Technical Note: Determination of formaldehyde mixing ratios in air with PTR-MS: laboratory experiments and field measurements

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Abstract. Formaldehyde (HCHO), the most abundant carbonyl compound in the atmosphere, is generated as an intermediate product in the oxidation of nonmethane hydrocarbons. Proton transfer reaction mass spectrometry (PTR-MS) has the capability to detect HCHO from ion signals at m/z 31 with high time-resolution. However, the detection sensitivity is low compared to other detectable species, and is considerably affected by humidity, due to back reactions between protonated HCHO and water vapor prior to analysis. We performed a laboratory calibration of PTR-MS for HCHO and examined the detection sensitivity and humidity dependence at various field strengths. Subsequently, we deployed the PTR-MS instrument in a field campaign at Mount Tai in China in June 2006 to measure HCHO in various meteorological and photochemical conditions; we also conducted intercomparison measurements by Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS). Correction of interference in the m/z 31 signals by fragments from proton transfer reactions with methyl hydroperoxide, methanol, and ethanol greatly improves agreement between the two methods, giving the correlation \[ [\text{HCHO}]_{\text{MAX-DOAS}} = (0.99 \pm 0.16) [\text{HCHO}]_{\text{PTR-MS}} + (0.02 \pm 0.38), \]
where error limits represent 95% confidence levels.

1 Introduction

Proton transfer reaction mass spectrometry (PTR-MS) is a technique that allows on-line measurements of volatile organic compounds (VOCs) at trace levels in air (Lindinger et al., 1998a, 1998b; de Gouw and Warneke, 2007). Proton transfer is an example of chemical ionization; it enables soft ionization of chemical species that have a proton affinity (PA) higher than that of the reagent species (i.e. water):

\[
\text{H}_3\text{O}^+ + \text{VOC} \rightarrow \text{VOC} \cdot \text{H}^+ + \text{H}_2\text{O} \tag{R1}
\]

PTR-MS allows monitoring of numerous VOCs of atmospheric interest with a high sensitivity (10–100 parts per trillion by volume (pptv)) and rapid response time (0.1–10 s). PTR-MS is potentially advantageous compared to gas chromatographic (GC) analyses because it does not require any sample treatment such as drying and/or preconcentration, and it is suitable for oxygenated VOCs, which are difficult to quantify from canister samples. PTR-MS is now used in many branches of atmospheric chemistry research, including air quality monitoring (e.g. Karl et al., 2001a, 2003a, 2003b; de Gouw et al., 2003), flux measurements (e.g. Holzinger et al., 1999; Karl et al., 2001b; Grabmer et al., 2004; Spirig et al., 2005), and oxidation studies (e.g. D’Anna et al., 2005; Paulsen et al., 2005; Lee et al., 2006a, 2006b).

Formaldehyde (HCHO) is an intermediate product in the oxidation pathways of nonmethane hydrocarbons emitted by anthropogenic and biogenic activities. In addition, formaldehyde is thought to be a probable carcinogen (Seinfeld and Pandis, 1998); this has heightened interest in atmospheric formaldehyde measurements, especially in urban areas. Reactions with hydroxyl radicals (OH) and photolysis are the main HCHO loss processes (Atkinson, 2000; Calvert et al., 2000):

\[
\text{HCHO} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O} \tag{R2}
\]

\[
\text{HCHO} + h\nu \rightarrow \text{H}_2 + \text{CO} (\lambda < 365 \text{ nm}) \tag{R3a}
\]

\[
\text{HCHO} + h\nu \rightarrow \text{H} + \text{HCO} (\lambda < 329 \text{ nm}) \tag{R3b}
\]
The HCO and H produced generate the hydroperoxy radical (HO$_2$) as follows:

$$\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO} \quad \text{(R4)}$$

$$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \quad \text{(R5)}$$

The photolysis channel (R3b) followed by reactions (R4) and (R5) is a net source of odd hydrogen radicals, HO$_x$ (HO$_x$=HO$_2$+OH+H). These species contribute to the formation of tropospheric ozone (O$_3$), a key chemical species in controlling the oxidizing capacity of the atmosphere.

Several techniques based on spectroscopic, chromatographic, and fluorometric methods are used for ambient measurements of HCHO. Differential Optical Absorption Spectroscopy (DOAS) (e.g. Lawson et al., 1990; Cárdenas et al., 2000; Grossmann et al., 2003; Hak et al., 2005), Fourier-Transform Infrared interferometry (e.g. Lawson et al., 1990; Cárdenas et al., 2000; Hak et al., 2005), and Tunable Diode Laser Absorption Spectroscopy (e.g. Harris et al., 1989; Fried et al., 1997, 2003; Zavala et al., 2006) are spectroscopic methods often used for in situ measurements, where the absorption by HCHO in the UV or IR regions is detected with a long-path setup such as a White cell system. The Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) is a relatively new technique, where scattered solar radiation is collected by telescope from different directions in order to derive the column densities of absorbing species. The vertical profile of HCHO in the troposphere can be measured by MAX-DOAS in combination with a radiative transfer model (Heckel et al., 2005). In chromatographic methods, HCHO is collected as a 2,4-dinitrophenylhydrazine (DNP) derivative, and then analyzed by high performance liquid chromatography (HPLC) (e.g. Tanner and Meng, 1984; Grosjean, 1991; Lee and Zhou, 1993; Gilpin et al., 1997). Other techniques include wet chemical fluorometric detection using the Hantzsch reaction, which requires the transfer of HCHO from the gas phase into the liquid phase and employs the fluorescence of 3,5-diacyetyl-1,4-dihydrolutidine at 510 nm, produced from the reaction of aqueous HCHO with a solution containing 2,4-pentadione and NH$_3$ (e.g. Steinbacher et al., 2004; Hak et al., 2005). Extensive intercomparison has been performed among these different techniques for ambient HCHO measurements, but the degree of agreement has varied from good to very poor, with no discernible patterns identified (e.g. Lawson et al., 1990; Gilpin et al., 1997; Cárdenas et al., 2000; Grossmann et al., 2003; Hak et al., 2005).

Various authors have detected HCHO with PTR-MS by monitoring ion signals of protonated HCHO (HCHO·H$^+$) at m/z 31 (Hansel et al., 1997; Holzinger et al., 1999; Karl et al., 2003b; Steinbacher et al., 2004; D’Anna et al., 2005; Lee et al., 2006a, 2006b); the protonated HCHO is created as follows:

$$\text{H}_3\text{O}^+ + \text{HCHO} \rightarrow \text{HCHO} \cdot \text{H}^+ + \text{H}_2\text{O} \quad \text{(R6)}$$

One of the potential advantages of measuring HCHO by PTR-MS in the field is the ability to simultaneously observe precursor molecules of HCHO, such as isoprene. However, HCHO has a PA only slightly higher than that of water, and so the exothermicity of reaction (R6) is small. Consequently, the reverse reaction of reaction (R6):

$$\text{HCHO} \cdot \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{HCHO} + \text{H}_2\text{O} + \text{H} \quad \text{(R–6)}$$

is not negligible (Hansel et al., 1997). The rate constant for the reverse reaction is several orders of magnitude lower than that of the forward reaction, but since the concentration of H$_2$O in the reactor is much higher than the concentration of HCHO, the overall rates of the forward and reverse reactions can be comparable. As a result, the protonation of HCHO is less efficient, and is expected to depend on the humidity of the sample air. There have been no experimental reports on the humidity dependence of HCHO detection by PTR-MS (de Gouw and Warneke, 2007). In addition, according to results from field measurements detecting ion signals at m/z 31 by PTR-MS, the correlation between independent measurements of HCHO by the PTR-MS and Hantzsch methods was poor (Steinbacher et al., 2004), suggesting that fragments of other compounds are present in the background, and interfere with the signal at m/z 31.

In the present work, we present detailed procedures for the calibration of PTR-MS for HCHO measurements, including determination of the detection sensitivity and its humidity dependence. We present an intercomparison of PTR-MS and MAX-DOAS techniques for ambient HCHO measurements made during an intensive field campaign at Mount Tai in China in June 2006. We discuss possible causes for background signals at m/z 31 in HCHO measurements performed by PTR-MS, and suggest a correction method for improving the agreement between PTR-MS and MAX-DOAS results.
Fig. 2. Mass spectrum of HCHO at three different drift tube $E/N$ ratios in dry conditions, obtained by the direct introduction method (a–c) and dynamic dilution method (d–f). (a–c): [HCHO]=1.02 ppmv; (d–f): [HCHO]=23.3 ppbv. Signals were normalized to a $H_3O^+$ intensity of $10^6$ cps, and background mass spectra without HCHO (obtained from $N_2$ (a–c) or zero air (d–f) only) were subtracted.

2 Experimental

2.1 PTR-MS instrument

The instrument used in the present work was a commercially available PTR-MS instrument (IONICON Analytik GmbH, Innsbruck, Austria). PTR-MS instruments have been described in detail elsewhere (e.g. Lindinger et al., 1998a, 1998b; de Gouw and Warneke, 2007). Briefly, the instrument consists of (1) a discharge ion source to produce the $H_3O^+$ ions; (2) a drift tube, in which the proton transfer reactions between $H_3O^+$ and VOCs take place; and (3) a quadrupole mass spectrometer for the detection of reagent and product ions.

In a hollow cathode discharge ion source, $H_3O^+$ ions were produced from a pure water vapor flow of 7.8 sccm. The air sample was introduced into the drift tube at a flow rate of 22 sccm; the drift tube pressure was held at 2.1 mbar. Most of the water vapor in the ion source was removed by a pump, but a small fraction of the water escaped into the drift tube, leading to an extra moistening of the sample air in the drift tube. The sampling inlet and drift tube were held at 105°C.

The drift tube consisted of stainless steel ring electrodes, separated by Teflon rings for electrical isolation. The ring electrodes were connected to a resistor network, which divided the overall drift voltage ($U_{\text{drift}}$) into a homogeneously increasing voltage and established a homogeneous electric field inside the drift tube. The electric field was applied along the drift tube in order to avoid substantial formation of cluster ions, $H_3O^+(H_2O)_n$, $n=1,2,\ldots$

$$H_3O^+ + H_2O \leftrightarrow H_3O^+ \cdot H_2O \quad (R7, R–7)$$

In the drift tube, trace gases such as VOCs in the sample air were available to be ionized by proton transfer reactions as shown earlier in reaction (R1). A fraction of the reagent ions ($H_3O^+, H_3O^+ \cdot (H_2O)_n$) and the product ions (VOC·$H^+$) was extracted through a small orifice into the quadrupole mass spectrometer. The ions were detected by a secondary electron multiplier (SEM) for ion pulse counting.

The count rate of the reagent ion, $i(H_3O^+)$, calculated from the count rate at $m/z$ 21 multiplied by 500, was typically $1 \times 10^7$ cps. Although the reactant VOCs are present in the low parts per million by volume (ppmv) range, the proton transfer reactions do not decrease $[H_3O^+]$ significantly; i.e. $[H_3O^+]>>[\text{VOC} \cdot H^+]$. Under these conditions, and if the reverse reaction of reaction (R1) is negligible, the count rate of the VOC·$H^+$ ions, $i(\text{VOC} \cdot H^+)$, can be calculated from

$$i(\text{VOC}^+)=i(H_3O^+)(1-e^{-k[\text{VOC}^+]t}) \approx i(H_3O^+)k[\text{VOC}^+]t, \quad (1)$$

where $t$ is the reaction time (the residence time of the reagent ions in the drift tube, typically 100 $\mu$s) and $k$ is the proton transfer reaction rate constant (typically $2 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$).

2.2 Laboratory calibration

Calibrations of HCHO were performed at three field strengths, $E/N$, of the drift tube: 108, 140, and 162 Td (Td=$10^{-17}$ cm$^2$ V molecule$^{-1}$), where $E$ is the electric field.
Table 1. Parameters of the PTR-MS instrument and HCHO calibrations.

<table>
<thead>
<tr>
<th>PTR-MS setup</th>
<th>U_{\text{drift}} (V)</th>
<th>T_{\text{drift}} (°C)</th>
<th>P_{\text{drift}} (mbar)</th>
<th>L_{\text{drift}} (cm)</th>
<th>t (µs)</th>
<th>E/N (Td)</th>
<th>KE_{\text{cm}} (eV)</th>
<th>Detection sensitivity of HCHO (ncps/ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400</td>
<td>105</td>
<td>2.1</td>
<td>9.2</td>
<td>114</td>
<td>108</td>
<td>0.10</td>
<td>Direct introduction (=m)^a 8.9±0.3 4.9±0.2 3.4±0.2</td>
</tr>
<tr>
<td></td>
<td>520</td>
<td>105</td>
<td>2.1</td>
<td>9.2</td>
<td>87</td>
<td>140</td>
<td>0.17</td>
<td>Dynamic dilution (=m)^b 3.4±0.6 1.8±0.2 1.2±0.2</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>105</td>
<td>2.1</td>
<td>9.2</td>
<td>76</td>
<td>162</td>
<td>0.23</td>
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</table>

<table>
<thead>
<tr>
<th>Humidity dependence</th>
<th>Experimental results: fitted to y=a/(x+b)</th>
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<tbody>
<tr>
<td></td>
<td>a (ncps mmol/mol)^c 1512±98 538±58 257±35</td>
</tr>
<tr>
<td></td>
<td>b (mmol/mol)^c 13.1±0.8 9.5±1.0 6.0±0.8</td>
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<tr>
<th>Estimations from kinetic parameters</th>
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<tr>
<td>k_{6} (10^{-9} cm^{3} molecule^{-1} s^{-1})^{d}</td>
</tr>
<tr>
<td>k_{-6} (10^{-11} cm^{3} molecule^{-1} s^{-1})^{d}</td>
</tr>
<tr>
<td>c (=k_{6}/k_{-6} [HCHO])^{e}</td>
</tr>
</tbody>
</table>

| m/n | 2.6 2.7 2.8 |
| c/a | 2.5 2.1 2.4 |

---

*a* Error limits represent 2σ of continuously observed ion signals at m/z 31.

*b* Error limits represent 95% confidence levels by t-test.

*c* Error limits represent 2σ.

*d* Data taken from Fig. 2 of Hansel et al. (1997).

*e* [HCHO]=23.3 ppbv.

Detection sensitivities of HCHO in dry conditions ([H_{2}O] <1 mmol/mol) were determined by two methods: (1) a direct introduction method and (2) a dynamic dilution method. In the direct introduction method, the inlet of the PTR-MS was connected directly to a standard gas mixture of HCHO/N_{2} (1.02 ppmv). In the dynamic dilution method, HCHO at 5–25 parts per billion by volume (ppbv) mixing ratios was produced by a dynamic dilution of the standard gas with zero air generated by a zero air supply (Model 111, Thermo Environmental Instruments Inc., Franklin, MA, USA). The dynamic dilution system was custom-built and consisted of two mass flow controllers (AERA, FC-795C @ 10 sccm (air) and FC-795C @ 5 slm (air), Advanced Energy Japan, Tokyo, Japan). The mass flow controllers were calibrated by film flow meters (Humronics Optiflow 420, Agilent Technologies, Santa Clara, CA, USA and VP-40, HORIBASTEC, Kyoto, Japan, respectively). The uncertainty of the derived concentration was typically 3%.

To vary the humidity in the sample, a humidity controller (SRG-1R-10, SHINYEI, Kobe, Japan) was connected to the line carrying zero air. The water vapor concentration of the moist air was estimated using an optical chilled mirror hygrometer (General Eastern, 1311DR-SR, GE Sensing, Billerica, MA, USA) between the humidity controller and the PTR-MS. The hygrometer was removed from the analysis line for measuring the detection sensitivities of HCHO. The moist air produced by the humidity controller was mixed with the HCHO standard gas in the dynamic dilution system and then introduced into the PTR-MS. We did not introduce the HCHO standard gas into the humidity controller because a large solubility into water is expected for HCHO (Zhou and Mopper, 1990).
The humidity dependence of the background signals at m/z 31, 33, and 47 was investigated in a separate experiment on zero air without added HCHO standard gas; no significant humidity dependence was found under these conditions.

Standard gases of HCHO, CH$_3$OH, and C$_2$H$_5$OH balanced with nitrogen (1.02 ppmv, 10.8 ppmv, and 9.56 ppmv, respectively, from Takachiho, Tokyo, Japan) and high-purity N$_2$ gas (>99.9995%, from Japan Fine Products, Kawasaki, Japan) were used as received. The HCHO concentrations in the standard gas were determined by the gas supplier (Takachiho) with precision of approximately 5%. However, the HCHO concentrations might decline, resulting in an underestimation of the HCHO detection sensitivity. Since the gas supplier guarantees an accuracy of 20% within 3 months, we used the standard gas within 100 d of receipt. In particular, between determinations of detection sensitivity in dry conditions (using the direct introduction method) conducted 30 and 100 d after the supplier tested the gas, we did not observe a significant decay in HCHO concentration in the standard gas.

Methyl hydroperoxide, CH$_3$OOH, was synthesized by methylation of hydrogen peroxide (Vaghjiani and Ravishankara, 1989). A reference mass spectrum of the CH$_3$OOH was obtained from the sample vapor. For methanol, ethanol, 2-propanol, n-butanol, and iso-butanol, reference mass spectra were obtained from vapors prepared by injecting liquid chemicals into a 5-liter Pyrex glass vessel (Aoki et al., 2007). Dimethyl sulfate (>95%), hydrogen peroxide (~30%), potassium hydroxide (>85%), sulphuric acid (47%), diethyl ether (>99.5%), and sodium sulfate (99.9%) were used for synthesis of CH$_3$OOH, and methanol (>99.8%), ethanol (>99.8%), 2-propanol (>99.9%), n-butanol (>99%), and isobutanol (>99%) were used to obtain preliminary reference mass spectra; these chemicals were all purchased from Wako Chemicals, Osaka, Japan.

2.3 Field measurement site and PTR-MS setup

Field measurements were made at the summit of Mount Tai in China (36.25° N, 117.10° E, 1534 m a.s.l.). Mount Tai is an isolated single mountain in the North China plain (Gao et al., 2005). The summit overlooks the city of Tai’an (population: 500 000), 10 km to the south. The city of Ji’nan (capital of Shandong province, population: 2.1 million) is situated 60 km to the north. There are many tourists on the mountain in the summer months (June–September); consequently, local emissions from small restaurants and temples are sometimes significant pollution sources. The PTR-MS was housed in a room on the ground floor of the station. The inlet was located approximately 10 m above the ground. A 1/4” Teflon line (4.0 mm ID and approximately 15 m long) was used as a sample line. The sample air was pumped at the flow rate of 2 L min$^{-1}$, with an estimated residence time of 6 s in the flow tube. An in-line particulate filter was used to prevent particles from entering the instrument. The voltage of the drift tube ($U_{drift}$) was set to 400 V and data were continuously recorded during 12–30 June 2006 using the PTR-MS instrument’s scan mode (from m/z 17 to m/z 300 with 0.1 s data collection at each step). Since the background signals at m/z 31 were 16.0±2.1 (2$\sigma$) ncps (normalized count per s; normalized to the H$_3$O$^+$ intensity of 10$^5$ cps), detection limits at S/N=2 were estimated to be 0.2–0.5 ppbv for a typical 5-s integration (0.1 s×50 scans during 30 min), depending on the ambient humidity (5.1–27.4 mmol/mol).

2.4 MAX-DOAS instrument setup

The MAX-DOAS system used in this work consisted of two main parts: a telescope unit placed outdoors and an indoor spectrograph (Andor Technology, Shamrock SR-303i-A) coupled with a two-dimensional CCD (charge coupled device) array detector (Andor Technology, DV-420A-0E; 1024×256 pixels). The telescope unit had five telescopes; all were directed south, but their elevation angles (ELs) differed; they were fixed at −5°, 5°, 10°, 20°, and 30°. The telescope with −5° EL looked down from Mount Tai toward Tai’an city, located at the foot of the mountain (126 m a.s.l.). The field of view (FOV) was estimated to be <1° for each telescope. To acquire a reference spectrum with the same instrument line shape as that of off-axis measurements, a mirror was periodically inserted into the FOV of each telescope, directing the viewing path to the zenith sky. A 6-min zenith-sky measurement was made automatically every 30 min. To achieve simultaneous multi-track acquisitions, the sunlight collected by the telescopes was directed to a spectrograph...
We next applied an aerosol retrieval algorithm (Irie et al., 2007) to the derived O$_4$ SCD values to determine the box-air mass-factor ($A_{box}$) vertical profile for each 30-min cycle. The algorithm utilizes the optimal estimation method (Rodgers, 2000) and a radiative transfer model, MCARaTS (Iwabuchi, 2006). In the radiative transfer modeling, we assumed a single scattering albedo of 0.90, an asymmetry parameter of 0.65, and a surface albedo of 0.10. The overall intrinsic error in the retrieved aerosol optical depth was assumed to be 30%, according to the estimate by Irie et al. (2007).

Using the calculated $A_{box}$ vertical profile, the HCHO SCD values were converted to a vertical profile by applying the nonlinear least-squares fitting method to the HCHO SCD values. For this conversion, a retrieval algorithm very similar to the aerosol retrieval algorithm (Irie et al., 2007) was applied to the HCHO SCD values. The algorithm is applicable to the HCHO retrieval because the nonlinearity of the forward model should be much lower than that of the aerosol retrievals. The lowest altitude of the vertical profile was set to 126 m a.s.l., corresponding to the surface level at Tai’an. The mean HCHO volume mixing ratios in the layer 1–2 km above the surface (referred to as HCHO(1–2 km) below) were compared to PTR-MS HCHO values. The layer corresponds to the layer 1126–2126 m a.s.l., the center of which is close to the mountaintop elevation. For each retrieval, the random error was estimated from the retrieval covariance matrix, according to Rodgers (2000). In this estimate, we used the measurement covariance matrix constructed from the residual that arose in fitting the HCHO SCD values, because it was much larger than the HCHO SCD error. The systematic error was estimated by making additional retrievals, for which the aerosol optical depth varied by ±30%. The mean values of the random and systematic errors estimated in this way are 0.64 and 0.17 ppbv, respectively, for the data set that is compared to PTR-MS measurements below.

3 Results and discussion

We considered the relative intensity of H$_3$O$^+$-H$_2$O to H$_3$O$^+$ (M37/M19) as a function of water vapor concentration (mmol/mol) in the sample air to examine whether the correction factors for HCHO determined in laboratory experiments could be applied to the field data (Fig. 1). There is obvious tight correlation, and the ratios obtained in the field measurements agreed closely with laboratory results. The relationship was similar to that reported by Ammann et al. (2006). The M37/M19 ratio does not approach zero as ambient water vapor concentrations approach zero because water vapor from the ion source exists in the drift tube in addition to water vapor from the sample air.
3.1 Laboratory calibration

3.1.1 Detection sensitivities under dry conditions

Mass spectra were obtained via the direct introduction method and the dynamic dilution method. For the spectra obtained by the direct introduction method, the HCHO concentration in the standard gas used was 1.02 ppmv; for the dynamic dilution spectra, the standard gas mixture was diluted with zero air in the ratio of 1:43; i.e. [HCHO]=23.3 ppbv. The mass spectra were taken with three different $E/N$ ratios. In all $E/N$ conditions, ion peaks of the protonated HCHO were the most strongly observed at $m/z$ 31 (Fig. 2). In addition to these protonated peaks, the protonated HCHO dimer, MMH$^+$, was observed at $m/z$ 61, especially with lower $E/N$ conditions in the drift tube.

Although the mass spectra obtained by the two HCHO introduction methods were similar, we found that the signal intensities of MH$^+$ were not proportional to the concentrations of HCHO introduced. Though signal intensity vs. HCHO concentration relationships were linear among various dynamic dilutions within each $E/N$ condition, extrapolated values from these data were not in agreement with the values obtained from the direct introduction method (Fig. 3). The detection sensitivities normalized to the H$_3$O$^+$ intensity of $10^6$ cps obtained in the direct introduction method were $8.9 \pm 0.3$, $4.9 \pm 0.2$, and $3.4 \pm 0.2$ ncp/ppbv at $U_{\text{drift}}=400$, 520, and 600 V, respectively. The sensitivities obtained in the dynamic dilution method were 2.6–2.8 times lower ($m/n$ ratio in Table 1) than those obtained in the direct introduction method, and were $3.4 \pm 0.6$, $1.8 \pm 0.2$, and $1.2 \pm 0.2$ ncp/ppbv at $U_{\text{drift}}=400$, 520, and 600 V, respectively (Table 1).

If the difference in the detection sensitivities is caused by saturation of the ion signal in the direct introduction method because the concentration of the 1.02 ppmv standard used in the direct introduction method is close to the upper limit of the linear dynamic range of the PTR-MS, the detection sensitivities from the direct introduction method should be lower than those from the dynamic dilution method. However, the reverse was observed. This suggests that there may have been losses of HCHO in the lines and/or a mass flow controller, which were used in the dynamic dilution method. We assume that the detection sensitivities obtained in the direct introduction method are better suited to accurate field measurement.

The detection sensitivities for HCHO calculated from Eq. (1) were 9.1, 7.0, and 6.1 ncp/ppbv at $U_{\text{drift}}=400$, 520, and 600 V, respectively, assuming the typical rate constant of reaction (R6) ($k=2 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$). The calculated value at $U_{\text{drift}}=400$ V, 9.1 ncp/ppbv, was very close to the calibrated value, 8.9±0.3 ncp/ppbv, but differences between the calculated and calibrated values for higher $U_{\text{drift}}$ become significant. This suggests that the backward reaction (R–6) becomes important, especially at high $E/N$ in the drift tube. Steinbacher et al. (2004) compared the HCHO sensitivity...
The regression lines (solid lines) were obtained by the reduced-major-axis (RMA) regression method. PTR-MS data, from which fragment ion signals at \( m/z \) 31 from methyl hydroperoxide and alcohols (methanol and ethanol) were subtracted.

The water vapor concentration in the drift tube can be divided into contributions from the ion source and the sample, i.e. \([\text{H}_2\text{O}] = [\text{H}_2\text{O}]_{\text{ion source}} + [\text{H}_2\text{O}]_{\text{sample}}\). Therefore, the humidity dependence of signal intensity can be fitted to an expression of the type

\[
y = \frac{a}{x + b}
\]

(4)

where

\[
a \equiv \frac{k_6}{k_{-6}} [\text{HCHO}]
\]

and

\[
b \equiv [\text{H}_2\text{O}]_{\text{ion source}}
\]

Next, we used a kinetic approach to evaluate the humidity dependence of the detection sensitivity of HCHO. In the drift tube, as HCHO reacts with \( \text{H}_2\text{O}^+ \) (R6), the concentration of the protonated HCHO increases until the rate of the backward reaction (R–6) balances the forward rate. If we assume that the equilibrium between \( \text{H}_2\text{O}^+ \cdot \text{HCHO} \), \( \text{HCHO}^+ \cdot \text{H}_2\text{O} \), and \( \text{H}_2\text{O} \) is reached by the end of the drift tube, the relationship between concentrations of \( \text{H}_2\text{O}^+ \), HCHO, \( \text{HCHO}^+ \), and \( \text{H}_2\text{O} \) can be given as follows:

\[
\frac{[\text{HCHO} \cdot \text{H}^+][\text{H}_2\text{O}]}{[\text{H}_2\text{O}^+][\text{HCHO}]} = \frac{k_6}{k_{-6}} = K
\]

(2)

where \( k_6 \) and \( k_{-6} \) represent rate constants of the forward and backward reactions (R6) and (R–6), respectively, and \( K \) is the equilibrium constant. Equation (1) can be modified as follows:

\[
\frac{[\text{HCHO} \cdot \text{H}^+]}{[\text{H}_2\text{O}^+]} \times 10^6 (\text{ncps}) = \frac{k_6}{k_{-6}} \cdot \frac{[\text{HCHO}](\text{ppbv})}{[\text{H}_2\text{O}](\text{mmol/mol})}
\]

(3)

The values of \( k_6 \) and \( k_{-6} \) were reported as a function of the energy in the drift tube: respectively, they were approximately \( 1.6 \times 10^{-9} \) and \( 1.0 \times 10^{-11} \) \( (U_{\text{drift}}=400 \text{ V}), 1.4 \times 10^{-9} \) and \( 2.9 \times 10^{-11} \) \( (U_{\text{drift}}=520 \text{ V}), 1.3 \times 10^{-9} \) and \( 5.0 \times 10^{-11} \) \( (U_{\text{drift}}=600 \text{ V}), \) in units of \( \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) (Hansel et al., 1997). Empirical values of \( c \) \( (c=k_6/k_{-6} \[
\text{[HCHO]\]) should be equal to the fitting parameter, \( a \), in Eq. (4), but the value of \( c \) was 2.1–2.5 times higher than the value of \( a \) (see \( c/a \), Table 1). This suggests losses of HCHO in the dynamic dilution system; we suggest that this is closely related to the differences in detection sensitivity observed in dry conditions. The values of \( c/a \) obtained from the kinetic parameters were very close to values of \( m/n \), the ratio of experimental detection sensitivities obtained by the direct introduction (=m) and dynamic dilution (=n) methods. The average ratio \( m/n)/(c/a) \) was calculated to be \( 1.2 \pm 0.3 \), where the indicated error limits represent 95% confidence levels by \( t \)-test, and the values of \( m/n \) and \( c/a \) were identical within the error limits. Therefore, we conclude that the detection sensitivity of HCHO obtained in the dynamic dilution method should be multiplied by \( m/n \), that is, the normalized detection sensitivity, \( S \) \( (\text{ncps/ppbv}) \), of HCHO and its humidity dependence at each \( E/N \) condition can be described as follows:

\[
S = \frac{m}{n} \cdot \frac{a}{[\text{H}_2\text{O}]_{\text{sample}}} + b \cdot \frac{1}{23.3}
\]

(7)

where ion counts are divided by 23.3 because the humidity dependence was measured with \([\text{HCHO}]=23.3 \) ppbv in the dynamic dilution method. The uncertainty of the calibrated data by this method was taken as \( \pm 25\% \). This value was the largest among the errors in \( m \) and \( n \) \( (\pm 3\%–6\% \) and \( \pm 11\%–16\% \), respectively).
respectively; see Table 1), errors originating from fitting to Eq. (3) (±9–18%; errors in the fitting, σy, are estimated from σy²=(δa/a)²+(δb/([H₂O]sample+b)²), and the error in the average of the ratio (m/n)/(c/a) (±25%).

The fitting parameter, b, represents the water vapor concentration from the ion source; it varied from 6 to 13 mmol/mol. The reason for the poor agreement between b values in different E/N conditions is not known. This poor agreement may be because the forward and backward reaction (R6) and (R–6) do not come to equilibrium by the end of the drift tube.

3.1.3 Possible interference in M31 signals

Steinbacher et al. (2004) found an inconsistency between PTR-MS and the Hantzsch monitor for ambient HCHO measurements. The disagreement may be partly explained by the humidity dependence of the detection sensitivity of HCHO, because Steinbacher et al. (2004) determined the HCHO concentrations by calculation. They observed different patterns by the two methods in diurnal variations of HCHO, and suggested the possibility of interferences from other compounds in the sample air. The possible interference of fragment ions from methyl hydroperoxide (CH₃OOH) was discussed, but the inconsistency was not fully explained.

In the present study, we investigated a reference mass spectrum of CH₃OOH. We observed the ion signals at m/z 31 as well as those of the protonated methyl hydroperoxide at m/z 49. The M31/M49 ratio was 0.92±0.06 at Udrift=400 V. Fragmentation is significant for the protonated methyl hydroperoxide, probably because an H₂O can be easily eliminated from protonated methyl hydroperoxide to produce methoxy cations.

In addition, ion signals at m/z 31 were observed in the analysis of methanol and ethanol by PTR-MS. The ion responsible is presumably CH₃OH⁺, which has the same mass as protonated HCHO. The M31/M33 and M31/M47 ratios were investigated at various mixing ratios from 20 to 100 ppbv, but remained constant at 0.0073±0.0002 and 0.045±0.004, respectively. Ion signals at m/z 31 were not observed for propanol and butanol, probably because an H₂O can be easily eliminated from protonated propanol and butanol to produce corresponding alkyl cations (Spanel and Smith, 1997), which do not have the structure of –CH₂OH.

3.2 Field measurements and comparison with MAX-DOAS

For the purpose of intercomparison between PTR-MS and MAX-DOAS, PTR mass spectra were averaged over each 30-min period. The uncorrected concentration of HCHO (ppbv) was determined as follows:

\[ [\text{HCHO}] = I_{31}/S_{400V} \]  

where \( I_{31} \) represents the ion intensity at m/z 31 normalized to the H₃O⁺ intensity of 10⁶ cps, and

\[ S_{400V} = \frac{169}{[\text{H₂O}]_{\text{sample}}+13.1} \]  

Error limits of the PTR-MS data were calculated by the following equation:

\[ \frac{\delta[\text{HCHO}]}{[\text{HCHO}]} = \sqrt{\left( \frac{\delta S_{400V}}{S_{400V}} \right)^2 + \left( \frac{\sqrt{T_{31}}}{I_{31}} \right)^2} \]  

where the value of 0.25 was used for \( \delta S_{400V}/S_{400V} \) and \( \sqrt{T_{31}} \) was used as the uncertainty of \( I_{31} \).

The mixing ratios observed during field measurements typically varied from 0 to 6 ppbv, except during the night of 12 June (Fig. 5). Diurnal variations, with a daytime maximum and nighttime minimum, were observed during 24 and 28 June. In addition, the HCHO concentrations were low on rainy days (e.g. from the night of 13 June to the morning of 14 June).

We compared HCHO mixing ratios determined by MAX-DOAS against those determined by PTR-MS, determining the slope and intercept of the regression line using the reduced-major-axis (RMA) regression method (Ayers, 2001). We used this method rather than the standard linear least squares regression because both data sets are measured variables, and thus are both subject to error. The RMA regression is a bilinear method that allows for errors in both variables. Without correction, most determinations of HCHO mixing ratios by PTR-MS are higher than those by MAX-DOAS (Fig. 6a). The best-fit line by the RMA regression method is largely shifted toward the PTR-MS–derived HCHO concentrations, providing a slope of 0.76±0.13 and an intercept of –0.35±0.43. Error limits of the slope and intercept represent 95% confidence levels.

Subsequently, the HCHO PTR-MS measurements were corrected by subtracting the fragment ions contributed by CH₃OOH from the ion signals at m/z 49, assuming that the observed ion signals at m/z 49 are attributable to CH₃OOH. However, this did not greatly improve the agreement between PTR-MS and MAX-DOAS (slope=0.78±0.13; intercept=–0.29±0.42). The averaged ion signals during the field measurements were 109, 894, 404, and 8 cps for m/z 31, 33, 47, and 49, respectively; the contribution of fragments from methanol and ethanol to the signals at m/z 31 was not negligible. The PTR-MS HCHO data were corrected again by subtracting the contributions of the fragment ions from methanol and ethanol from the ion signals at m/z 31, assuming that the observed ion signals at m/z 33 and 47 were attributable to methanol and ethanol, respectively, i.e.
where $I_{31}^{\text{corr}}$ is $I_{31} - \alpha_{49} \times I_{49} - \alpha_{33} \times I_{33} - \alpha_{47} \times I_{47}$ and $\alpha_X$ represents a ratio of M31/MX. Error limits of the PTR-MS data were derived by the following equation:

$$\frac{\delta [\text{HCHO}]}{[\text{HCHO}]} = \sqrt{\left( \frac{\delta S_{400V}}{S_{400V}} \right)^2 + \left( \frac{\delta I_{31}^{\text{corr}}}{I_{31}^{\text{corr}}} \right)^2}$$

(12)

where

$$\left( \frac{\delta I_{31}^{\text{corr}}}{I_{31}^{\text{corr}}} \right)^2 = \left( \sqrt{I_{31}} \right)^2 + \sum_X \left[ \left( \frac{\delta I_X}{I_X} \right)^2 + \frac{\delta \alpha_X}{\alpha_X} \right] (\alpha_X \cdot I_X)^2$$

(13)

Values of 0.25, 0.07, 0.03, and 0.09 were used for $\delta S_{400V}/S_{400V}$, $\delta \alpha_{49} \delta \alpha_{49}$, $\delta \alpha_{33} \delta \alpha_{33}$, and $\delta \alpha_{47} \delta \alpha_{47}$, respectively, and $\sqrt{I_X}$ was used as the uncertainty of $I_X$.

After these corrections were applied, the PTR-MS-derived HCHO mixing ratios were decreased accordingly (Figs. 5, 6b). The corrections greatly improved the agreement between MAX-DOAS and PTR-MS. The data gathered along the x=y line; indeed, the RMA-derived regression slope was very close to 1 (slope=0.99±0.16) and the RMA-derived regression intercept was very close to 0 (intercept=0.02±0.38). And, though significant differences occasionally occurred between the two determinations, this is to be expected, due to the fact that the air mass measured by the in situ PTR-MS technique was considerably different from that measured by the remote sensing MAX-DOAS technique.

4 Conclusions

The detection sensitivity of HCHO and its humidity dependence by the PTR-MS were determined in laboratory experiments at three drift tube $E/N$ ratios: 108, 140, and 162Td. We observed a discrepancy in detection sensitivities measured in dry conditions by two methods: (1) a direct introduction method, in which standard gas of HCHO/N$_2$ (1.02 ppmv) was analyzed directly, and (2) a dynamic dilution method, in which the HCHO/air mixture analyzed was produced by a dynamic dilution of the standard gas with zero air. The detection sensitivities obtained in the dynamic dilution method were approximately 2.7 times less than those obtained in the direct introduction method.

The detection sensitivity of PTR-MS for HCHO decreased with increasing humidity in all $E/N$ conditions. The detection sensitivities for HCHO were determined as a function of the water vapor concentration in the sample, [H$_2$O]$_{\text{sample}}$ (mmol/mol):

$$S(\text{ncps/ppbv}) = \frac{169}{\text{[H}_2\text{O]}_{\text{sample}}+13.1} \text{ for KE}_{\text{cm}}=0.10 \text{ eV}$$

$$S(\text{ncps/ppbv}) = \frac{62.4}{\text{[H}_2\text{O]}_{\text{sample}}+9.5} \text{ for KE}_{\text{cm}}=0.17 \text{ eV}$$

In an intensive field campaign at Mount Tai in China in June 2006, most of the HCHO values determined by the calibrated PTR-MS method were higher than the corresponding MAX-DOAS values; this was partly caused by interference of fragment ions from methyl hydroperoxide, methanol, and ethanol. By subtracting the contribution of these fragment ions from the ion signals at m/z 31, the agreement between the PTR-MS data and the MAX-DOAS data was considerably improved.

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