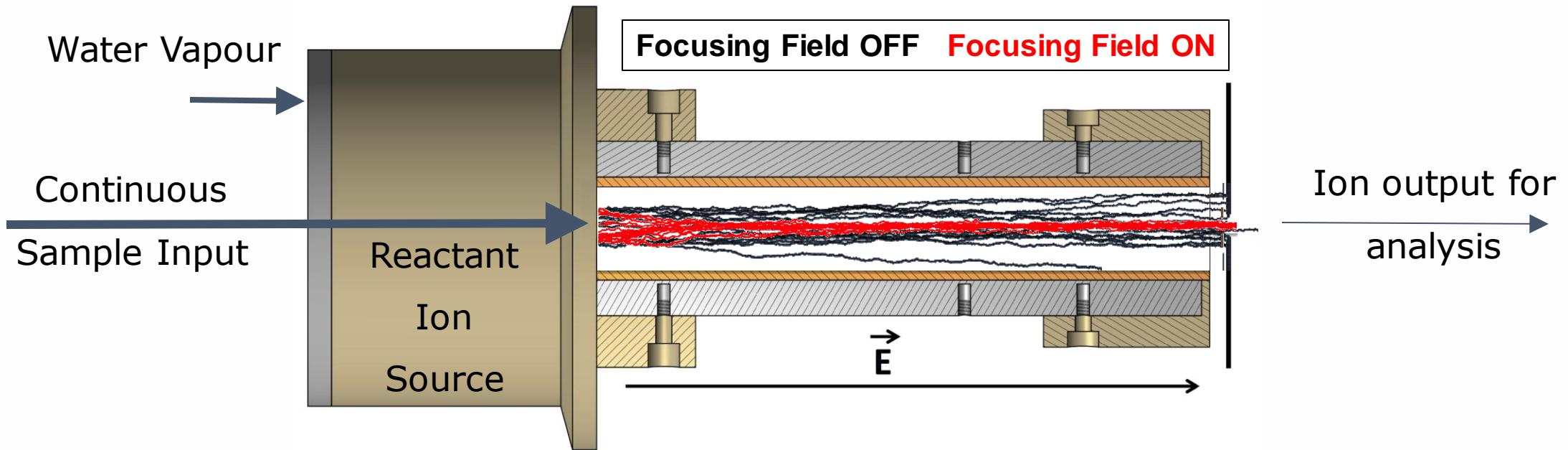
1. Redesign the **reagent ion source** for more ions
2. Radically new **ion molecule reactor** for higher ion transmission (**sensitivity**)
3. Improve the **mass analyzer** for better **separation** (resolution)

Vocus has:

- Better sensitivity
- Better mass resolution
- More compact
- Calibration system included

Ion Molecular Reactor with RF focusing

Vocus

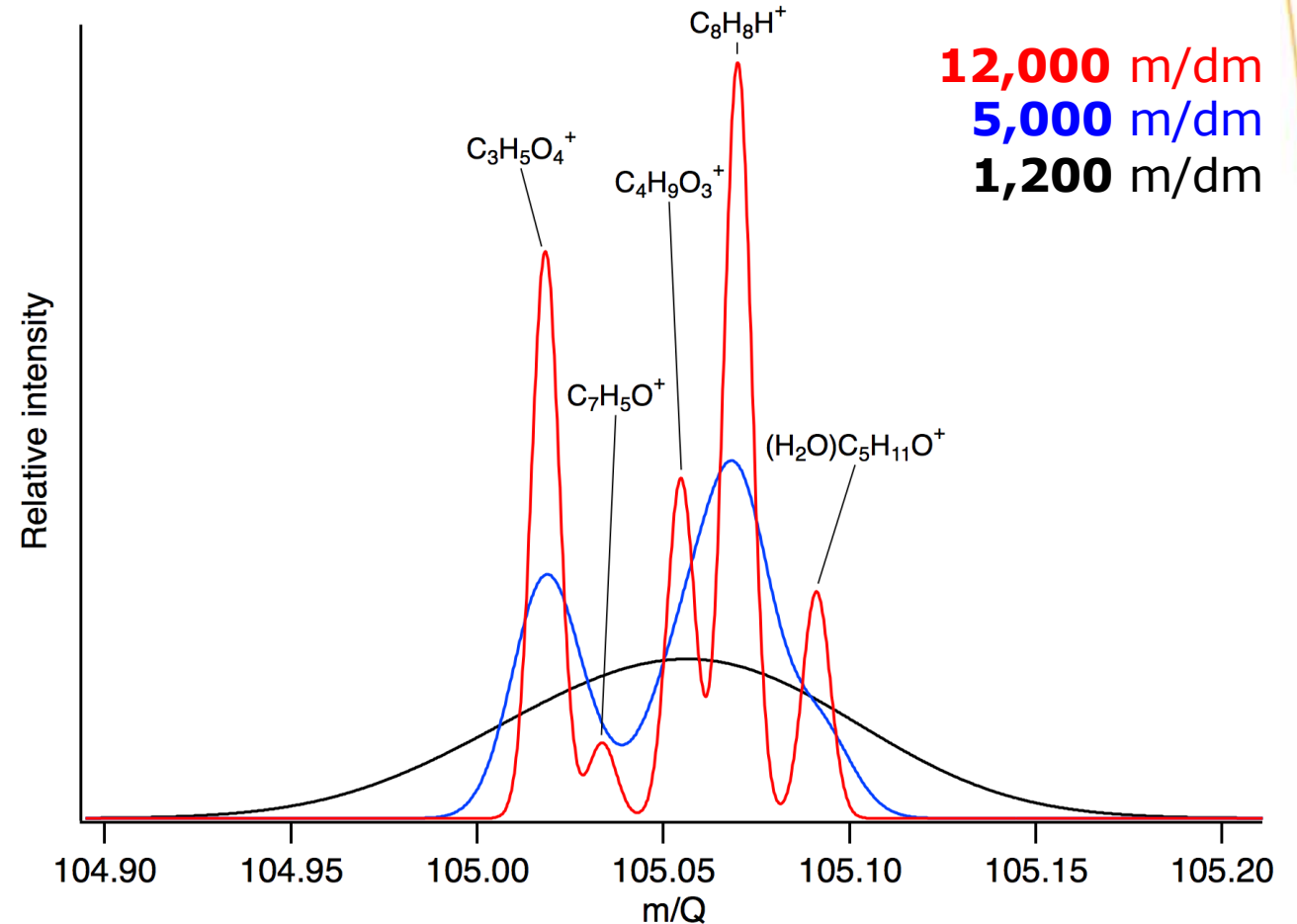


- Vocus is a patented technology developed at TOFWERK combining both a bright ion source and focusing reactor, maximizing chemical ionization and detection efficiency.
- **The result: Sensitivity boost of >10x** utilizing ion focusing which eliminates ion losses, pushing the level of detection and precision of VOC measurements to new limits.

Mass Analyzer with more Resolution

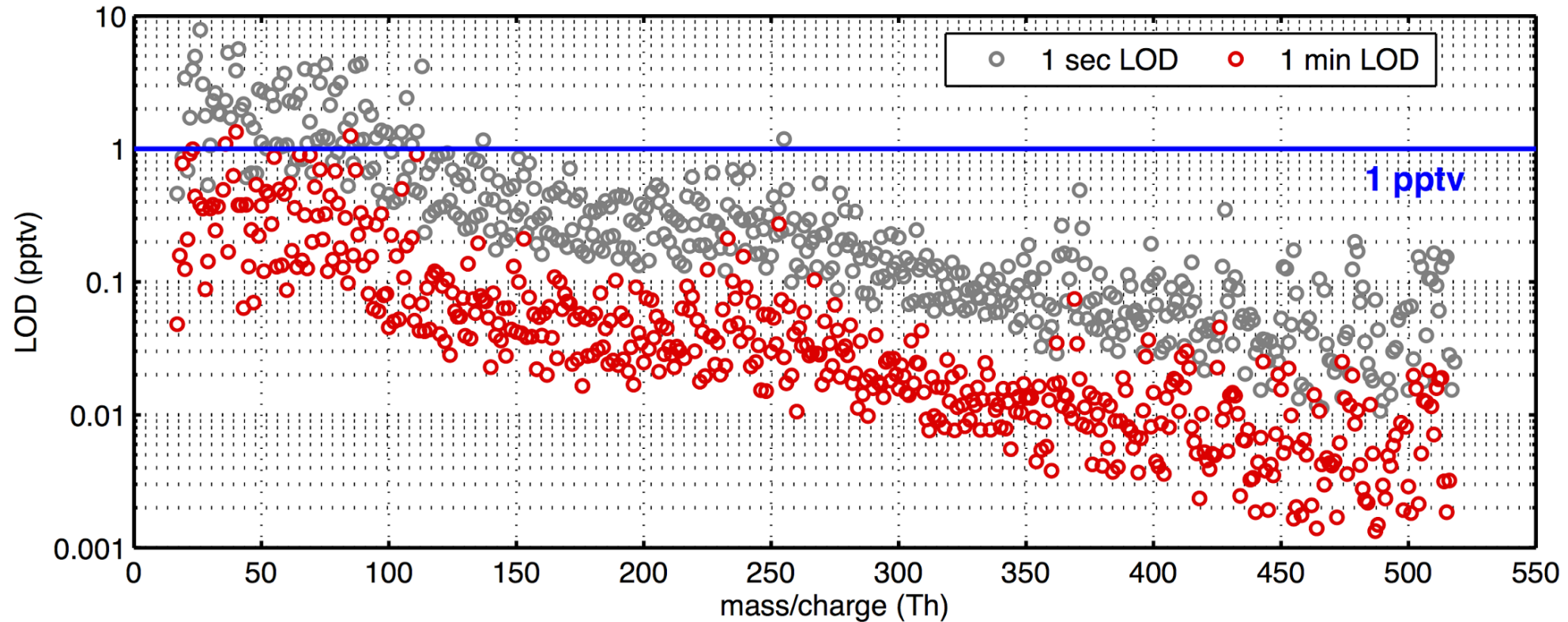
Vocus

- Example mass spectrum from air measured in the Netherlands during ACTRIS by a VOCUS 2R (**red**)
- The spectrum is re-sampled to simulate the same spectrum, at different TOF resolutions (**blue** and **black**)
- **The VOCUS 2R allows quantitative analysis and robust isobar separation even in complex samples.**



Sub-ppt level of detection

Vocus



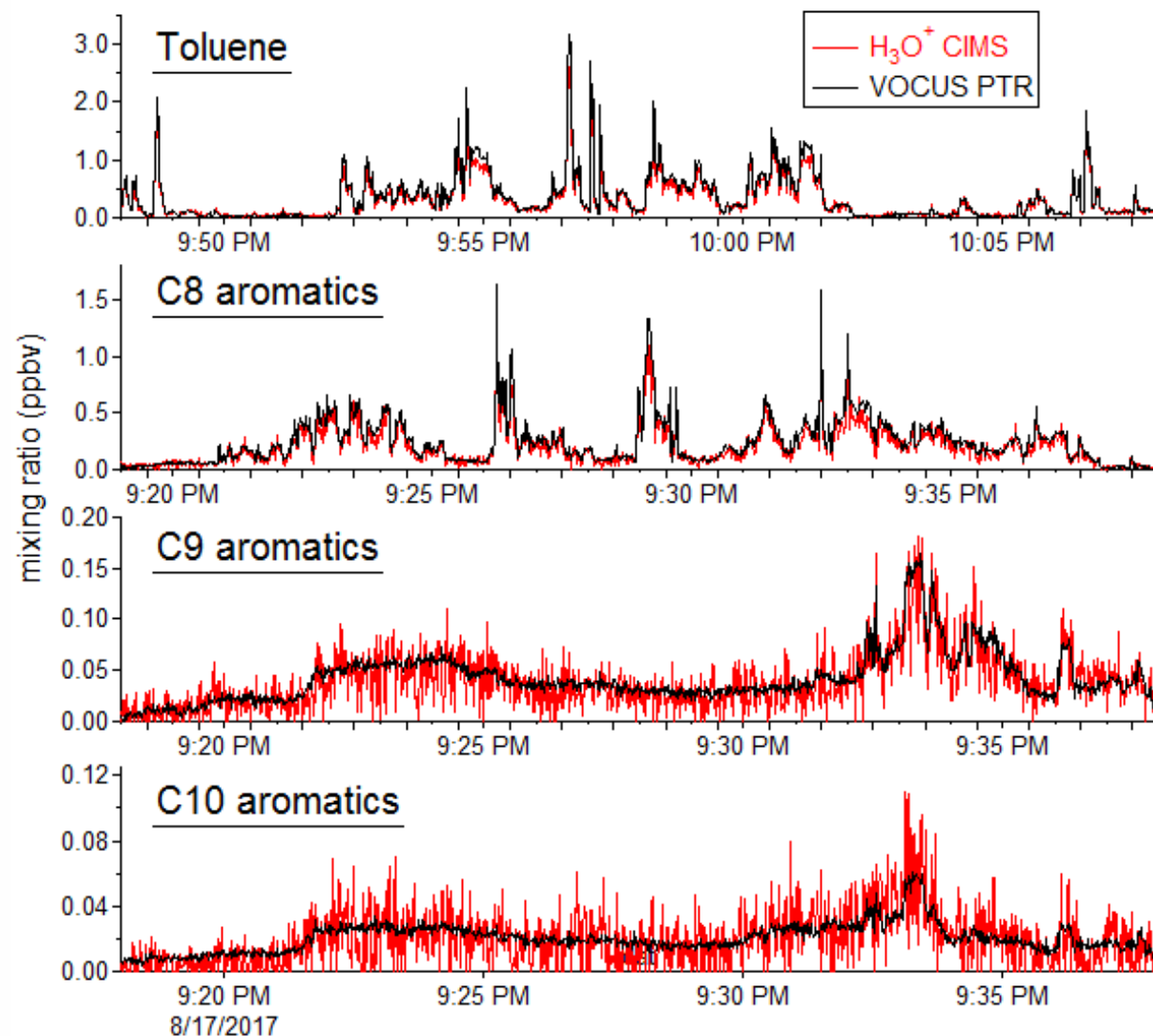
- For the first time, **sub-ppt level of detection in seconds is possible**, raising the bar for VOC analysis speed and high throughput analysis

Signal-to-Noise

Vocus

- 1 Hz, sampling of ambient air in Boulder, Colorado, USA showing quantitative response
- VOCUS (**black**) side-by-side sampling with the NOAA* PTR-TOF (**red**), which is recognized as most sensitive PTR-MS in literature *Atmos. Meas. Tech.*, 9, 2735–2752, 2016
- **The sensitivity of VOCUS yields better precision faster, especially at low concentrations.**

*NOAA PTR-TOF was the most sensitive PTR-TOF for atmospheric measurement before Vocus introduction

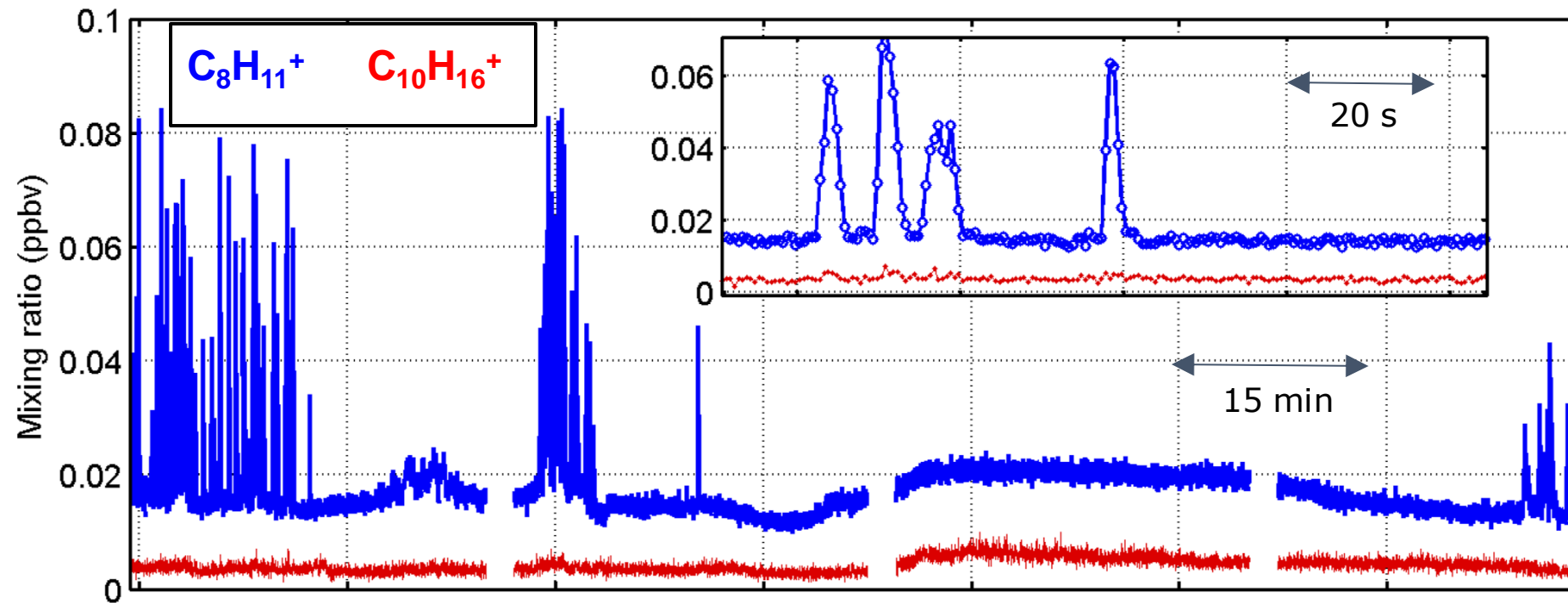


Data courtesy of Carsten Warneke, Joost DeGouw, Abby Koss

TOFWERK

High frequency atmospheric measurements

Specs



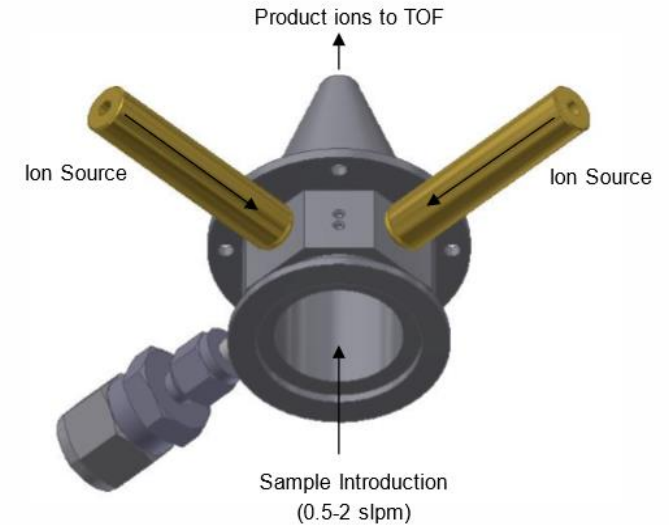
- **Vocus measurements at 2 Hz show excellent signal to noise.**
- **Using real time analysis it is possible to catch really fast event in VOCs measurement.**

Convert Vocus into an API-TOF

- The Vocus has a “medium pressure interface” between the ion source and the TOF analyzer
- The Vocus is therefore a MPI-TOF
- But: the Vocus can be converted into an API-TOF (atmospheric pressure interface – TOF)
- The modular design allows to quickly change from MPI-TOF to API-TOF

Sources compatible with the API-TOF and their main applications :

- APCI positive and negative mode (chlorine compounds, pesticides, explosives...)
- DART (ionization of solids and liquids)
- ESI (electrospray ionization)
- EESI (analysis of aerosol particles)
- AI (**A**mbient **I**ons - more dedicated for inorganic gas)
- many more atmospheric pressure ion sources



Example of an APCI source

Online TD-GC-MS

VOCs

The most popular analytical tool for VOCs measurement is probably **T**hermal **D**esorption (TD) coupled to **G**as **C**hromatography (GC) **M**ass **S**pectrometry (MS).



Lab TD-GC-MS (Perkin Elmer)

GC-MS is a powerful analyzer able to separate, identify and quantify gaz compounds but lack in sensitivity for ppb/ppt level measurement. Thermal desorption is an enrichment technique use to trap VOCs in a sorbent at low temperature. Then the sorbent is heated to inject them in the GC-MS, enhancing the limit of detection.

TD-GC-MS and VOCUS PTR-TOF are most of the time presented as competitor because both can measure really low levels of VOCs.

In fact they are complementary, thanks to their specific weakness and strength.

PID and FID detector

VOCs



PID Detector
(Ionsciences)

PID and FID detector are also commonly use to monitor VOCs in environmental applications.

Photo **I**onization **D**etector is a common tool to detect Total VOCs. It can be portable and detect up to 1 ppb. The measurement is real time and it is a portable detector with no utility.



Total VOC analyzer
(Thermofisher)

Flame **I**onization **D**etector is used to measure Total VOCs in online measurement. The response is real time and limit of detection can go up to 50 ppb. It is a simple and very stable instrument.

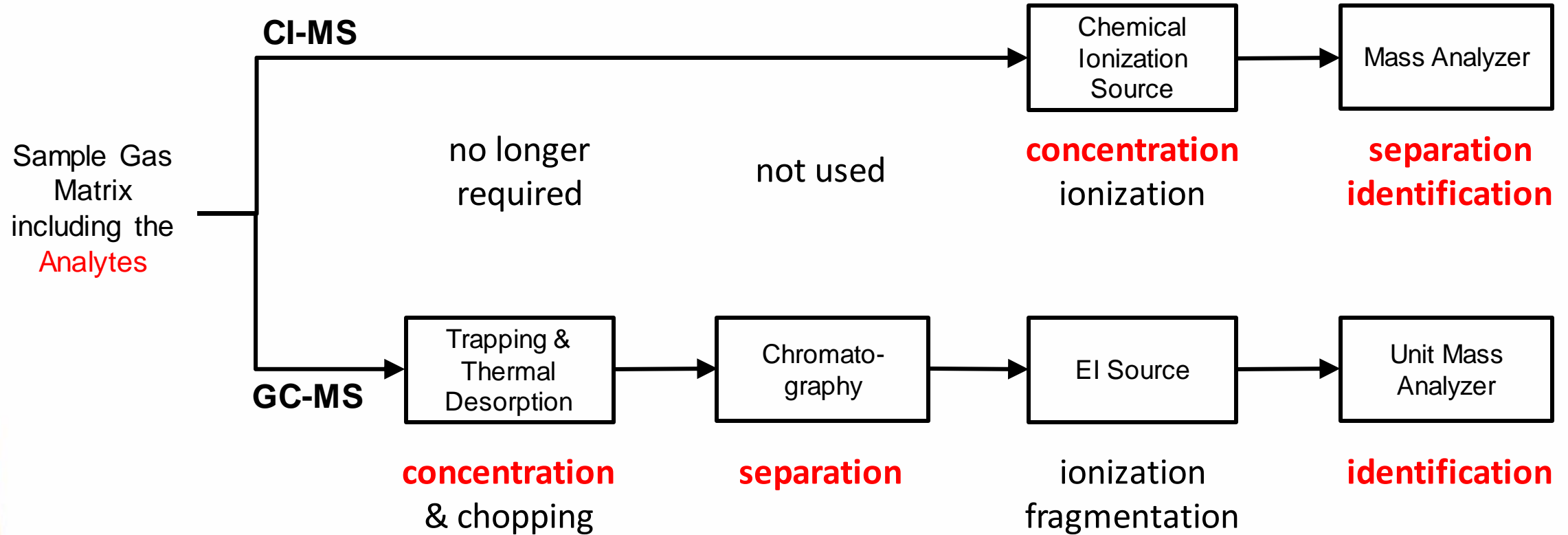
Main performance comparison

VOCs

	PID	Vocus	TD-GC-MS
Sensitivity	1 ppb	1 ppt (1 min average)	5 ppt
Temporal resolution	2 s	100 ms to 1 min	20 mins or more
Affect by humidity	At really high level	Mostly no	Yes depending sorbent
Identification	No	Yes, hard in complex gas	Yes even in complex gas
Quantitation	Yes average	Yes	Yes
Utility gas	No	No	Carrier gas
Field deployable	Portable	Transportable	Transportable

CI-MS vs. TD-GC-MS

Comparison



- GC-MS and CI-MS are two methods for analyzing air samples
- The essential steps are: **concentration**, **separation**, **identification**

Comparison TD-GC-MS / Vocus

VOCs

	TD-GC-MS	Vocus PTR-TOF
Temporal resolution	20 mins or more	100 ms to 1 s typically
Substances covered	Alkanes, alkenes, some species with functional groups	Alkanes*, alkenes*, many species with functional groups
Specificity	High	Medium (no isomeric separation)
Sensitivity	High depending the sorbent	High depending reactant ions
LOD (ppbV)	0.005 in 20 min or more	<0.005 in 1 minute average
Precision	±5%	±10%
Standards required for quantification	Often many (>100)	Semi-quantitative w/o external calibrant
Retrospective analysis	Not in SIM mode	Yes
Automation	Automatic	Automatic
Field deployable	Yes	Yes

* short-chain alkanes and alkenes can be detected using O₂⁺ as the CI agent.

Comparison TD-GC-MS / Vocus

VOCs

	TD-GC-MS	Vocus PTR-TOF
Identification	Yes	Yes but more difficult
Online measurement	Averaging VOCs during trapping + separation time inside the column	Real time, can monitor fast-changing events up to 10ms
Lab measurement	Trapping and then analysis	No sample prep, insanely productive
Lab sampling	Compatible with cylinder, tedlar bag...	Compatible with cylinder, tedlar bag...
Affected by humidity	Yes depending trap used	No
Formaldehyde	Challenging	Yes
Polycyclic aromatic hydrocarbons (PAHs)	Challenging, high boiling point are a problem	Yes
Amines gas	Challenging	Yes
Chlorinated gas	Challenging	Yes, Trichloroanisole is a good example
Sulfurs based	Challenging	Yes

Various intercomparisons show promising outcomes

Comparison

Table 4. Intercomparisons between PTR-MS and alternative methods in this study and the comparison with previous other studies.

Compound	<i>m/z</i>	Alternative method	Slope	Intercept (ppbv)	<i>r</i>	Sampling area type	Reference
Formaldehyde	31	MAX-DOAS	1.01	−0.02	NA	mountain area	Inomata et al. (2008)
		DOAS	1.17	NA	0.84	urban area	Warneke et al. (2011b)
		Hantzsch	1.35	NA	0.74	urban area	Warneke et al. (2011b)
		DNPH-HPLC	NA	NA	NA	in chamber	Wisthaler et al. (2008)
		DNPH-HPLC	1.00	−0.03	0.79	urban roadside area	This study
Acetaldehyde	45	PIT-MS	1.25	NA	0.87	in chamber	Warneke et al. (2011a)
		online GC-MS	1.56	−0.17	0.93	on ship	de Gouw et al. (2003)
		DNPH-HPLC	NA	NA	NA	in forest	Müller et al. (2006)
		DNPH-HPLC	1.10	0.83	0.75	urban roadside area	This study
Acetone	59	AP-CIMS	1.18	0.06	0.94	in flight	Sprung et al. (2001)
		online GC-MS	1.00	−0.05	0.98	on ship	de Gouw et al. (2003)
		online GC-MS/FID	1.03	−0.44	0.90	urban area	Wang et al. (2014)
		DNPH-HPLC	NA	NA	NA	in forest	Müller et al. (2006)
		DNPH-HPLC	0.76	1.88	0.60	urban roadside area	This study
MEK	73	online GC-MS	2.51	0.02	0.95	on ship	de Gouw et al. (2003)
		offline canister	0.85	0.06	NA	in flight	de Gouw et al. (2006)
		online GC-MS/FID	1.39	−0.18	0.89	urban area	Wang et al. (2014)
		DNPH-HPLC	0.88	0.36	0.93	urban roadside area	This study
Benzene	79	offline canister	0.82	0.11	0.91	suburban area	Warneke et al. (2001)
		online GC-MS	1.12	0.00	0.96	on ship	de Gouw et al. (2003)
		online GC-ITMS	0.85	0.00	0.97	suburban area	Kuster et al. (2004)
		online GC-QMS	0.97	0.00	0.92	suburban area	Kuster et al. (2004)
		online GC-FID	0.82	0.03	NA	suburban–urban area	Kato et al. (2004)
		offline canister	0.96	0.07	0.98	urban area	Rogers et al. (2006)
		offline canister	1.08	0.01	0.87	in flight	de Gouw and Warneke (2007)
		offline canister	1.05	−1.16	0.65	urban area	Jobson et al. (2010)
		DOAS	1.22	0.39	0.61	urban area	Jobson et al. (2010)
		online GC-MS/FID	0.80	0.07	0.96	urban area	Wang et al. (2014)
		online GC-FID	1.23	−0.03	0.95	urban roadside area	This study
		offline canister	1.05	−0.03	0.62	urban roadside area	This study
Toluene	93	offline canister	1.18	−0.07	0.96	suburban area	Warneke et al. (2001)
		online GC-MS	1.08	0.01	0.99	on ship	de Gouw et al. (2003)
		online GC-ITMS	0.91	0.00	0.98	suburban area	Kuster et al. (2004)
		online GC-QMS	0.81	0.10	0.95	suburban area	Kuster et al. (2004)
		online GC-FID	0.52	0.16	NA	suburban–urban area	Kato et al. (2004)
		offline canister	0.99	0.02	0.99	urban area	Rogers et al. (2006)
		offline canister	0.88	0.00	0.90	in flight	de Gouw and Warneke (2007)
		offline canister	0.94	−0.43	0.66	urban area	Jobson et al. (2010)
		DOAS	0.60	0.81	0.55	urban area	Jobson et al. (2010)
		online GC-MS/FID	0.94	0.05	0.99	urban area	Wang et al. (2014)
C ₂ -benzenes	107	online GC-FID	1.01	0.02	0.96	urban roadside area	This study
		offline canister	0.78	0.19	0.96	urban roadside area	This study
		online GC-MS	3.20	0.01	0.98	on ship	de Gouw et al. (2003)
		online GC-ITMS	1.02	0.00	0.97	suburban area	Kuster et al. (2004)
		online GC-FID	0.58	0.00	NA	suburban–urban area	Kato et al. (2004)
		offline canister	0.86	0.00	0.91	in flight	de Gouw et al. (2006)
		offline canister	1.31	−0.40	0.99	urban area	Rogers et al. (2006)
		offline canister	0.86	−0.01	0.91	in flight	de Gouw and Warneke (2007)
		offline canister	0.91	0.18	0.61	urban area	Jobson et al. (2010)
		DOAS	0.59	0.04	0.58	urban area	Jobson et al. (2010)
		online GC-MS/FID	0.87	0.09	0.98	urban area	Wang et al. (2014)
		online GC-FID	1.02	0.31	0.96	urban roadside area	This study
		offline canister	0.67	0.38	0.92	urban roadside area	This study

CI-MS concept: use better MS

Conclusion

- **No chromatography!**

- no sample preparation
- no trapping
- no thermal desorption

instead use:

1. **Selective Ionization**

- concentration

2. **Soft Ionization**

- simple spectra
- less interferences

3. **High Mass Resolution**

- resolve remaining interferences
- for identification via mass accuracy

- **Capabilities**

- Can measure challenging species for TD-GC-MS
- no sample preparation
- no trapping
- no thermal desorption
- Fast
- Real-time
- Sensitive
- Quantitative
- Simple
- Can still be coupled with GC

- **Problems**

- Very complex samples → couple to GC
- Some molecules invisible → use other chemistry
- Still more peaks than GC (isotopes)

❖ Calibration of trace-level species can be really challenging.

- **How to generate them properly? How to manage reactive species? What is the accuracy and precision of the calibration?**

❖ Big data is happening!

- Analyzers nowadays can detect ultra traces of gas but how it is true ? Do we lose information or quantity somewhere in the system ?
- Once you reach the ppt world you detect basically everything. The amount of datas is gigantic. Data processing cannot be human anymore.
- **What is relevant ? VOCs are changing everywhere with new materials and new products.**