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# Development and characterization of a High-Temperature Proton-Transfer-Reaction Mass Spectrometer (HT-PTR-MS)

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## Abstract

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We have developed a High-Temperature Proton-Transfer-Reaction Mass Spectrometer (HT-PTR-MS) in which both the ion source and the ion drift tube can be continuously operated at temperatures up to 250 °C. The instrument was characterized in a high 5  $E/N$ -mode (130 Td) and in a low  $E/N$ -mode (87 Td) at an operating temperature of 200 °C. Instrumental sensitivities and  $2\sigma$ -detection limits were on the order of 50–110 cps/ ppb and 100 ppt (1 s signal integration time), respectively. The HT-PTR-MS is primarily intended for measuring “sticky” or semi-volatile trace gases. Alternatively, it may be coupled to a particle collection/thermal desorption apparatus to measure 10 particle-bound organics in near real-time. In view of these applications, we have measured instrumental response times for a series of reference compounds.  $1/e^2$ -response times for dimethyl sulfoxide, ammonia and monoethanolamine were in the sub-second to second regime.  $1/e^2$ -response times for levoglucosan, oxalic acid and cis-pinonic acid ranged from 8 to 370 s.

## 15 1 Introduction

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is a highly sensitive, real-time analytical technique for detecting volatile organic compounds (VOCs) in air, which was developed in the mid-nineties in the laboratories of the Institute of Ion Physics at the University of Innsbruck (Hansel et al., 1995). PTR-MS combines the concepts 20 of soft, non-fragmenting chemical ionization of organics via proton transfer reactions from  $H_3O^+$  ions (Hunt and Ryan, 1972) and of quantitative product ion formation in an ion drift tube (McFarland et al., 1973).  $H_3O^+$  ions are produced in a glow discharge ion source and injected into an ion drift tube which is continuously flushed with analyte air. Organic molecules become protonated in collisions with  $H_3O^+$  ions 25 and are subsequently subjected to mass spectrometric analysis. Most Innsbruck-type PTR-MS instruments use quadrupole mass spectrometers for analysis, but recently

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more sophisticated mass spectrometric instrumentation (including cylindrical/linear ion traps, time-of-flight mass spectrometers) has become available (Prazeller et al., 2003; Warneke et al., 2005; Mielke et al., 2008; Jordan et al., 2009a). In the field of atmospheric chemistry, PTR-MS is nowadays a well-established technique that is routinely used for on-line detection of small VOCs such as methanol, acetone, isoprene, benzene and toluene (see recent review by de Gouw and Warneke, 2007). It is implicitly known in the PTR-MS user community that PTR-MS instruments perform poorly for compounds that readily adsorb or condense onto surfaces. The combination of a low sampling flow through the drift tube (15–20 ml/min), stainless steel surfaces in the inlet and in the drift tube, and a relatively low maximum continuous operating temperature (120 °C) promote surface losses and memory effects. The maximum operating temperature is limited by the thermal stability of vacuum gaskets and insulating spacers used in the ion source and in the drift tube. Older generation instruments used Viton gaskets, while newer generation instruments (from now on referred to as standard instruments) use Teflon PTFE gaskets (Steinbacher et al., 2004). At continuous operating temperatures above 120 °C, Teflon PTFE slowly deforms which leads to leaking and ultimately to instrument failure. Furthermore, fluoropolymers and fluorocarbon elastomers show increased outgassing at elevated temperature which increases the instrumental background and deteriorates the limit of detection. Here, we report on the development and characterization of a High-Temperature Proton-Transfer-Reaction Mass Spectrometer (HT-PTR-MS) that can continuously be operated at temperatures up to 250 °C. The HT-PTR-MS is primarily intended for measuring “sticky” or semi-volatile trace gases. In the future, it will be combined with a particle collection/thermal desorption apparatus to measure particle-bound organics in near real-time. In view of these applications, we have performed instrumental response time tests with a series of reference compounds (dimethyl sulfoxide, monoethanolamine, ammonia, levoglucosan, oxalic acid and cis-pinonic acid). Most of this species are of atmospheric relevance and the development of on-line chemical ionization detection methods for these compounds is highly desirable.

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## 2 Experimental

### 2.1 The High-Temperature Proton-Transfer-Reaction Mass Spectrometer (HT-PTR-MS)

The HT-PTR-MS is schematically shown in Fig. 1. It has a similar set-up as the standard PTR-MS instrument. The most important modification was the use of a resistive glass drift tube (Photonis Inc., Sturbridge, MA, USA) instead of a segmented drift tube consisting of stainless steel rings with Teflon PTFE insulating spacers. The use of a resistive glass drift tube ensures a high homogeneity in the electric drift field. Thornberry et al. (2009) have previously used a resistive glass drift tube in their PTR-MS type instrument. We used a glass drift tube of 150 mm length (ID: 8.3 mm; OD: 10.9 mm) with an end-to-end resistivity of 20 G $\Omega$ . The resistive glass drift tube was coupled to the electro-optic entrance lens and exit lens using an electrically conductive flexible graphite foil (SIGRAFLEX<sup>®</sup>, SGL Group, Wiesbaden, Germany). A MACOR<sup>®</sup> hollow cylinder was used to keep the drift tube in place. Resistive glass can, in principle, be operated up to a maximum temperature of 400 °C. Sealing materials have, however, lower maximum operating temperatures (see Table 1) and we can currently not heat the drift tube to temperatures higher than 250 °C. For the studies reported herein, we used a continuous operation temperature of 200 °C. The drift tube temperature was measured directly at the surface of the resistive glass tube. The pumping configuration was the same as in the standard instrument: the drift tube was pumped by a TMH 071P turbomolecular pump (Pfeiffer Vacuum, Asslar, Germany), the detection region was differentially pumped by an TMH 071P turbomolecular pump (Pfeiffer Vacuum, Asslar, Germany) and by a Varian Turbo-V 300HT MacroTorr turbomolecular pump (Varian Vacuum Technologies, Torino, Italy). A QMA 400 (Pfeiffer Vacuum, Asslar, Germany) quadrupole mass spectrometer was used for mass spectrometric analysis. The range of the drift tube operation parameters was the same as in the standard instrument: 2.0–2.4 mbar drift tube pressure, 80–140 Td reduced electric field  $E/N$  (with  $E$  being the electric field across the drift tube and  $N$  being the gas number

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density;  $1 \text{ Td} = 10^{-17} \text{ cm}^2 \text{Vmolecule}^{-1}$ ). We typically used two operating conditions: 130 Td (600 V, 2.00 mbar, 200 °C; from now on referred to as the high *E/N*-mode) and 87 Td (400 V, 2.00 mbar, 200 °C; from now on referred to as low *E/N*-mode). In the standard instrument, the segmented drift tube is slightly bent. The glow discharge ion source produces energetic photons and the bending prevents them from reaching the detection region. Since we used a straight glass drift tube, the design of the ion source had to be changed to avoid photon noise. The single on-axis hollow cylinder cathode used in the standard instrument was replaced by three off-axis hollow cylinder cathodes each with an inner diameter of 4 mm. We used an exit anode lens with 5 one central orifice of 0.8 mm diameter and three 0.5 mm diameter orifices which were aligned with the cathode hollow cylinders. A water vapor flow of  $8 \text{ cm}^3 \text{ min}^{-1}$  was supplied to the ion source via a low- $\Delta p$  flow controller (Bronkhorst High-Tech BV, Ruurlo, NL). The ion source was manufactured from stainless steel, the spacers were made of PolyEtherEtherKetone (PEEK). Kalrez® Spectrum™ 6375 O-rings were placed outside 10 the PEEK rings to provide additional vacuum sealing (see also Fig. 1). The use of PEEK and Kalrez® currently limits the maximum operating temperature of the HT-PTR-MS to 250 °C. A detailed overview of all the materials used for the construction of the HT-PTR-MS and their maximum continuous operating temperatures is given in Table 1. The inlet of the HT-PTR-MS was made of a 35 µm critical orifice placed on a 30 mm 15 long passivated stainless steel tube (OD: 3.175 mm) (Sulfinert®, Restek, Bellefonte, MA, USA). The orifice was pumped at 80 ml/min by a scroll pump (Triscroll 600, Varian Vacuum Technologies, Torino, Italy). A lower-capacity pump can be used in combination with a smaller critical orifice. A flow of 15 ml/min was delivered to the drift tube while the overflow of 65 ml/min was branched off into the scroll pump (see Fig. 1). Both 20 the ion source and the drift tube were enclosed in a stainless steel cylinder (ID: 90 mm) surrounded by a heating jacket heated to 250 °C. Superwool® 607 (Thermal Ceramics, Morgan Crucible, Windsor, UK) was used as thermal insulation material.

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## 2.2 Set-up for instrument calibration

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The HT-PTR-MS was calibrated using a calibration gas standard (Air Env., Denver, CO, USA) containing 1.00 ppm of acetone, 1.02 ppm of methyl ethyl ketone, 0.70 ppm of hexanal and 0.28 ppm of decanal (accuracy:  $\pm 5\%$  for each of the compounds).

5 We only targeted oxygenated hydrocarbons in our calibration studies. The standard was dynamically diluted to ppb levels using humidified zero air. Humidified zero air (2000–3000 ml/min) was produced by passing pressurized air over a Pt/Pd catalyst (Pt/PtO<sub>2</sub>/Pd/PdO, EnviCat<sup>®</sup> VOC 5528, Süd-Chemie, Munich, Germany) operated at 380 °C. The air was humidified using a water bubbler at 20 °C.

## 10 2.3 Set-up for response time measurements

The critical orifice inlet was continuously flushed with heated (120–180 °C) humidified zero air (2000–3000 ml/min). A  $\mu$ l-syringe (Hamilton 1705RN, 50  $\mu$ l) was placed into the stream of zero air at a distance of 2 mm from the critical orifice to spike the zero air with different test compounds at different concentration levels. A constant liquid sample flow was injected using a syringe pump (Harvard Apparatus Pico Plus, Holliston, MA, USA). Chemicals used were dimethyl sulfoxide ( $\geq 99.9\%$ , Sigma-Aldrich), ammonia (25% in H<sub>2</sub>O, Merck), monoethanolamine ( $\geq 99.5\%$ , Sigma-Aldrich), levoglucosan ( $\geq 98\%$ , Sigma Aldrich), oxalic acid ( $\geq 99\%$ , Sigma Aldrich), cis-pinonic acid ( $\geq 98\%$ , Sigma-Aldrich). Pure compounds were diluted in distilled water to achieve approximately 100 ppm mixing ratio in solution. After achieving a steady-state ion signal from the spiked compound, the needle was mechanically removed from the zero air flow and the fall-off of the ion signal was monitored. HT-PTR-MS sampling times were compound specific and ranged from 20 ms to 1 s.

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#### 3.1 Ion source performance

Typical reagent ion count rates in the new HT-PTR-MS were  $7 \times 10^6$  cps of  $\text{H}_3\text{O}^+$  ions (1.2%  $\text{O}_2^+$  impurity) in the high  $E/N$ -mode and  $4.5 \times 10^6$  cps  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$  ions (0.7%  $\text{O}_2^+$  impurity) in the low  $E/N$ -mode. We limited the ion source discharge current to 3.5 mA. A minimum of 50% increase in the primary ion signal output was obtained at discharge currents  $> 8$  mA. Previous experience has shown that higher discharge currents reduce the lifetime of PTR-MS ion sources. We thus kept the discharge current relatively low to avoid frequent servicing. In addition, the quadrupole mass spectrometer was optimized for the detection of high  $m/z$ -signals which results in a reduced detection efficiency for the primary ions. If only optimized for primary ion signal output and detection, our new HT-PTR-MS achieved similar primary ion signal intensities as standard PTR-MS instruments ( $> 10^7$  cps).

#### 3.2 Sensitivity

We calibrated the instrument with a series of oxygenated VOCs including acetone, methyl ethyl ketone, hexanal and decanal. Monofunctional oxygenates are not the primary target analytes of a HT-PTR-MS instrument. The sensitivity of the PTR-MS for a specific compound does, however, primarily depend on the dipole moment and on the molecular weight of the analyte molecules. The studied carbonyls may thus serve as proxies for multifunctional compounds of lower volatility with similar dipole moments and molecular weights. Figure 2 shows calibration curves obtained in the low  $E/N$ -mode. For acetone ( $m/z$  59) we observed a sensitivity of 112 cps/ppb. A similar sensitivity was observed in the high  $E/N$ -mode when the primary ion signal was significantly higher (see paragraph 3.1). We have refrained from normalizing the sensitivity as it is frequently done in the PTR-MS user community. Normalized sensitivity is not a useful parameter to characterize and compare PTR-MS instruments because it

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does not reflect differences in primary ion signal intensities. It is again pointed out that the instrument was not optimized for the detection of low  $m/z$ -signals. Under optimized conditions we achieved acetone sensitivities up to 200 cps/ppb, which is comparable to the performance of standard instruments we deploy in our laboratory. High-end commercial PTR-MS instruments can reach carbonyl sensitivities up to 600 cps/ppb (Jordan et al., 2009b). Sensitivities close to 100 cps/ppb were observed for methyl ethyl ketone ( $m/z$  73) and hexanal ( $m/z$  101 and dehydration fragment at  $m/z$  83). A factor of 2 drop in sensitivity was measured for decanal ( $m/z$  157). Decanal has a similar dipole moment as the other investigated carbonyls which should, in theory, lead to a similar instrumental sensitivity. It is, however, well-known in the PTR-MS community that the QMA 400 mass analyzer strongly discriminates ion signals with  $m/z > 110$  (e.g. Kim et al., 2009). At  $m/z$  200 the detection efficiency is typically only 5–10% of the detection efficiency obtained at  $m/z$  100. When operated in the high  $E/N$ -mode, no protonated ions were observed for both hexanal and decanal. This is not the case for standard instruments when operated at comparable  $E/N$ -levels. Our findings suggest that high-temperature operation (200 °C vs. 25 °C) induces fragmentation of protonated hexanal and decanal. A similar effect has been observed in standard instruments for protonated isoprene when the drift tube temperature was raised from 25 °C to 50 °C. To avoid extensive fragmentation, we recommend operating the HT-PTR-MS in the low  $E/N$ -mode. For oxygenated VOCs we do not expect any humidity dependence in sensitivities even if the instrument is operated in the low  $E/N$ -mode. Oxygenates react at similar rates with both  $\text{H}_3\text{O}^+$  and  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$  ions. Thus, even if relative abundances of  $\text{H}_3\text{O}^+$  and  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$  ions vary with humidity, product ion count rates remain identical or very similar. We spiked ~10 ppb of our carbonyl mix into completely dry and humid air (90% RH, 25 °C), respectively. For both conditions we observed identical signal responses to within  $\pm 5\%$ .

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### 3.3 Instrumental background and detection limit

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The operation of PTR-MS instruments at elevated temperatures is known to increase the instrumental background due to material outgassing and desorption of surface impurities. Figure 3 shows the instrumental background of the HT-PTR-MS recorded after 5 start-up (grey) and after one-week of continuous operation (black) when background levels were at quasi steady-state. Even at steady-state the instrument had elevated background levels ( $> 10^2$  cps) for low  $m/z$ -signals ( $m/z < 80$ ). These are, however, not the target analytes of a HT-PTR-MS instrument. Semi- or non-volatile species have 10 higher molecular weights. In the mass spectral region above  $m/z$  100, background levels were typically below 10 cps (with only few major exceptions, e.g.  $m/z$  106, 109, 123, 125, 149). A 7 cps background converts into a  $2\sigma$ -detection limit of 100 ppt (signal integration time: 1 s, high  $m/z$  sensitivity:  $\sim 50$  cps/ppb).

### 3.4 Response time

We define the response time as the time required to observe a  $1/e^2$ -signal decay after 15 instant removal of the analyte from the sampling air ( $1/e^2$ -response time). For compounds that do not adsorb or condense onto surfaces, the PTR-MS response time is determined by the time required to exchange the sampling air in the inlet and in the drift tube. Standard PTR-MS instruments have a response time of  $\sim 0.15$  s for pure 20 hydrocarbons (Wisthaler et al., 2006). A minor tailing effect is observed for small oxygenated hydrocarbons such as methanol or acetone. For the HT-PTR-MS we measured an upper limit in the response time of  $\sim 0.10$  s for methanol and acetone with no observable tailing. The HT-PTR-MS instrument is primarily intended for measuring “sticky” or semi-volatile trace gases. It is planned to combine it with a particle collection/thermal desorption apparatus to measure particle-bound organics in near real-time. In view 25 of these applications, a set of reference compounds was chosen to perform instrumental response time tests. Most of the tested compounds are of atmospheric relevance and have been previously studied using the standard instrument (published and

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unpublished data). We can thus refer to these results for comparison. Memory effects are known to be concentration-dependent and our response time tests spanned at least one order of magnitude in analyte concentrations. Initial signal count rates (reported in the figure legends) can be converted into approximate ( $\pm 50\%$ ) volume mixing ratios using a sensitivity value of 50 cps/ppb. A more accurate quantification would require detailed studies on ion fragmentation patterns and mass discrimination effects. Signals were normalized to the steady-state starting signal to better compare the results obtained at different analyte levels. Response times were only measured in a humid air matrix. The results of the instrumental response time tests are summarized in Fig. 4.

As a general feature we found that response times tend to increase with decreasing analyte concentration. Dimethyl sulfoxide (DMSO), a gas-phase oxidation product of dimethyl sulfide (DMS) involved in marine aerosol formation, contains the sulfinyl group which readily binds to active surface sites. Standard PTR-MS instruments have DMSO response times on the order of minutes (unpublished results from our laboratory). Figure 4a shows that the HT-PTR-MS time response for DMSO was 0.4 s. Ammonia ( $\text{NH}_3$ ) plays an important role in the atmospheric nitrogen cycle and in particle formation. Norman et al. (2007) reported a  $1/e^2$  time response in the 15-to-30 s regime using a standard instrument that had been optimized for  $\text{NH}_3$  measurements. We observed  $\text{NH}_3$  response times in the range of 0.2 to 0.3 s (Fig. 4b). Monoethanolamine (MEA) was chosen as a gaseous reference compound with two functional groups ( $-\text{OH}$  and  $-\text{NH}_2$ ). MEA response times in the standard instrument are on the order of several minutes (unpublished data from our laboratory). Response times on the order of 5–18 s were obtained with the new HT-PTR-MS instrument (Fig. 4c). Levoglucosan is a particle-bound marker for biomass burning with a vapor pressure of  $7 \times 10^{-5}$  mbar at 70 °C (Oja and Suuberg, 1999). Figure 4d shows that the HT-PTR-MS time response for levoglucosan is on the order of 8 to 54 s. Oxalic acid is the simplest dicarboxylic acid and it is typically used as a reference compound in aerosol studies. We observed a response time for oxalic acid in the range between 11 and 79 s (Fig. 4e). Cis-pinonic acid is a particle-bound oxidation product of  $\alpha$ -pinene with an estimated vapour pressure of

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$7 \times 10^{-7}$  mbar at room temperature (Bilde and Pandis, 2001). Response times between 1 and 6 min were obtained with the HT-PTR-MS instrument (Fig. 4f). This finding implies that near real-time detection should be possible even for very low vapor pressure compounds.

## 5 4 Conclusions and outlook

We have developed a HT-PTR-MS instrument in which both the ion source and the ion drift tube can be continuously operated at temperatures up to 250 °C. The instrument was characterized in a high  $E/N$ -mode and in a low  $E/N$ -mode at an operating temperature of 200 °C. Instrumental sensitivities and limits of detection of the HT-PTR-MS instrument were of similar order to those observed in standard PTR-MS instruments. Instrumental response times for compounds that readily adsorb or condense onto surfaces (“sticky” or low-volatility compounds) were significantly reduced and were in the sub-second to a few-minutes time regime. Potential applications of the new HT-PTR-MS include on-line measurements of “sticky” or semi-volatile atmospheric trace gases (e.g. flux measurement of ammonia or amines), direct sampling of hot process gases (e.g. sampling of stack gas, exhaust gas, biomass burning gas), and the coupling to a particle collection/thermal desorption apparatus for the analysis of non-volatile organic species (e.g. Thornberry et al., 2009). A further improvement in instrument sensitivity and specificity can be obtained if the high-temperature ion source and drift tube are coupled to an orthogonal time-of-flight (oTOF) mass analyzer (Jordan et al., 2009a). As discussed in Sect. 3.2, the QMA 400 quadrupole mass spectrometer negatively discriminates high  $m/z$ -signals, which is not the case for oTOF mass analyzers. In addition, the use of a high mass resolution oTOF-analyzer will provide the exact mass (sum formula) of the analyte (Graus et al., 2010).

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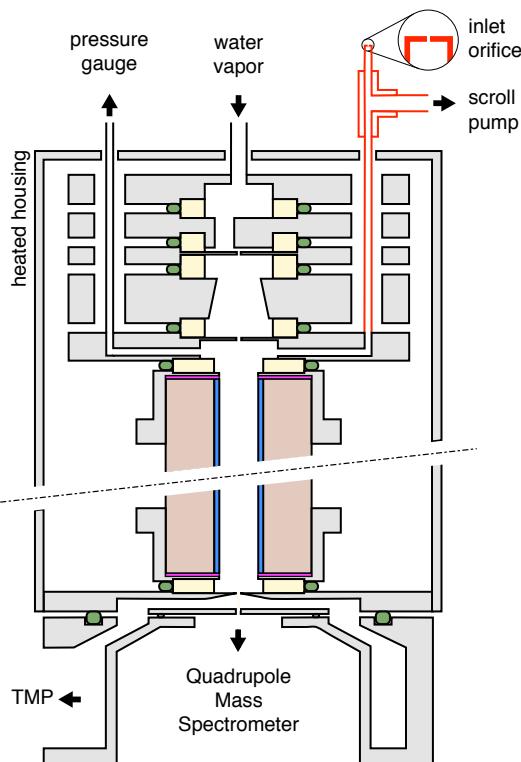
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**Table 1.** Materials used in the HT-PTR-MS and their maximum continuous operation temperatures ( $t_{\max}$ ).

Material	Use	$t_{\max}$ / °C
Kalrez® Spectrum™ 6375	sealing	275
VICTREX® PEEK™ 450G	sealing	260
MACOR®	drift tube holder	800
Flexible graphite	electrically conductive sealing of the drift tube	450
Resistive glass	drift tube	400

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**Fig. 1.** Scheme of the ion source and the resistive glass drift tube in the HT-PTR-MS. Material color-coding: stainless steel (grey), PEEK (yellow), Kalrez® (green), flexible graphite (magenta), resistive glass (blue), MACOR® (light brown), passivated stainless steel (red).

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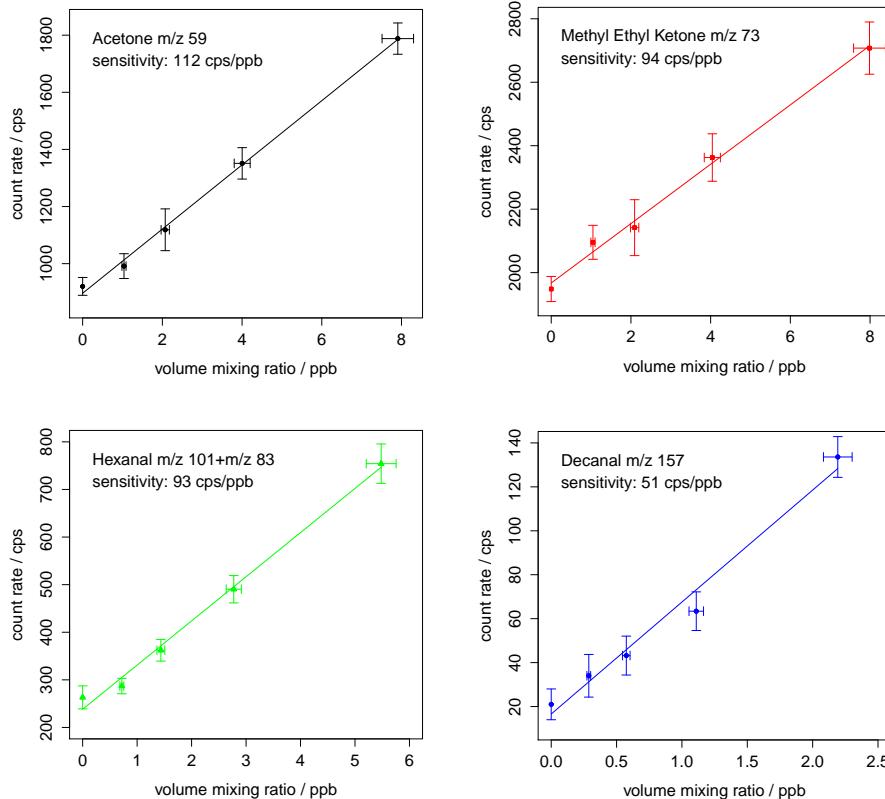
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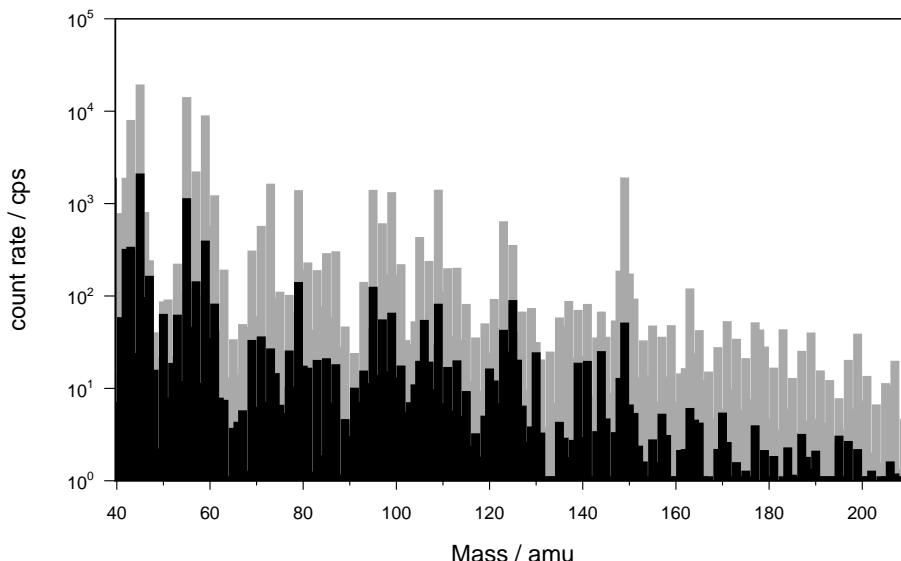
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**Fig. 2.** Calibration curves for acetone, methyl ethyl ketone, hexanal and decanal measured at 87Td and 200°C drift tube temperature.

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**Fig. 3.** Instrumental background mass spectrum of the HT-PTR-MS recorded after start-up (grey) and after one-week of continuous operation (black); both mass spectra were recorded at an HT-PTR-MS operational temperature of 200 °C.

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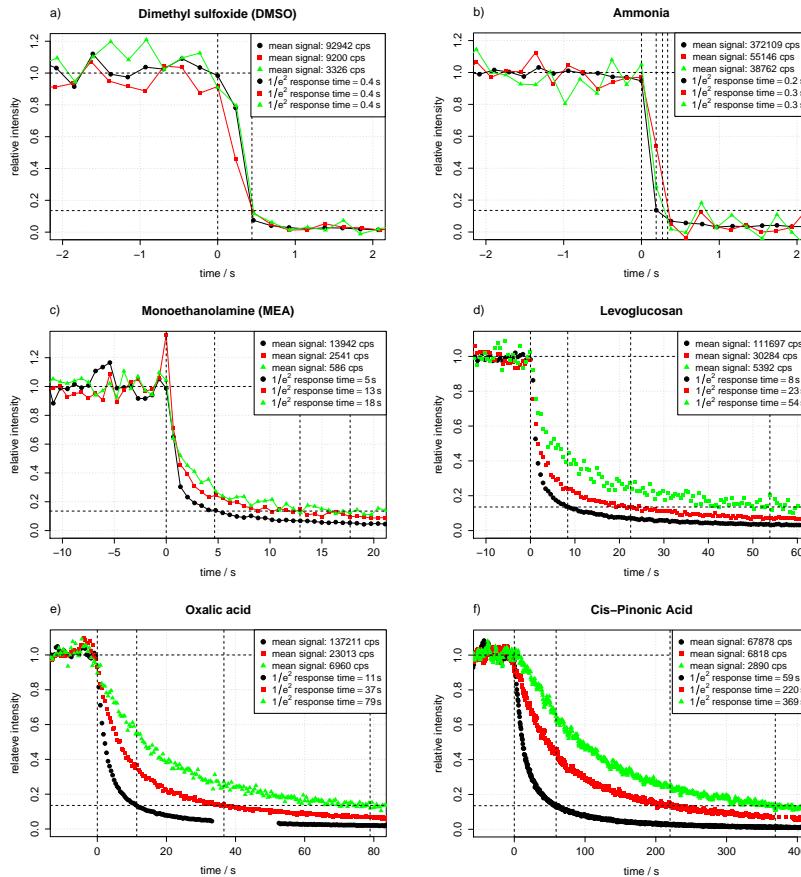
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**Fig. 4.** HT-PTR-MS response times for dimethyl sulfoxide ( $m/z$  79), ammonia ( $m/z$  18), monoethanolamine ( $m/z$  62), levoglucosan ( $m/z$  85), oxalic acid ( $m/z$  91), and cis-pinonic acid ( $m/z$  185).

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