



Bridging temporal resolution and molecular specificity with a compact GC-PTR for the measurement of volatile organic compounds

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Abstract. Volatile organic compounds (VOCs) play important roles in atmospheric chemistry and air quality, but
10 measurements often require a tradeoff between temporal resolution, molecular specificity, and instrument size and complexity. Online chemical-ionization mass spectrometry provides sensitive, rapid measurements but can be affected by isomeric contributions, fragmentation, and other ion-chemistry interferences, whereas gas chromatography (GC) provides molecular separation and specificity at lower temporal resolution. Here, we present a compact, low-power VOC measurement system that combines *in-situ* gas chromatography and thermal desorption (TD) preconcentration with a newly developed ultracompact
15 proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS) equipped with a novel vacuum-ultraviolet (VUV) ion source. The complete system occupies a 50 x 65 x 55 cm space, weighs < 70 kg, and consumes < 600 W of power during typical operation. The instrument combines high-time resolution, direct PTR measurements with periodic chromatographic measurements for regular molecular speciation. The system was operated continuously for 30 days in Thun, Switzerland with stable calibrant response (average variation of 3.5%) during the ambient measurement period, with demonstrated direct-PTR
20 limits of detection (LODs) of 13 – 136 ppt (1-min) and GC-PTR LODs of 0.1 – 4.0 ppt (1 L sample) across 11 calibrants. Together, these results demonstrate a complementary approach to instrument miniaturization in which reduced detector performance can be offset by upstream analytical separation and preconcentration. In this configuration, the direct PTR measurement provides high-time resolution observations, while periodic chromatographic measurements provide molecular specificity, sensitivity enhancement, and information on analyte-specific ion chemistry and interferences. By reducing the size,
25 power requirements, and operational complexity, this system provides a pathway toward broader deployment of chemically specific VOC measurements at long-term monitoring sites, on mobile platforms, and in locations where infrastructure or reliable power is limited, to investigate emission sources, atmospheric processing, and the formation of secondary pollutants.



1 Introduction

30 Volatile organic compounds (VOCs) are a diverse group of carbon-containing compounds that predominantly exist in the gas phase under typical atmospheric conditions (Atkinson and Arey, 2003; Goldstein and Galbally, 2007). Their emissions sources are extensive, both biogenic and anthropogenic, and temporally and spatially dynamic (Guenther et al, 1995; Gu et al., 2021; Liu et al., 2026). Due to their exceptionally broad range of chemical structures and physical properties, VOCs exhibit widely varying fates once emitted to the atmosphere, both in terms of chemical reactivity and overall lifetime (Atkinson and Arey, 35 2003; Ziemann and Atkinson, 2012). Detailed, accurate monitoring of VOCs is needed to provide insight into emission sources and patterns, oxidation processes including photochemistry and radical cycling, and the formation of secondary pollutants such as tropospheric ozone and secondary organic aerosol (He et al., 2019; Hui et al., 2025). These observations are also critical for identifying changes in emission patterns, evaluating the effectiveness of emission mitigation strategies, constraining atmospheric chemistry models, and gauging the overall impact of VOC emissions on air quality, climate, and health impacts 40 (Warneke, 2012; Li et al. 2019; Liu et al., 2026).

Despite these needs, analytical techniques capable of making high-quality VOC measurements have historically been divided between methods offering high molecular specificity and those offering high time resolution, with both relying on sophisticated and expensive instruments that require substantial infrastructure and expertise for deployment, operation, and data analysis. This bifurcation stems from the use of online or offline gas chromatography (GC) systems coupled with mass spectrometric 45 (MS) or other types of detectors (e.g., flame ionization) versus the use of online chemical ionization mass spectrometry (Lerner et al., 2017; Yuan et al., 2016; Koss et al., 2016; Xu et al., 2022). The online, or offline, GC methods provide highly accurate, chemically specific, measurements but typically at the cost of time resolution (e.g., once per hour for an online system, once per day for an offline system due to the labor-intensive nature). Online chemical ionization mass spectrometry techniques offer high time resolution (e.g., 1 s) data but at the cost of specificity, as these methods cannot provide molecular structure 50 information regardless of mass resolving power.

In particular, proton transfer reaction mass spectrometry paired with time-of-flight technology (PTR-TOF-MS), has been widely used for the detection of VOCs in a variety of environments and measurement platforms (de Gouw and Warneke, 2007; Graus et al., 2010; Sekimoto and Koss, 2020). This broad adoption of the technique is due to its high sensitivity, wide dynamic range, time response, and weak or negligible humidity dependence (Yuan et al., 2017). Furthermore, PTR detection offers the 55 ability to estimate analyte sensitivities using empirical approaches based on proton transfer reaction rate coefficients (k_{PTR}) in combination with instrument specific characterization, such as ion transmission efficiencies and product ion distributions (PIDs) (Jensen et al., 2023). This approach can reduce the reliance on direct calibration with authentic standards for individual analytes, providing a practical advantage over other chemical-ionization techniques. However, this technique cannot offer molecular structure information and is known to be impacted by detection interferences such as fragmentation, cluster 60 formation, and mixed ionization schemes that complicate data analysis and interpretation (Coggon et al., 2024; Link et al., 2025; Zhang et al., 2025; Feng et al., 2026).



The combination of *in situ* GC with PTR-TOF-MS provides complementary analytical capabilities, leveraging the high sensitivity and temporal resolution of PTR-TOF-MS with the molecular separation and identification afforded by GC (Ditto et al., 2025; Rogers et al., 2025). Integrating these approaches offers molecular specificity while retaining the ability to characterize rapid temporal variability in VOC concentrations, providing a more comprehensive description of VOC composition than either technique alone. In addition to providing isomer-level resolution of ambient VOC measurements, GC separation prior to PTR ionization enables the characterization of PIDs for individual analytes (Link et al., 2025). These PIDs can be used to identify and quantify analyte-specific interferences, aiding interpretation and providing a means of increasing the accuracy of direct, non-specified PTR-TOF-MS measurements (Vermeuel et al., 2023; Coggon et al., 2024). Additionally, chromatographic pre-separation can expand the analytical scope of PTR-based methods by enabling the detection and quantification of VOCs that may otherwise be difficult to distinguish or quantify, including compounds classified as hazardous air pollutants (HAPs) or emerging species of interest such as volatile chemical products (VCPs) (Robinson et al., 2025; Link et al., 2025).

Across research and monitoring communities, there is a growing need for analytical instrumentation that reduces the barriers to field deployment and operation while maintaining high-quality data capable of meaningful outputs. This includes instrumentation that is more compact, incorporates fewer variables to simplify setup and operation, requires less maintenance, and consumes less power and other resources (Dobrecevic et al., 2026). Here, we present a compact, integrated VOC measurement platform that combines an *in-situ* GC with thermal desorption (TD) preconcentration and a newly developed ultracompact PTR-TOF-MS. The complete system occupies a 50 x 65 x 55 cm space, weighs < 70 kg, and consumes < 600 W of power during typical operation, substantially reducing the infrastructure requirements associated with conventional high-performance VOC instrumentation. The ultracompact PTR-TOF-MS contains a novel vacuum-ultraviolet (VUV) PTR ion source, which enhances instrument robustness, enabling stable, long-term operation with minimal maintenance. Coupling the *in-situ* GC system with PTR-TOF-MS enables automated acquisition of both direct measurements at high temporal resolution (e.g., 1 s) and periodic molecular speciation measurements. Importantly, integration of the online TD-GC compensates for some of the lower performance specifications of the ultracompact PTR-TOF-MS relative to larger, higher-performance systems. The use of chromatographic pre-separation reduces the reliance on high mass-resolving power for compound identification and quantitation, allowing a low-resolution TOF analyzer to be used without sacrificing the ability to resolve important analytical interferences. The TD-GC system also enhances sensitivity through sample preconcentration.

The instrument acquired ambient-air measurements continuously for more than four weeks during Spring 2025 in Thun, Switzerland. These measurements demonstrate the operational stability of the system and the value of combining continuous, high-time resolution VOC measurements with regular molecular speciation. By reducing the size, power requirements, and operational complexity of PTR-based VOC measurements, this platform expands opportunities for deployment at long-term monitoring sites, on mobile platforms, and in locations with limited access to infrastructure. Such deployments can increase spatial coverage and enable coordinated measurements to investigate local, regional, and global patterns in VOC emissions and atmospheric chemistry.



2 Methods

2.1 Instrument description

The proton transfer reactor time-of-flight mass spectrometer (PTR-TOF-MS) described in this work is a newly developed ultracompact detector (Tofwerk AG). A schematic of the system and its coupling with a thermal desorption gas chromatograph (Aerodyne Research), described below, is shown in Fig. 1. Hereafter this system will be referred to as ultracompact PTR, or compact GC-PTR, for conciseness. The ultracompact PTR system is housed in a standard 6U, 19" rack-mount chassis (483 x 266 x 560 mm), weighs 30 kgs, and is powered solely by 24 VDC requiring 270 W of power at start-up. The system operates with typical resolving power of 1200 $m/\Delta m$ at m/z 100, exemplary instrument sensitivities and limits of detection (LOD) are given in Table 1 and are described below.

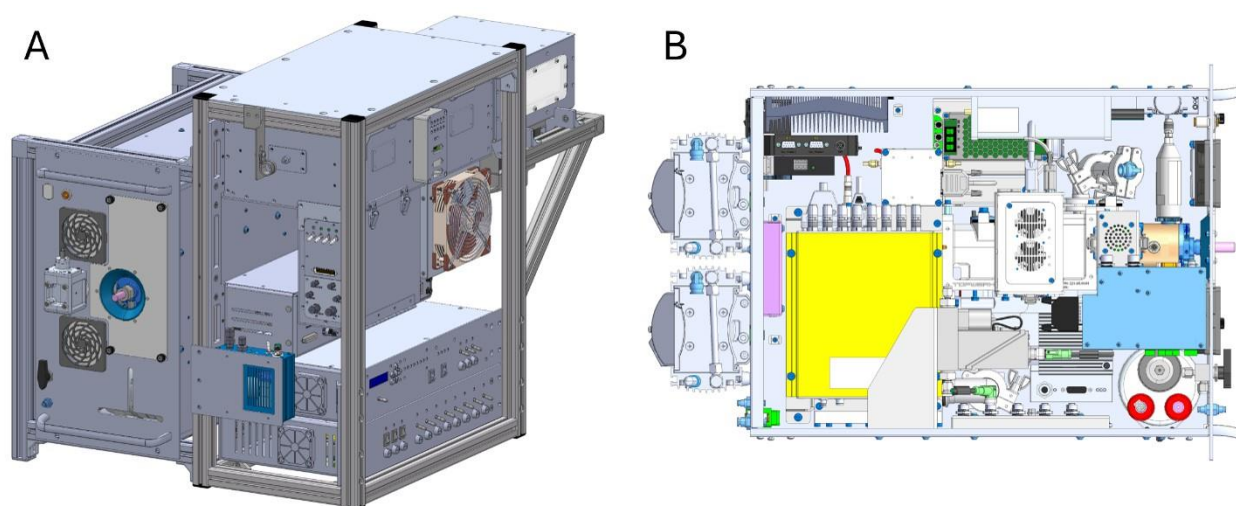
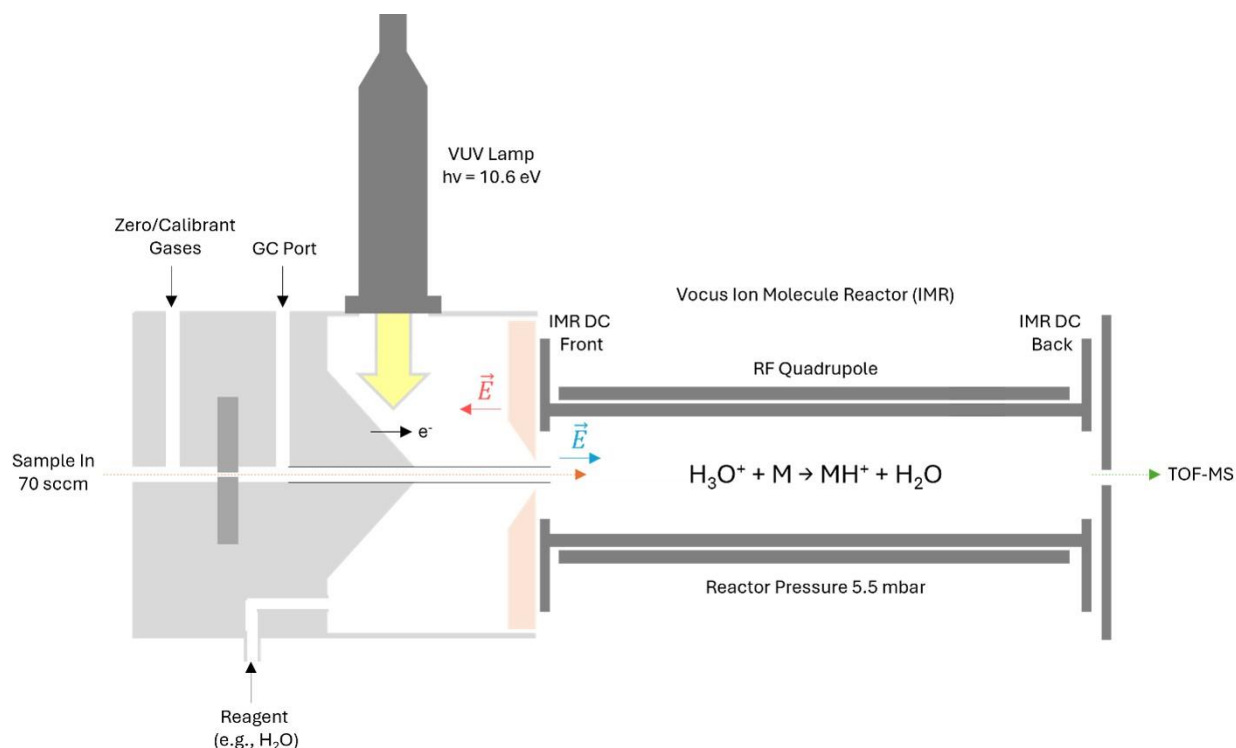


Figure 1. (a) Model rendering of the TD-GC system coupled with the ultracompact PTR-TOF-MS and (b) detailed rendering of the ultracompact PTR-TOF-MS.

Compared to previously described PTR-TOF-MS systems developed by Tofwerk AG (Krechmer et al., 2018), the ultracompact PTR described here has modified electronic and vacuum systems to allow for the size reduction of the instrument. The vacuum system consists of 2 diaphragm pumps (MD1, VACUUBRAND) and a split-flow turbo pump (SF80, Pfeiffer), where one diaphragm pump is used to back the turbo pump while the other is attached to the ion source to maintain fore pressure control in the reactor region. While the ion molecular reactor (IMR) is identical to that used in previous systems (Krechmer et al., 2018), this system employs a VUV-PTR ion source. A schematic of the VUV-PTR ion source coupled to the IMR is shown in Fig. 2. This ion source operates by illuminating a stainless-steel surface with VUV radiation, generating photoelectrons. These photoelectrons are then accelerated using an applied electric field to ionize the desired reagent.



120 **Figure 2. Schematic of the VUV PTR ion source coupled with the ion molecule reactor (IMR).**

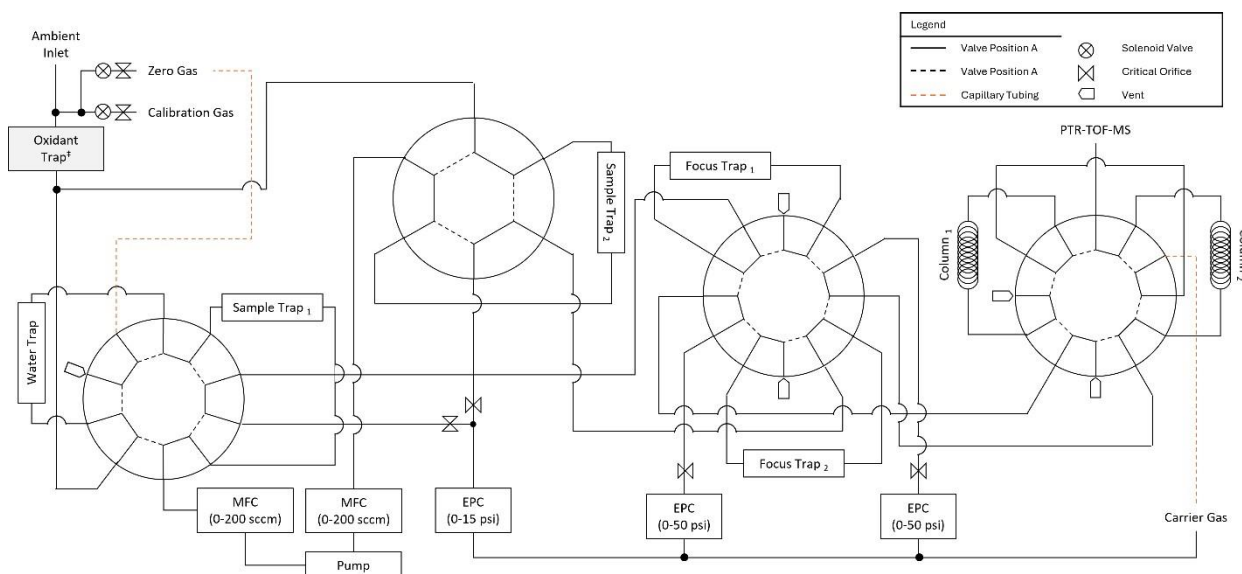
In this system water vapor flows at $5 \text{ cm}^3 \text{ min}^{-1}$ into the source to generate H_3O^+ for subsequent analyte ionization. The sample flow into the PTR inlet is controlled by a sapphire pinhole. In this study, the orifice employed, the pressure downstream, and the pressure drop of the ambient inlet, resulted in a $60 \text{ cm}^3 \text{ min}^{-1}$ sample flow into the reactor. The PTR was operated with an
 125 IMR pressure of 5.5 mbar, a direct current (DC) gradient of 930 V, and an RF focusing voltage of 400 V. Under these operating conditions, we estimate an effective reduced electric field (E/N) of 110 Td in the IMR.

To compensate for the low mass resolving power of the ultracompact PTR, address complexities in PTR data that occur upon ionization (e.g., fragmentation), and resolve isomeric species, the system was coupled with an online gas chromatography (GC) system equipped with two-stage thermal desorption (TD) preconcentration (Aerodyne Research). A previous version of
 130 the TD-GC system was described by Claflin et al. (2021), but the system is described here in detail to reflect changes in design and instrument function.

The TD-GC system designed for coupling with PTR detectors has two different flow path options, a single channel separation (Fig. S1) and a dual channel separation (Fig. 3). The choice between these flow paths depends on the desired data output and available labor, with key considerations including the target compound volatility range, duty cycle constraints, and
 135 maintenance requirements. The range of species resolved is dependent on the type of column installed, the temperature program



applied, and the thermal desorption traps utilized in the preconcentration step. Each of these three items are easily modified in the system, depending on the species desired to be resolved.



140 **Figure 3. TD-GC flow path schematics of dual channel systems.**

Both flow-path designs provide the same basic system functionality: sample preconcentration followed by chromatographic separation. Sample air is pulled into the instrument via a miniature diaphragm pump placed downstream of a mass flow controller (range: 0-200 sccm). The sample flow is initially collected onto the first stage of the TD preconcentration system, which is a sorbent tube. The flow rate and length of sample collection onto the sorbent tube is user defined, typically 50-100 sccm for 1-10 min. After the sample collection onto the sorbent tube, the system performs a post-collection water purge where dry zero gas (e.g., UHP nitrogen) is forward-flushed across the sorbent tube. The sample is then transferred to the second stage of the TD preconcentration system by backflushing the sorbent tube with carrier gas (e.g. helium) while the tube is subjected to a user defined temperature ramp to desorb the analytes. The second stage of the TD preconcentration system is a focus trap which further preconcentrates the analyte onto a smaller mass of adsorbent. After collection onto the focus trap, the sample is then flash-heated into carrier gas to the head of the GC column for subsequent separation via a user defined chromatographic temperature ramp. It should be noted that preconcentration system is equipped with a Peltier cooler (TE Technology) for sub ambient sample collection, tested down to -10°C but typically operated between $10 - 15^{\circ}\text{C}$. All internal wetted surfaces of the TD-GC, meaning any surface the analyte contacts, are inert materials, consisting of passivated stainless-steel tubing and fittings (e.g., Sulfinert, Restek) along with PFA tubing and Teflon fittings.

The single channel separation TD-GC is equipped with two sorbent tubes in the first stage of the TD preconcentration system. The sorbent tubes can be exposed to atmospheric species that cause degradation of the adsorbent material over time (e.g.,



water, oxidants, acids) and therefore require more frequent replacement (e.g., every 300 cycles) versus the focusing trap which is protected from exposure to these species. With the single channel separation TD-GC system, the method is designed to alternate between each sorbent tube during ambient sampling resulting in a system that requires hands-on maintenance half as often as a system equipped with a single sorbent tube. Both sorbent tubes are desorbed to the same focusing trap, with subsequent separation onto a single GC column.

For the dual channel separation TD-GC, the system is equipped with two different GC columns that operate in parallel. Typically, these are two different columns, each optimized for different volatility ranges. For this flow path, each separation channel has its own dedicated sorbent tube and focusing trap. The system is equipped with two mass flow controllers to individually control the sample flow to each sorbent tube. The benefit of this design is that each channel's sample can either be collected in parallel (e.g., sample the same air mass) or in series (e.g., to have greater total sampling time coverage), with each channel's sampling period being individually controlled.

For both the single and dual channel separation flow paths, the TD-GC systems are equipped with a three-inlet design, this allows sampling of ambient air, zero gas (e.g., UHP nitrogen or zero air), and calibration gas to be automated via software sequencing. The flow of the zero gas and calibration gases into the system are controlled by critical orifices mounted upstream of solenoid valves.

The TD-GC systems are coupled to a PTR by a heated transfer line, typically operated at 125 °C (Fig. S2). On the ultracompact PTR, the heated transfer line connects to a low-pressure port which is downstream of the sapphire pinhole (Fig. 2). During chromatographic separations, the column eluent flows to this port in $\sim 2 \text{ cm}^3 \text{ min}^{-1}$ carrier gas while the PTR inlet is overflowed with zero air. This design ensures that all the GC eluent is sampled into the PTR IMR with low, stable backgrounds supplied by the PTR inlet zero air overflow. During direct PTR operation, a small amount of carrier gas ($\sim 1 \text{ cm}^3 \text{ min}^{-1}$) is flowing through the heated transfer line to continuously flush the flow path for cleanliness and to avoid dead volume. This flow of carrier ($\sim 1 - 2 \text{ cm}^3 \text{ min}^{-1}$) has been shown to not interfere with the ion chemistry occurring in the IMR.

When the TD-GC is operated in an environment that has consistently high levels of reactive gases (e.g., ozone), an oxidant trap upstream of the first stage of preconcentration is utilized to prevent sampling artifacts (Helmig, 1997). Within the oxidant trap, the sample is flowed through a quartz tube with $\sim 1 \text{ g}$ of preconditioned NaSO_3 at a temperature of 35 °C. Directly before use, the NaSO_3 aliquot is heated to 80 °C for 1 hour with ambient air flowing through. This conditioning step drives off contaminants adsorbed while the NaSO_3 was in storage. The NaSO_3 aliquot is replaced with the same maintenance cycle as the TD preconcentration sorbent tubes.

The TD-GC system used in this study had the following operating parameters and specifications: the TD-GC system was a dual channel separation system. The first channel was equipped with a 15 m MXT-QBOND PLOT column (Restek) with 5 m of MXT-1 (Restek) column guard attached to both ends of the PLOT column to act as a particle trap. To further protect the GC and PTR instruments from PLOT particle migration, frits were installed before the upstream column guard, and after the downstream column guard. This channel, termed high volatility, was optimized to resolve $\text{C}_3 - \text{C}_6$ hydrocarbons, and $\text{C}_1 - \text{C}_4$ OVOCs. The second channel, termed mid volatility, was equipped with a 30 m MXT-624 column (Restek) optimized to resolve



$C_5 - C_{12}$ hydrocarbons, and $C_2 - C_{10}$ OVOCs. Each channel was equipped with multi-bed adsorbent sorbent tubes and focusing traps (Markes International) consisting of Tenax TA / Graphitized Carbon / Carboxen 1000 adsorbents. These multi-bed traps are optimized for $C_{2/3} - C_{30}$ hydrocarbons and OVOCs, including halocarbons, siloxanes, nitrogen and sulfur containing species. It should be noted that the use of multi-bed traps can help to reduce, but not eliminate, sampling artifacts associated with single bed Tenax sorbent tubes. The use of multi-bed traps in tandem with the oxidant trap, described above, is done to minimize sampling artifacts, ensured by routinely sampled instrument blanks and calibrations.

For this study, sample air was first pulled through the TD-GC system by both mass flow controllers for 60 seconds to purge dead volume in the internal inlet flow path. The sample flow was then routed to both sorbent tubes simultaneously for active sample collection for 10 minutes at $100 \text{ cm}^3 \text{ min}^{-1}$ per channel. The sorbent tubes were each held at 20°C during the sample collection period. After the sample collection, the sorbent tubes were purged with zero gas (UHP N_2) for 120 s at $40 \text{ cm}^3 \text{ min}^{-1}$ to reduce the level of trapped water. After purging, each sample was transferred via a helium backflush to its designated focusing trap by ramped heating of the sorbent tube to 300°C in 60 s followed by a 30 s hold at 300°C . After the transfer to the focusing trap, the analyte was held at 15°C until injection by flash heating to 300°C onto the designated GC column. For the high volatility channel, the sample was injected while the column was held at 50°C , the column was then ramped to 100°C at $40^\circ \text{C min}^{-1}$, then to 150°C at $46^\circ \text{C min}^{-1}$, followed by a 5.5 min hold at 150°C , resulting in a 7.8 minute chromatogram. For the mid volatility channel, the sample was injected while the column was held at 35°C , after a 2.6 min hold at 35°C the column was ramped to 100°C at $41^\circ \text{C min}^{-1}$, then to 150°C at $15^\circ \text{C min}^{-1}$, and finally to 235°C at $34^\circ \text{C min}^{-1}$, resulting in a 10-minute chromatogram. After each separation the columns were backflushed to clean the path, the MXT-QBOND at 200°C for 200 s and the MXT-624 at 235°C for 160 s. UHP helium was used as the carrier gas for transfers between the preconcentration traps and for both chromatographic separations.

2.2 Sampling design

As shown in Fig. S2, the PTR and the TD-GC house separate inlets for ambient sampling. For this study, both the PTR and the TD-GC were subsampling from a 5 m, 3/8" OD (1/4" ID) PFA ambient inlet. To reduce the residence time on the ambient inlet, two supplemental inlet pumps, each set to pull 1.5 SLPM, were installed on the ambient inlet downstream of 1) the PTR and 2) the TD-GC inlets. This design is required as both the PTR and the TD-GC overflow their respective instrument inlets when conducting zero or calibration periods.

Figure 4 provides an example of the sampling methodology used for this project, where the system was set to operate on a 90-minute duty cycle. During each 90 min cycle, the PTR system acquired direct-PTR data for 65 min; for 10 min within this period, the TD-GC preconcentration system simultaneously collected a sample. The last 25 minutes of the cycle were devoted to detection of the chromatographically separated samples. This sampling strategy, where the TD-GC sample is collected during direct-PTR data acquisition, allows the chromatographically resolved data to be directly compared to the non-specified data. An example of a similar sampling method for a system equipped with a 1-channel TD-GC system is also provided in Fig. S3.



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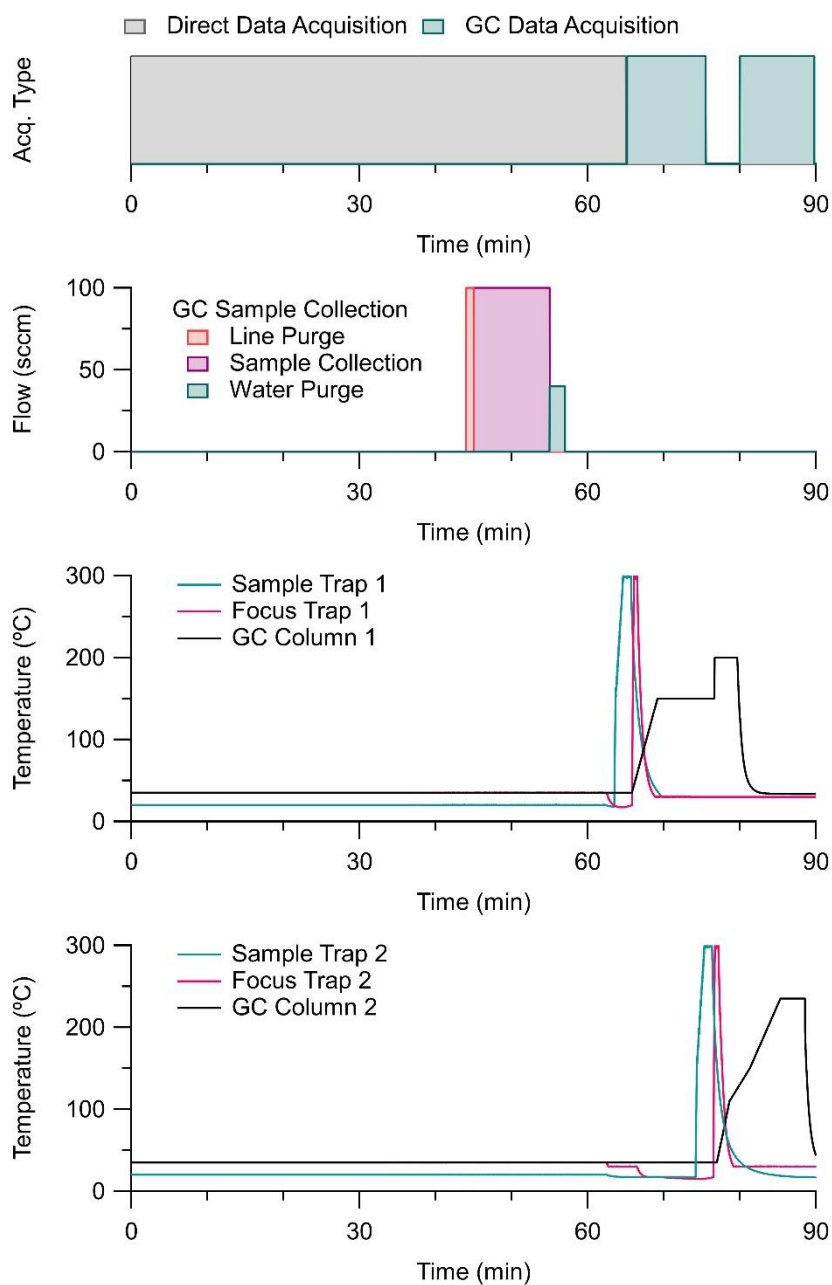


Figure 4. Sampling methodology for a dual channel TD-GC coupled with PTR-TOF-MS. The cycle overview is split into four axes for ease of visualization. Methodology shown is an example, all timings, flow rates, heat rates, etc. can be modified depending on use case.



230 2.3 Calibrations

For instrument calibration, both the PTR and TD-GC were simultaneously connected to an 11-component calibration mixture consisting of 1 ppm per analyte diluted with UHP N₂, list of analytes given in Table 1. The TD-GC utilizes inline dynamic dilution with zero gas (UHP N₂) to further dilute the calibration gas to 1.8 ppb before collection in the preconcentration system. For this study, the TD-GC system collected both calibrant and instrument zero samples (UHP N₂) for 10 min at 100 cm³ min⁻¹, identical to how the ambient samples were collected. During the measurement period, the TD-GC system conducted daily calibrations which consisted of two consecutive calibrations with preceding and the succeeding system zeros. The TD-GC zero and calibration periods were set to occur on a rolling schedule, every 26.5 hours, to avoid interfering with diurnal profiles. Aside from the daily GC-PTR calibration checks, the PTR conducted direct multi-point calibrations (delivered calibrant concentration range of 3 – 15 ppb) at the start and end of the measurement project. During the ambient measurement period, direct instrument zeros were measured for 2 min by the PTR every hour.

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2.4 Data analysis

Operation of the TD-GC is controlled via a Labview-based stand-alone executable (National Instruments Inc, Aerodyne Research) installed on the TOF-MS computer. The PTR was operated with TofDAQ v.1.99 acquisition software (Tofwerk AG). The mass spectral data acquired from the PTR was integrated as unit mass resolution data, undergoing no post-collection mass spectral fitting. After background correction and removal of instrument zero periods, the direct mass spectral data, which was acquired at 1 Hz, was averaged to 1 min time resolution. Chromatographic data was acquired at 5 Hz, and chromatographic integrations of the TD-GC data were done using TERN chromatographic analysis software (version 2.3.0, Aerodyne Research) (Isaacman-VanWertz et al., 2017).

For this study, a procedure employed previously (Karbiwnyk et al., 2003; Lerner et al., 2017; Claffin et al., 2021) for GC-EI-MS (gas chromatography coupled to electron ionization mass spectrometers) data was utilized to normalize both the GC-PTR and the direct-PTR data. This normalization uses long-lived halocarbons present in the atmosphere to account for drift in sensitivity due to changes in detector response. In this study, ambient carbon tetrachloride (CCl₄), resolved by the GC, was used. This halocarbon demonstrated no significant variation in its temporal behavior over the course of the measurement period, indicating no local source which would impact its effectiveness as a normalization agent. For the GC-PTR data, a normalization factor (NF) was calculated for each sample by dividing the chromatographic peak area for CCl₄ by the average CCl₄ response from the measurement period. The GC-PTR data was then corrected by dividing the integrated peak areas by this NF. In some cases, it may also be necessary to correct for variations in preconcentrated sample volumes, however for this study this correction was not necessary as the variability in collected volume was negligible. To normalize the direct-PTR data, the NF generated from the GC-PTR data was expanded onto the direct-PTR time basis (1 min), then linearly interpolated between GC sample collection times. The direct-PTR ion data were then divided by this direct-PTR NF. It should be noted

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that CCl_4 is detected by the PTR as the fragment CCl_3^+ (m/z 117), an ion which has other atmospheric contributors, consequently GC pre-separation is a necessary component to this normalization method for PTR data.

Calibration results for the system, for both direct-PTR and GC-PTR modes, including analyte list, quantitation ion used, instrument sensitivities, limits of detection (LODs), and standard deviations in analyte response over the measurement period (30 days) are provided in Table 1. It should be noted that the sensitivities given for direct- and GC-PTR are in different units; normalized counts per second per ppb (ncps ppb^{-1}) and normalized counts per ppb (ncts ppb^{-1}), respectively. To directly compare the two sensitivities in the same unit, differences in sample flow rates and sample collection timing for each method must be considered (Claflin and Lerner, 2023), this will be discussed in Section 3a. After normalization, the ambient data was converted to mixing ratio by dividing the normalized signal by the normalized sensitivity (Table 1).

2.5 Sampling site description

Ambient sampling demonstrated in this work was conducted in Thun, Switzerland ($46^\circ 45' 4.25''\text{N}$, $7^\circ 37' 17.98''\text{E}$) at Tofwerk AG (Fig. S4). The instruments were deployed on the top floor where an ambient inlet was installed at an approximate height of 20 m from the ground to sample from the side of the building. The system made continuous measurements for 30 days, February 27 – March 28, 2025. During this time the average daily ambient temperature maxima and minima were 11.1 ± 4.4 °C and 2.5 ± 3.4 °C, respectively. Dominant wind direction was from the west/northwest, with regular contribution of stronger winds from the southeast across Lake Thunersee.

3 Results

3.1 System performance

The compact GC-PTR system reports two data streams: direct-PTR and GC-PTR. Each of these data streams has their own associated analyte sensitivities and limits of detection (LODs). Table 1 reports the sensitivities, LODs, and standard deviations in calibrant response for 11 VOCs commonly reported by PTR methods. The standard deviations in calibrant response represent a 10-day continuous measurement period that was not impacted by external events (e.g., power outage, maintenance events on the ambient inlet).

With PTR ionization detection schemes, VOC sensitivity is a function of analyte proton affinity, ion mass due to transmission effects, and depends on the extent of fragmentation and cluster formation that the compound undergoes upon ionization (Sekimoto et al., 2017; Jensen et al., 2023). The direct-PTR sensitivities for the ultracompact PTR described in this study range from 401 ncps ppb^{-1} to 1769 ncps ppb^{-1} depending on the compound (ncps, normalized counts per second). The 1-min averaged LOD for the direct-PTR data range from 13 ppt to 136 ppt. The direct-PTR LODs are a function of the compound sensitivity and the standard deviation in the background signal of that ion.



Table 1. Quantification ions, measured sensitivities, limits of detection, and normalized standard deviations in calibrate response for both the direct-PTR and GC-PTR measurements.

Calibrant	Quantitation Ion [MH ⁺]	Direct-PTR		GC-PTR		Standard Deviation (%) ^c
		Sensitivity (ncps ppb ⁻¹)	Limit of Detection (ppt, 1 min avg) ^a	Sensitivity (ncts ppb ⁻¹)	Limit of Detection (ppt, 1 L) ^b	
acetonitrile	42	1073	98	1.01E+06	0.63	2.2
acetaldehyde	45	817	62	5.25E+05	4.01	3.4
acrylonitrile	54	1784	18	1.75E+06	0.20	2.4
acetone	59	1769	27	1.92E+06	0.98	4.9
isoprene	69	479	95	5.05E+05	3.56	3.3
methyl ethyl ketone	73	1416	13	1.67E+06	0.21	6.2
benzene	79	649	121	7.30E+05	0.43	1.1
toluene	93	910	58	1.02E+06	0.11	2.0
m-xylene	107	1116	41	1.33E+06	0.07	3.9
1,2,4-trimethylbenzene	121	1034	136	1.23E+06	0.19	7.1
α-pinene	137	401	46	4.33E+05	0.45	1.4

^a Direct-PTR limits of detection (LOD) were calculated as 3 times the 1-minute standard deviation in signal divided by the sensitivity.

^b GC-PTR LODs were calculated as 3 times the standard deviation of the baseline multiplied by the full width at half maximum (FWHM) of the chromatographic peak and then divided by the sensitivity.

^c Normalized standard deviation of calibrant response across continuous 10-day measurement period not impacted by external events (e.g., power outage, ambient inlet maintenance).

The GC-PTR sensitivities follow the same trend as the direct-PTR sensitivities, but are a different magnitude, ranging from 4.25×10^5 ncts ppb⁻¹ to 1.90×10^6 ncts ppb⁻¹ depending on the analyte (ncts, normalized counts). The GC-PTR sensitivities are a function of the sensitivity of the detector, here the ultracompact PTR and of the sample volume preconcentrated by the GC. For this study, each sensitivity represents a 1 L sample collected in 10-min by the GC system. Claflin and Lerner (2023) offer a discussion of the comparison between direct-PTR and GC-PTR sensitivities. The relationship between the direct-PTR and GC-PTR sensitivities demonstrated in this study, including their conversion to a unified unit basis (cts per mL of air sample), is shown in Fig. S5. In their native units, the GC-PTR and direct-PTR sensitivities demonstrate a linear relationship ($R^2 = 0.924$) with the GC-PTR being a factor 1102 times more sensitive than the direct-PTR mode. However, when the differences in sampling flows and sample collection times are considered, the sensitivities from the two modes fall on the 1:1 line. This unification is useful as both an instrument performance check and to show that a sensitivity demonstrated by one mode (e.g., GC-PTR) can be directly applied to data in the second mode (e.g., direct-PTR). This is beneficial as the GC offers an efficient way to calibrate across many species, including isomers, at once; using complex, multi-component gas standards for example. The relative standard deviations in calibrant response are reported in Table 1, ranging from 1.1 – 7.1 % with an average of 3.5 % across the 11 analytes reported. The GC-PTR LODs range from 0.07 ppt to 4.01 ppt for the calibrants listed. The GC-PTR



315 LODs are a function of the compound sensitivity, the chromatographic full width half maximum (FWHM), and the standard deviation in the baseline of the chromatogram surrounding the analytes elution time for the quantification ion used.

While the compact system has lower sensitivities and higher LODs for the direct-PTR data, this direct data is representative of lumped ion signals, meaning the sum of isomers or multiple contributing species, where 1-min LODs on the order of 50 ppt are not unreasonable for many environments (e.g., urban and remote forested regions) where concentrations of VOCs are typically 10 – 1000 ppt (Liu et al., 2025; Hellén et al., 2018). The low LODs demonstrated for the speciated data, on the order of 1 ppt, demonstrated by the GC-PTR data offer the ability to obtain highly detailed information on the molecular level including in environments where some isomers may be present in low concentrations. The low LODs for speciated data is important as some species present in low concentrations may contain molecular structures that make them more active in terms of reactivity or SOA and O₃ formation potentials (Kwok and Atkinson, 1995; Ziemann and Atkinson, 2012). Resolving temporal variations in low-concentration species may also aid source apportionment and the characterization of loss processes. System product ion distributions (PIDs) were also evaluated to determine whether the VUV ion source utilized in the ultracompact PTR generated similar distributions to PTR systems equipped with plasma ionization sources. Figure S6 shows exemplary PIDs for a variety of atmospherically relevant VOCs, all detected in ambient air immediately before the 30-day measurement intensive discussed throughout this work. For the comparison of the PIDs between the VUV and plasma PTR ion sources, the TD-GC system was attached to two different PTR-TOF-MS; one equipped with a plasma source and one with the VUV source. The TD-GC then alternated ambient and calibration samples between the two detectors to observe the PIDs generated from each system. For this comparison, each PTR system was operated with an estimated E/N of 110 with similar mass transmission curves, verified by the extent of monoterpene fragmentation, charge transfer ion formation from aromatics, and cluster ion formation of acetone. As shown in Fig. S6, the PIDs generated from each PTR system were similar and showed no significant bias toward enhanced fragmentation or cluster formation in one system versus the other. Also, the composition of the PIDs formed for each compound was identical, meaning the same fragment ions were formed (e.g., C₆H₇⁺ being the dominant fragment ion from ethyl benzene in both cases). This comparison demonstrates that measurements conducted with the new VUV PTR ion source can be directly compared to previous, or future, work conducted with plasma PTR sources, as long as the operating conditions (e.g., E/N) of the PTR system are well characterized and defined.

340 3.2 Ambient measurements

As an example of the chromatographic resolution applied during this study, Fig. 5 demonstrates separations of both the calibration mixture (Fig. 5A) and an ambient sample (Fig. 5B) for reference. These chromatograms were resolved on the second channel of the GC system which was equipped with the MXT-624 column, operated to resolve C₅ – C₁₂ alkanes/alkenes, C₆ – C₁₀ aromatics, and C₁ – C₁₀ oxygenates in 500 seconds for this study. In Fig. 5, only the ions associated with species present in the calibration mixture are shown to offer a simple visual example of the volatility and functionality span of a typical separation that is paired with PTR for the analysis of ambient air by the GC-PTR system.



Figure 5 (C-L) shows a sub-set of the ambient data for both the direct measurement of the associated quantitative ion (Table 1) and the chromatographically resolved species for each of the species present in the calibration mixture for which system sensitivities were directly measured, except α -pinene which will be discussed in detail later. For most of these examples (Fig. 5 C-J) the direct data is compared to a single compound that was chromatographically resolved from the ambient data. For example, the m/z 45 ion directly measured is compared only to the GC resolved acetaldehyde, without considering contributions to the ion signal from other isomers or interferences from other species due to the formation of that ion as a fragment or a water cluster. For the C_8 and C_9 aromatic data shown, the various contributing isomers were fit separately in the chromatographic data and each isomer's concentration was summed to compare to the measurement of the corresponding direct ion. For the C_8 aromatics, to convert these signals to concentration, the calculated sensitivity for m-xylene was also applied to o-xylene and p-xylene (which co-elutes with m-xylene) isomers, while a sensitivity of 6.55×10^5 ncts/ppb was applied to the ethyl benzene isomer. This lower sensitivity for ethyl benzene was calculated based on the ratio of protonated molecular ion detected versus the dominant fragment ion (m/z 107 / m/z 79) in the chromatographically resolved data. Similar for the C_9 aromatics, the sensitivity measured for 1,2,4-trimethyl benzene was applied to 1,3,5-trimethyl benzene and 1,2,3-trimethyl benzene, while a sensitivity of 6.0×10^5 ncts/ppb was applied for the i-propyl benzene and n-propyl benzene isomers to account for their non-negligible fragmentation upon ionization.

To quantitatively compare the agreement between the direct and the chromatographically resolved ambient data, the direct data was averaged onto the GC sample collection time basis so that the two data types could be directly compared; this comparison is shown in Fig. S7. In these correlation plots, the dark blue data points represent the subset of data shown in Fig. 5, while the light blue data points include the comparison for the entire data set. The 1:1 line is shown in all plots in red as a reference. The statistics for these correlations for the subset of data shown in Fig. 5 are given in Table S1. The slope and intercept values were calculated using orthogonal distance regression (ODR) to account for error in both the direct and GC-resolved data, whereas the R^2 values were calculated using standard linear regression.

As seen from these correlations, the agreement between the chromatographically resolved compound(s) and the associated direct ion is very good ($R^2 \geq 0.980$) for acetonitrile, acetone, toluene, the C_8 and C_9 aromatic sums, and the sum of monoterpenes. The comparisons for these species also demonstrate slopes between 0.88 – 1.22 with intercepts near zero, meaning the high time resolution data is well attributed by the specified compounds resolved by the GC. The benzene data shows good correlation ($R^2 = 0.856$) but with a slope of 2.02. Interferences to the m/z 79 ion are well documented (Coggon et al., 2024; Link et al., 2025), with common sources being ethyl substituted aromatics. The overestimation of benzene from m/z 79 in the direct data in this study further corroborates the need for careful designation of this ion to benzene without GC pre-separation.

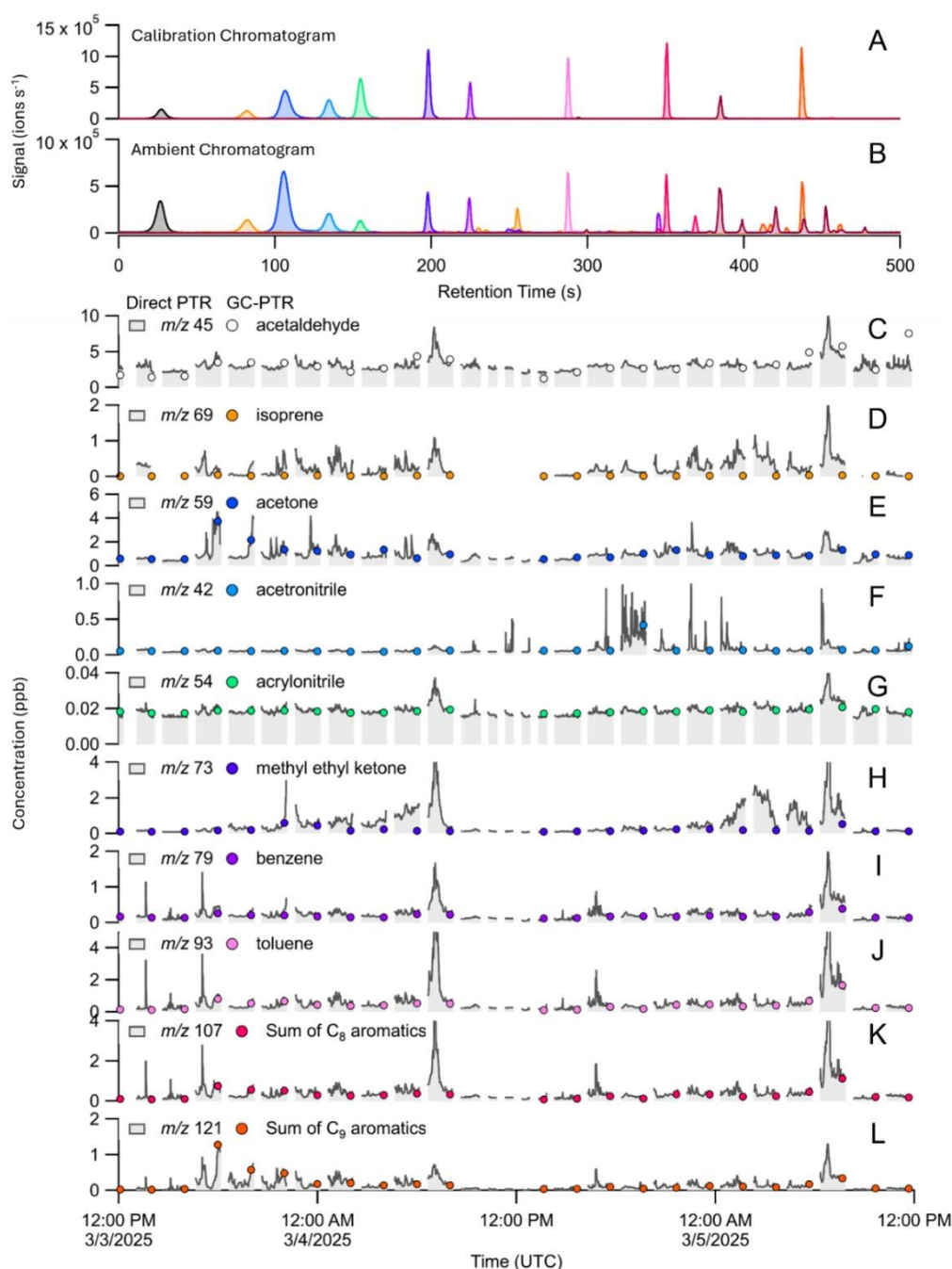


Figure 5. Exemplary (a) calibration and (b) ambient chromatograms resolved by the compact GC-PTR. Timeseries sub-set of each of the calibrant species detected in ambient air, where the direct-PTR measurement (signal averaged to 1 min) of the quantitation ion is shown in gray and the GC-PTR resolved compound(s) are shown in color (c – l). The C₈ aromatic sum (k) reported by the GC is the sum of m-, p-, and o-xylenes and ethyl benzene. The C₉ aromatic sum (l) reported by the GC is the sum of 1,2,4-, 1,3,5-, 1,2,3-trimethyl benzenes, n-propyl benzene, and i-propyl benzene.



385 Both acetaldehyde and acrylonitrile demonstrate intermediate correlations with R^2 of 0.605 and 0.645, respectively. The m/z
45 ion measured in direct mode can have contributions from multiple isomers (e.g., acetaldehyde, ethylene oxide, vinyl
alcohol) or interferences, here the GC measurement of acetaldehyde is the dominant contribution to the detected m/z 45 signal,
however, a modified chromatographic method to resolve the other isomers and identify the interferences would be an
improvement for the correlation in the future. On average across the entire measurement period, the directly measured m/z 45
390 signal is 1.4 times higher than the resolved acetaldehyde, with discrepancy having a diurnal pattern that peaks in the early
afternoon. To resolve which compound(s) are contributing to this daily enhancement in m/z 45 beyond the contribution from
acetaldehyde, further analysis would be warranted to quantify the other isomers and interferences.

The ambient levels of acrylonitrile detected during this measurement period were low, generally approaching 20 ppt. These
levels are in line with previous reports of background concentrations in environments without strong point sources, such as
395 industry or traffic (Kramer et al., 2025). The mid-tier correlation between the direct and GC resolved measurement is likely a
function of the ambient concentrations being near the detection limit of the instrument, not due to the presence of interfering
species in this scenario.

The correlation between the chemically resolved and directly measured data for isoprene and methyl ethyl ketone (MEK) do
not demonstrate good agreement (R^2 of 0.149 and 0.188, respectively) during this period. In the case of isoprene (Fig. 5D), the
400 GC measurement of isoprene is consistently lower than the measured m/z 69 ion. The direct measurement of m/z 69 is at least
a factor of 1.5 times higher than the resolved isoprene for over 90% of the entire measurement period, with an average factor
of 28.9 times higher. This is due to the fragmentation of larger species upon ionization resulting in the generation of the m/z
69 signal, these interferences cannot be distinguished without pre-separation of the sample. Another possible cause of
interference is the presence of isobars (e.g., $C_5H_9^+$, $C_4H_5O^+$ for m/z 69) which the low mass resolving power of the ultracompact
405 PTR cannot resolve. For these cases, the system must rely on the pre-separation of the GC for accurate quantification. The
difficulty in accurately measuring isoprene by PTR methods without pre-separation has been previously discussed (Coggon et
al., 2024). An example of the interference to m/z 69 from fragmentation of larger species, in this example the interferences are
predominately long chain aldehydes, is shown in Fig. S8. Here, we show the utility of periodic speciation of the PTR data to
regularly observe the variability and magnitude of the interference, which can provide a mechanism to correct the direct data
410 or to report certain species on the lower (GC) time basis with quantitative accuracy.

The lack of agreement between the direct and speciated data for MEK could be attributed to the presence of both isomers and
interferences due to fragmentation of larger species. MEK has many possible isomers, including tetrahydrofuran and butanal,
all of which would contribute to the direct measurement of m/z 73 without distinction if present in the ambient sample. Figure
5H demonstrates that during certain time periods, nominally all the m/z 73 signal measured directly by the PTR can be
415 attributed to MEK, while at other times MEK only contributes $\sim 10\%$ to the direct signal. Figure S9 shows the m/z 73 ion
allocation across the measurement period. As shown in the exemplary chromatogram, in this dataset, the cause of the
discrepancy is due to interference from fragmentation of larger species upon ionization, not from isomeric contributions. As
the interference source(s) contributed substantially to the signal at m/z 73 from March 3 – 5, these events influence the



correlation shown in Fig. S7 and reported in Table S1. If the entire measurement period is used, where MEK is generally the
420 dominant contributor to m/z 73, the correlation is enhanced to give an R^2 of 0.882 with a slope of 1.46.

It should be expressly noted that the extent of GC-PTR and direct-PTR agreement for individual species/ions can vary significantly depending on the environment and can also be temporally variable, depending on isomer contributions and contributions from species that result in interfering signals.

Figure 6 demonstrates the mass balance that can be obtained when all isomers, or contributions from interfering species, are
425 accounted for in the chromatographic data and then compared to the direct PTR data. During the ambient measurement period, 11 monoterpenes were resolved by the GC system with varying contributions to the m/z 137 ion signal. For comparison with the direct-PTR data, where a single sensitivity was used, each isomer was assumed to have the same sensitivity as α -pinene. The average fragmentation ratio (m/z 81 / (m/z 81 + m/z 137)) across the different isomers was 0.61 ± 0.09 , spanning 0.50 (tricyclene and β -ocimene) to 0.75 (carene and the unidentified isomer), α -pinene demonstrated a fragmentation ratio near the
430 average of 0.59, which aided the justification of this assumption.

Figure 6 (top panel) shows the direct-PTR data, averaged to 1 min time resolution, along with the summed concentrations of each of the monoterpene isomers resolved by the GC system. The relationship between direct and GC data is shown in Fig. S7, where the correlation has a slope of 1.02 and R^2 of 0.954 across the entire dataset. This level of agreement indicates that there are no significant contributions to the m/z 137 signal detected by the PTR that were not resolved by the GC during this
435 measurement period.

The speciated monoterpene concentrations are shown in Fig. 6 (middle panel), with their contributions relative to the total concentration shown in Fig. 6 (bottom panel). It should be noted that the white gaps in the GC data are due to zero and calibration periods, which were conducted daily during this project to characterize detector stability.

The measurement intensive occurred during the early spring season (March 2025) in Thun, Switzerland where the average
440 daytime maximum temperature was 11.0 ± 4.4 °C and the average nightly minimum temperature was 2.5 ± 3.4 °C. These measurements occurred either before or in the very early stages of the spring transition (green-up) which began in early- to mid-April in the region (MétéoSuisse, 2025). While a shift in total emissions corresponding to a seasonal transition during this measurement period was not observed (Hellén et al., 2018), there was significant variability in the relative contribution of each isomer to the total composition. The average standard deviation in the relative contribution of the 6 most abundant
445 isomers, each of which contributed to at least 10% of the total composition on average, was 31%. For the most abundant isomers, the average contribution and percent variabilities are as follows: α -pinene (0.32, 19%), β -pinene (0.18, 22%), camphene (0.12, 25%), limonene (0.11, 45%), γ -terpinene (0.11, 45%), and α -phellandrene (0.10, 30%).

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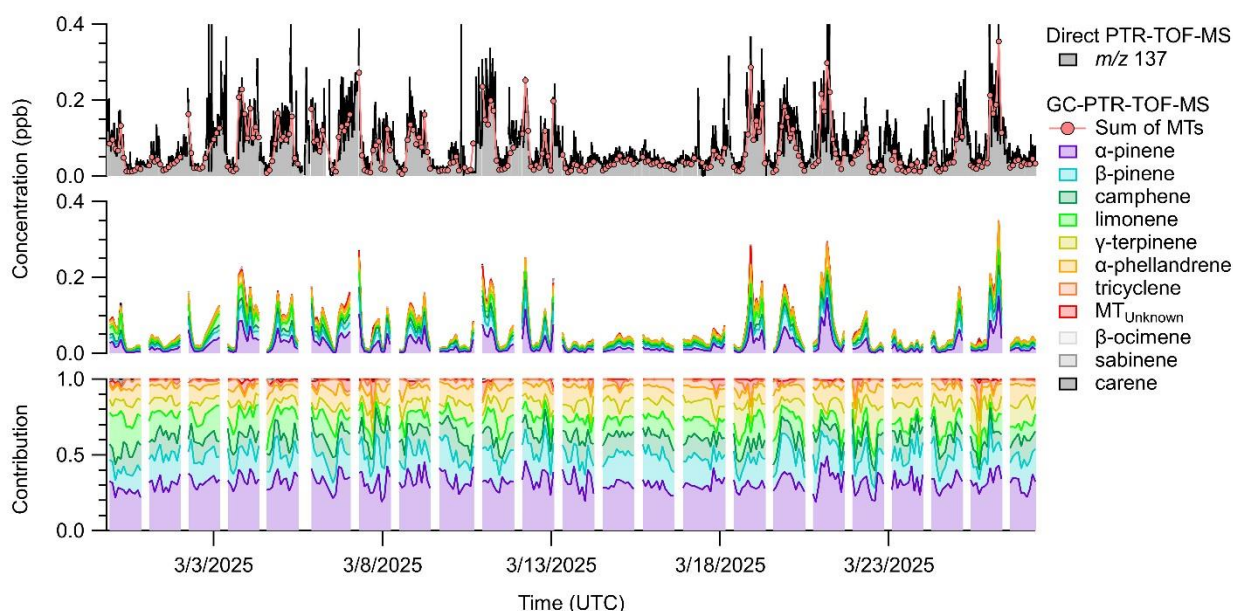


Figure 6. Top panel: ambient time series of m/z 137 measured by direct-PTR averaged to 1 min (gray) and the sum of monoterpene isomers resolved by the GC-PTR (pink) for the 30-day measurement period. Middle panel: speciated ambient time series of monoterpenes by the GC-PTR. Bottom panel: contributions of the speciated monoterpenes to the total monoterpene concentration over the ambient measurement period. White spaces in the middle and bottom panels are periods when the GC system was conducting daily zero and calibration periods.

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The periodic speciated data allows the analysis of isomer resolved diurnal profiles and wind correlations which aid in the understanding of emission sources and loss processes. As shown in Fig. S4, the dominant wind direction during the measurement period was from the west/northwest where the area immediately to the west of the measurement site consists of residential and commercial buildings, with periodic strong contributions from the southeast (across Lake Thunersee). Figure 7 provides an example speciated wind rose plot for α -pinene and limonene. The population of α -pinene measurements skews higher under easterly to southerly winds, particularly in the late evening (Fig. S10) signaling a temporally significant impact from the lake. Enhancements in both α -pinene and limonene are observed from the west/northwest, occur in the early morning, signaling a difference in emission source.

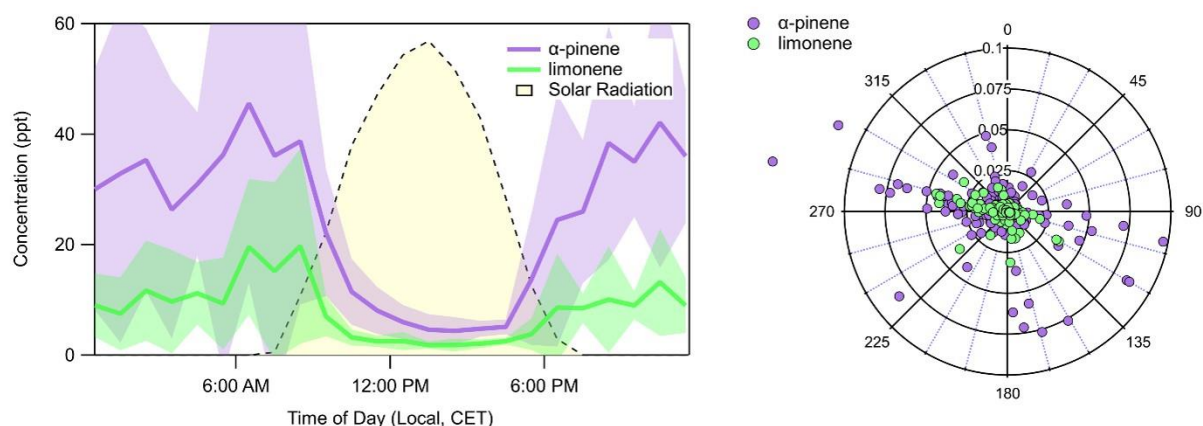
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The diurnal profiles of each of the monoterpene isomers, along with their sum, are shown in Fig. 7 and Fig. S11. Each of the isomers, along with their sum, show the general behavior of increasing concentration in the evening, around 18:00 CET, building to a steady state concentration overnight, followed by a decrease in the morning around 08:00 CET. Biogenic monoterpene emissions are known to be temperature dependent (Bourtsoukidis et al., 2024), which causes their emissions to continue into the evening. This coincides with decreasing boundary layer height and diminished reactive pathways at night (Finlayson-Pitts and Pitts, 2000), resulting in the increase and stable concentrations observed overnight. In the morning,



475 dilution due to boundary layer growth along with the initiation of photochemical reactions contribute to the observed decrease in concentration (Song et al., 2024). Of the monoterpenes reported from this measurement period, limonene also demonstrates a recurring morning enhancement between 06:00 and 08:00 CET. This early morning enhancement, corresponding to westerly winds, indicates either an anthropogenic or biogenic source unique to the emission of limonene.



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Figure 7. Diurnal profiles (left) and wind rose diagrams (right) for α -pinene and limonene during the 30-day ambient measurement period. The wind rose shows the distribution of isomer concentration with respect to wind direction, where the length of each spoke represents compound concentration in parts per billion (ppb).

485 Aside from the use of the speciated data to generate wind correlations or diurnal patterns that may help with source apportionment and distinguishing loss processes, the speciated data also allows for the accurate calculation of the oxidant reactivity (e.g., with OH radicals) and the O₃ and SOA formation potentials of an air mass, where each isomers contribution can vary significantly (Atkinson et al., 1986; Lee et al., 2006; Fry et al., 2014; Friedman and Farmer, 2018).

4 Conclusions

490 We developed and demonstrated a compact, integrated system for atmospheric VOC measurements that combines *in situ* gas chromatography, thermal desorption (TD) preconcentration, and an ultracompact PTR-TOF-MS equipped with a VUV ion source.

The 30-day ambient deployment in Thun, Switzerland, demonstrated stable operation under field conditions, with normalized calibration responses varying by 1.1–7.1% across the 11 calibration compounds, averaging 3.5%. These results demonstrate the potential for compact, low-power analytical platforms to reduce the infrastructure requirements that can otherwise limit the deployment of advanced VOC instrumentation.

495 The TD-GC provides sample preconcentration and molecular separation before detection, reducing reliance on the mass-resolving power of the PTR while simultaneously improving sensitivity and providing isomer-resolved measurements. The



compact GC-PTR measurements achieved detection limits of 0.1–4.0 ppt for 1 L samples, compared with 13–136 ppt for the
500 1-min direct-PTR measurements. Importantly, the chromatographic measurements provided information needed to interpret
the direct PTR signals, including compound-specific product-ion distributions and the contributions of isomers and
fragmentation products. For example, the direct m/z 69 signal substantially overestimated chromatographically resolved
isoprene, with the direct signal averaging 28.9 times the resolved isoprene concentration, demonstrating how unresolved ion
chemistry can materially affect quantitative interpretation. In contrast, the summed monoterpene measurements showed strong
505 agreement between the two measurement modes (slope = 1.02, $R^2 = 0.954$), while the GC measurement revealed variability in
the contributions of individual monoterpene isomers otherwise missing from the direct measurement.

Together, these results demonstrate a complementary approach to instrument miniaturization in which reduced detector
performance can be offset by upstream analytical separation and preconcentration rather than requiring all performance
specifications to be achieved within the detector itself. In this configuration, the direct PTR measurement provides high-time
510 resolution observations, while periodic chromatographic measurements provide molecular specificity, sensitivity
enhancement, and information on analyte-specific ion chemistry and interferences. This approach allows a compact detector
to retain useful analytical capabilities while reducing system size, power consumption, and operational complexity.

The combination of compact instrumentation and periodic pre-separation provides a pathway toward broader deployment of
chemically specific VOC measurements at long-term monitoring sites, on mobile platforms, and in locations where
515 infrastructure or reliable power is limited. Expanding deployment in this manner could increase the spatial and temporal
coverage of VOC observations while retaining the molecular information needed to investigate emission sources, atmospheric
processing, and the formation of secondary pollutants.

Data availability

The data generated and analyzed during this study are not publicly available because they were collected and used for the
520 development and validation of an instrument for a private company. The data are available from the corresponding author
upon reasonable request, subject to applicable confidentiality and data-use restrictions.

Author contributions

The ultracompact PTR and VUV PTR ion source were designed by UR, FLH, VY, and JT. The TD-GC systems were designed
by MSC, BML, and JJ. The experiments were designed and carried out by MSC and FLH. The data was analyzed by MSC.
525 MSC prepared the manuscript with contributions from all co-authors.



Competing interests

The authors declare the following competing financial interest(s): MSC, FLH, UR, VY, BML, DW, MC, and JJ are current or former employees of either Aerodyne Research or ToFwerk AG which manufacture and supply both the TD-GC systems and the compact chemical ionization mass spectrometer described in this work.

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