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Formaldehyde measurements by Proton Transfer Reaction – Mass Spectrometry (PTR-MS): correction for humidity effects

A. Vlasenko^{1,2,*}, A. M. Macdonald², S. J. Sjostedt¹, and J. P. D. Abbatt¹

¹Department of Chemistry, University of Toronto, Toronto, Canada

²Science and Technology Branch, Environment Canada, Toronto, Canada

* now at: Science and Technology Branch, Environment Canada, Toronto, Canada

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Correspondence to: A. Vlasenko (alexander.vlasenko@ec.gc.ca)

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Formaldehyde measurements can provide useful information about photochemical activity in ambient air, given that HCHO is formed via numerous oxidation processes. Proton transfer reaction mass spectrometry (PTR-MS) is an online technique that allows measurement of VOCs at the sub-ppbv level with good time resolution. PTR-MS quantification of HCHO is hampered by the humidity dependence of the instrument sensitivity, with higher humidity leading to loss of PTR-MS signal. In this study we present an analytical, first principles approach to correct the PTR-MS HCHO signal according to the concentration of water vapor in sampled air. The results of the correction are validated by comparison of the PTR-MS results to those from a Hantzsch fluorescence monitor which does not have the same humidity dependence. Results are presented for an intercomparison made during a field campaign in rural Ontario at Environment Canada's Centre for Atmospheric Research Experiments.

1 Introduction

Formaldehyde (HCHO) is an important atmospheric constituent that can be emitted directly or produced in-situ via oxidation of hydrocarbons. It is one of the most abundant oxygenated volatile carbonyls in the boundary layer with mixing ratios from ~ 100 ppt in polar pristine regions (Hutterli et al., 1999; Riedel et al., 1999; Sumner et al., 2002) up to 10–50 ppbV in a polluted urban environment (Dasgupta et al., 2005; Garcia et al., 2006; Grosjean, 1991). The primary gas-phase atmospheric sinks for HCHO are reaction with OH and photolysis. Depending on the atmospheric conditions, the overall tropospheric HCHO lifetime is estimated to be only hours during the daytime, when the photolysis rate and OH concentration are at a maximum. The products of HCHO photolysis and OH reaction eventually produce the HO₂ radical, which is an important atmospheric HO_x constituent known to contribute to the formation of tropospheric ozone.

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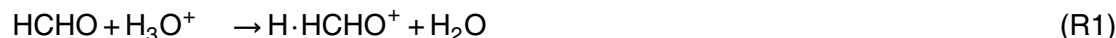
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Several analytical techniques have been deployed to detect atmospheric HCHO including: cartridge collection followed by offline analysis (Grosjean and Fung, 1982), on-line gas to liquid trapping followed by derivatization and fluorescent detection (Kelly and Fortune, 1994), Fourier transform infrared spectroscopy FTIR (Tuazon et al., 1980), differential optical absorption spectroscopy DOAS (Lawson et al., 1990) and MAX-DOAS (Heckel et al., 2005) and tunable diode laser absorption spectroscopy (Fried et al., 1998; Harris et al., 1989). Recently, proton transfer mass spectrometry (PTR-MS) was used to measure ambient concentrations of HCHO (Karl et al., 2003; Steinbacher et al., 2004). The advantages of the PTR-MS technique include high time resolution and an ability to simultaneously detect a large number of VOC compounds (Lindinger et al., 1998), which could also be atmospheric HCHO precursors (e.g. isoprene, monoterpenes, ketones, etc).

Formaldehyde is detected with PTR-MS by monitoring the ion signal of protonated H·HCHO⁺ at *m/z* 31 which is formed via reaction R1. Thermodynamically, this proton transfer is favourable since the proton affinity (PA) of HCHO (170.4 kcal/mol) is higher than that of water (165.2 kcal/mol) (Hunter and Lias, 2005).



However the difference of PA is small so that the reaction of protonated HCHO with water (R1a) becomes relevant and reduces the sensitivity of detection. Hansel et al. (1997) investigated the kinetics of the H₃O⁺ proton-transfer reaction to HCHO including the back reaction in a selected-ion flow tube experiment (SIFT). Several studies reported the humidity dependence of PTR-MS detection using comparison with other techniques. Generally, their results suggested the significant (a factor of 3 to 5) underestimate of HCHO concentrations by PTR-MS which can be improved by taking into account reaction R1a (Christian et al., 2004; Karl et al., 2003; Steinbacher et al., 2004). Good agreement was observed between HCHO concentrations measured by specially modified PTR-MS (i.e. the water leakage from ion source was reduced by

enhanced pump-down), Hantzsch monitors and DOAS methods during special VOC intercomparison chamber tests (Wisthaler et al., 2008). Another interesting approach to improve HCHO sensitivity was to remove water vapour from the air sample by a cold trap installed upstream of the PTR-MS inlet (Jobson and McCoskey, 2009). In a recent report, Inomata et al. (2008) suggested a method to correct the PTR-MS sensitivity with respect to sample air humidity assuming equilibrium between (R1) and (R1a) in the drift tube (Inomata et al., 2008). In the present study, we extend this approach and propose a correction that can be applied over a wider humidity range. The results are discussed by comparing ambient HCHO measurements by PTR-MS and the Hantzsch monitor.

2 Experimental

2.1 PTR-MS instrument

The instrument used in this study was acquired from Ionicon Analytik GmbH (Innsbruck, Austria). A detailed description of the measurement principle and performance is given elsewhere (de Gouw and Warneke, 2007). Briefly, the instrument consists of an ion source, a drift-tube reaction chamber and a quadrupole mass spectrometer (QMS) (Balzers QMG422). H_3O^+ ions are generated in the hollow cathode discharge from pure water vapour flowing at 6 sccm. Most of this vapour is pumped away by a turbo pump immediately after leaving the ion source, and only a small fraction escapes to the drift-tube. Sample flow (25 sccm) is introduced at the entrance of the drift-tube, where H_3O^+ + VOC ion-molecule reactions take place. During this study the drift tube was operated at 2.13 mbar pressure and the electric field was maintained at 600 V difference. The value for E/n (E being the electric field strength and n the air density inside drift tube) in the drift tube is kept at about 135 Townsend (Td). The electrical field maintains a controlled ion velocity in the drift-tube, which reduces the clustering

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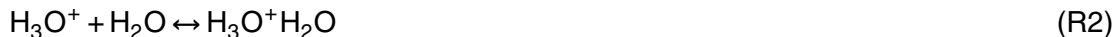
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of water ions:



The drift voltage also determines the ion reaction time t , which is calculated to be 9×10^{-5} s for our system. The PTR-MS inlet system and the drift-tube were maintained at 50 °C to minimise wall losses. At the end of the drift tube the ions are extracted through a collision dissociation chamber into the QMS where they are detected by a secondary electronic multiplier (MasCom GmbH).

2.2 Hantzsch monitor

The mixing ratio of HCHO was measured continuously using an instrument built in-house (Macdonald et al., 2001) based on a fluorescence technique similar to the Hantzsch monitor (Kelly and Fortune, 1994). HCHO was stripped from the air into a H_2SO_4 aqueous solution in a 28-turn glass coil with a liquid flow of $0.8 \text{ mL} \times \text{min}^{-1}$ and airflow of $2 \text{ L} \times \text{min}^{-1}$. The dissolved HCHO was then reacted with a ketone (2,4-pentanedione, 0.01 M) in a solution of 6 M ammonium acetate and 0.16 M acetic acid. The ammonium acetate is both a source of ammonia for the reaction and a buffering agent. Formation of the reaction product, 3,5-diacetyl 1,4-dihydrolutidine (DDL), took place in a reaction coil, heated to 80 °C, with a residence time of 30 s. The DDL product was measured with a fluorescence detector (GTI/Spectrovision model FD-100) with a Xenon flash lamp, a 254 nm interference filter in the excitation path, and a combination of GG 19 and GG 435 Schott glass filters in the emission path. The instrument lag time was about 180 s, and the response time was 90 s. The instrument was calibrated daily with liquid standards, which varied by less than 5% over the study period. A permeation-dilution system containing α -polyoxymethylene (α -POM) was also used to provide gas-phase standards. The permeation rate was determined gravimetrically

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over a three-month period. Zero measurements were done hourly by diverting the ambient air through a cartridge packed with charcoal and molecular sieve. The limit of detection was defined as 3 times the standard deviation of the instrument zeros and was approximately 200 pptv. The instrument performance was tested during an intensive HCHO intercomparison campaign and very good agreement was found with TDL systems for variable atmospheric conditions (Macdonald et al., 1999).

2.3 Laboratory experiments

Two types of laboratory experiments were performed to study the signal response of the PTR-MS measurement at m/z 31 with a controlled known mixing ratio of HCHO. In the first experiment the mixing ratios of HCHO were calculated from PTR-MS signals using such parameters as reaction rate constant, reaction time, and ion transmission and were compared to the mixing ratios prepared by flow dilution. Three different mixing ratios of HCHO were prepared using a permeation-dilution system comprised of a permeation source (VICI Metronics Inc.) and mass flow controllers (MKS). Synthetic air passed over the permeation tube, containing α -polyoxymethylene (permeation rate 52.6 ng/min at 70 °C) at $1 \text{ L} \times \text{min}^{-1}$. This flow was diluted by another flow from a mass flow controller (MKS), and then was sampled simultaneously by the Hantzsch monitor and PTR-MS.

In the second type of experiment, the PTR-MS response was studied as a function of water vapour concentration in the sampling flow. A constant mixing ratio of HCHO was provided using the same permeation source kept at constant temperature and $1 \text{ L} \times \text{min}^{-1}$ flow of nitrogen. This flow was diluted by $1 \text{ L} \times \text{min}^{-1}$ humidified nitrogen flow which passed through a fritted bubbler containing deionised water. The bubbler was held in a constant temperature water bath. The humidified flow was saturated with respect to water which was tested by reducing the flow through the bubbler. By changing the temperature of the bubbler it was possible to keep all flows constant and vary the mixing ratio of water vapour in the sample flow from 3 to 21 hPa in order to cover the range relevant to atmospheric conditions. The concentration of water

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vapour was calculated using the literature (Haar et al., 1984) and the flow dilution ratio. The calculated values were in excellent agreement (within 2%) with data measured by a hygrometer (VWR International, accuracy $\pm 1\%$) installed downstream of the flow mixing point.

2.4 Field measurement

Field measurements were made at the Environment Canada Centre for Atmospheric Research Experiments (CARE: 44.23 N, 79.78 W; 251 m a.s.l.) in Egbert, Ontario. The details of the measurement location are published elsewhere (Vlasenko et al., 2009) so here we present only a brief summary. CARE is located in a rural area consisting of mixed forest and farmland, located about 70 km north of Toronto. There are minimal local pollution sources and the prevailing winds are commonly from the northwest, in which case the air can be exceedingly clean having its source in Northwestern Ontario and the Upper Great Lakes region. With south/southwesterly flow, the air comes from Toronto and Southern Ontario, a large metropolitan and industrial region of close to 8 million people. Measurements were made from 14 May to 15 June, 2007. Inlets were located approximately 1 m above the roof of a sampling building and ambient air was sampled through a 7.5 m long PFA tube with 0.6 cm outer diameter. For the PTR-MS, a total inlet flow of 4.4 lpm flow was pulled with a diaphragm pump, restricted by a needle valve. The residence time in the inlet line is 1.3 s. The PTR-MS sampled part of the main flow (200 sccm) through a heated 0.2 cm OD silcosteel line. Instrument background checks were performed regularly (14 times) by installing a charcoal cartridge (Supelco) upstream of the PTR-MS inlet line. Data presented in this paper were deduced by linearly interpolating the charcoal backgrounds from point to point. The inlet for the Hantzsch monitor also employed an inlet line filter with 5 micron pore size.

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3 Results and discussion

A kinetic treatment is introduced to describe the ion-molecule reactions of HCHO, H₃O⁺ and H₂O in the drift tube. Then an approach is presented to determine the concentration of water in the drift tube originating from the ion source. The results of HCHO PTR-MS laboratory measurements are compared to the data from Hantzsch monitor for dry conditions. Finally, the results of the field intercomparison are discussed.

3.1 Drift tube kinetics

The kinetics of HCHO protonation (R1) and deprotonation (R1a) in the drift tube can be solved analytically using the assumption of constant concentrations of H₂O and H₃O⁺. Our main focus is the effect of water vapour so we neglect ion losses in the drift tube. The concentration of protonated HCHO ions at a given reaction time t is as following, a standard expression for the kinetics of both forward and reverse reactions of the same process:

$$[\text{H}^+ \cdot \text{HCHO}] = [\text{H}_3\text{O}^+] \frac{k_{\text{R1}}[\text{HCHO}](1 - e^{-(k_{\text{R1}}[\text{HCHO}] + k_{\text{R1a}}[\text{H}_2\text{O}])t})}{k_{\text{R1}}[\text{HCHO}] + k_{\text{R1a}}[\text{H}_2\text{O}]} \quad (1)$$

k_{R1} and k_{R1a} are rate constants of reactions R1 and R1a, respectively, and [HCHO], [H₃O⁺] and [H₂O] are concentrations of HCHO, hydronium ions and water in the drift tube.

Equation (1) can be simplified knowing that typical atmospheric conditions mixing ratios of HCHO are smaller than 10 ppbV, and the ambient water vapor mixing ratio is higher than 0.1 hPa. In addition, the rate constants $k_{\text{R1}} = 1.4 \times 10^{-9} \text{ cm}^3/\text{s}$ and $k_{\text{R1a}} = 3 \times 10^{-11} \text{ cm}^3/\text{s}$ are known (Hansel et al., 1997). Then, $k_{\text{R1a}}[\text{H}_2\text{O}] \approx k_{\text{R1}}[\text{HCHO}]$ and $k_{\text{R1a}}[\text{H}_2\text{O}] + k_{\text{R1}}[\text{HCHO}] \approx k_{\text{R1a}}[\text{H}_2\text{O}]$, assuming that most of the water comes from the ambient surroundings:

$$[\text{H}^+ \cdot \text{HCHO}] = [\text{H}_3\text{O}^+] \frac{k_{\text{R1}}[\text{HCHO}](1 - e^{-k_{\text{R1a}}[\text{H}_2\text{O}]t})}{k_{\text{R1a}}[\text{H}_2\text{O}]} \quad (2)$$

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It is worth noting that an equivalent equation has been proposed independently (Eq. 6 in Knighton et al., 2009) to explain the change in PTR-MS detection efficiency change with regard to humidity for HCN, another VOC molecule which has a proton affinity similar to formaldehyde.

The sensitivity of the PTR-MS signal as a function of the water vapor concentration in the drift tube can be expressed by normalising the concentration of protonated HCHO to the signal at dry conditions ($[H_2O]_{dry}$) when the concentration of water vapor in the drift tube is minimal:

$$\frac{[H^+ \cdot HCHO]}{[H^+ \cdot HCHO]_{dry}} = \frac{[H_2O]_{dry}(1 - e^{-k_{R1a}[H_2O]t})}{[H_2O](1 - e^{-k_{R1a}[H_2O]_{dry}t})} \approx \frac{(1 - e^{-k_{R1a}[H_2O]t})}{[H_2O]k_{R1a}t} \quad (3)$$

Equation (3) is simplified using the fact that for most dry conditions observed experimentally the concentration of water molecules in the drift tube $[H_2O]_{dry} \sim 1 \times 10^{13}$ molecules/cm³ (this concentration corresponds to the case when sampling flow is water-free and all H₂O in the drift tube is originated from the ion source. See later discussion). In addition, the typical reaction time is 100 μs, so that $k_{R1a}[H_2O]_{dry}t \ll 1$ and thus, the exponent in the denominator can be expanded.

The sensitivity dependence to water in Eq. (3) is time dependent and differs from the one derived by (Inomata et al., 2008), who assumed R1 and R1a are at equilibrium. The time dependence becomes important under dry conditions when the concentration of water is lower and the equilibrium is not reached within typical reaction times. This effect is illustrated in Fig. 1 where the concentration of H⁺ · HCHO ions, calculated according to Eq. (2), is plotted as a function of time for two concentrations of water vapor in the drift tube. One sees that at higher H₂O concentrations the production of H⁺ · HCHO does not depend on reaction time. At a lower H₂O concentration the equilibrium is reached only at times larger than 1×10^{-3} s which is an order of magnitude higher than typical drift tube conditions. Also plotted is the concentration of H⁺ · HCHO ions when the reverse reaction, R1a, does not proceed. Overall, it is seen that the reaction system consisting of reactions R1 and R1a has kinetic constraints reaching

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equilibrium at lower $[\text{H}_2\text{O}]$.

Another illustration of how the sensitivity can be affected by H_2O concentration is shown in Fig. 2. The calculated concentrations of $\text{H}^+ \cdot \text{HCHO}$ ions (Eq. 1) are normalised by equilibrium values and plotted as a function of water partial pressure. For practical reasons the water amount is expressed in the hPa units corresponding to the levels in the sample flow. Modelling results suggest that equilibrium for R1 and R1a in the drift tube is reached for H_2O mixing ratios higher than 10 hPa. Below this value the kinetic constraint should be considered. Different sets of initial conditions (concentrations of HCHO and H_3O^+) were used in the simulations as a sensitivity test, but no deviation from predicted behavior was observed.

Summarizing the results of the drift tube kinetic simulations, we conclude that for typical PTR-MS conditions there should be a strong water concentration dependence of $\text{H}^+ \cdot \text{HCHO}$ ions produced in Reactions R1 and R1a. The equilibrium approach is not accurate for dry conditions and the PTR-MS signal at m/z 31 needs to be corrected taking into account the time dependent term in Eq. (3).

3.2 Determination of water concentration in the drift tube originating from the ion source

To account for the effect of water vapor in the drift tube it is necessary to know the H_2O concentration. It was reported earlier (Inomata et al., 2008) that the total H_2O concentration is a sum of water vapour that is entering the drift tube with the sample flow and also that emanating from the ion source: $[\text{H}_2\text{O}]_{\text{drift tube}} = [\text{H}_2\text{O}]_{\text{sample}} + [\text{H}_2\text{O}]_{\text{ion source}}$. The contribution from the sample flow can be estimated by measuring the absolute humidity of sample air and adjusting for the pressure drop from ambient to drift tube conditions. $[\text{H}_2\text{O}]_{\text{ion source}}$ requires special attention because it was not measured directly during routine PTR-MS data acquisition.

To determine the concentration of water vapor in the drift tube that originates from the ion source we use the PTR-MS signal at m/z 37 which corresponds to the $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$ cluster concentration. In particular, we fit field data for m/z 37 as a function of humidity

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in the sample air with a second-order polynomial (Ammann et al., 2006). We then extrapolate to the condition when the sample flow is dry, where one estimates that the residual signal m/z 37_{dry} ≈ 400 ncps arises from $[\text{H}_2\text{O}]_{\text{ion source}}$ (see Fig. 3). We point out that the extrapolated value of the m/z 37 signal for dry conditions is in excellent agreement with the value measured in a separate experiment using synthetic air as a sample gas (shown as the green shaded region in the inset of Fig. 3). Assuming linear dependence of m/z 37 in the limited range shown in the insert we estimate that the increase of $[\text{H}_2\text{O}]$ 0.3 hPa (from 0 to 0.3) corresponds to m/z 37 increase of 400 ncps (from 400 to 800). This is equivalent to the m/z_{dry} signal observed at $[\text{H}_2\text{O}]_{\text{sample}}$, therefore we can estimate that $[\text{H}_2\text{O}]_{\text{ion source}} \approx 0.3$ hPa. The value of 0.3 hPa humidity in the sample flow corresponds to 3% of total drift tube pressure. This corresponds well to the additional pressure increase that we observe when the water flow is turned on through the ion source.

The amount of water originating from the ion source of the PTR-MS used in this work is significantly smaller than that reported earlier for other instruments. For example, Ammann et al. (2006) published the range of normalized m/z 37 values of $3\text{--}5 \times 10^4$ ncps and another value is 7×10^4 ncps (de Gouw and Warneke, 2007). Smaller values, $\sim 1.5 \times 10^4$ ncps, can also be found in the literature (Inomata et al., 2008; Steinbacher et al., 2004) but these values are still a factor of three higher than observed in our study. Such a wide range of protonated water dimer concentrations for dry conditions can be explained by the difference in PTR-MS operation settings, namely drift tube pressure and voltage. It was shown that the observed m/z 37 signal count depends strongly on those two parameters (Warneke et al., 2001). The main reason for the very low $[\text{H}_2\text{O}]_{\text{ion source}}$ concentration for the PTR-MS used in this study is the recent change to the ion source downstream pumping made by the instrument manufacturer (Armin Hansel personal communication).

3.3 Comparison with Hantzsch monitor at dry conditions

A starting point for comparison of the PTR-MS HCHO measurement with the Hantzsch monitor is under dry conditions when the influence of the backward reaction R1a is minimal. Using synthetic air as a buffer gas with addition of a known amount of HCHO, the response of the PTR-MS was measured. Under pseudo first order conditions the signal at m/z 31 was then converted to HCHO mixing ratio with the assumption of negligible depletion of reagent H_3O^+ :

$$[\text{HCHO}]_{\text{ppbV}} \approx \frac{1}{k_{\text{R1}} t} \frac{(m/z\ 31 - m/z\ 31_{\text{background}}) / \tau_{m/z\ 31}}{500 m/z\ 21 / \tau_{m/z\ 21}} \frac{10^9}{n} \quad (4)$$

where $m/z\ 31_{\text{background}}$ is signal measured in synthetic air; $\tau_{m/z\ 31}$ and $\tau_{m/z\ 21}$ are transmission factors for $\text{H}^+ \cdot \text{HCHO}$ and $\text{H}_3^{18}\text{O}^+$ ions, respectively, and the factor 500 is used to account for the fact that the $\text{H}_3^{18}\text{O}^+$ isotope is measured as the reagent ion instead of $\text{H}_3^{16}\text{O}^+$. For the calculation we used a literature value $\tau_{m/z\ 31} / \tau_{m/z\ 21} = 1.4$ (Ammann et al., 2004) which is in good agreement (within 10%) with the manufacturer's data for the particular instrument.

Figure 4 shows the results of HCHO mixing ratio calculations from the PTR-MS measurement compared to values detected by the Hantzsch monitor. While there is excellent agreement between both methods one sees that the measurements slightly (14%) underestimate HCHO mixing ratios derived from the permeation source rate. A possible reason for that can be wall losses on the way from the HCHO source delivery to the instruments as well as instrumental collection efficiency issues: losses on silcosteel lines for PTR-MS and gas-to-liquid stripping efficiency for Hantzsch monitor.

3.4 Laboratory experiment

The results of water influence on the PTR-MS signal response are given in Fig. 5. There is a significant drop of HCHO signal as a function of sample humidity. The data

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suggest that the best agreement between measurement and calculation is found for the backward reaction rate constant, k_{R1a} , between $5\text{--}7 \times 10^{-11} \text{ cm}^3/\text{s}$, about a factor of two higher than the literature value of $3 \times 10^{-11} \text{ cm}^3/\text{s}$. This is a small discrepancy, and could possibly be due to either an energy dependence in the rate constant, to uncertain reaction times, or, perhaps, to an error in the literature value. Also, we note that the model and measurements disagree most at high humidities, perhaps due to another process of H^+HCHO formation taking place that is not accounted by the calculation. As humidity increases in the drift tube so does the concentration of protonated water dimers. The latter react with HCHO by direct protonation or through ligand switching reactions and subsequent collisional dissociation of the organic water cluster (Jobson and McCoskey, 2009). If we assume that the dimer reaction rate is 75% that of H_3O^+ (Midey et al., 2000) and use the signal at m/z 37 to estimate the dimer fraction relative to the monomer, we are able to explain a 6% difference between measurement and calculation at the highest humidity. Nevertheless, even with these uncertainties, using a rate constant of $6 \times 10^{-11} \text{ cm}^3/\text{s}$ matches the observations to an accuracy of better than 20%.

As a reference, the PTR-MS response is shown for other VOC species - toluene, benzene and acetone. There is little change with regard to humidity change for all compounds. This result is different from literature data (Warneke et al., 2001) where a significant decrease of the PTR-MS response for aromatics (especially for toluene) was found. The results for acetone however are in agreement – the mass spectrometer signal at m/z 59 is not affected significantly as humidity changes in the sample flow.

3.5 Field study intercomparison

The formaldehyde mixing ratio was calculated from the PTR-MS signal and compared to data measured by the Hantzsch monitor (Fig. 6). One approach, defined as not corrected, was to apply a single response factor of 8.5 ncps/ppbV (i.e. see Fig. 4; m/z 31_{background} signal was interpolated between charcoal measurements) for the whole field study dataset. A second approach was to correct the data for the

humidity dependent sensitivity (Eq. 3) based on the kinetics parameters determined in laboratory experiments. The concentration of water vapour in the sample flow was calculated from the measurements of air relative humidity and ambient temperature. The humidity corrected data agree much better with the Hantzsch measurement, with a linear slope only 5% higher than the 1:1 line. This is a small overestimate that might possibly be due to contribution of methyl hydroperoxide (MHP) CH_3OOH , which has been suggested as an interference at m/z 31 (Inomata et al., 2008). Median measured concentrations of MHP have ranged from 1.1 ppbv in Korea (Hong et al., 2008) to (0.18 ppbv) in Antarctica (Frey et al., 2009). The quantitative estimate of this contribution, however, was not studied in this work. The influence of other interferences, such as those resulting from fragmentation of protonated methanol and formic acid is believed to be small. For example, no interference from methanol was found when it was introduced from a calibration standard we have used in our lab.

4 Conclusions

We conclude by noting that laboratory, field and modeling studies all show that PTR-MS detection of formaldehyde at m/z 31 is strongly dependent on ambient water vapor concentration. With the help of kinetic modelling, it is shown that the assumption of equilibrium for the water-formaldehyde ion cluster system is limited for sample air humidity higher than 15 hPa. And so, we propose an analytic, time-dependent correction to be used to correct the PTR-MS signal at m/z 31 in order to obtain the absolute concentration of formaldehyde in the ambient sample. Based on the results of a field study, agreement to within 5% is found between PTR-MS corrected data and the Hantzsch monitor data for HCHO mixing ratios ranging from about 0.5 to 5 ppbv.

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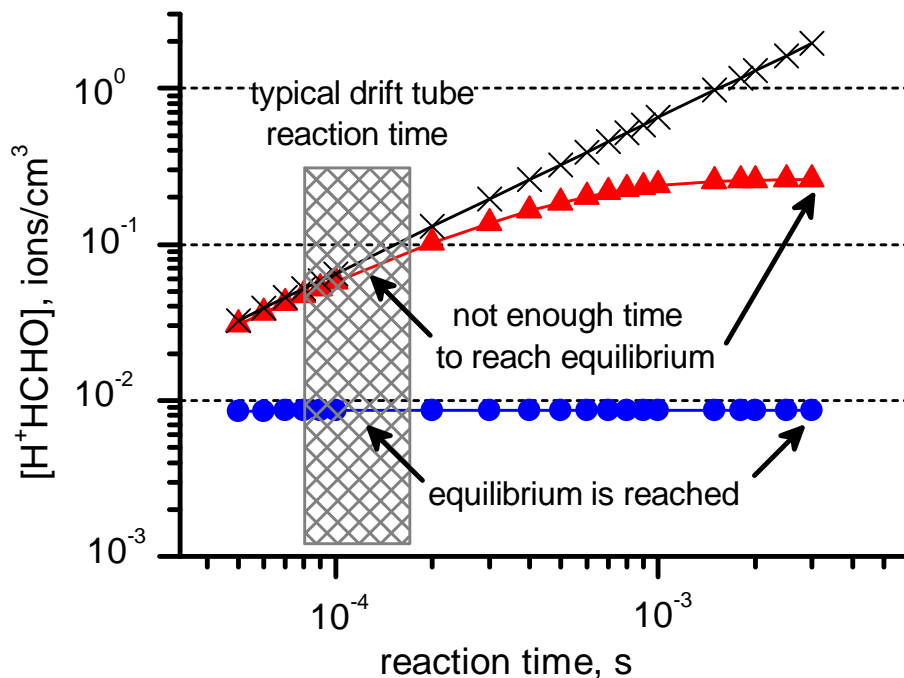


Fig. 1. Concentration of product ions $H^+\cdot HCHO$ as a function of reaction time for different scenarios. For all runs: $[HCHO] = 5 \times 10^7$ molecules/cm³, $[H_3O^+] = 1 \times 10^4$ ions/cm³ (Steinbacher, 2004). Crosses correspond to the case when only the forward R1 reaction is considered and k_{R1a} is set to zero. Circles ($[H_2O] = 1.5 \times 10^{15}$ molecules/cm³) and triangles ($[H_2O] = 5 \times 10^{13}$ molecules/cm³) correspond to the case where both the forward and reverse reactions, R1 and R1a, take place. Shaded area represents reaction times typical for the drift tube.

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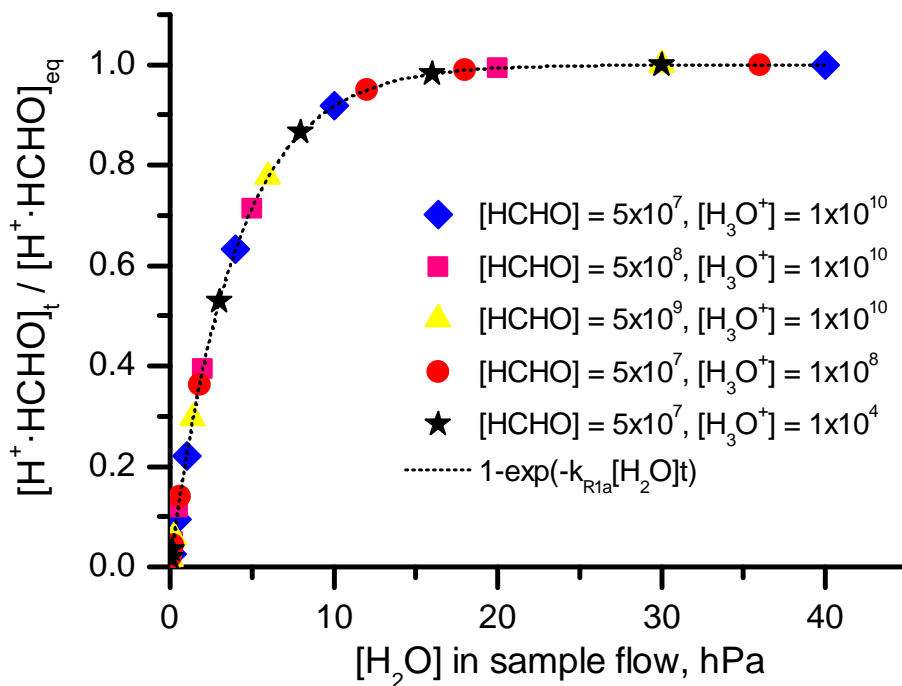


Fig. 2. Calculated concentration of $\text{H}^+\cdot\text{HCHO}$ ions normalized by corresponding equilibrium concentration shown as a function of water vapor amounts in the sample flow. Dotted line corresponds to the time dependent term in Eq. 2. Symbols correspond to calculations assuming various initial concentrations of HCHO and reagent ion in the drift tube. Reaction time is set to 1×10^{-4} s in accord with drift tube reaction time. Concentrations indicated in units of molecules cm^{-3} .

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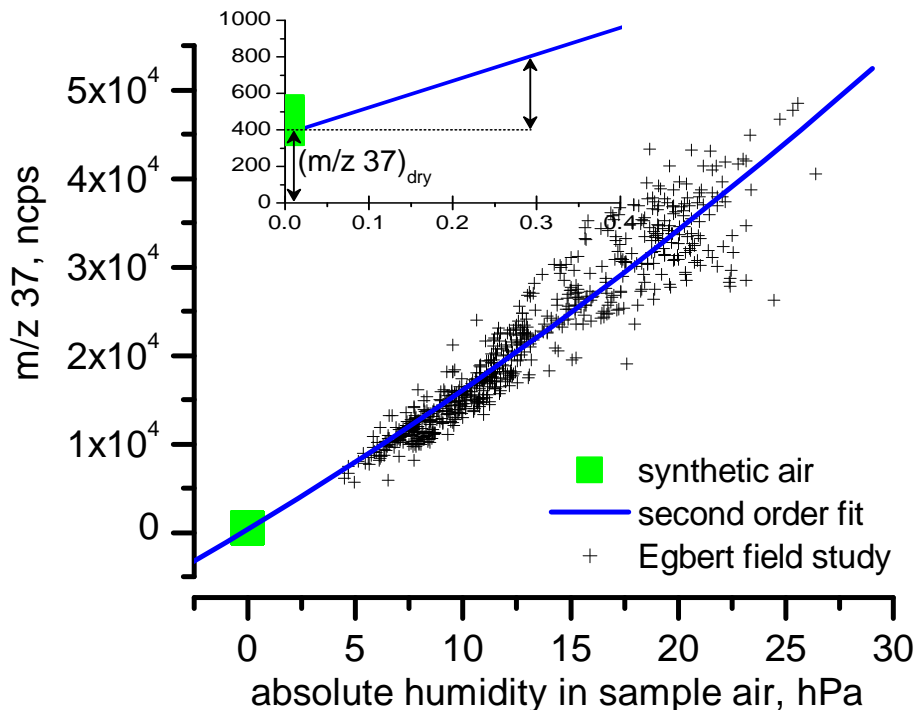


Fig. 3. Signal of m/z 37 (units are normalized counts ncps signal, i.e. m/z 37 normalized by m/z 21) as a function of sample air absolute humidity. Crosses represent field data. Solid green box corresponds to synthetic air. The line is a second order regression fit $Y = A + B1 \cdot X + B2 \cdot X^2$ with the following parameters $A=368$, $B1=1460$, $B2=11$, with an $R^2=0.97$. The insert describes the manner by which the H_2O concentration in the drift tube is estimated for the dry sample air condition.

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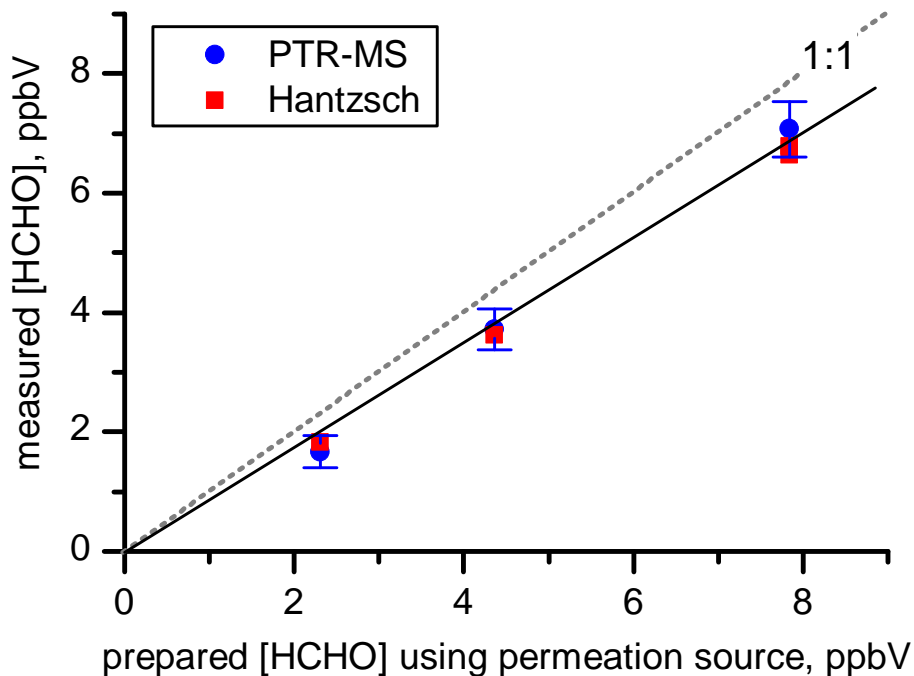


Fig. 4. Comparison of HCHO mixing ratio measurements by the PTR-MS and Hantzsch monitor using a permeation HCHO source and synthetic air as the carrier gas. The Hantzsch monitor HCHO mixing ratios are calculated using a liquid calibration standard (squares). PTR-MS mixing ratios are calculated from m/z 31 signal using Eq. 4 (circles).

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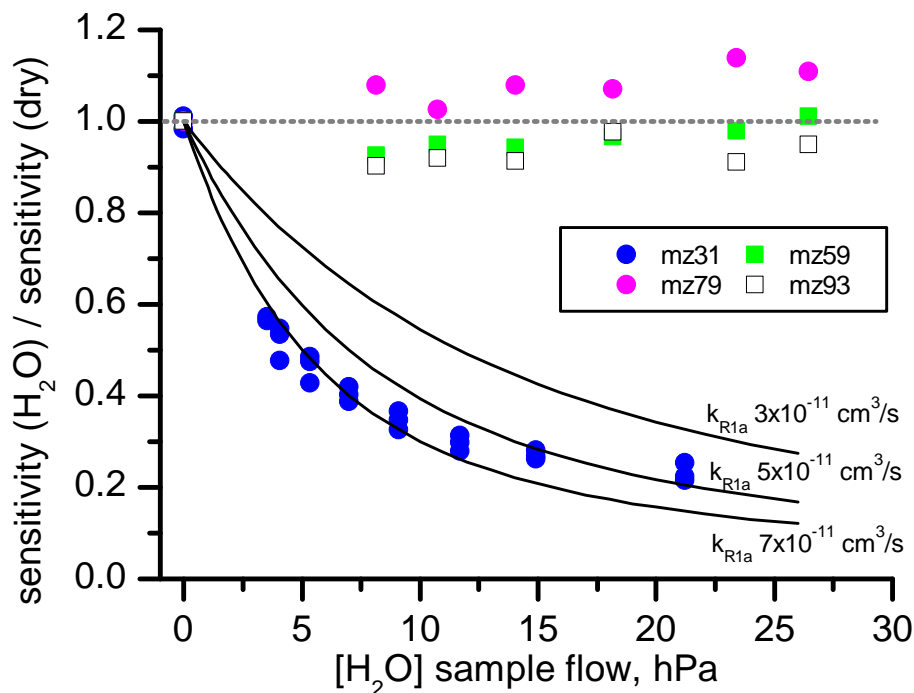


Fig. 5. Sensitivity of HCHO PTR-MS signal] m/z 31 as a function of sample flow water amount. Data points for m/z 59, 79 and 93 correspond to signals of acetone, benzene and toluene, respectively. Lines are the calculated dependence according to Eq. 3, using the labeled rate constants for the reverse reaction, R1a. Mixing ratios of formaldehyde, acetone, benzene, toluene are about 17, 10, 10, 10 ppbV, respectively.

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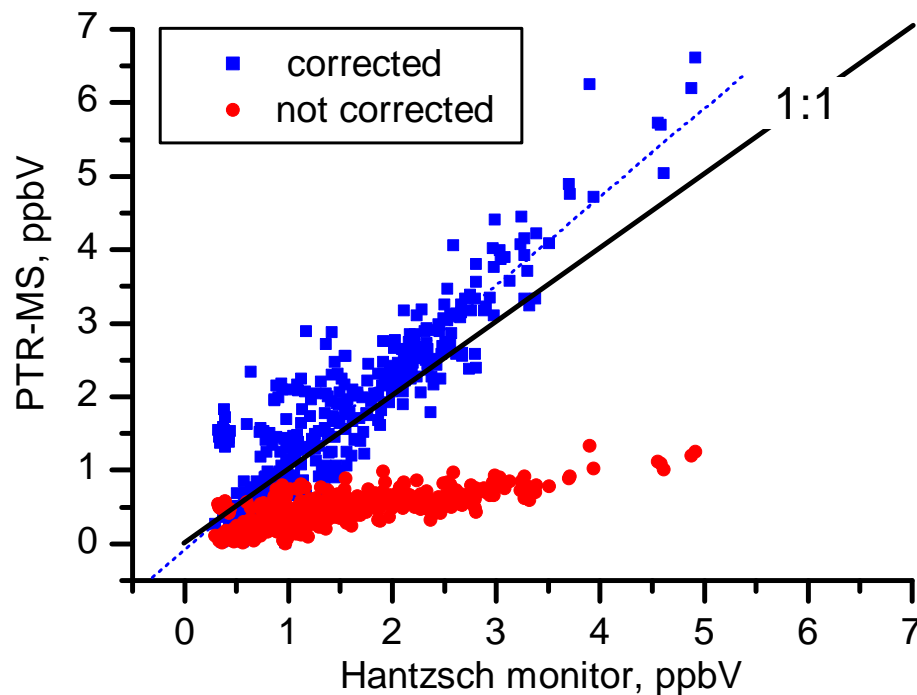


Fig. 6. Intercomparison of formaldehyde detection by PTR-MS and the Hantzsch monitor for the Egbert 2007 dataset.

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