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# High Resolution PTR-TOF: Quantification and Formula Confirmation of VOC in Real Time

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We present the unprecedented capability to identify and quantify volatile organic compounds (VOCs) by means of proton transfer reaction time-of-flight (PTR-TOF) mass spectrometry on-line with high time resolution. A mass resolving power of 4000–5000 and a mass accuracy of 2.5 ppm allow for the unambiguous sum-formula identification of hydrocarbons (HCs) and oxygenated VOCs (OVOCs). Test masses measured over an 11-wk period are very precise ( $SD < 3.4$  ppm) and the mass resolving power shows good stability ( $SD < 5\%$ ). Based on a 1 min time resolution, we demonstrate a detection limit in the low pptv range featuring a dynamic range of six orders of magnitude. Sub-ppbv VOC concentrations are analyzed within a second; sub-pptv detection limits are achieved within a few tens of minutes. We present a thorough characterization of our recently developed PTR-TOF system and address application fields for the new instrument. (J Am Soc Mass Spectrom 2010, 21, 1037–1044) © 2010 American Society for Mass Spectrometry

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Proton transfer reaction (PTR) for soft chemical ionization of different organic compounds has been used for many years. In the late 1990s, scientists from the University of Innsbruck reported on the development of proton transfer reaction mass spectrometry (PTR-MS), a combination of a PTR drift tube and a quadrupole mass spectrometer (Quad-MS), which allows for, in principle, fast detection of volatile organic compounds (VOCs) [1, 2]. Sensitivity, detection limit, and time resolution of PTR-MS have improved significantly since those early days. Field deployable PTR-MS instruments now reach detection limits of typically 10 pptv at an integration time of a few seconds per compound. PTR-MS readily detects traces of most hydrocarbons (HCs) and their oxygenated derivatives (commonly classified as oxygenated VOCs; OVOCs) present in air samples. Consequently, PTR-MS has found numerous applications in atmospheric chemistry, biology, and other scientific fields such as food technology and medicine, where HCs and OVOCs play an important role. Measurements of VOCs in the earth's atmosphere using PTR-MS have been recently reviewed by de Gouw and Warneke [3]. Since atmospheric samples may contain thousands of VOCs, even PTR-MS mass spectra are hard to interpret due to the large number of peaks and the lack of discrimination between isobaric compounds by quad-MS instruments, which commonly have unity mass resolution.

Various approaches have been reported to improve the selectivity by combining the PTR-ionization with more powerful separation techniques. The GC-PTR-MS approach, i.e., coupling a chromatographic column to a PTR-MS instrument [4–6], allows for greater selectivity than PTR-MS alone, but sample pretreatment steps are necessary and the sampling frequency is strongly reduced to only one per 30 min. PIT-MS [7–9], PTR-LIT [10], and QqQ-MS [11] couple the PTR ionization with a 3D quadrupole ion trap, a linear ion trap, and triple quadrupole MS, respectively. These ion trap instruments utilize collision induced dissociation on previously isolated ions of a certain mass of interest to distinguish between isomeric species. All these approaches are practical for target analysis, where quantitative information about a few specific compounds is required, but have a limited applicability for on-line VOC analysis to target complex gas matrixes containing thousands of VOCs.

Recently, several groups reported the coupling of a chemical ionization unit to a time of flight mass spectrometer [12–15]. Mass resolving power,  $m/\Delta m$ , well in excess of 1000 (CIR-TOF-MS) [12] and detection limits in the 100 pptv range for 1 min integration time [14] were achieved. The increased mass resolution allowed the separation of a limited number of exemplified isobaric VOCs that quadrupole PTR-MS cannot distinguish. Detection limits, however, are about two orders of magnitude poorer compared with conventional PTR-MS. Proton transfer reaction mass spectrometry with its variety of technical approaches and numerous applications was reviewed by Blake and coworkers [16].

In collaboration with Ionicon Analytik, we recently developed a PTR-TOF instrument with a mass resolu-

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tion that is better than those previously reported [12–16], and a detection limit that is at least one order of magnitude lower than of those demonstrated in the literature [14, 16]. Application examples of the commercially available PTR-TOF system were shown by Jordan and coworkers [17]. Here, we demonstrate the improved sensitivity of our PTR-TOF, give carefully evaluated detection limits, and thoroughly discuss its identification capability by exact mass measurement with regards to HCs and OVOCs.

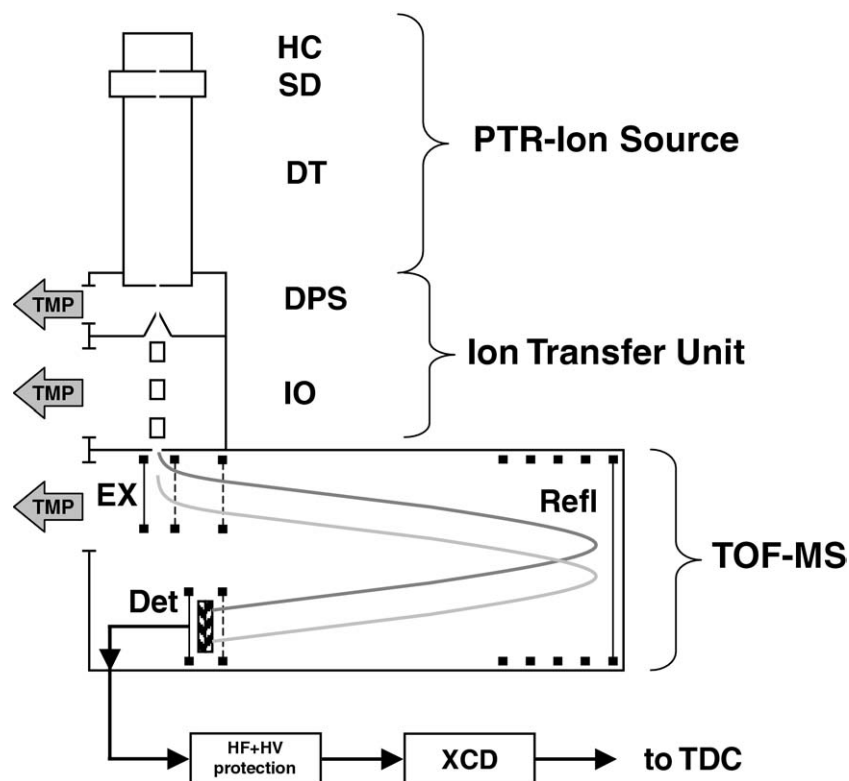
## Experimental

The PTR-TOF system (Figure 1) consists of a proton transfer reaction (PTR) ion source (Ionicon Analytik GmbH, Innsbruck, Austria) and an orthogonal acceleration, reflectron time-of-flight mass spectrometer (TOF-MS; Tofwerk AG, Thun, Switzerland).

As the working principle of the PTR ionization technique was already described by Hansel and coworkers [1], only the parameters relevant for the coupling are given here. The PTR-ion source is typically operated at  $E/N$  ( $E$  being the electric field strength in volts per centimeter,  $N$  being the number density in molecules per cubic centimeter, in the reaction cell) of  $120 \cdot 10^{-17} \text{ Vcm}^2$ . A drift tube pressure of  $\sim 2 \text{ mbar}$

provides sufficient reactive collisions between the proton donor ions and the trace organic compounds. In contrast the TOF-MS must be operated at high vacuum ( $< 1 \times 10^{-6} \text{ mbar}$ ) to ensure a collision free passage of the ions through the flight tube. A differentially pumped ion transfer unit couples the PTR-ion source with the TOF-MS, allows for keeping up both pressure regimes, and maintains the sample flow through the drift tube.

The mass analyzer used in this instrument is a high mass resolution, orthogonal acceleration, reflectron TOF-MS (G-TOF platform; Tofwerk AG). Vacuum ports were customized according to the needs of a high-pressure ion source. The interface for the PTR-ion source and the geometry of the ion extraction into the first differential pumping stage were optimized for ion transmission and thus sensitivity. The ion optics is an Einzel-lens system that collimates the ions to a virtually parallel beam. At the end of the ion optics, the ions enter the pulser through an aperture. All ions are periodically extracted every  $30 \mu\text{s}$  from the ion beam in orthogonal direction. After acceleration and passage through a field-free region the ions are reversed in a reflector and thereby refocused in the detector plane where they are detected by multi-channel-plates (MCP; Burle Industries Inc., Lancaster, PA, USA). An amplifier-



**Figure 1.** Schematic representation of the PTR-TOF instrument. External ion source with hollow cathode (HC) and source drift (SD) region. Proton transfer reactions take place in the drift tube (DT). Through a differential pumping stage (DPS) ions enter the ion optics (IO), which forms a virtually parallel ion beam. At the extractor (EX) ions are pulsed orthogonally towards the reflectron (Refl) and are refocused into detector (Det) plane. The signal is preprocessed by an amplifier/discriminator unit (XCD) to generate individual ion counting events processed by a time to digital-converter (TDC).

discriminator (Ionwerks XCD; Ionwerks Inc., Houston, TX, USA) amplifies the MCP signal by a factor of 50 and triggers the input channel of the time-to-digital converter (TDC, 0.1 ns minimum bin width; based on high-performance TDC as described by Christiansen and coworkers [18]) if the signal exceeds the threshold level (typically 30–40 mV). Optimization of the MCP gain setting and threshold level allows for effective electronic noise suppression. This increases the signal-to-noise ratio and hence improves the limit of detection (LOD) of the PTR-TOF.

The data acquisition system comprises a personal computer (PC), a TDC, and a timer-card. The data acquisition software TofDaq (version 1.72; Tofwerk AG) controls the timing of the pulser and the TDC, acquires the raw data and stores series of mass spectra according to the chosen data structure in HDF5 format together with meta-information on the data acquisition.

Data reduction was done with routines for peak search, peak fit, and mass scale assignment programmed in Matlab R2007b, 7.5 (The MathWorks Inc., Natick, MA, USA). In the following, we refer to those routines as data evaluation software version 2 (DESV2). Those routines are described in detail by Müller and coworkers [19]. DESV2 uses the  $^{18}\text{O}$  isotope peaks of  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{OH}_3\text{O}^+$  as well as the product ion peaks of 1,4-dichlorobenzene and 1,2,4-trichlorobenzene as nodes for the mass scale assignment. The chlorobenzene compounds were continuously added into the gas inlet from a diffusion cell.

## Results and Discussion

### Mass Accuracy, Mass Precision, and Resolving Power

A thorough characterization of the mass accuracy and mass precision is of crucial importance for the instru-

ment's capability to determine the atomic composition of protonated VOCs by exact mass measurement. Temperature variations of the TOF-MS can cause a slow change in the length of the ion's flight path over time. Therefore, a frequent calibration of the mass scale is important. This was accomplished by adjusting the mass scale assignment to four known peaks present in all mass spectra. Only mass spectra with congruent mass scales can be added up without the smearing out of mass peaks. Such integration over several spectra may be desirable to increase the signal-to-noise ratio.

The quality and stability of the PTR-TOF's mass measurement was determined by introducing a suite of VOCs in ppbv volume mixing ratios (VMR) into the instrument. Besides the two chlorinated aromatic compounds, we added VOCs from a standard gas to the instrument's inlet (see sensitivity calibration below). For each VOC, the theoretical exact mass,  $(m/z)_{\text{exact}}$  of  $\text{VOC.H}^+$  was derived from its atomic composition and used as evaluation mass for the mass accuracy and precision (Table 1). To each resulting PTR-TOF mass peak, DESV2 assigns its measured mass number (position of the peak center,  $(m/z)_{\text{empirical}}$ ). We utilized 1-min mass spectra which were taken on 17 occasions, six at each time, over a period of 11 wk resulting in 102 individual 1-min mass spectra. From this dataset, we computed statistical parameters similar to Sack and coworkers [20]. Table 1 compares the evaluation mass and the measured mass (being the mean value of all 102 measured mass numbers for each individual test peak). It lists the deviation (DEV) of each measured mass from the evaluation mass as well as the standard deviation (SD) of each test mass time-series in both absolute and relative units.

The relative mass deviation is found to be smaller than 2.5 ppm for all test masses. Consequently we assume that the mass accuracy of the PTR-TOF is also in

**Table 1.** Accuracy and precision of the measured mass of protonated VOCs over an 11-wk period

Trivial name	Prot. ion	Evaluation mass [m/z]	Measured mass [m/z]	DEV [ $10^{-3}$ m/z]	SD [ $10^{-3}$ m/z]	DEV [ppm]	SD [ppm]	CR [ppm]
Methanol	$\text{CH}_5\text{O}^+$	33.03349	33.03353	0.04	0.1099	1.24	3.33	7.90
Acetonitrile	$\text{C}_2\text{H}_4\text{N}^+$	42.03383	42.03386	0.03	0.1018	0.65	2.42	5.49
Acrolein	$\text{C}_3\text{H}_5\text{O}^+$	57.03349	57.03361	0.12	0.1174	2.10	2.06	6.22
Acetone	$\text{C}_3\text{H}_7\text{O}^+$	59.04914	59.04915	0.01	0.1190	0.15	2.02	4.19
Isoprene	$\text{C}_5\text{H}_9^+$	69.06988	69.07005	0.17	0.1313	2.48	1.90	6.28
2-Butanone	$\text{C}_4\text{H}_9\text{O}^+$	73.06479	73.06490	0.11	0.1158	1.54	1.59	4.72
Benzene	$\text{C}_6\text{H}_7^+$	79.05423	79.05435	0.12	0.1304	1.56	1.65	4.86
Toluene	$\text{C}_7\text{H}_9^+$	93.06988	93.07000	0.12	0.1382	1.30	1.48	4.26
Hexanone	$\text{C}_6\text{H}_{13}\text{O}^+$	101.09609	101.09622	0.13	0.1362	1.29	1.35	3.99
Xylenes <sup>a</sup>	$\text{C}_8\text{H}_{11}^+$	107.08553	107.08556	0.03	0.1463	0.27	1.37	3.01
$\alpha$ -Pinene	$\text{C}_{10}\text{H}_{17}^+$	137.13248	137.13245	-0.03	0.2045	-0.22	1.49	3.20
1,2-DCB isotopes <sup>b</sup>	$\text{C}_6\text{H}_5\text{Cl}_2^+$	146.97628	146.97637	0.09	0.2267	0.60	1.54	3.68
		148.97336	148.97357	0.21	0.3903	1.39	2.62	6.63
1,2,4-TCB isotopes <sup>c</sup>	$\text{C}_6\text{H}_4\text{Cl}_3^+$	180.93731	180.93724	-0.07	0.1690	-0.37	0.93	2.23
		182.93438	182.93413	-0.25	0.2997	-1.34	1.64	4.62

<sup>a</sup>Mix of 1,2-xylene and 1,3-xylene.

<sup>b</sup>DCB = dichlorobenzene.

<sup>c</sup>TCB = trichlorobenzene.

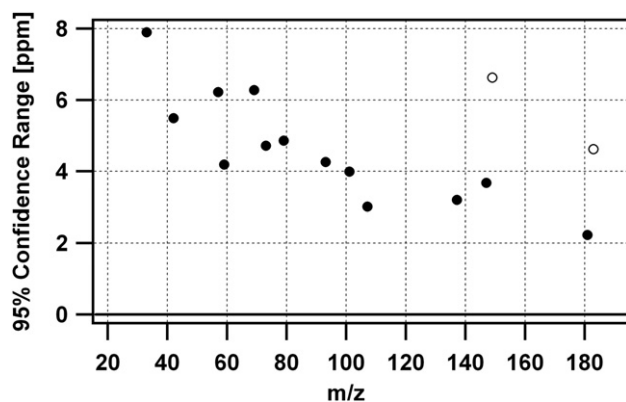
the range of 2.5 ppm when a statistically relevant number of spectra is used for the accurate mass measurement. Looking into the measured mass numbers of individual spectra, we found that they do not show any trend over the 11-wk period (data not shown). They are normally distributed around the mean measured mass, which allows the simple calculation of a confidence range (CR) for the expected deviation of the mass measured from a single mass spectrum. On a 95% confidence level, individually measured masses deviate less than  $|\text{DEV}| + 2 \times \text{SD}$  from the exact mass. With 7.9 ppm CR is largest for methanol (33.03349  $m/z$ ) and shows a decreasing trend towards higher masses (Figure 2).

The only exceptions to this trend are the 148.9734 and 182.9344  $m/z$  isotope peaks of dichlorobenzene and trichlorobenzene, respectively, which are displayed as different markers in Figure 2. The fact that the main peaks and the respective  $(m/z)+2$  isotope peaks have similar intensities led us to the hypothesis that chlorobenzene products from charge-transfer with ion source impurities such as  $\text{O}_2^+$  or  $\text{NO}^+$  could interfere with the PTR product peaks. With the low fraction of primary ion impurities ( $<1\%$ ), however, it is unlikely that those impurity peaks have any significant influence on the mass measurement of the main and  $(m/z)+2$  isotope peaks of the chlorinated aromatics. Further investigation is needed to solve this discrepancy.

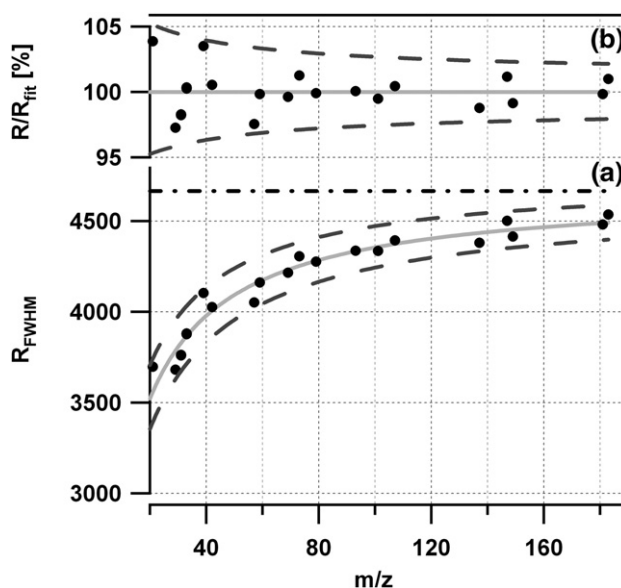
The capability to separate mass peaks of ions with differing exact masses is characterized by the mass resolving power  $R_{\text{FWHM}}$ . For a mass peak with peak center at  $(m/z)_{\text{empirical}}$

$$R_{\text{FWHM}} = (m/z)_{\text{empirical}} / \Delta(m/z)_{\text{FWHM}} \quad (1)$$

$\Delta(m/z)_{\text{FWHM}}$  being the peak's full width at half maximum (FWHM). Figure 3a shows the mass resolution of the PTR-TOF between 20 and 190  $m/z$ . The mass resolution increases with increasing mass number. A similar behavior was shown by other users of the TOFWERK



**Figure 2.** 95% confidence ranges (CR) for the ion masses measured in a single individual 1-min mass spectrum. Open circles are  $(m/z)+2$  isotopes of chlorinated aromatics, all other data are displayed as full circles.



**Figure 3.** Mass dependency of the resolving power. (a) Black circles depict  $R_{\text{FWHM}}$  of individual mass peaks. The grey line is the best fit according to a 0.7 ns jitter of the absolute time-of-flight determination. Dashed lines are the 95% confidence margins for the prediction of  $R_{\text{FWHM}}$  (prediction band). For the analysis of the  $R_{\text{FWHM}}$ 's mass dependency according to Coles and Guilhaus [22], see Supplemental Information, Figure S-1. (b) Deviation of  $R_{\text{FWHM}}$  of individual peaks (black circles) measured by PTR-TOF in percent relative to the best fit resolution (grey line) along with the 95% prediction band (grey dashed line) of the fit.

high-resolution TOF-MS [21] and is a consequence of the statistical uncertainty of the absolute time-of-flight determination [22]. The analysis according to Coles and Guilhaus [22] is presented in Figure S-1 (Supplemental Information, which can be found in the electronic version of this article). The mass resolution  $R_{\text{FWHM}}$  is higher than 4000 for peaks at masses greater than 40  $m/z$  and increases towards an asymptotic value of 4660. Consequently two peaks at 157  $m/z$  or less with a mass difference of 0.036 are separate by at least their FWHM; a 10% broadening of such overlapping, equally high peaks can be determined up to 445  $m/z$  (see Supplemental Information, Figure S-2 for the appearance of overlapping peaks). Note that to any given measured mass, the mass resolution has a very narrow prediction band (dashed lines in Figure 3a and b in absolute units and relative units, respectively). This is important for the identification capability of the instrument as the lower margin of the 95% prediction band marks the limit for the recognition of single peaks, i.e., an individual mass peak with a resolution lower than the margin is unlikely ( $P < 0.025$ ) originating from a single ion species of a certain exact mass. This exhibits a criterion for the determination whether a peak can be treated as single peak or whether a multi-peak analysis needs to be considered. For peaks at 20  $m/z$  or greater, the lower margin deviates less than 5% from the mass resolution (see Figure 3b). The prediction band is narrowing down strictly with increasing  $m/z$ .

In terms of long-time stability (11-wk period) we found that PTR-TOF measures ion masses with excellent accuracy (mean deviation < 2.5 ppm) and precision (SD < 3.4 ppm). The  $R_{FWHM}$  of each test mass in Table 1 showed a slightly decreasing trend (less than 0.2% per day) and a scatter of less than 5% ( $1\sigma$ ). This demonstrates the excellent performance of the PTR-TOF over long time periods.

### Sensitivity, LOD, Precision

For the determination of the sensitivity of the PTR-TOF, we diluted a calibration gas standard (Apel Riemer Environmental Inc., Denver, CO, USA; containing ~1 ppmv of each VOC listed in Table 2 in high grade  $N_2$ ) dynamically with scrubbed air using two calibrated mass flow controllers (MFC). VOCs in a VMR range of 0 to 10 ppbv were applied. The sensitivity of the PTR-TOF for a certain compound was determined from the slope of the linear fit through the scattered plot of signal intensities versus VMR. With an uncertainty of the gas standard concentrations of less than 5%, we estimate the total accuracy of the sensitivity calibration to be 13% or better. The limit of detection (LOD) was determined as the  $3\sigma$  uncertainty of the zero calibration. The quantification precision is the experimental standard deviation of the respective mass signal intensity in a number of spectra at a constant VOC VMR. Here we used a series of six 1-min spectra at constant MFC settings with corresponding VMRs in the range of 1 ppbv to 3 ppbv per compound. Sensitivity, LOD and precision values are listed in Table 2.

For the interpretation of signal intensities it is important to take the duty cycle at the respective mass into account. The geometrical duty cycle (the ratio of MCP length and the longitudinal separation of extractor and MCP) and the mass-dependent duty cycle (square root of the ratio of respective mass and the maximal mass on the mass scale) combine to a total duty cycle, which strongly suppresses the detection of light ions. At a typical extraction frequency of 33.3 kHz (30  $\mu$ s flight time corresponding to the highest detectable ion mass of 314  $m/z$ ) the total duty cycle for ions at 21  $m/z$  is 0.075

and reaches 0.29 at 314  $m/z$ . Changing the pusher frequency to lower values increases the upper mass range limit but at the same time reduces the duty cycle for lower masses. Detected signal intensities of the primary ions (determined from the count rates of  $^{18}O$  isotopes of the  $H_3O^+$  and  $H_2OH_3O^+$ ) are typically  $1.6 \times 10^6$  Hz and  $3.8 \times 10^5$  Hz, respectively. Primary ion intensities as well as sensitivities (see Table 2) are somewhat higher than reported by Jordan and coworkers [17]. The LOD for  $S/N = 3$  and at 1 min integration time of PTR-TOF spectra ranges from 8 pptv for isoprene to 65 pptv for methanol. Even for 1 s integration time of PTR-TOF mass spectra a LOD in the sub-ppbv range was achieved. If a lower LOD is desired, co-adding a series of stored 1 s mass spectra (e.g., over a period of 10 to 30 min) allows for a LOD in the ppqv range by post-experimental data processing. From the calibration setup, we estimate a sensitivity uncertainty of less than 13%, thus resulting in an accuracy of the VMR determination of the calibrated VOCs of 13% or better. As PTR is an unselective ionization method, a multitude of compounds can be analyzed. In reasonable time, however, one can carry out calibration experiments for only a limited number of VOCs of interest. Sensitivities of uncalibrated VOCs may be estimated from known sensitivities by analogy to similar calibrated VOCs or can be derived solely theoretically from the reaction rate constant for the PTR [2, 23]. In this case, the accuracy for the quantitative measurement must be estimated individually. The precision of concentrations measurement in the standard addition experiment at VOC VMRs < 3 ppbv is in the range of 1.0% to 3.4% at 1 min time resolution (Table 2).

### Separation and Identification of Isobaric Species

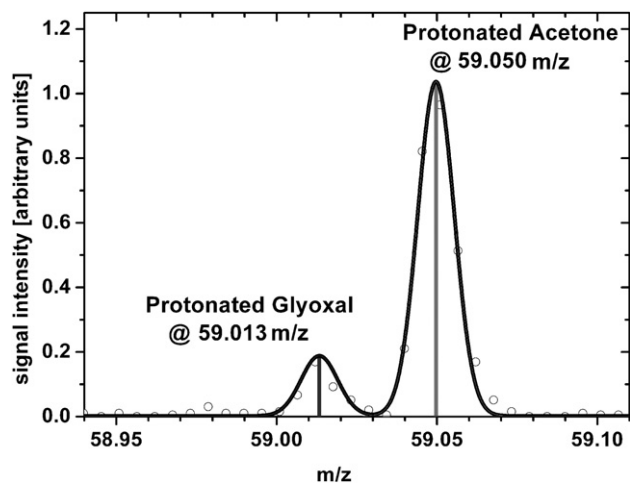
PTR-ionization is a soft chemical ionization technique that preserves in many cases the chemical structure of the VOC during ionization. In any non-dissociative proton transfer case,  $VOC.H^+$  directly reflects the atomic composition of the respective VOC. In the following, we demonstrate the separation capability of the PTR-TOF with two examples and deduct general rules

**Table 2.** Sensitivity, detection limit, and precision of the PTR-TOF for a suite of VOCs

Trivial name	Protonated ion	$(m/z)_{exact}$	$\varepsilon$ [Hz×ppbv <sup>-1</sup> ]	LOD <sup>†</sup> [pptv]	Precision <sup>†,‡</sup>
Methanol	CH <sub>5</sub> O <sup>+</sup>	33.03349	26.9	65	3.4%
Acetonitrile	C <sub>2</sub> H <sub>4</sub> N <sup>+</sup>	42.03383	55.3	21	1.1%
Acrolein	C <sub>3</sub> H <sub>5</sub> O <sup>+</sup>	57.03349	66.7	21	1.5%
Acetone	C <sub>3</sub> H <sub>7</sub> O <sup>+</sup>	59.04914	66.3	25	1.1%
2-Butanone	C <sub>4</sub> H <sub>9</sub> O <sup>+</sup>	73.06479	72.0	20	1.4%
Hexanone	C <sub>6</sub> H <sub>13</sub> O <sup>+</sup>	101.09609	74.7	12	1.4%
Benzene	C <sub>6</sub> H <sub>7</sub> <sup>+</sup>	79.05423	43.7	12	2.1%
Toluene	C <sub>7</sub> H <sub>9</sub> <sup>+</sup>	93.06988	52.5	16	1.6%
m-, o-Xylenes	C <sub>8</sub> H <sub>11</sub> <sup>+</sup>	107.08553	54.4	17	1.0%
Isoprene	C <sub>5</sub> H <sub>9</sub> <sup>+</sup>	69.06988	44.4	8	2.2%
α-Pinene	C <sub>10</sub> H <sub>17</sub> <sup>+</sup>	137.13248	45.7	9	2.1%

<sup>†</sup>Based on 1 min integration period.

<sup>‡</sup>t VOC VMRs in the range of 1 ppbv and 3 ppbv.



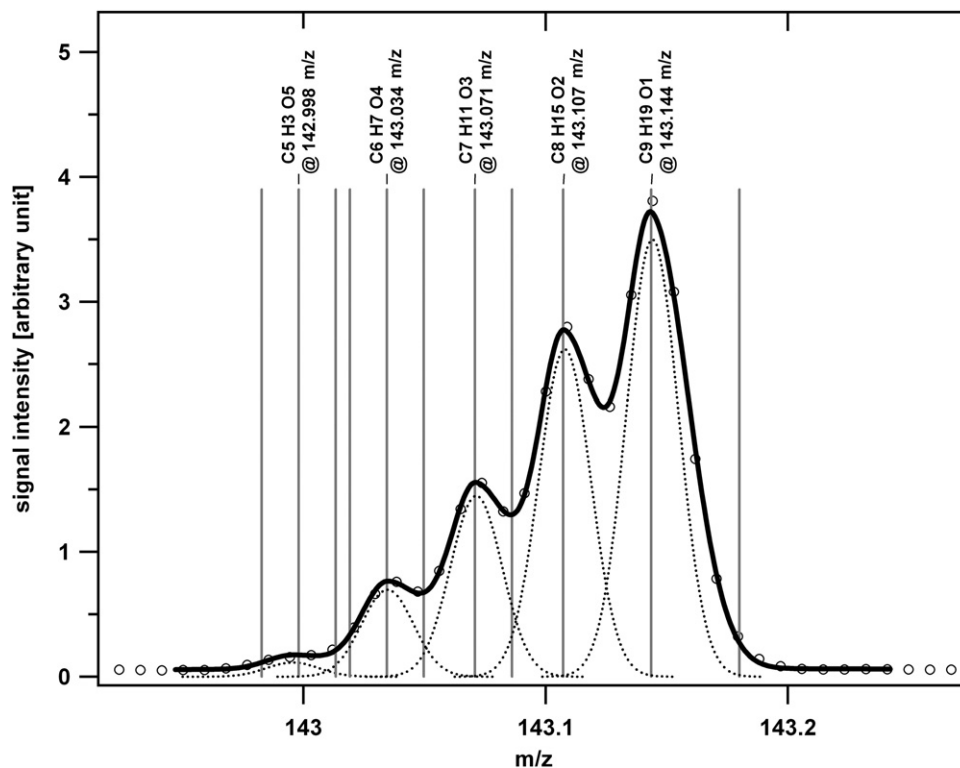
**Figure 4.** Separation of glyoxal and acetone. Measured ion signal (open circles) of an acetone and glyoxal mixture and modified-Gaussian fitted peaks (black line) with measured centroid masses (vertical lines) at 59.013 and 59.050  $m/z$ , respectively.

for the unambiguous identification of ion compositions  $C_xH_yO_z^+$  from fundamental considerations of valence rules and the mass accuracy of the PTR-TOF.

**Figure 4** shows the separated peaks of protonated glyoxal ( $CH(O)CH(O)H^+$ ) and protonated acetone ( $CH_3C(O)CH_3H^+$ ). Individual concentrations of glyoxal

and acetone in this mixture can be derived from the respective peak area under the fitted curve.

**Figure 5** shows a small part of a PTR-TOF mass spectrum at nominal mass 143 obtained during a series of photo-oxidation experiments performed at the environmental chamber of the Paul Scherer Institute (PSI). The details of the 1,3,5-trimethylbenzene (TMB) photo-oxidation experiments are published elsewhere [unpublished work: Müller et al. (2010)]. This work was presented at the AGU Conference 2009 in Vienna. An abstract is available at <http://meetingorganizer.copernicus.org/EGU2009/EGU2009-10242.pdf>. A manuscript for the submission to a peer-reviewed journal is in preparation]. TMB and its photo-oxidation products were monitored with a time resolution of 1 min. The spectra of the whole TMB photo-oxidation experiment (410 min between light on and light off) were co-added to obtain a sum spectrum containing all detectable products at lowest possible signal-to-noise ratios. The multi-peak fitting procedure clearly separates at least five mass peaks. Neighboring peaks are separated by 0.036, which corresponds to the mass difference of  $CH_4$  (16.0308 u) and O (15.9944 u). This mass difference indicates that the unknown compounds at nominal mass 143 can be assigned to different isobaric oxygenated hydrocarbons containing one, two, three, four, and five oxygen atoms.



**Figure 5.** Oxygen number in OVOCs. Measured ion signal (open circles) of PTR-TOF to photo-oxidation products of TMB averaged over 410 min. Multi-peak fit (black line) and contributing peaks (dotted lines) along with matching candidates for  $C_xH_yO_z^+$  assignment (vertical lines)—all potential candidates are listed in the Supplemental Information, Table S-4.

The separation of a mass peak from neighboring peaks is an essential prerequisite for the identification of its sum formula. Every mass peak that is considered to originate from a single ion species can be assigned with an atomic composition by matching the measured mass with a list of candidate compositions (e.g.,  $C_xH_yO_z^+$ ) and taking valence rules into consideration. We produced a complete list of combinations ( $x, y, z$ ) that represent ions  $C_xH_yO_z^+$  in the mass range of 33 to 800 sorted by increasing  $m/z$  (for index boundaries and limits for the saturation number see Supplemental Information, Figure S-3) and plotted the distances between consecutive combinations versus their exact mass (Figure S-3). Let MA be the instrument's mass accuracy and  $(m/z)_{\text{empirical}}$  an individually measured mass of a peak. The assignment of the peak at  $(m/z)_{\text{empirical}}$  with  $C_xH_yO_z^+$  is unambiguous if there is only one candidate  $C_xH_yO_z^+$  within the interval  $[(1 - \text{MA}) \times (m/z)_{\text{empirical}}, (1 + \text{MA}) \times (m/z)_{\text{empirical}}]$ . To turn this into a more general rule, we look at the minimum distance between candidates in certain mass ranges (red line in Figure S-3).

Table 3 shows upper mass range margins, the respective minimum distance of  $C_xH_yO_z^+$  peaks in those mass intervals, and the required mass accuracy for an unambiguous assignment of an atomic composition. The PTR-TOF fulfills those mass accuracy requirements up to 373  $m/z$  when a series of statistically significant spectra is recorded and up to 265  $m/z$  for individual 1-min mass spectra. Under these very general limitations for candidates, however, assumption of a single separate mass peak must be checked on an individual basis for peaks at 109  $m/z$  or greater. For masses below 109  $m/z$ , non-separate peaks are readily identified by a 10% broadening (see mass resolution).

In many cases, quasimolecular peaks of HCs and OVOCs are separated solely by 0.036 (see Figures 4 and 5). Under these premises, the demonstrated mass resolution and mass accuracy of the PTR-TOF are sufficient to identify such peaks up to 445  $m/z$ . It is important to note that the identification capability of the PTR-TOF is not only a matter of its mass accuracy and mass resolution but also depends strongly on the restrictions that are applicable to the candidate list. For a mass peak to be assigned to a particular VOC, one must always demonstrate that the assigned candidate has at least one neutral representative that forms  $\text{VOC.H}^+$  upon protonation. Particular care must be taken when analyzing complex mixtures of VOCs and when dissociative pro-

ton transfer cannot be excluded. For the accurate quantification of fragmenting VOCs fragmentation patterns must be established for those compounds in question.

## Summary

In this paper, we describe the performance of the recently developed high-resolution PTR-TOF instrument. This PTR-TOF instrument has a high sensitivity (primary ion signal  $> 10^6$  Hz), which makes it applicable for fast on-line VOC analysis, where low LOD and high time resolution have to be achieved at the same time, e.g., 0.1 s for eddy covariance flux measurements [19]. In addition, our instrument has a high mass resolution of 4400  $m/\Delta m$  (FWHM) and a mass accuracy of 2.5 ppm. This mass accuracy and the excellent mass precision are sufficient to be unambiguously matched to  $C_xH_yO_z^+$  candidates for peaks up to 373  $m/z$  when a statistically relevant number of spectra are recorded; based on a single 1-min spectra, an assignment of  $C_xH_yO_z^+$  candidates is still feasible for peaks up to 265  $m/z$ . Peaks separated by 0.036 (O in exchange of  $\text{CH}_4$ ) are identified for mass peaks below 445  $m/z$ . The measured mass range of the PTR-TOF can be increased at the cost of duty cycle for the low masses. The detection efficiency of larger masses (less volatile compounds) is strongly enhanced in PTR-TOF compared with PTR-Quad-MS due to the measurement principle. The PTR-TOF allows quantifying a variety of organic compounds at trace levels and greatly expands the capabilities to conduct problem solving for environmental science, food technology, and life sciences.

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## Appendix A Supplementary Material

Supplementary material associated with this article may be found in the online version at doi:10.1016/j.jasms.2010.02.006.

**Table 3.** Mass accuracy requirements for  $C_xH_yO_z^+$  identification

Upper mass range margin [ $m/z$ ]	Minimum distance [ $m/z$ ]	MA [ppm]
61	0.0364	298
109	0.0153	70
265	0.0059	11
373	0.0035	4.7
637	0.0024	1.8

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