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Short communication

A high resolution and high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS)

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ABSTRACT

Proton-transfer-reaction mass spectrometry (PTR-MS) developed about 10 years ago is used today in a wide range of scientific and technical fields allowing real-time on-line measurements of volatile organic compounds in air with a high sensitivity and a fast response time. Most instruments employed so far use quadrupole filters to analyze product ions generated in the reaction drift tube. Due to the low mass resolution of the quadrupoles used this has the disadvantage that identification of trace gases under study is not unambiguous.

Here we report the development of a new version of PTR-MS instruments using a time-of-flight mass spectrometer, which is capable of measuring VOCs at ultra-low concentrations (as low as a few pptv) under high mass resolution (as high as 6000 m/Δm in the V-mode) with a mass range of beyond 100 000 amu. This instrument was constructed by interfacing the well characterized and recently improved Ionicon hollow cathode ion source and drift tube section with a Tofwerk orthogonal acceleration reflectron time-of-flight mass spectrometer. We will first discuss the set-up of this new PTR-TOF-MS mass spectrometer instrument, its performance (with a sensitivity of several tens of cps/ppbv) and finally give some examples concerning urban air measurements where sensitivity, detection limit and mass resolution is essential to obtain relevant data.

1. Introduction

Volatile organic compounds (VOCs) in the atmosphere are emitted from different biogenic and anthropogenic sources. The production, storage and use of fossil fuel products as well as intensive agriculture and biomass burning leads to an increasing change of the atmospheric composition. Deposition processes and important photochemical reactions are removing and changing the VOC composition in the atmosphere. Photochemical reactions are dominated by the hydroxyl radical (OH) which is produced by photons from water during the daytime. The reactions of VOCs with the OH radical require different time scales from minutes to months. For many established analyzers a sample preparation and accumulation over some time is necessary which results in bad time resolution. Proton-transfer-reaction mass spectrometry (PTR-MS) has overcome some of the disadvantages of traditional GC measurements and is by now a well established mass spectrometric technique used in a wide variety of fields including besides fundamental mass spectrometry, atmospheric science, medical and biotechnological applications, food and flavour science and industrial monitoring [1–4]. PTR-MS was developed as a new method for quantitative trace gas analysis in the nineties by Lindinger et al. at the Institut für Ionenphysik in Innsbruck and immediately overcame some of the disadvantages of gas chromatographic methods, however at the cost of chemical detail [1,2]. Over the past 10 years much has been unravelled about the performance, response and specificity of PTR-MS instruments and present day knowledge in particular concerning field measurements of atmospheric VOCs has been summarized in the seminal review by de Gouw and Warnecke [4].

Besides the many advantages, one of the drawbacks of PTR-MS is the fact that only the nominal mass-to-charge ratio of the protonated parent ion (or product ion) can be determined, which is a useful quantity but does not always allow a unique identification of the VOCs under study. The presence of several different species on the same nominal mass, cluster ion formation and parent ion fragmentation may lead to complications in the interpretation of ion signals measured. Various ways have been developed to overcome these complications (including specially designed drift tubes, ion traps and triple quads and coupling of PTR-MS with GC [5]), the most obvious one is however the use of a high resolution mass

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spectrometer instead of the quadrupole mass filter used in most of the more than 150 commercial instruments worldwide in operation. Time-of-flight (TOF) mass spectrometry not only eliminates the necessity to select a subset of ions to be monitored in a specific experiment, but it usually has a mass resolution which allows the separation of most nominally isobaric ions. The major obstacle so far using TOF in combination with PTR-MS was the difficult coupling situation and the significant loss of sensitivity encountered thereby.

In 2004 Blake et al. [6] were the first to report the successful coupling of a reflectron TOF mass spectrometer with a radioactive ion source in combination with a drift tube. Nevertheless, typical mass resolutions achieved were 1200 m/Δm and thus were not sufficient in most cases to separate nominally isobaric species. Moreover, due to a variety of reasons, one being the duty cycle achieved, the highest H_3O^+ primary ion count rate obtained was appr. 10^4 cps, which is over four orders of magnitude, lower than that of high sensitivity Ionicon quadrupole PTR-MS instruments. This led to a low sensitivity of about 0.17 cps/ppbv for H_2S with detection limits in the ppbv range for integration times of around 1 min. One year later Ennis et al. [7] reported on the development of a reflectron PTR-TOF instrument incorporating a hollow cathode ion source allowing the detection of trace gas components at concentrations as low as 1 ppbv on a timescale between 10 and 60 s. Nevertheless, with a sensitivity of 3.7 cps/ppbv for toluene the instrument was still about two orders of magnitude lower than the commercially available quadrupole PTR-MS instruments. As in the above case, the instrument barely allowed the separation of nominally isobaric ions, the example given at mass 47 in the paper being protonated ethanol and formic acid, and a large number of NO^+ and $O_2{}^+$ ions were produced which makes the interpretation of PTR mass spectra more complicated. Very recently, Inomata et al. [8] and Tanimoto et al. [9] reported the construction of a PTR-TOF instrument involving a linear time-of-flight mass spectrometer with a mass resolution of about 100 m/Δm in combination with a novel discharge ion source, allowing a higher drift tube pressure and a detection limit just below 1 ppbv for 1 min integration times.

A clear disadvantage of PTR-TOF is that the ions produced in the drift tube need to be pulsed into the time-of-flight region. In a conventional PTR-MS instrument a constant current of primary ions and consequently product ions, is generated, and these ions are usually injected into the quadrupole on line and in constant ion mode. Injecting these ions into a TOF can only be done in ion packages and so far at the cost of large ion losses and thus loss of sensitivity as compared to the commercially available quadrupole instruments. Here we report the development and one of the first deployments of a new version of PTR-TOF-MS instruments, which is capable of measuring VOCs at ultra-low concentrations (as low as a few pptv) under high mass resolution (over 6000 m/Δm in the V-mode (see Fig. 1 for a schematic demonstration of the V- and the W-mode and Fig. 2 for an estimation of the maximum mass resolution)). This instrument was constructed by interfacing the well characterized and recently improved [10] Ionicon hollow cathode ion source and drift tube section with a Tofwerk orthogonal acceleration reflectron time-of-flight mass spectrometer. We will first discuss the set-up of this new PTR-TOF-MS mass spectrometer instrument, its performance and finally give some examples concerning urban air measurements where sensitivity, detection limit and mass resolution are essential to obtain relevant data.

2. Instrument description

The present proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS) is an instrument based on the design of

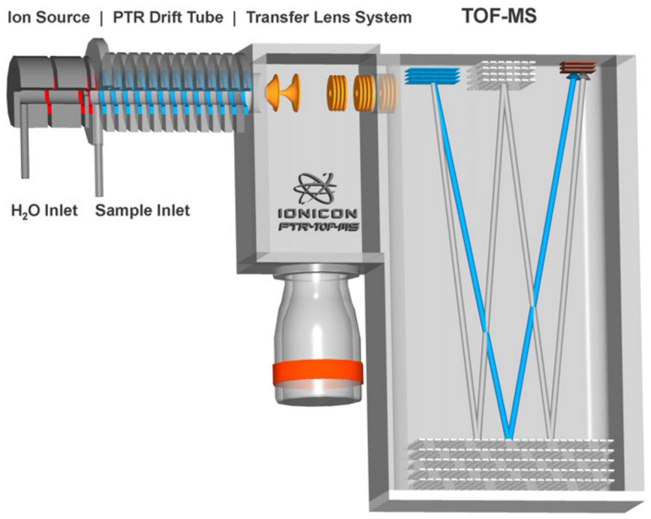

Fig. 1. Schematic drawing of the PTR-TOF-MS instrument, consisting of the hollow cathode discharge ion source, the drift tube reaction chamber, the transfer lens system and the reflectron time-of-flight mass spectrometer. Additionally the two modes of operation of the TOF are outlined, namely the V- and the W-mode.

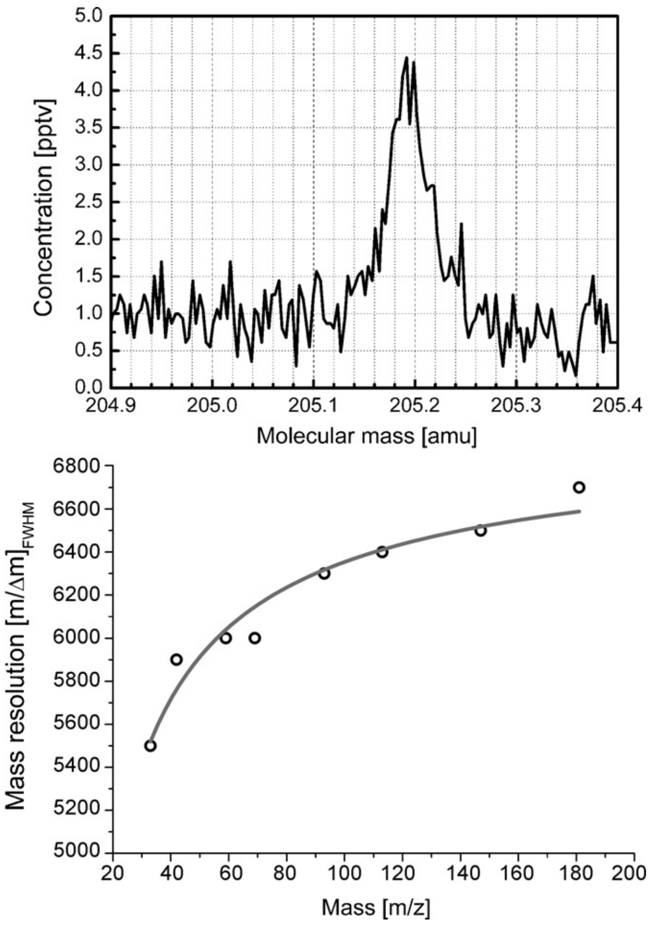

Fig. 2. Upper panel: PTR-TOF-MS spectrum of sesquiterpene demonstrating the low background for an extremely small signal from an urban air sample. The signal has been obtained by averaging 10 measuring cycles each running for a 4 min integration time. The *y*-axis is calculated via the well known conditions in the drift tube (pressure, temperature, length, reagent ion current, etc.). Lower panel: Measurement of mass resolutions for several compounds using a calibration gas mixture. By fitting the measurement points via $y = a \times x^{1/(2+b\times x)}$ the maximum achievable resolution at high mass can be estimated to be 6976 ± 85 m/Δm (FWHM).

Table 1
Reaction rate constants, measured count rates, concentration in calibration sample, sensitivity (cps/ppbv) and relative transmission (normalized to the primary ion current at mass 21, which is chosen because of detector saturation at the extremely high count rates at mass 19) for nine compounds in the mass range from 79 to 181 amu.

Protonated molecular mass (*m*/*z*)	Reaction rate coefficient ($\times 10^{-9}$ cm^3/s)	Count rate (cps)	Concentration in sample (ppbv)	Sensitivity (cps per ppbv)	Transmission factor relative to mass 21
Reagent ion (21)		481 000			1.00
Benzene (79)	2.02	1 763	133	13	2.68
Toluene (93)	2.13	1 797	101	18	3.36
Styrene (105)	2.30	1 826	90	20	3.59
Xylene (107)	2.29	7 546	372	20	3.59
Chlorobenzene (113)	2.35	1 749	78	22	3.91
Trimethylbenzene (121)	2.20	4 545	199	23	4.23
Dichlorobenzene (147)	2.30	4 151	172	24	4.27
Dichlorobenzene (149)	2.30	2 712	110	24	4.36
Trichlorobenzene (181)	2.30	961	37	26	4.54

the commercially available high sensitivity quadrupole PTR-MS instrument from Ionicon [10,11]. The instrument was constructed by interfacing the well characterized and recently improved [10] Ionicon hollow cathode ion source and drift tube section with a Tofwerk orthogonal acceleration reflectron time-of-flight mass spectrometer. An instrument schematic of this PTR-TOF-MS is given in Fig. 1. The PTR-TOF-MS in its current commercially available version [11] (an exploratory prototype version with a detection limit of 20 pptv for 1 min integration time has been constructed and tested in the Institut für Ionenphysik [12] in collaboration with Ionicon achieving a mass resolution of up to 5500 thereby demonstrating clear separation of protonated glyoxal and acetone at mass 59) is mounted in a single mobile rack, where the mass spectrometer, the ion source and drift tube system, the vacuum system (2 split-flow turbo pumps and 1 foreline backing pump) and the whole electronics including the pulse generator are integrated. The rack dimensions are 55 cm × 130 cm × 78 cm (W × H × D) and the whole instrument weighs approximately 170 kg. The data acquisition and analysis system is situated in an external desk top computer and display system.

In the hollow cathode ion source H_3O^+ reagent ions are produced from water vapour introduced as reagent gas from a liquid water sample holder. Reagent ions are entering the adjacent drift tube section, where the sample to be analyzed is continuously injected (via a gas inlet system with adjustable flow between 50 and 1000 sccm and adjustable temperature between 40 and 150 °C) with typical pressures maintained in the drift tube between 2.2 and 2.4 mbar. In this drift tube (adjustable temperature between 40 and 120 °C) proton transfer reactions occur between hydronium ions and VOCs and the outgoing protonated VOCs ions then enter, via a specially designed transfer lens system, the pulse extraction region of the orthogonal acceleration reflectron time-of-flight mass spectrometer. Here ions are accelerated into the TOF section at a typical repetition rate of up to appr. 80 kHz. The mass-to-charge ratios of the ions are determined from the flight times measured and each extraction pulse generates a complete mass spectrum for the time interval (mass range) chosen, and each mass spectrum is processed by a fast data acquisition board in combination with a desk top computer.

Several facts are responsible for the fast response time (smaller than 100 ms), high sensitivity (up to several tens of cps/ppbv, see Table 1) and low detection limit (down to a few pptv, see Fig. 2 showing a mass scan for sesquiterpene from urban air) achieved in the present instrument as compared to the previously reported TOF set-ups [7–9]. Most importantly, the extremely low detection threshold is due to the interplay of the higher duty cycle of the TOF-MS designed by Tofwerk, the specially designed transfer lens system, the dimensions of the pulse extraction region, and the low background noise of the multichannel-plate. Moreover, especially rewarding is the fact that (i) in contrast to quadrupole mass filter detection, where the transmission of ions is strongly deteriorating with increasing mass (usually a factor of 2 when going from mass 21 to 100), in the present case sensitivity (i.e., overall transmission relative to the primary ion) is increasing when going from 21 to larger masses (see Table 1, where the transmission factor is seen to increase by about a factor of 5 when going from 21 to 181 using a standard gas mixture as sample gas), and (ii) the certified (by the manufacturer Tofwerk) mass range accessible for the present instrument is in excess of 100 000 amu. From extended measure-

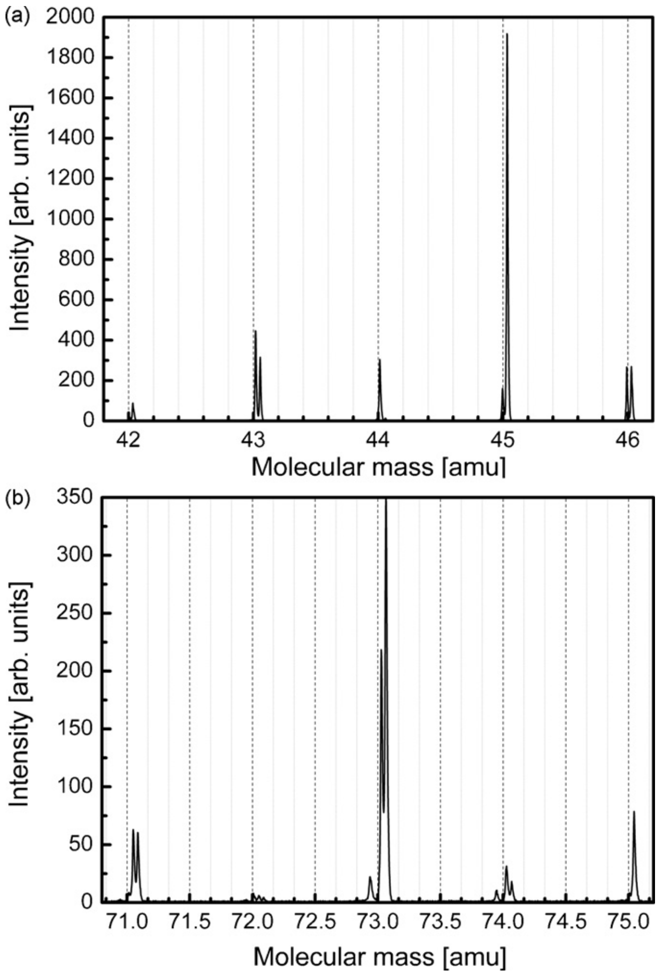

Fig. 3. Two examples of PTR-TOF-MS mass spectra of an urban air sample covering the mass range between 42 and 46 (a) and 71 and 75 (b). The mass spectra have been obtained by averaging 10 measuring cycles each running for a 4 min integration time.

ments with calibrated gas samples (as the ones given in Table 1) we can confirm linearity of response over a concentration range from about 10 pptv up to 10 ppmv, this is similar to the performance of the commercially available high sensitivity quadrupole PTR-MS instruments from Ionicon.

To demonstrate the extraordinary mass resolution of over $6000\,\mathrm{m}/\Delta\mathrm{m}$ we measured several compounds from a calibration gas standard (mixture from Restek) with an optimised PTR-TOF-MS instrument in V-mode. In Fig. 2 eight measurement points (each one obtained by fitting a Gaussian function to the peak and dividing the position of the peak by its full width at half maximum) are displayed and it can be clearly seen that the resolution is strongly increasing in the mass range from 30 to about 100 m/z. The respective fit function gives a maximum mass resolution of approximately $7000\,\mathrm{m}/\Delta\mathrm{m}$. It is clear that W-mode operation gives an even higher resolution.

3. Urban air measurements

In order to demonstrate the performance and some of the specific advantages of the presently available PTR-TOF-MS, i.e., high mass resolution, high sensitivity, ultra-low detection limit, we have carried out measurements of the urban air just outside of our Technikerstrasse laboratory. Innsbruck is a typical moderate-sized alpine city (population appr. 150 000) and the Ionicon laboratory is located appr. 7 km from the city center at the outskirts of the city opposite to the airport. One of the major traffic connections into the city is passing the laboratory just 100 m away. Besides VOCs from the airport grassland and the city in general, substantial VOC pollutants are expected in this environment from the adjacent road depending on the specific traffic situation. Urban air is sampled over a number of days (see below) during a stable, mostly sunny inversion like, relatively warm winter weather situation (−3 °C during night time and about 8 °C during daytime) via a heated Peek sampling tube (inner diameter of 1 mm and the length of about 3 m) from just outside the laboratory building (appr. 5 m above ground) directly into the PTR-TOF-MS instrument.

Fig. 3 shows as an example two mass spectra covering a range from 42 to 46 and 71 to 75 amu, respectively, recorded during daytime within a 40 min period (average of ten 4 min scans). As can be seen from this figure at each nominal mass a signal is present. As a matter of fact expanded views of some of the peak structures recorded at mass resolutions of about $4000\,\mathrm{m}/\Delta\mathrm{m}$ (operating the instrument in V-mode) given in Fig. 4 immediately reveal that each nominal mass consists of several clearly resolved peaks indicating the presence of multiple species at a single nominal mass. Such a situation, the occurrence of scrambling of several species at one nominal mass has been discussed in detail in the case of atmospheric VOC research by de Gouw and Warnecke [4], and the only way to handle this complex situation were additional measurements and intercomparisons with GC-FID or GC-PTR-MS (see also [5]). Nevertheless, it has been mentioned that some species will not be detected by these alternatives, for instance when they cannot be collected in the cryo-cooled sample trap, if they dissociate as a result of the heating during the injection, or if they are not separated by the column used [4].

As shown in Fig. 4a–d, in the present case we can distinguish and detect simultaneously in urban air at nominal mass 43 protonated ketene at 43.0184 and protonated propene at 43.0548, at nominal mass 57 protonated methylketene at 57.034 and protonated butene at 57.0704, at nominal mass 69 protonated furan at 69.034 and pro-

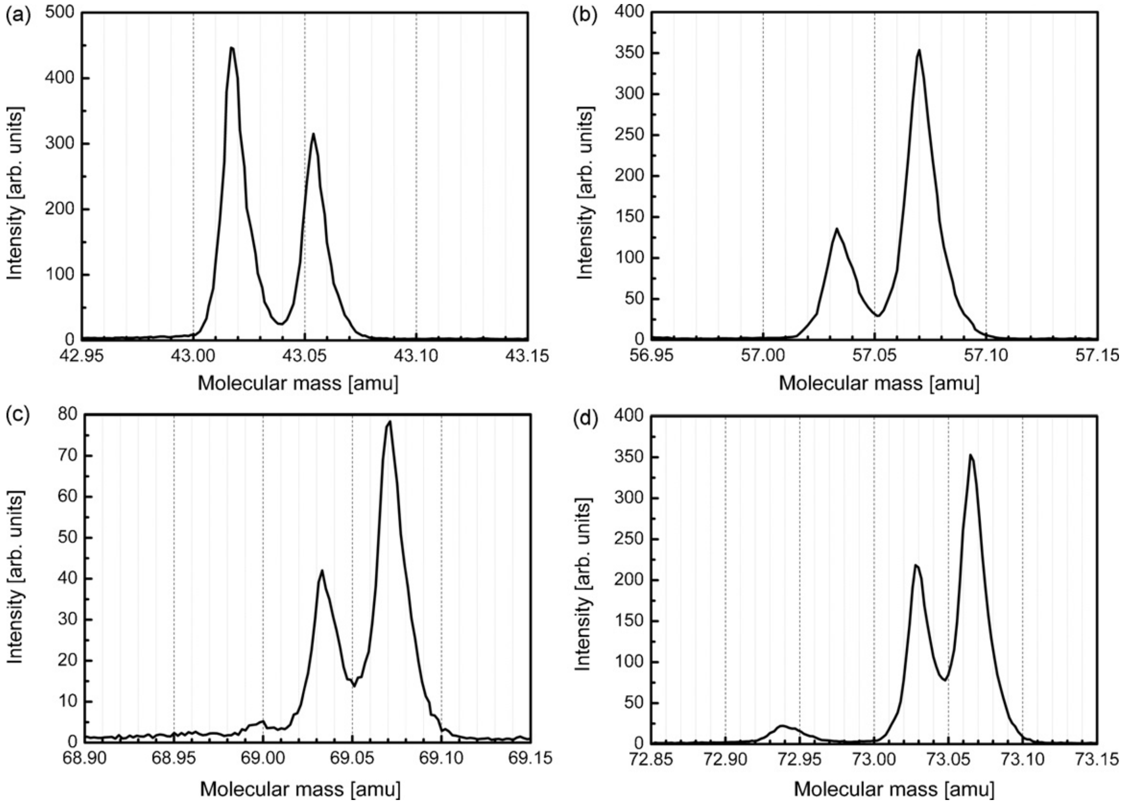

Fig. 4. Expanded views of the PTR-TOF-MS mass spectra given in Fig. 3 demonstrating the ability of the present set-up to distinguish multiple mass peaks (here and below we give the most likely mass identifications) present at one nominal mass, i.e. (a) at mass 43 protonated ketene at 43.0184 and protonated propene at 43.0548, (b) at nominal mass 57 protonated methylketene at 57.034 and protonated butene at 57.0704, (c) at nominal mass 69 protonated furan at 69.034 and protonated isoprene at 69.0704 (with a small unidentified species at around 69.000) and (d) at nominal mass 73 protonated methyethylketone at 73.0653 and two unidentified species at around 73.030 and 72.940.

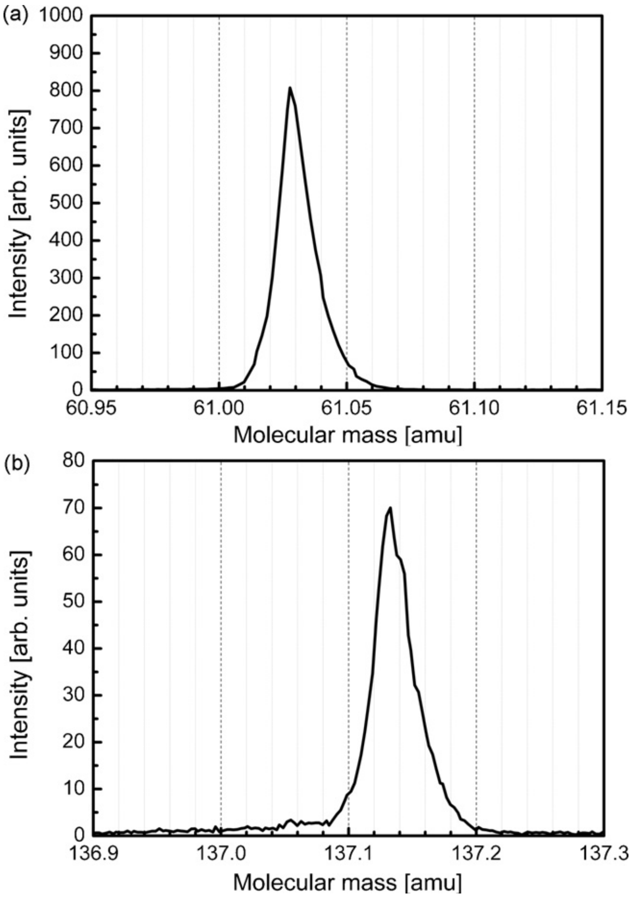

Fig. 5. PTR-TOF-MS spectrum of acetic acid (a) and terpene (b) from an urban air sample. The signal has been obtained by averaging 10 measuring cycles each running for a 4 min integration time. In this case only a single mass peak is present at these nominal masses.

tonated isoprene at 69.0704 (with a small unidentified species at around 69.000) and at nominal mass 73 protonated methyethylketone at 73.0653 and two unidentified species at around 73.030 and 72.940. It is interesting to note, that in particular when measuring isoprene, multiple (biogenic) species can contribute to the signal at the nominal mass 69 including 2- and 3-methyl-butanal, 2-methyl-3-buten-2-ol and 1-penten-3-ol and other unidentified species in urban air [4,13,14]. Here we can identify the chemical species at least according to their sum formula from the exactly measured mass, showing that here the overwhelming source at mass 69 is isoprene in accordance with measurements of de Gouw et al. [15] for fresh and aged urban emissions. It is also quite noteworthy, that in some cases we only detect one single peak at a nominal mass in urban air, e.g., see Fig. 5a and b, with acetic acid at mass 61.290 and terpene at mass 137.133. Furthermore, one overriding conclusion from the present measurements is that identification of species and measurements of multiples at a nominal mass can be carried out also at very low concentrations, e.g., see sesquiterpene measured in the urban air sample at the exact mass of 205.1956 and at concentrations in the few pptv range as shown in Fig. 2. The mass spectrum in Fig. 2 also demonstrates the excellent signal/noise ratio that can be achieved with longer data acquisition times (here giving a 40 min average) with background values below the 1 pptv level.

Finally, we would like to present here the results of absolute concentration measurements yielding the temporal variations of some major VOCs (traffic and biogenic compounds) present in the urban air over a 3-day period, starting on Friday, 18 January 2008 at around noon and lasting until Monday, 21 January 2008 evening (Fig. 6). In this case data points plotted correspond to 4 min sampling (integration) times. The panels in Fig. 6 are ordered roughly according to the concentrations of the compounds detected ranging from about 8 ppbv for the maximum signal of ethanol at mass 45.034 (top panel) to about 10 pptv for the maximum signal of sesquiterpene at a mass of 205.1956 (bottom panel). Several features can be deduced from these results. Almost all compounds exhibit definitive variations over the daily 24 h period, some VOCs show rather regular patterns with one, two or more maxima, some VOCs show rather irregular patterns with temporal variation on a short time scale (thus fully exploiting the time resolution of the set-up) due to wind gusts. It is interesting to note that some biogenic compounds like terpene and sesquiterpene (Fig. 6g) go through a build up phase starting at the late afternoon reaching a broad maximum around midnight and then a minimum at around next day before lunchtime. This behaviour can be explained by the very high reaction rates of these two compounds with OH radicals. The production of OH radicals is caused by sunlight and occurs just during the daytime which leads to a reduced half-life of these compounds during daytime of about 1 h even in winter when there is not too much sunlight. The emission of these compounds, however, occurs also over night when no OH radicals are present thereby leading to higher concentrations at this time due to the much longer lifetimes.

In contrast, engine exhaust related components, like benzene, toluene, xylene and propylbenzene with isomers (Fig. 6d) and butylbenzene with isomers (Fig. 6h) exhibit several traffic related peaks, the diurnal bimodal peak situation (morning traffic and evening traffic) especially clearly visible on Monday. The half-life of these compounds is several days due to the lower reaction rate constants with OH radicals and so they show usually lower concentrations at the early morning and over the weekend when emissions are lower.

Finally, it is particularly noteworthy, that in some cases the temporal behaviour of two compounds having the same nominal mass is quite different, in this case mass separation as achieved in the present case is of utmost importance, a vivid example of this can be seen in Fig. 6e where methylketene at mass 57.034 takes a quite different behaviour over the 3-day period than butene at mass 57.0704, in contrast furan at mass 69.034 shows a rather similar dependence as isoprene at 69.0704 except for a strong deviation on Monday morning which shows a strong increase for isoprene. In summer when isoprene emissions are much higher this may be different. Similar large differences at least in magnitude are present for other isobaric pairs, e.g., see in Fig. 6f (the two species located at mass 75.081 and 75.0446). Given these results, the differing behaviour observed and documented here for the first time highlights and demonstrates possible applications of PTR-TOF-MS in emission studies under complex primary source conditions.

In concluding, the present study clearly demonstrates the great potential of the newly developed time-of-flight PTR-MS. In contrast to commercially available quadrupole PTR-MS instruments, the PTR-TOF-MS described here can generate entire mass spectra (snapshots) of complex trace gas mixtures on short response times (smaller 100 ms) with high mass resolution (in V-mode up to 7000, in W-mode even higher resolutions but with lower sensitivity are possible) and with virtually no upper mass limit (confirmed range of over 100 000 amu). In addition the present instrument is highly sensitive (even for large masses yielding several tens of cps/ppbv) and features an extremely low detection limit (a few pptv). This will make this instrument a useful and valuable tool for trace gas analysis in all kind of fields, including atmospheric and environmental science, food and flavour science, medical applications and industrial monitoring.

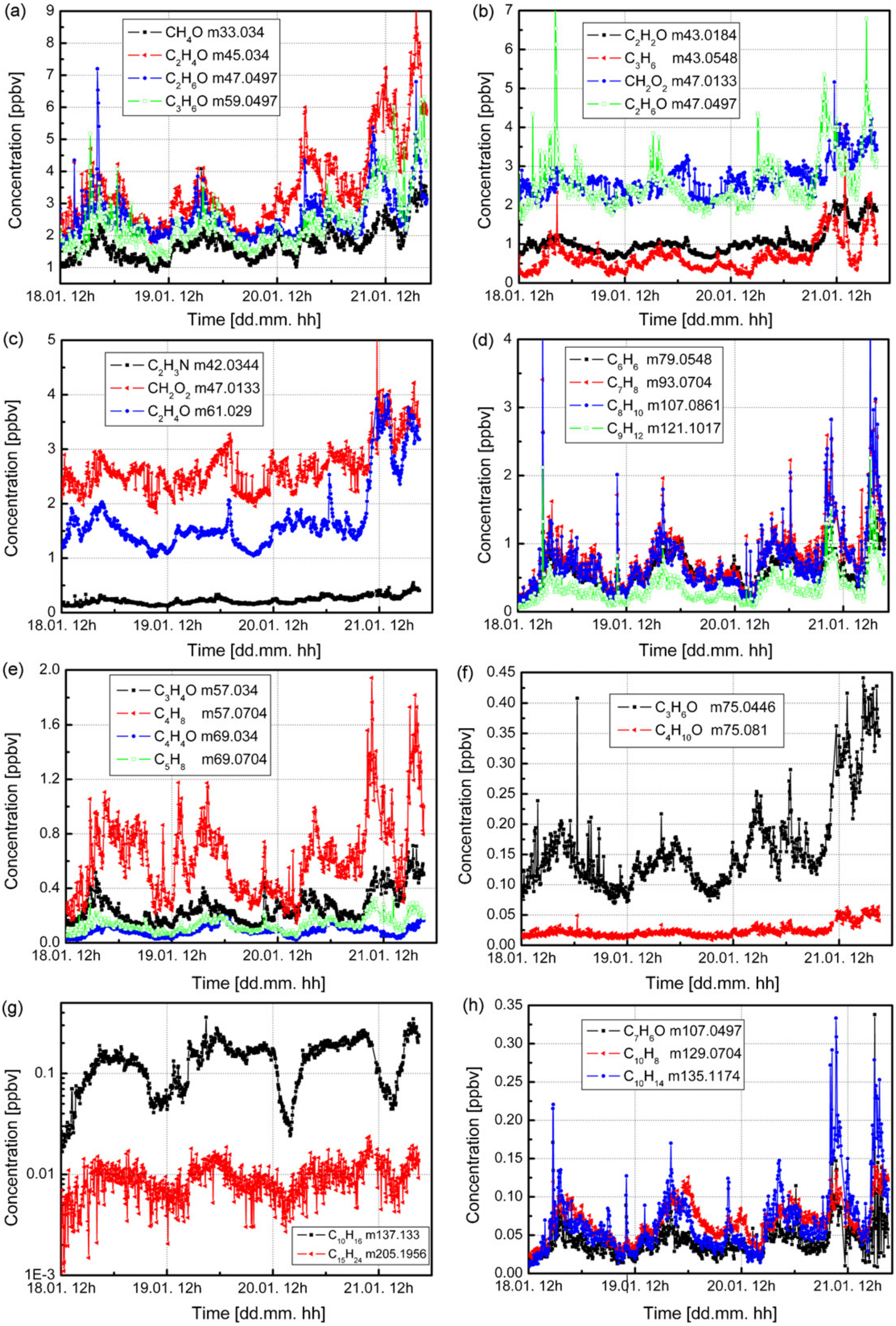

Fig. 6. Temporal variations of VOCs present in urban air measured with PTR-TOF-MS over a 3-day period, starting on Friday, 18 January 2008 at around noon and lasting until Monday, 21 January 2008 evening. Single data points have been obtained with a 4 min integration time: (a) methanol at 33.034, acetaldehyde at 45.034, ethanol at 47.0497 and acetone at 59.0497; (b) ketene at 43.0184, propene at 43.048, formic acid at 47.0133 and ethanol at 47.0497; (c) acetonitrile at 42.0344, formic acid at 47.0133 and acetic acid at 61.029; (d) benzene at 79.0548, toluene at 93.0704, xylene at 107.0861 and propylbenzene with isomers at 121.1017; (e) methylketene at 57.034, butene at 57.0704, furan at 69.034 and isoprene at 69.0704; (f) $C_3H_6O_2$ likely acetic acid methyl ester and formic acid ethyl ester at 75.0446 and $C_4H_{10}O$ likely dimethylethanol at 75.081; (g) terpene at 137.133 and sesquiterpene at 205.1956; (h) benzaldehyde at 107.0497, naphthalene at 129.0704 and butylbenzene with isomers at 135.1174.

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