Atmospheric
Measurement
Techniques

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A compact PTR-ToF-MS instrument for airborne measurements of volatile organic compounds at high spatiotemporal resolution

M. Müller[1], T. Mikoviny[2,3,5], S. Feil[4], S. Haidacher[4], G. Hanel[4], E. Hartungen[4], A. Jordan[4], L. Märk[4], P. Mutschlechner[4], R. Schottkowsky[4], P. Sulzer[4], J. H. Crawford[2], and A. Wisthaler[1,5]

[1]Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Innsbruck, Austria
[2]Chemistry and Dynamics Branch, Science Directorate, NASA Langley Research Center, Hampton, VA, USA
[3]Oak Ridge Associated Universities, Oak Ridge, TN, USA
[4]Ionicon Analytik GmbH, Innsbruck, Austria
[5]Department of Chemistry, University of Oslo, Oslo, Norway

Correspondence to: A. Wisthaler (armin.wisthaler@uibk.ac.at)

Abstract. Herein, we report on the development of a compact proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) for airborne measurements of volatile organic compounds (VOCs). The new instrument resolves isobaric ions with a mass resolving power ($m/\Delta m$) of ~ 1000, provides accurate m/z measurements ($\Delta m < 3$ mDa), records full mass spectra at 1 Hz and thus overcomes some of the major analytical deficiencies of quadrupole-MS-based airborne instruments. 1 Hz detection limits for biogenic VOCs (isoprene, α total monoterpenes), aromatic VOCs (benzene, toluene, xylenes) and ketones (acetone, methyl ethyl ketone) range from 0.05 to 0.12 ppbV, making the instrument well-suited for fast measurements of abundant VOCs in the continental boundary layer. The instrument detects and quantifies VOCs in locally confined plumes (< 1 km), which improves our capability of characterizing emission sources and atmospheric processing within plumes. A deployment during the NASA 2013 DISCOVER-AQ mission generated high vertical- and horizontal-resolution in situ data of VOCs and ammonia for the validation of satellite retrievals and chemistry transport models.

1 Introduction

Volatile organic compounds (VOCs) are ubiquitous in the Earth's troposphere, and many of them are intimately involved in HO_x-NO_x-O_3 chemistry and in secondary organic aerosol formation. VOCs potentially impact regional air quality and global climate, which puts them among the key target species of many field measurement campaigns. Airborne measurements of VOCs put a high demand on instrumental sensitivity, time response and robustness. VOC mixing ratios range from levels of less than 1 pptV (1 pptV $= 10^{-12}$ v / v) in the upper or remote atmosphere to double or even triple digit ppbV (1 ppbV $= 10^{-9}$ v / v) levels in biomass burning or industrial plumes. Sampling from a jet aircraft at typical ground speeds of 100 to 200 m s^{-1} converts into a spatial resolution of 6 to 12 km for a 1 min measurement. The ultra-fast Trace Organic Gas Analyzer (TOGA), an airborne gas chromatograph (GC), collects 40 s integrated samples every 2 min; whole air sampling (WAS) grabs 1 min integrated samples into a pre-evacuated canister every 1–2 min during intensive sampling periods (Hornbrook et al., 2011, and references therein). This is often too low when operating over urban areas, in the proximity of point sources (e.g., forest or agricultural fires or industrial sources) and during extensive vertical profiling, i.e., when it is essential to be able to resolve large gradients over very small distances. Higher frequency measurements of a large set of VOCs can only be achieved via direct chemical ionization mass spectrometry (CIMS). In direct CIMS, the sample is not subjected to time-intensive preconcentration procedures and chromatographic separation, but it is directly and continuously introduced into an ion-molecule reactor for ionization. Analyte-specific ions are then monitored at high time

resolution (1–10 Hz) using a mass spectrometer (MS). Airborne direct CIMS was pioneered by F. Arnold's group in the mid-1980ies (Arnold and Hauck, 1985) and was followed by a breakthrough in the form of proton-transfer-reaction mass spectrometry (PTR-MS) (Crutzen et al., 2000). In the past 16 years, PTR-MS instruments have been successfully deployed on a variety of research aircraft, and the reader is referred to the thorough review by de Gouw and Warneke (2007) and the references given therein. The PTR-MS instruments that were hitherto flown on research aircraft used quadrupole filters for mass analysis. The quadrupole mass spectrometer (QMS) is usually operated in the selected ion monitoring (SIM) mode, i.e., a series of preselected m/z signals are sequentially measured for 0.5 to 1.0 s. For 10 analytes, it is this transfers into an overall time resolution of 5 to 10 s which causes the PTR-MS to be slower than most 1 Hz airborne air pollution sensors (e.g., O_3, NO, NO_2, CO, CH_4, etc.). Only on rare occasions has full mass spectral information been acquired at the expense of lower time resolution (e.g., Williams et al., 2001). QMS-based instruments are also not capable of distinguishing isobaric ions, i.e., ions with the same nominal mass but different exact masses (Murray et al., 2013), which often limits the specificity of the measurement. Prominent examples include protonated formic acid ($CH_3O_2^+$) and protonated ethanol ($C_2H_7O^+$), both detected at m/z 47, and protonated isoprene ($C_5H_9^+$) and protonated furan ($C_4H_5O^+$), both detected at m/z 69. An additional analytical deficiency of QMS-based instruments is their poor detection sensitivity for higher-molecular-weight analytes ($> m/z$ 150) caused by increased losses of heavier ions in the quadrupole filter.

A number of groups have used orthogonal acceleration time-of-flight mass spectrometers (oa-TOF-MS) in combination with a glow-discharge drift tube ion source (Blake et al., 2004; Ennis et al., 2005; Tanimoto et al., 2007; Jordan et al., 2009; Graus et al., 2010). None of those instruments has yet been deployed on an atmospheric chemistry research aircraft which is a particularly challenging measurement platform (short power-up time, shocks and vibrations during takeoff and landing, variable pressure and temperature in the cabin, contamination with polluted air at the airport, etc.). Herein, we report on the development and performance of a compact proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) that has flown on the NASA P-3B Airborne Science Laboratory during the DISCOVER-AQ mission (http://discover-aq.larc.nasa.gov). We show that the newly developed instrument is capable of generating full mass scan information at 1 Hz and of resolving a series of isobaric interferences known from conventional PTR-QMS studies. Examples of field data are presented to demonstrate the analytical power of the new airborne PTR-ToF-MS instrument in characterizing point emissions of VOCs and in measuring vertical trace gas profiles at high spatial resolution.
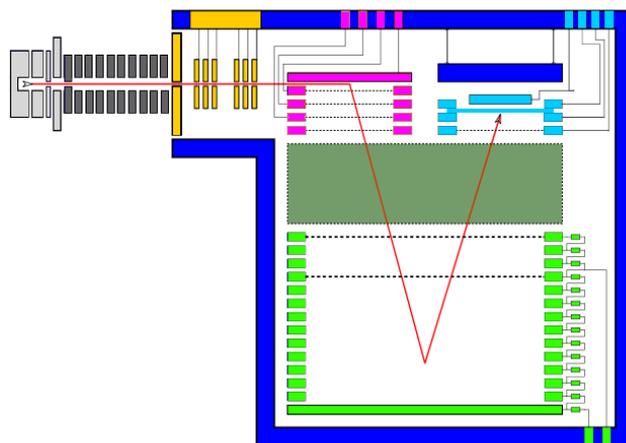
Figure 1. Schematic drawing of the newly developed compact PTR-ToF-MS instrument. The color-coded components are as follows: glow discharge (light grey), ion drift tube (dark grey), ion transfer optics (dark yellow), orthogonal ion accelerator (magenta), field-free time-of-flight region (olive green), double-stage ion mirror (light green), post-accelerator and multichannel plate (MCP) detector (light blue). The ion path is shown in red. Housing and mounting parts are shown in deep blue.

2 Experimental

The new airborne PTR-ToF-MS instrument (Fig. 1) includes (i) a direct chemical ionization source (glow discharge–ion drift tube), (ii) ion transfer optics that deliver ions from the drift tube to the MS, (iii) a newly developed compact oa-TOF-MS for ion mass analysis, (iv) a vacuum system that reduces the pressure in the ion source and in the mass spectrometer, (v) a data acquisition system that records all instrument operation parameters and the mass spectra, (vi) an aircraft inlet system that delivers outside air to the instrument in the aircraft cabin and (vii) an in-flight zeroing and calibration system. Each of these components is described in detail below. The instrument is installed in a double-bay 19 inch aircraft rack (~ 140 cm in height; see Fig. S1 in the Supplement) and has an overall weight of approximately 340 kg and an overall power consumption of 1.2 kW.

2.1 Ion source

The instrument is equipped with the conventional glow-discharge–drift-tube ion source housed in a thermostat-controlled (50 °C) enclosure. H_3O^+ ions generated in a glow discharge from pure water vapor axially drift through an ion-molecule reactor (pressure: 2.30 mbar; drift voltage: 550 V). Sampling air is supplied to the reactor via a capillary tube whose inlet is maintained at a pressure of 290 mbar using an electronic pressure controller (Bronkhorst High-Tech B.V., Ruurlo, NL). In the reactor, VOCs with a higher proton affinity than water are ionized via nondissociative proton transfer reactions with the H_3O^+ ions. The yield of protonated

analyte ions is linear for VOCs in their typical atmospheric concentration range. The ionization method, its technical details and limitations, and its application for atmospheric VOC measurements has been thoroughly reviewed by de Gouw and Warneke (2007).

2.2 Ion transfer lenses

The ion transfer optics guide the ions from the ion-molecule reactor to the orthogonal extraction region of the MS and consist of a drift tube extraction lens and two einzel lens stacks for ion beam transfer and focusing. The first lens following the drift tube extraction lens acts as a skimmer lens. The total voltage gradient across the ion transfer lens system is about 40 V.

2.3 oa-ToF-MS

A conventionally designed compact oa-ToF-MS is used for mass analysis (Fig. 1). The multistage orthogonal ion accelerator consists of a pusher and four mesh electrodes (reference, pull, grid and drift tube cage). Ions are typically extracted at 80 kHz with a maximum extraction frequency of 120 kHz. After V-shaped reflection in a double stage ion mirror the ions are post-accelerated before impinging on a multichannel plate (MCP) stack operated between 2000 and 2700 V. The extending dead time of the MCP is between 1.2 and 1.4 ns. The flight tube has a total length of only 190 mm, which is why this instrument is called the compact PTR-ToF-MS.

2.4 Vacuum system

Fine and high vacuum is maintained by three turbomolecular pumps coupled to the ion-molecule reactor (~ 2 mbar), the ion transfer lens system (few 10^{-5} mbar) and the oa-ToF-MS ($< 10^{-6}$ mbar), respectively. A four-stage diaphragm pump backs the turbo pumps. The turbomolecular pumps and the oa-ToF-MS are spring-mounted for shock and vibration isolation (Fig. 2).

2.5 Data acquisition system

The MCP signals are sent to a constant fraction discriminator (CFD) and a time-to-digital converter (TDC) with a minimum bin time of 27.43 ps. The bin time used is 219.48 ps. The non-extending dead time of the CFD–TDC system is 5.5 ns. At 80 kHz and a total acceleration voltage of 2300 V, the mass spectrum ranges from m/z 10 to m/z 214, containing 43 286 data bins. A Labview®-based data acquisition software generates time-of-flight mass spectra with customary spectral integration times ranging from 50 ms to 1 min. The mass spectra are displayed in real time with several diagnostic options (zooming, averaging, m/z calibration, single peak fitting and mass resolution diagnosis). In addition, the time series of selected m/z signals can be displayed in
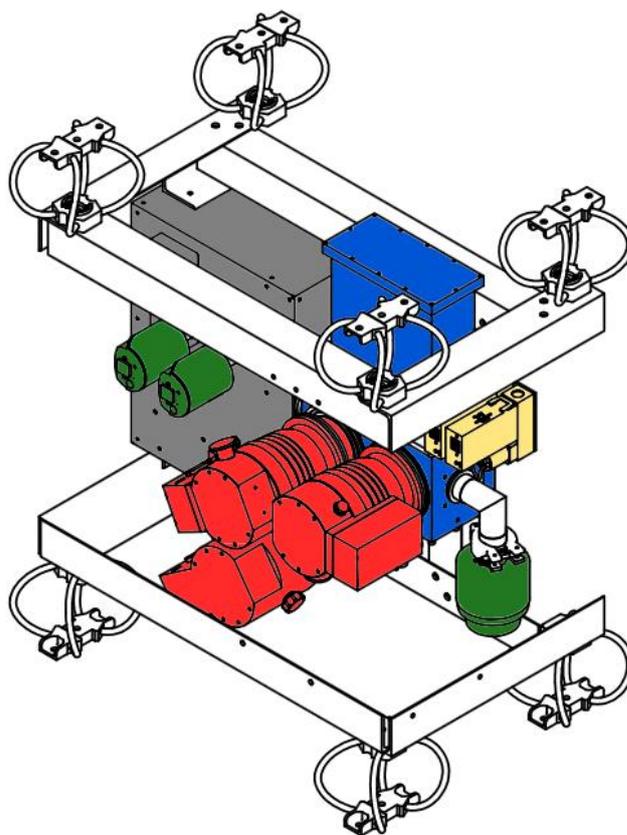
Figure 2. 3-D sketch of the compact PTR-ToF-MS as mounted in the P-3B flight rack. The color-coded components are as follows: thermostatted enclosure housing the glow discharge–ion drift tube (grey); ion transfer optics and ToF-MS flight tube (blue); turbomolecular pumps (red); pressure gauges (green) and electronic mass flow and pressure controllers (yellow).

real time. The mass spectral data and all operational parameters of the instrument are saved into hdf5 files (The HDF Group, Hierarchical Data Format, version 5, 1997–2013; http://www.hdfgroup.org/HDF5/). The user defines the maximum length of the hdf5 files either by time or by number of spectra.

2.6 Inlet system

A 50 cm long inlet probe, mounted on a window plate, extends outside the boundary layer of the airplane. The outermost section of the winglet contains a heated copper block. A ~ 2 m long heated silanized stainless steel line extends from the inlet probe to the instrument rack. The inlet line temperature is set to 45 °C. The inlet line is directly coupled to a three-stage diaphragm pump (Vacuubrand GmbH + CO KG, Wertheim, Germany), with the inlet flow being measured by an electronic flow meter (Bronkhorst High-Tech B.V., Ruurlo, NL). The flow ranges from 19 slpm at 3000 m altitude to 27 slpm at 300 m altitude.

2.7 In-flight zeroing and calibration system

Outside air is sampled through a separate air inlet into a swing piston compressor (KNF Neuberger, Freiburg, Germany). The pressurized side of the compressor is maintained at 1200 mbar using an electronic pressure controller (Bronkhorst High-Tech B.V., Ruurlo, NL). The compressor feeds a noble metal (Pt/Pd) catalyst (Parker Balston, Haverhill, MA) maintained at a controlled temperature of 320 °C. The flow through the catalyst is controlled to 2 slpm using a downstream electronic flow controller (Horiba STEC, Kyoto, Japan). The catalyst efficiently destroys all VOC in the air without affecting the humidity levels of the matrix. For instrument zeroing, this flow of VOC-free air is periodically backflushed via the main sampling inlet. Zeroing is carried out at different altitude levels to determine the humidity dependence of the instrumental background signals. For in-flight calibration, the flow of VOC-free air is spiked with ~ 5 ppbV of the target VOCs. Spiking is also carried out at different altitudes to characterize any humidity dependence of instrumental response factors. We use a certified custom-made 11-component VOC mixture (~ 1 ppmV of methanol, acetonitrile, acetaldehyde, acetone, isoprene, methyl ethyl ketone, benzene, toluene, m-xylene, 1,3,5-trimethylbenzene, α-pinene; Apel Riemer Environmental Inc., Broomfield, CO, USA) for instrument calibration. Based on our experience, ppmV levels of oxygenated VOCs are stably preserved in a treated aluminum cylinder for at least 1 year, and dynamic dilution generates accurate low-ppbV calibration gas mixtures. The small compressed gas cylinder (length: 513 mm; diameter: 133 mm) containing the VOC standard is placed in a thermostat-controlled (40 °C) enclosure. An electronic mass flow controller with a piezoelectric control valve (Horiba STEC, Kyoto, Japan) is used to deliver a constant calibration gas flow of 10 sccm throughout the entire flight. A three-way stainless steel ball valve (Parker-Hannifin, Jacksonville, AL, USA) is used to divert the calibration gas flow into the zero air flow or discard it into an exhaust line. A multipoint calibration in the 0–15 ppbV range is carried out on the ground before each flight. The accuracy of the mixing ratios in the standard (± 5 %) and the accuracy of the calibration and dilution flows (± 1 %) define the total accuracy of the measurement; this is ± 5.1 %. Based on our experiences from various intercomparison and validation exercises, we conservatively increase this value to ± 10 %. A schema of the in-flight zeroing and calibration system is given in the Supplement (Fig. S2)

2.8 Organic acids and ammonia measurements

Formic acid (detected at m/z 47.013) and acetic acid (detected at m/z 61.028) were calibrated post-campaign using a liquid standard nebulization device (LCU, Ionicon Analytik, Innsbruck, Austria) which has been described in detail by Fischer et al. (2013). The accuracy of the data is ± 10 %.

Ambient ammonia was detected at m/z 18.033 (NH_4^+) in spite of a high intrinsic background from the ion source. The isobaric peak at m/z 18.010 (H_2O^+) was clearly resolvable. Data accuracy is ± 35 % based on a calibration with an NOAA permeation source (Neuman et al., 2003) performed during ground operation. PTR-ToF-MS ammonia data agreed well with data obtained using a Picarro G2103 instrument (see Fig. S3 in the Supplement). More details regarding airborne ammonia measurements by PTR-ToF-MS will be given in a forthcoming publication.

2.9 Post-flight data analysis

The PTR-TOF Data Analyzer software (https://sites.google.com/site/ptrtof/) is used for data analysis (Müller et al., 2013, and references therein). This software corrects ion count rates, accurately calibrates the mass axis, separates isobaric ions and lists the m/z values of detected ions. It generates highly time-resolved (0.1–1 s) data using the stick spectra approach, wherein signals are counted in dynamic m/z intervals and scaled to more accurate 1 min data. We use a non-extending dead time of 5.5 ns, an extending dead time of 1.2 ns, 1 min spectral averaging for cumulative peak analysis and a residual analysis factor of 3 as input parameters. The intrinsic $H_3^{18}O^+$, $H_3^{18}O^+(H_2O)$ and $H_3^{18}O^+(H_2O)_2$ signals (m/z 21.022, m/z 39.033 and m/z 55.039) are used for mass axis calibration and reference peak shape determination. The data are further processed using the PTR-TOF Data Plotter which is an analysis module in the PTR-TOF Data Analyzer toolbox. This software subtracts instrumental backgrounds and applies instrumental response factors. The final output is the time series of volume mixing ratios of selected VOCs.

3 Results

3.1 Sensitivity, detection limit and precision

Table 1 summarizes the typical performance characteristics obtained from a calibration with the diluted 11-component VOC mixture. Instrument sensitivities range from 60.4 cps ppbV^{-1} for methanol to 148.9 cps ppbV^{-1} for 1,3,5-trimethylbenzene. 2σ detection limits for 1 Hz data are between 0.05 ppbV for 1,3,5-trimethylbenzene and 0.45 ppbV for methanol. The higher detection limits for methanol and acetaldehyde are due to an elevated chemical background. The instrument cannot be kept continuously under vacuum during an airborne campaign (overnight power down), which causes an elevated chemical background on a series of oxygenated VOC signals. This background is, however, low for signals with $m/z > 70$, and detection limits are generally below 0.1 ppbV. The 1σ absolute precision at 1 ppbV for 1 Hz data ranges from 0.06 ppbV for 1,3,5-trimethylbenzene to 0.48 ppbV for methanol. The 1σ relative precision at 10 ppb for 10 Hz data ranges from

Table 1. 1 Hz measurement performance results (measured accurate m/z, calculated exact m/z, instrumental sensitivity, 2σ detection limit and precision at 1 ppbV) for a set of 11 VOCs.

Compound name	Measured m/z	Exact m/z	Sensitivity (cps ppbV^{-1})	Detection limit (ppbV)	Precision (ppbV)
Methanol	33.034	33.033	60.4	0.45	0.48
Acetonitrile	42.033	42.034	113.2	0.10	0.11
Acetaldehyde	45.031	45.033	87.9	0.32	0.25
Acetone	59.045	59.049	125.2	0.09	0.08
Isoprene	69.065	69.070	62.2	0.12	0.12
Methyl ethyl ketone	73.061	73.065	136.4	0.07	0.07
Benzene	79.051	79.054	78.7	0.08	0.10
Toluene	93.064	93.070	102.2	0.07	0.07
m-Xylene	107.090	107.086	130.0	0.05	0.07
1,3,5-Trimethylbenzene	121.110	121.102	148.9	0.05	0.06
α-Pinene	137.140	137.132	65.7	0.08	0.10

± 8 to $\pm 16\%$ (data not included in the table). Figure 3 shows the calibration curves obtained for four aromatic VOCs (benzene, toluene, m-xylene, 1,3,5-trimethylbenzene), two biogenic hydrocarbons (isoprene, α-pinene) and four oxygenated compounds (methanol, acetaldehyde, acetone, methyl ethyl ketone). The performance achieved is sufficient to generate 1 Hz VOC data in the continental boundary layer. 10 Hz eddy covariant airborne flux measurements should be possible for selected species. In the remote boundary layer and the upper troposphere, longer signal integration times may be required.

3.2 Mass resolving power and mass accuracy

The typical mass resolving power ($m/\Delta m$) at full-width half maximum (FWHM) for methanol and acetone is 900 and 1200, respectively. Although this is significantly lower than reported for Ionicon's high-end PTR-TOF 8000 instrument, a series of important isobaric peaks can be resolved in post-analysis using the cumulative peak approach (Müller et al., 2011; Titzmann et al., 2010). We show this using the example of protonated methanol, CH_5O^+, with a calculated exact m/z of 33.033, and protonated molecular oxygen, HO_2^+, with a calculated exact m/z of 33.003. HO_2^+ ions are formed from endothermic proton transfer reactions during ion extraction into the high-vacuum region. The HO_2^+ abundance is humidity-dependent, which causes the instrumental background of PTR-QMS systems at m/z 33 to vary with absolute humidity. $^{17}OO^+$ ions with a calculated exact m/z of 32.994 cannot be resolved from HO_2^+ ions at a mass resolving power of 900, and only a broadened HO_2^+ peak is observed. In our instrument, the $^{17}OO^+$ contribution to the HO_2^+ peak was typically on the order of 15 %. Figure 4a depicts two 1 min average PTR-ToF-MS mass spectra around m/z 33. The data obtained during instrument zeroing are shown as cyan crosses; the calibration data (10 ppbV of methanol) are shown as black crosses. The corresponding

color lines visualize the fitting results obtained using the PTR-TOF Data Analyzer software. Vertical lines indicate the peak centroid position, i.e., the measured accurate m/z for HO_2^+ (m/z 33.005, in blue) and the protonated methanol signal CH_5O^+ (m/z 33.034, in red). These results demonstrate that two isobaric peaks at m/z 33 are well-resolved even with a relatively low mass resolving power of 900. The absolute mass accuracy of the measurement, i.e., the difference between the calculated exact m/z and the measured accurate m/z, is less than 2 mDa. The mass accuracy is limited by the mass resolving power of the instrument, by the presence of isobaric peaks, by the accuracy of the mass axis calibration and by the obtained signal-to-noise ratio. Further details are discussed in Müller et al. (2011).

Figure 4b shows the 1 Hz time series of the two isobaric signals obtained during a multistep calibration. Methanol volume mixing ratios supplied were 10, 0, 1, 2, 3, 4, 5 and 10 ppbV. The methanol spike between 0 and 1 ppbV occurred when a valve was manually opened. This time series demonstrates that the HO_2^+ signal is not affected by any short- or long-term variation in the CH_5O^+ signal. Data analysis with the PTR-TOF Data Analyzer software reliably resolves the two isobaric signals. An analogous argumentation can be made for protonated carbon dioxide, CHO_2^+, with a calculated exact m/z of 44.997 and protonated acetaldehyde, $C_2H_5O^+$, with a calculated exact m/z of 45.033.

Further examples of resolvable isobaric signals include organic isobars such as protonated formic acid, $CH_3O_2^+$, with a calculated exact m/z of 47.013, and protonated ethanol, $C_2H_7O^+$, with a calculated exact m/z of 47.049. The differentiation between protonated isoprene, $C_5H_9^+$, with a calculated exact m/z of 69.070 and protonated furan, $C_4H_5O^+$, with a calculated exact m/z of 69.033 is of particular interest to the PTR-MS community. Furan is known to be emitted from biomass burning (e.g., Hornbrook et al., 2011, and references therein), which complicates the interpretation of the PTR-QMS m/z 69 signal in fire plumes. Figure 5a shows a
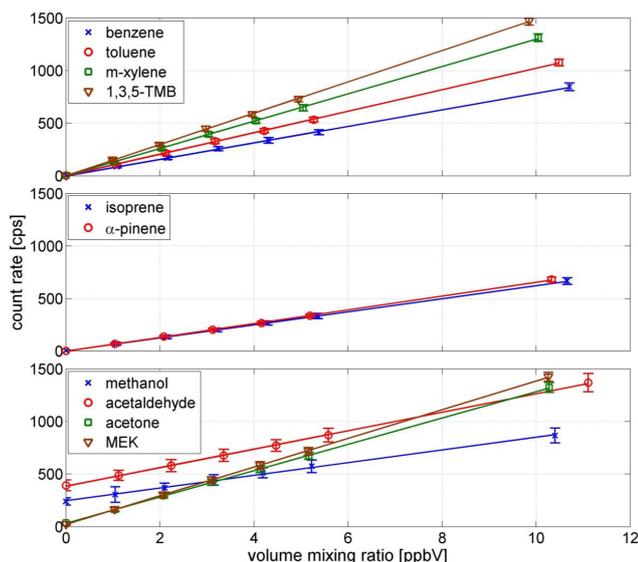
Figure 3. Calibration curves for aromatic VOCs (top), biogenic VOCs (center), and oxygenated VOCs (bottom). Signals measured are ion count rates at m/zs of the protonated molecules. Error bars indicate the precision of the 1 Hz data.

1 min average PTR-ToF-MS mass spectrum around m/z 69 obtained on 29 September 2013, when the NASA P-3B overflew an agricultural crop residue fire near Dublin, GA, USA. Two distinct peaks are observed: a dominating peak centered at m/z 69.034, which corresponds to $C_4H_5O^+$ (protonated furan), and a smaller $C_5H_9^+$ peak at m/z 69.070 on its right shoulder, corresponding to protonated isoprene and isomers (e.g., pentadienes or methylbutadienes). Figure 5a also shows that furan is only present in the plume; outside the plume only isoprene is observed. The 1 min time series of the two isobaric signals recorded during the overflight is shown in Fig. 5b. We have included the time series of acetonitrile to identify the encounters with the biomass burning plume. Our results confirm findings from previous biomass burning laboratory studies which identified furan as the dominating species detected at m/z 69 (e.g., Hornbrook et al., 2011, and references therein).

The examples given have already demonstrated the excellent absolute mass accuracy of the measurements in the lower mass range, i.e., where the mass axis is calibrated using the intrinsic m/z 21.022, 39.033 and 55.039 signals. We also note that, in the lower mass range, the measured accurate m/z is highly reproducible with 2σ variations in the range between 0.5 and 2 mDa (3 mDa for methanol). For VOCs with a higher m/z value, e.g., α-pinene with a calculated exact m/z of 137.132, the absolute mass accuracy is lower (8.0 mDa in the case of α-pinene). The addition of an external mass calibrant with $m/z > 100$ would significantly improve the accuracy of measured m/zs for higher molecular weight ions.
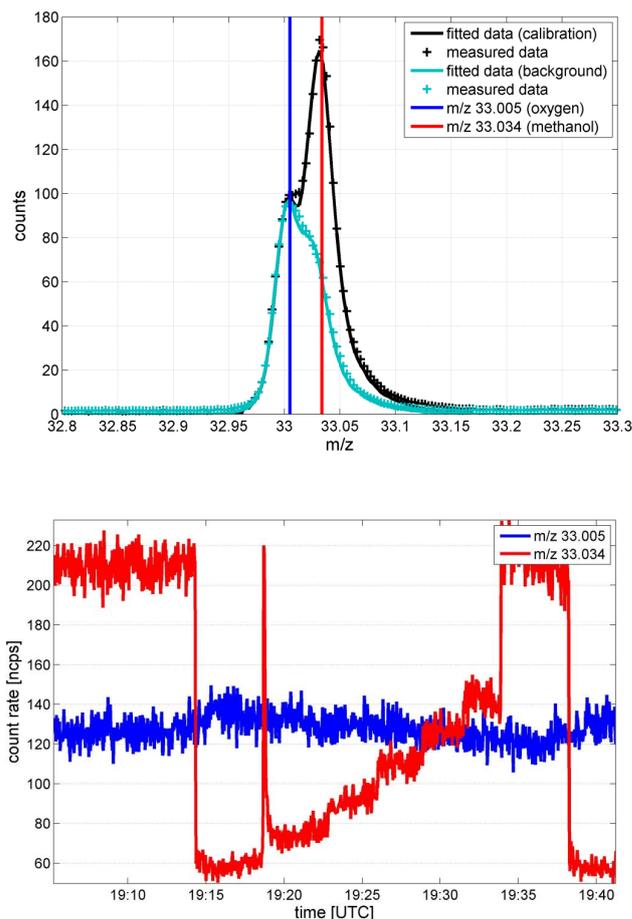
Figure 4. Resolution of isobaric HO_2^+ (m/z 33.005, protonated molecular oxygen) and CH_5O^+ (m/z 33.034, protonated methanol) ions in a 1 min average mass spectrum (top) and the time series of the two signals obtained during a multipoint calibration with methanol (bottom).

At higher m/z it also becomes more difficult to resolve isobaric peaks, but a lot of other factors (e.g., peak shape, stability of the peak shape, signal-to-noise) play an equally important role. Peak resolvability needs to be assessed on a case-by-case basis.

We conclude that the new airborne PTR-ToF-MS instrument, which was originally conceived for nominal mass analysis only, performed unexpectedly well in resolving isobaric peaks and measuring accurate m/z values.

3.3 Field data

The high-time-resolution PTR-ToF-MS data are particularly useful for determining $\Delta VOC / \Delta CO$ (or $\Delta VOC / \Delta CO_2$) emission ratios from point sources (e.g., from forest or agricultural fires, industrial and traffic sources) or enhancement ratios in pollution plumes. This is particularly true for small-scale plumes (< 1 km) which are not resolvable with slower analytical techniques including PTR-QMS. Figure 6 shows

Figure 7. Scatterplot of furan and isoprene (for interferences see text) versus acetonitrile as obtained from a 30 s transect of an agricultural crop-burning plume. Lines and ratios were obtained from a bivariate regression analysis.
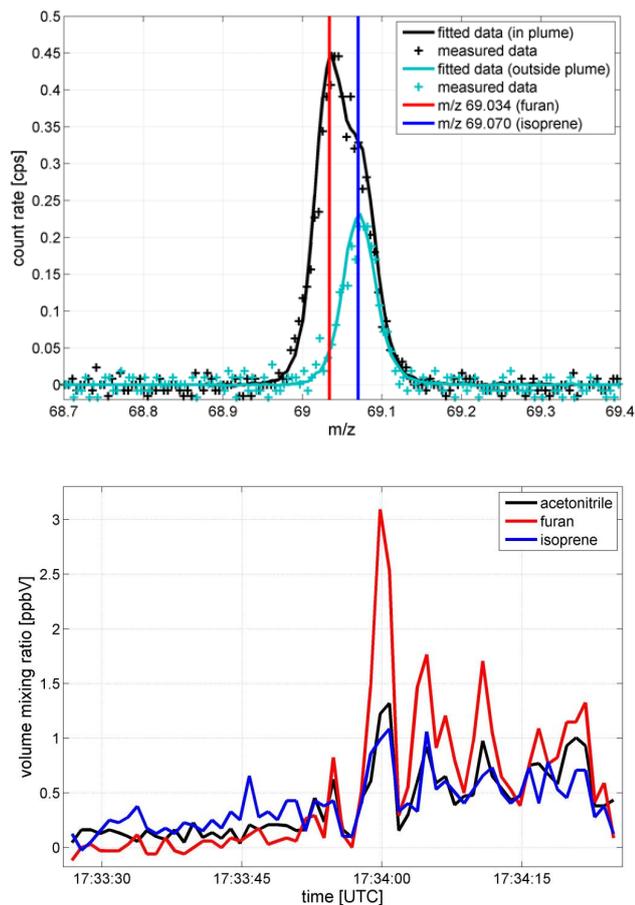
Figure 5. Resolution of isobaric $C_4H_5O^+$ (m/z 69.034, protonated furan) and $C_5H_9^+$ (m/z 69.070, protonated isoprene) ions (1 min signal average) measured in an agricultural crop-burning plume. The signal obtained outside the plume is included for comparison (top). Time series of furan, isoprene (for interferences see text) and acetonitrile obtained during transect of an agricultural crop-burning plume on 23 September 2013 near Dublin, GA, USA (bottom).
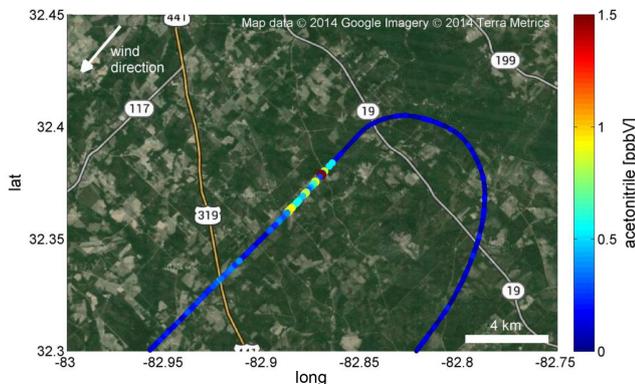
Figure 6. High-spatial-resolution data of acetonitrile during transect of an agricultural crop-burning plume on 23 September 2013 near Dublin, GA, USA.

the geographic extension of the crop residue fire plume intercepted near Dublin, GA, USA, on 29 September 2013. Enhanced acetonitrile concentrations (> 200 pptV) are observed over a flight path of 4.5 km. CO data are typically recorded at 1 Hz which results in about 40 data points within the plume. The new PTR-ToF-MS instrument provides VOC data at the same rate, which allows deriving emission or enhancement ratios for both identified compounds and unidentified m/z signals. Since CO data are not yet available for this flight, we use acetonitrile as our reference compound to derive two emission ratios as $\Delta X / \Delta CH_3CN$ from the scatterplot shown as Fig. 7. We find that Δfuran / Δacetonitrile is 1.70, while Δisoprene / Δ acetonitrile is only 0.66. Biogenic isoprene outside the plume causes the positive y axis offset in the isoprene data regression line. The negative y axis offset in the furan data regression line is caused by background levels of acetonitrile ubiquitously found in the atmosphere. It is noted that the isoprene signal includes contributions from isomeric hydrocarbons (e.g., pentadienes or methylbutadienes) known to be emitted from fires. It is not within the scope of this paper to put these results in a broader scientific context. These data are shown to demonstrate that even a 40 s (or less) plume transect is sufficient to derive VOC emission or enhancement ratios and to correlate PTR-ToF-MS signals to data from any other fast air pollutant sensor.

Figure 8 shows all enhanced m/z signals in the agricultural fire plume. The m/z signals that are usually monitored by conventional PTR-QMS are highlighted in dark grey. It becomes immediately evident that conventional PTR-QMS measurements only account for a fraction of the emitted organic mass and that more research needs to be done to identify the remaining signals. The use of PTR-ToF-MS supersedes the need for preselecting the signals to be monitored, which is an important prerequisite for generating new scientific knowledge.
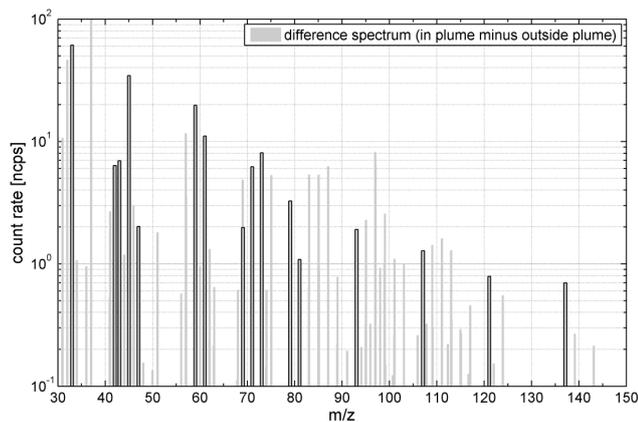
Figure 8. Full mass spectrum (m/z 30–150) obtained during a 30 s transect of an agricultural crop plume. The atmospheric background measured outside the plume has been subtracted from the in-plume data. The signals highlighted in dark grey indicate the signals that are typically recorded by conventional PTR-QMS. The signals in light grey are unidentified organic compounds (with the exception of m/z 32, 36 and 37).

Figure 9a shows data from an urban overflight on 21 January 2013 over Bakersfield, CA, USA. Elevated toluene concentrations are seen east of Highway 99 (Golden State Highway) and in the vicinity of Bakersfield Municipal Airport. The corresponding time series is shown in Fig. 9b. Two toluene spikes are visible at 21:23:55 UTC (highway) and 21:24:50 UTC (airport). Notably, elevated C_8-alkylbenzene and benzene levels are only seen from the traffic source and not over the airport. The toluene-to-benzene ratio derived from a bivariate regression analysis of the 5 s traffic emission spike is 4.0. This value is in good agreement with ratios from ambient and emission inventory data previously reported for nearby sites (Reid et al., 2007). These data are shown to exemplify the value of airborne PTR-ToF-MS measurements in identifying and characterizing point sources of VOCs in an urban environment.

Figure 10 shows vertical profiles of ammonia and three VOCs (methanol, formic acid and acetic acid) as obtained during the NASA DISCOVER-AQ mission in January and early February 2013 over Fresno, CA. We focus on these four species as they are currently also observable from space with the Tropospheric Emission Spectrometer (TES) and Infrared Atmospheric Sounding Interferometer (IASI) instruments and are thus of interest to the satellite-remote-sensing community and to NASA. The 1 Hz ammonia data suffer from a poor detection limit (13 ppbV) due to a high intrinsic background. The acetic acid data are potentially biased by a glycolaldehyde interference. Glycolaldehyde, an isomer of acetic acid, is directly emitted from biomass burning or photochemically formed from isoprene and 2-methyl-3-buten-2-ol (MBO) (St. Clair et al., 2014, and references therein). Given that no biomass burning markers were observed and
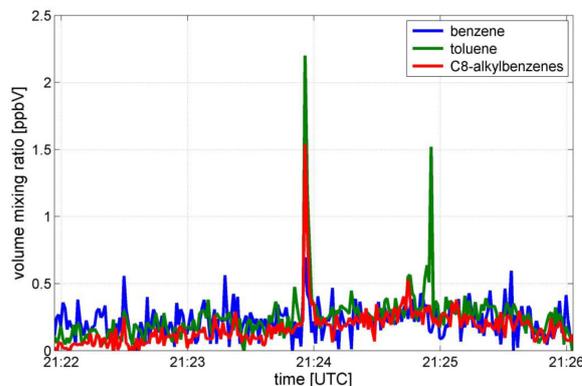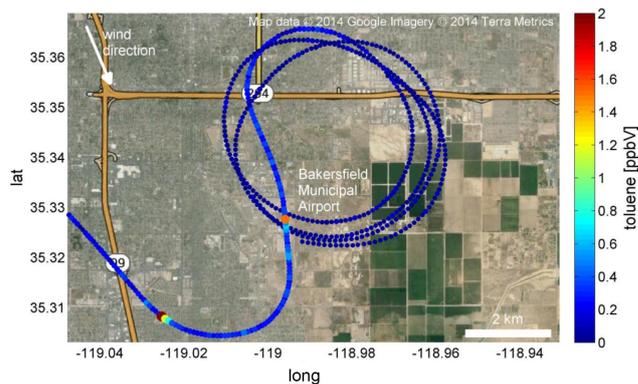
Figure 9. High-spatial-resolution data (top) of toluene during an urban overflight, obtained on 21 January 2013 over Bakersfield, CA, USA, and corresponding time series of benzene, toluene and C_8-alkylbenzenes (xylenes plus ethylbenzene).

that biogenic emissions are low in winter, we expect the glycolaldehyde interference to be small. Formic acid is reported for the first time; the 1 Hz detection limit is 1.1 ppbV, due to isobaric interferences. The data in black include all 28 profiles (22 for ammonia) measured during 10 research flights over a period of 3 weeks. A single profile, starting at 20:03:27 UTC on 22 January 2013, is shown in red. These data demonstrate the capability of the new airborne PTR-ToF-MS to generate high-vertical-resolution (down to 8 m) VOC data for the validation of satellite retrievals and chemistry transport models. All PTR-ToF-MS data are publicly available at the NASA Langley Research Center (LaRC) Airborne Science Data Center for Atmospheric Composition (http://www-air.larc.nasa.gov/index.html).

4   Conclusions

An airborne PTR-ToF-MS instrument for high spatiotemporal VOC measurements (1 Hz, 110 m horizontal, 8 m vertical) has been successfully developed, and the first airborne PTR-ToF-MS data have been reported. 2σ-detection limits
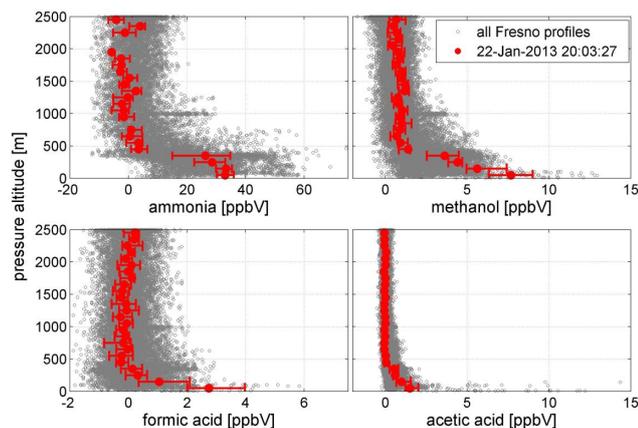
Figure 10. Vertical profiles of methanol, acetic acid, ammonia and formic acid as obtained during the NASA DISCOVER-AQ mission in January and February 2013 over Fresno, CA, USA. Grey dots include data from all flights, red dots refer to data from a single profile (100 m bins, median with upper and lower quartile) measured on 22 January 2013 started at 20:03 (UTC).

range from tens to hundreds of pptV, which makes the instrument well suited for 1 Hz VOC measurements in the continental boundary layer. Longer signal integration times (up to 10 s) are required when measuring in the remote boundary layer and in the upper troposphere. To be able to measure at 1 Hz even under clean conditions, the instrument sensitivity needs to be increased by at least one order of magnitude. A recent study by Sulzer et al. (2014) has demonstrated that such a sensitivity increase can realistically be achieved. Still, our new instrument records full mass spectra at 1 Hz, which constitutes a significant improvement over conventional airborne PTR-QMS measurements. It allows studying continental VOC point sources even if the resulting plumes are spatially constrained to less than 1 km. We have also shown that the instrument is capable of resolving important isobaric ion pairs in the low-mass range. Future instrument improvements should aim at an improved mass resolution for better isobar distinction. Deployment of the new instrument during the NASA DISCOVER-AQ mission generated vertical profile data of VOCs for satellite retrievals and chemistry transport model validation. Future deployments may include airborne eddy-covariance flux measurements of VOCs.

The Supplement related to this article is available online at doi:10.5194/amt-7-3763-2014-supplement.

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