# SAMPLE DEHUMIDIFICATION TO ENHANCE FORMALDEHYDE DETECTION BY A PROTON TRANSFER REACTION MASS SPECTROMETER

By

Jacob K. McCoskey

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the thesis of JACOB K. MCCOSKEY find it satisfactory and recommend that it be accepted.

Bertram T. Jobson, Ph.D., Chair

George Mount, Ph.D.

Shelley Pressley, Ph.D.

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#### ABSTRACT

by Jacob K. McCoskey, M.S. Washington State University August 2009

Chair: Bertram T. Jobson

A custom built inline sample dehumidifier was connected to a Proton Transfer Reaction – Mass Spectrometer to increase the sensitivity of the PTR-MS to formaldehyde. With the dehumidifier in place, water vapor in the sample line was controlled to a dew point as low as -50 °C resulting in increased sensitivity of the PTR-MS to formaldehyde and near removal of water vapor dependent sensitivity of several measureable volatile organic compounds (VOC's), including formaldehyde. Through laboratory testing of the dehumidifier, the optimal operating tube temperature and flow through the tube were determined to be -30 °C and ~ 250 sccm respectfully. At a drift tube field intensity of 120 Td and a drift tube pressure of 2.4 mbar, the normalized sensitivity of the PTR-MS to formaldehyde increased from 8 ncps/ppbV at a dew point of ~11 °C to 35 ncps/ppbV at a dew point of -30 °C. The dehumidifier was implemented during field measurements of formaldehyde during the 2009 SHARP campaign at the University of Houston. Formaldehyde concentrations show diurnal variation and intermittent pollution episodes. The mean mixing ratio for the measurement period was ~

iii

2ppbV with peaks as high as ~ 12 ppbV. The detection limit for formaldehyde implementing the dehumidifier was 244 pptV and 105 pptV at a drift tube field intensity of 120 and 80 Td, respectively.

Abstract	III
List of Tables	VII
List of Figures	VIII
Chapter 1: Introduction	1
1.1. Formaldehyde in the Troposphere	1
1.2. Methods of Measurement	2
1.3. Proton Transfer Reaction Mass Spectrometer Theory of Operation	5
Chapter 2: Experimental	19
2.1. Calibration Gas Mixtures	
2.2. Humidity Source	
2.3. Dehumidifier Design: Peltier Cooler	
2.4. Dehumidifier Design: Immersion Cooler	
2.5. Software Control	
Chapter 3: Results and Discussion	
3.1. The Kinetics of Formaldehyde detection by the PTR-MS	
3.2. Influence of Dehumidifier Temperature on Formaldehyde Sensitivity	
3.3. Sample Flow through the Dehumidifier	
3.4. Drift Tube Optimization	44
3.5. Houston Experiment	47
3.6. Detection Limits	56
3.7. Precision	64
Chapter 4: Summary and Future Work	68

# TABLE OF CONTENTS

ography73
-----------

# LIST OF TABLES

Table 1.1         The ratio of measured to calculated formaldehyde concentratios for SAPHIR
intercomparision (Wisthaler et al., 2008)
Table 1.2 Theoretical and measured normalized sensitivities (*Dew Point = $-30 \text{ °C}$ ) 13
Table 3.1 Forward $(k_{cap f})$ and Reverse $(k_r)$ Rate Constants for the $H_3O^+ + HCHO$
Reaction listed with drift tube field intensity and mean kinetic energy ( $KE_{cm}$ ) between
formaldehyde and $H_3O^+$
Table 3.2 The dipole moment ( $\mu_D$ ), polarizability ( $\alpha$ ), and Henry's constant ( $k_H$ ) of
VOC's found in the calibration mixture
Table 3.3 The PTR-MS drift tube configurations for the two detection limit experiments.
Table 3.4. Detection limits of the PTR-MS measuring at ambient dew point and dew
point = -30 °C
Table 3.5. The normalized sensitivities at two dehumidifier temperatures and two drift
tube intensities. 63

## LIST OF FIGURES

Figure 1.1 The PTR-MS is composed of three general parts: 1) hollow cathode ion
source 2) drift tube 3) quadrupole mass spectrometer
Figure 1.2 Proton affinity versus molecular weight for trace atmospheric gases. VOC's
with a proton affinity greater than water undergo direct proton transfer from $\mathrm{H_3O^+}$ and
VOC's with a proton affinity greater than the water dimer undergo direct proton transfer
from $H^+(H_2O)_2$
Figure 1.3 A typical mass scan for ions $m/z = 21$ to $m/z = 150$ taken in zero air
Figure 1.4 PTR-MS mass scan of Mexico City air during morning rush hour 16
Figure 1.5 PTR-MS mass spectrum of forest air 17
Figure 2.1 Air flow diagram of the experimental setup: $1 =$ sample preparation, $2 =$
dehumidifier section, $3 =$ detection section. 19
Figure 2.2 Water vapor mixing ratio verses the count rate of the first water cluster.
Dashed line is a linear fit to the data
Figure 2.3. The operational flow diagram of dehumidifier system illustrates the
dehumidifier, valves, flow controlling devices, calibration devices, and the
calibration/zero electronic box. NO denotes normally open position of valves
Figure 3.1 Normalized sensitivity vs. water vapor mixing ratio for $Td = 108$

Figure 3.5 Formaldehyde normalized sensitivity versus sample dew point	at 2.4 mbar
drift pressure and 120 Td illustrating an abrupt change in sensitivity betwee	en -30 °C and -
25 °C	

Figure 3.8 Ion signal versus time for six different dehumidifier temperatures. The formaldehyde signal changes significantly when sample air is diverted through the trap.

Figure 3.14 Thirteen VOC's in the calibration mixture were sampled every 12 hours at both ambient dew point and a dew point of -30 °C. The calibration transition from ambient dew points to a dew point of -30 °C was characterized by a sharp decrease in water cluster count rates indicating a drop in water vapor. Formaldehyde count rates rose sharply due to the drop in water vapor.

Figure 3.16. Formaldehyde measurements of the SHARP campaign for May, 2009 are displayed in the time series. The formaldehyde time series for the first two weeks of May (top) displays a strong diel cycle, while the last two weeks of May (bottom) are heavily influenced by strong pollution episodes. 54

Figure 3.17 The formaldehyde, acetaldehyde, and isoprene time series were collected during the month of May at the 2009 SHARP project in Houston, Texas and displays diurnal variation and pollution events characteristic of the region. The drift tube field intensity of the time series on the left and right are 120 Td and 80 Td, respectively...... 56

#### **CHAPTER 1: INTRODUCTION**

#### 1.1. Formaldehyde in the Troposphere

Atmospheric formaldehyde is one of the most abundant aldehydes in the atmosphere (Muir and Shirazi, 1996) originating from both primary and secondary sources. Primary sources of formaldehyde include emission from vehicle exhausts and industrial sources. Formaldehyde is also directly emitted from vegetation (Kesselmeier et al., 1997, Seco et al., 2008). Biomass burning (Karl et al., 2007) is a source of formaldehyde on local and regional scales. In urban regions, formaldehyde is produced photochemically as an oxidation product of many volatile organic compounds (VOC), and urban mixing ratios range from 0.1 to 100 ppbV (Baez et al., 1995; Grutter et al., 2004; Possanzini et al., 2002; Dasgupta et al., 2005;. Pang and Mu, 2006). In rural areas dominated by biogenic emissions from trees, formaldehyde is produced primarily from the photooxdation of biogenic hydrocarbons such as isoprene (Sumner et al, 2001). Background tropospheric mixing ratios of formaldehyde of ~ 100 pptv are maintained through the OH initiated oxidation of atmospheric methane (Lowe and Schmidt, 1983). At high concentrations formaldehyde is considered a health risk (Cogliano et al., 2004).

The photochemical importance of formaldehyde in atmospheric chemistry is the reactivity with OH and the fact that it readily photolyzes to produce  $HO_2$  radicals. In urban atmospheres  $HO_2$  production from formaldehyde photolysis can be an important source of radicals and impact ozone production rates. Through photolysis and reaction

with OH, formaldehyde is consumed, producing both CO and intermediates (HCO) for production of  $HO_x$  (Lowe and Schmidt, 1983; Atkinson, 2000).

#### **1.2.** Methods of Measurement

Several techniques exist to quantify formaldehyde concentrations, which include spectroscopic techniques, fluorescence techniques and chromatographic techniques. Formaldehyde absorbs in both the ultra violet (240 nm -360 nm) and the infared (3.5 um and 5.7 um) and is readily analyzed using tunable diode laser absorption spectroscopy (TDLAS) (e.g. Sewell et. al., 1994; Freid et. al., 1997), differential optical absorption spectroscopy (DOAS) (e.g. Lawson et al., 1990; Hak et al., 2005; Wisthaler et al., 2008; Inomata et al., 2008), and Fourier transform infrared spectroscopy (FTIR) (e.g. Lawson et al., 1990; C'ardenas et al., 2000; Hak et al., 2005). The methods are capable of high time resolution and have a limit of detection that ranges from less than 100 ppt to roughly 5 ppb. They typically employ a long path length either open to the atmosphere (FTIR, DOAS) or they are operated using a closed cell with a long folded path length (TDLAS). The Hantzsch method is a wet chemical technique commonly implemented for formaldehyde quantification (e.g. Steinbacher et al., 2004; Hak et al., 2005, Fan & Dasgupta, 1994). In this method formaldehyde is scrubbed from the air sample by a denuder and reacted to form a dihydropyridine derivative that fluoresces in the ultra violet. The method has low pptV limit of detection with a sample acquired every 5-10minutes. The chromatographic method (e.g. Tanner and Meng, 1984; Grosjean, 1991; Lee and Zhou, 1993; Gilpin et al., 1997, Fung & Grosjean, 1981) uses high performance liquid chromatography (HPLC) to quantify formaldehyde through reaction of HCHO

with dinitrophenylhydrazine (DNPH) to form a derivative compound. The technique is implemented with either cartridges or through an automated solution apparatus. The limit of detection of this method ranges between 100 - 400 pptV. The disadvantage is the low time resolution due to grab sample collection and the chromatographic analysis.

Intercomparisons have been conducted to evaluate the agreement of the different techniques with varied results (Lawson et. al.; 1990, Gilpin et al., 1997; Cardenas et al., 2000; Hak et al., 2005; Wisthaler et al., 2008). The most recent intercomparison was conducted by Wisthaler et al. 2008. Five instruments comprising 4 techniques sampled formaldehyde and other VOC's from the atmosphere simulation chamber SAPHIR. The instruments included a broadband DOAS, DNPH cartridges, two commercially available Hantzsch monitors, and a proton transfer reaction mass spectrometer (PTR-MS). All instruments were compared to calculated values of formaldehyde introduced into the simulation chamber with dry air, humid air, and humid air containing 100 ppbV of ozone. For each type of air, the experiment was repeated three times, for a period of three hours. The ratio of the measured concentrations to the calculated concentrations is listed in Table 1.1 (Wisthaler et al., 2008) for each of the experiments. Generally, the instruments underestimated the formaldehyde concentrations of the chamber for dry and humid air, but overestimated the formaldehyde concentrations when ozone was added to the chamber. Wisthaler et al., 2008 concluded that the overall agreement between the techniques was fair and that PTR-MS based measurements of HCHO are possible.

**Table 1.1** The ratio of measured to calculated formaldehyde concentratios for SAPHIR

 intercomparision (Wisthaler et al., 2008).

Instrument	Dry Air	Humid Air	Humid Air + O <sub>3</sub>
Hantzsch AL4021	$0.82 \pm 0.07$	$0.77\pm0.24$	$1.1 \pm 0.25$
Hantzsch MA-100	$1.11 \pm 0.20$	$0.84\pm0.23$	$1.0 \pm 0.45$
DNPH-HPLC	$0.25\pm0.20$	$0.68\pm0.23$	$0.88\pm0.24$
BB-DOAS	-	-	$1.3 \pm 0.03$
PTR-MS	$0.77\pm0.02$	$0.74\pm0.23$	$1.5 \pm 0.23$

The PTR-MS has not been widely used to measure HCHO due to an overall low sensitivity to HCHO that is also dependent on water vapor concentration. There are several reports of PTR-MS based measurements of HCHO which try to account for humidity dependence of the sensitivity (Hansel et al., 1997; Holzinger et al., 1999; Karl et al., 2003; Steinbacher et al., 2004; D'Anna et al., 2005; Lee et al., 2006a, 2006b; Inomata et al., 2008; Seco et al., 2008; Taipale et al, 2008). The most thorough and convincing investigation is that reported by Inomata et al. (2008). Inomata reported formaldehyde sensitivity as a function of both humidity and drift tube reaction kinetics and presented evidence showing positive interferences from methyl hydroperoxide, ethanol, and methanol. With the positive interferences removed and a correction for the humidity dependence, Inomata demonstrated good agreement between PTR-MS and multi axis differential optical absorption spectroscopy (MAX-DOAS) formaldehyde data (slope =  $0.99 \pm 0.16$ , intercept =  $0.02 \pm 0.32$ ) for ambient measurements at a rural site in China.

#### **1.3.** Proton Transfer Reaction Mass Spectrometer Theory of Operation

The PTR-MS detects VOC's down to pptV levels through positive chemical ionization using  $H_3O^+$  as the reagent ion.  $H_3O^+$  will transfer a proton to compounds with proton affinities greater than that of water.

$$H_3O^+ + R \rightarrow RH^+ + H_2O \qquad \qquad R1.1$$

 $H_3O^+$  is perfectly suited for trace gas measurements in air due to no reaction with the primary components of air (N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub>, CH<sub>4</sub>) and exothermic, non-dissociative reaction with an assortment of VOC's (Lindinger, et al., 1998). Ideally, the PTR-MS mass spectrum is an M+1 mass spectrum where M is the molecular weight of the neutral organic R. In practice the mass spectrum is more complicated to interpret due to some species undergoing dissociative protonation reactions, creating lower molecular weight fragment ions.

The PTR-MS is comprised of three general sections: 1) a hollow cathode ion source generates  $H_3O^+$  ions, 2) a drift tube where the  $H_3O^+$  reagent ions react with sample air, and 3) a quadrupole mass spectrometer that mass filters and counts ions with a secondary electron multiplier (Figure 1.1). The SEM counts are averaged over a period of time, typically referred to as the dwell time. As the dwell time is increased, recorded measurements are less frequent and more precise.



**Figure 1.1** The PTR-MS is composed of three general parts: 1) hollow cathode ion source 2) drift tube 3) quadrupole mass spectrometer

In the ion source, water vapor flows though the hollow cathode at 7 sccm, controlled by a low pressure drop mass flow controller. A DC potential of 460 volts is applied across the anode and cathode, causing the ionization of water vapor and creation of the ions  $O^+$ ,  $H^+$ ,  $H_2^+$ ,  $OH^+$ , and  $H_2O^+$  (Hansel et al, 1995). The intensity of the ionization can be controlled by varying the source current. Typically the source is operated at 7 mA. These ions then react with  $H_2O$  vapor in a secondary drift chamber to form  $H_3O^+$  (Hansel, 1995). The  $H_3O^+$  ions are extracted into the drift through a small pin hole orifice and the water vapor is pumped away from the secondary drift and exhausted. Pressure in the secondary drift is similar to that of the drift tube (~ 2 mbar). Typical  $H_3O^+$  count rates for the high sensitivity version of the PTR-MS used in these experiments was 5 x 10<sup>6</sup> Hz. These counts rates are high enough to cause detector saturation, so the <sup>18</sup>O isotope of  $H_3O^+$  is monitored instead (m/z = 21), and multiplied by the isotope ratio of <sup>16</sup>O to <sup>18</sup>O of  $H_3O^+$  (490) to yield  $H_3O^+$  count rates of the <sup>16</sup>O isotope.

The ion source also produces ions, such as  $O_2^+$  and  $NO^+$  which undergo fast charge transfer reactions with organics (Hansel et al., 1995). These ions originate from air diffusing back from the drift tube into the ion source. The abundance of these ions are minimized by tuning the water vapor flow, the current to the hollow cathode and potentials of the secondary drift rings and extraction ring into the drift tube. In the experiments described within this thesis,  $O_2^+$  was kept below 2% of the reagent ion and  $NO^+$  was kept below 0.1% of the reagent ion. Typically, the count rate of the interference ions are monitored and if the interference exceeds allowed tolerances, the ion source is retuned to return the interference ion abundances to specifications.

In the drift tube,  $H_3O^+$  reacts with VOC's in the air sample that is continuously pulled through the drift tube at ~ 15 sccm. The drift tube is 9.2 cm long, with an interior volume of ~ 65 cm<sup>3</sup>. The drift tube consists of a series of stainless steel rings separated by Teflon spacers. The rings are connected in series with a 150 KOhm resistor. A DC potential of 400-600 volts is applied to the sample ring at the top of the drift tube. The applied potential creates a uniform electric field in the drift tube (~ 66 V /cm) and causes the ions to move under the force of this field towards the extraction pinhole at the other

end of the drift tube. The drift tube is pressure controlled by adjusting the inlet pressure that connects to the sample extraction ring. The purpose of the drift tube is to reduce the hydration of the reagent ions (R1.2) and  $RH^+$  ions (R1.3) by giving the ions sufficient kinetic energy that collisions with neutrals cause dissociation (R1.4).

$$H_3O^+ + H_2O \rightarrow H^+(H_2O)_2$$
 R1.2

$$RH^+ + H_2O \rightarrow H^+(R)(H_2O)$$
 R1.3

$$H^{+}(H_2O)_2 + N_2 \rightarrow H_3O^{+} + H_2O + N_2$$
 R1.4

The ratio of the electric field strength E (V/cm) to the molecular number density N (molecules cm<sup>-3</sup>) is a critical metric describing drift tube reaction conditions. The number density is controlled by varying the pressure in the drift tube. The ratio E/N is expressed in the units of Townsends (Td),  $1 \text{ Td} = 1 \times 10^{-17} \text{ V cm}^{-2}$ . Typical operating ranges are 110 to 140 Td. This range strikes a balance between excessive hydration at low Td numbers and excessive fragmentation of RH<sup>+</sup> following protonation at high Td numbers. In this operating regime the first proton bound water cluster H<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub> is typically less than 10% of the H<sub>3</sub>O<sup>+</sup> ion signal.

Ions are formed from the VOC's in one of three methods; (a) direct transfer of a proton from  $H_3O^+$ , (b) direct transfer of a proton from a proton bound water cluster such as  $H^+(H_2O)_2$ , or (b) indirect transfer of a proton through a ligand switching reaction with a proton bound water cluster. VOC's with a proton affinity greater than water accept a proton during a collision with  $H_3O^+$ . The proton affinity of water is 692 KJ/mol (de

Gouw and Warneke, 2007). All known proton transfer reactions that are exothermic proceed at the collisional rate ( $k_c \sim 2 \ge 10^{-9}$  molecule<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup>). Direct proton transfer reactions with the proton bound dimer H<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub> can also occur if the VOC has a proton affinity greater than the water dimer, calculated to be 830 KJ/mol (Kawai et al., 2003). Figure 1.2 illustrates the proton affinities of many VOC's compared to the proton affinity of water and the water dimer.



**Figure 1.2** Proton affinity versus molecular weight for trace atmospheric gases. VOC's with a proton affinity greater than water undergo direct proton transfer from  $H_3O^+$  and VOC's with a proton affinity greater than the water dimer undergo direct proton transfer from  $H^+(H_2O)_2$ .

Protonation can also occur due to ligand switching reactions whereby an organic becomes incorporated into a water cluster which then dissociates, leaving behind the proton bound organic.

$$H^{+}(H_{2}O)_{2} + R \rightarrow H^{+}(R)(H_{2}O) + H_{2}O$$
 R1.5

$$H^+(R)(H_2O) \rightarrow RH^+ + H_2O$$
 R1.6

Such switching reactions (R1.5) are thought to be fast if exothermic, and can be an important pathway for producing protonated organics when the water cluster concentration is high relative to  $H_3O^+$ .

The conversion of VOC's by direct proton transfer from  $H_3O^+$  is given by

$$[RH^{+}] = [H_{3}O^{+}]_{0}(1 - e^{-k[R]t})$$
1.1

where, *k* is the ion-molecule rate constant, *t* is the reaction time, and  $[H_3O^+]_0$  is the initial reagent ion concnetration (Hansel et al, 1995, Lindinger, et al., 1998). Only a small fraction of  $H_3O^+$  reacts with organics, so equation 1.1 can be re-written as

$$[RH^{+}] \approx kt[H_{3}O+]_{0}[R]$$
 1.2

The rate constant *k* can be obtained from either published values (Anicich, 2003) or calculated from theory (Su and Chesnavich, 1982). The reaction time, *t*, is the average time for an ion to traverse the length of the drift tube and is determined by the drift velocity,  $v_d$ 

$$v_d = \mu^* E \tag{1.3}$$

where  $\mu$  is the mobility of the ion within the sample gas (air) in the drift tube and E is the electric field of the drift tube. The ion mobility is generally reported as  $\mu_0$  at a standard

temperature ( $T_o$ ) of 273.15 K and a standard pressure ( $p_o$ ) of 1 atm resulting in an expanded form of equation 1.4 (Gouw et al., 2003)

$$v_d = \mu_o \frac{p_o}{p} \frac{T}{T_o} E = \mu_o N_o \frac{E}{N}$$
 1.4

where  $N_o$  is the sample gas number density in the drift tube at standard pressure and temperature and N is the number density at drift tube pressure and temperature. Knowing the length of the drift tube (L), *t* is represented in equation 1.5.

$$t = \frac{L}{v_d} = \frac{L}{\mu_o N_o} \left(\frac{E}{N}\right)^{-1}$$
 1.5

The drift tube field intensity (E/N) determines the reaction time *t*. Lower drift field intensities yield proportionally longer reaction times and a greater conversion of neutral organics to ions. However, if the field intensity is too low,  $H_3O^+$  ions are converted into proton bound water clusters,  $H^+(H_2O)_n$ , and instrument sensitivity is reduced.

The sensitivity of a PTR-MS is usually expressed in terms of a normalized sensitivity parameter that takes into account the  $H_3O^+$  ion count rate. The  $H_3O^+$  ion count rates can depend on the age of the ion source, drift conditions, and applied detector voltage. Thus the sensitivity,  $RH^+$  count rate per ppbV of R, is normalized to the reagent ion count rate expressed in millions of  $H_3O^+$  to allow ease of comparison between different experiments and instruments. The normalized sensitivity (ncps) is calculated from equation 1.6 (de Gouw and Warneke, 2007)

$$NCPS = \frac{RH_{Cal}^{+} - RH_{Zero}^{+}}{MR_{R} \left(\frac{H_{3}O^{+}}{10^{6}}\right)} = 10^{-3} \frac{kL}{\mu_{o}N_{o}} \frac{N^{2}}{E} \frac{T_{RH^{+}}}{T_{H_{3}O^{+}}}$$
 1.6

where  $RH_{cal}^+$  is the count rate of species R during a calibration period,  $RH_{zero}^+$  is the count rate of species R during introduction of zero air,  $MR_R$  is the mixing ratio of species R (units of ppbV) introduced into the drift tube, and  $H_3O^+$  is the reagent ion count rate (typically of the order of 5 x 10<sup>6</sup> Hz).  $T_{RH^+}$  and  $T_{H3O^+}$  are the transmission efficiencies of the respective ions. The transmission efficiencies are determined by 1) extraction of ions through optics from the drift tube to the quadrupole 2) transmission of ions through the quadrupole to the SEM and 3) detection efficiency of the SEM. Transmission efficiencies are difficult to determine experimentally so the sensitivity of the PTR-MS is best determined by external calibration with a compressed gas mixture. Mixing ratios from ambient data are determined from the raw ion signal using normalized sensitivities

$$MR = \frac{RH_{ambient}^{+} - RH_{Zero}^{+}}{NCPS\left(\frac{H_{3}O^{+}}{10^{6}}\right)}$$
1.7

To get the best measurement performance from the PTR-MS instrument high absolute reagent ion count rates are desired along with large values of normalized sensitivity.

Table 1.2 lists theoretical and measured normalized sensitivities for a drift tube field intensity of 120 Td. at ambient and -30 °C dew points (\* indicates dew point = -30 °C). The theoretical sensitivities were calculated using equation 1.6 and the measured normalized sensitivities were calculated from calibration and zero air measurements taken during April and May, 2009 at the SHARP campaign in Houston, Texas. The measured normalized sensitivity of formaldehyde is much lower than the theoretical normalized sensitivity due to the presence of water vapor in the sample stream. With the water vapor removed, the normalized sensitivity of formaldehyde is greatly increased as demonstrated by the measured normalized sensitivities at the dew point = -30 °C. The value for  $\alpha$ -pinene is much less that calculated because it fragments. At higher masses the ion transmission is falling rapidly, resulting in lower measured sensitivities. This effect is apparent for 1,3,5-trimethylbenzene.

	Theoretical ncps/ppbV	Measured ncps/ppbV	
VOC Ions	120	120	120*
Formaldehyde	8.82	3.54	11.32
Methanol	7.54	10.44	10.23
Acetonitrile	13.02	18.08	17.30
Acetaldehyde	10.07	14.18	13.63
Acetone	9.66	15.34	14.67
Isoprene	9.29	10.10	9.49
Methyl vinyl ketone	11.68	8.70	8.09
Methyl ethyl ketone	10.91	19.29	18.36
Benzene	9.28	9.86	9.76
Toluene	10.15	10.07	9.76
Styrene	11.06	10.63	10.25
<i>p</i> -xylene	10.72	9.27	8.86
1,3,5-trimethylbenene	11.32	8.63	8.23
α-pinene	11.57	3.17	3.00

**Table 1.2** Theoretical and measured normalized sensitivities (\*Dew Point = -30 °C)

Figure 1.3 illustrates the zero air background spectrum. The mass scan is from m/z = 21 to m/z = 150 at a 1 second dwell time and a drift tube intensity of 120 Td. For methanol (m/z = 31) and acetone (m/z = 59), the background count rate is significant. Using

Figure 1.3, the raw signal for ambient methanol at a confidence level greater than 95 % would only be ~ 21 Hz on top of the ~ 110 Hz background signal. Therefore, the DL of methanol for the methanol signal in figure 1.3 assuming a theoretical sensitivity of ~ 8 ncps/ppbV and a H<sub>3</sub>O<sup>+</sup> signal of ~ 2 x 10<sup>6</sup> Hz would be ~1.3 ppbV. Interference ions can also influence the background and, consequently, the detection limit of the measurements. As illustrated in Figure 1.3,  $O_2^+$  and NO<sup>+</sup> have very large signal intensities relative to other mass signals making the contribution from isotopes to interferences substantial. <sup>16</sup>O<sup>17</sup>O<sup>+</sup> contributes to the background of methanol at m/z = 33 (de Gouw and Warneke, 2007) and NO isotopes can contribute to formaldehyde backgrounds at m/z = 31 (Steinbacher et al., 2004).



Figure 1.3 A typical mass scan for ions m/z = 21 to m/z = 150 taken in zero air.

Also displayed in Figure 1.3 is the first and second water cluster m/z = 37 and m/z = 55. The first water cluster <sup>18</sup>O isotope has significant signal intensity at m/z = 39 and is commonly used to measure the first water cluster to avoid damage to the detector. The ceramic based secondary electron multipliers sold by ETP and used in this work have been observed to age faster when exposed to masses with high signal intensities, such as the first water cluster at m/z = 37.

Figure 1.4 shows a mass spectrum of Mexico City air to illustrate the organic composition of urban air as observed by the PTR-MS. The data were collected at a downtown site during rush hour as part of the 2006 MILAGRO field experiment. Most peaks in the mass spectrum represent the M+1 peak. Strong ion signals are observed for aromatic compounds: benzene (m/z = 79), toluene (m/z = 93), C<sub>2</sub>-alkyl benzenes (m/z = 107), C<sub>3</sub>-alkyl benzenes (m/z = 121), and C<sub>4</sub>-alkyl benzenes (m/z = 135). Strong ion signals are also observed for oxygenated compounds: methanol (m/z = 33), acetaldehyde (m/z = 45); and acetone (m/z = 59). The formaldehyde ion signal (m/z = 31) is clearly present although a weaker signal compared to other species. Many ions in the PTR-MS mass spectrum have not been identified and are likely ion fragments from larger organics. Examples of such fragmentation are the ion m/z = 81, produced from monoterpenes (m/z = 137), and the ion at m/z = 43 which is a common fragment ion formed in dissociative proton transfer reactions.



Figure 1.4 PTR-MS mass scan of Mexico City air during morning rush hour.

Figure 1.5 shows a PTR-MS mass spectrum from a remote forested area, the University of Michigan Biological Station (UMBS) located near Pellston, Michigan. PTR-MS data were collected at the FASET tower site during July, 2006. Fewer ions are present in the spectrum compared to an urban environment. The organic composition of air at this site is dominated by organics emitted from trees and their oxidation products. Isoprene (m/z = 69) and its first and second generation photoproducts, methacrolein and methyl vinyl ketone (m/z = 71), hydroxyacetone (m/z = 75), and formaldehyde (m/z = 31), are readily apparent in the mass spectrum. Strong ion signals for methanol (m/z = 33), acetone (m/z = 59), and monoterpenes (m/z = 137) are also evident. The  $\beta$ -pinene oxidation product nopinone (m/z = 139) is also detectable.



Figure 1.5 PTR-MS mass spectrum of forest air.

These spectra illustrate the wide range of compounds that can potentially be measured by the PTR-MS. Importantly, the PTR-MS is sensitive to many oxygenated compounds such as alcohols and aldehydes that are difficult to measure by gas chromatography methods. Being able to quantify formaldehyde with the PTR-MS would be valuable since one technique would then be able to measure both formaldehyde and a broad range of formaldehyde precursors and related photoproducts to better understand formaldehyde sources and chemistry in the atmosphere. However, formaldehyde is difficult to quantify due to a negative water vapor dependence. As a result the PTR-MS is not very sensitive to formaldehyde and the sensitivity varies with ambient humidity.

In this paper we present work describing the application of a dehumidifier system to remove water vapor from the air sample inlet to the PTR-MS, resulting in improved sensitivity to formaldehyde. We will show the capability to operate the drift tube of the PTR-MS at low drift tube field intensities while remaining free of water cluster interferences and increasing sensitivity for many VOC's. We will also demonstrate improved precision of formaldehyde and lower detection limits from many compounds in our calibration mixture.

### **CHAPTER 2: EXPERIMENTAL**

The experimental setup consisted of three major sections, the sample preparation section, the dehumidifier section, and the detection section with each labeled 1, 2 and 3 respectively in Figure 2.1. A humidified sample composed of formaldehyde and an assortment of other VOC's was created in the sample section and then passed to the dehumidifier section, where water was removed from the sample stream. After drying the sample stream, the stream was passed to the detection section where a PTR-MS measured VOC and humidity concentrations.



Figure 2.1 Air flow diagram of the experimental setup: 1 = sample preparation, 2 = dehumidifier section, 3 = detection section.

#### **2.1.** Calibration Gas Mixtures

The sample preparation section consisted of a set of calibration sources, flow controllers, a humidifier, and a Vaisala relative humidity sensor (HMP50). The formaldehyde source was a KinTek permeation tube placed inside a permeation oven set to 80 °C. The permeation rate of the formaldehyde source was 64 ng/min  $\pm$  5 %. Dry nitrogen was flowed over the permeation tube at 20 sccm and the flow was controlled by a needle valve. A multicomponent VOC calibration gas mixture produced by Scott-Marrin was introduced into the sample stream through a mass flow controller at a flow of 10 sccm. Scott-Marrin reports a blend tolerance +/- 5% for the calibration mixture. This VOC calibration mixture contained 13 VOC's at 2 ppmV mixing ratio. This mixture was diluted to yield 20 ppbV mixing ratios for testing of the cold trap. All flows were measured with a DryCal model DC-2 primary flow meter (Bios International Corporation) which has an accuracy of  $\pm$  0.75 %.

### 2.2. Humidity Source

Humidifying the air stream was done by combining a moist nitrogen flow at 100% humidity for the given room temperature and a dry nitrogen flow. The total flow of the humidity source was kept constant at 1000 sccm and the water vapor concentration of the total flow was varied by adjusting the ratio of the moist nitrogen flow to the dry nitrogen flow. The water vapor introduced into the sample stream ranged from trace amounts to  $\sim$  30 mmol/mol. The second water cluster (H<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub>) was monitored as a surrogate for humidity present in the sample. Figure 2.2 illustrates the positive correlation of water vapor mixing ratio with the second water cluster at a drift tube field intensity of 120 Td.

A liner regression was fit to the data giving a slope of  $1.8 \times 10^{-4} \pm 1.7 \times 10^{-6}$  (mmol/mol)/Hz and an intercept of  $0.85 \pm 0.11$  mmol/mol.



**Figure 2.2** Water vapor mixing ratio verses the count rate of the first water cluster. Dashed line is a linear fit to the data.

The nitrogen flows of the two streams were regulated by a set of mass flow controllers. The moist stream was created by a humidifier, which was a curved 3 foot long by 1 inch inside diameter glass tube. The tube was half full of distilled water and sat parallel to the test bench. The tube created a 1 inch by 36 inch flat water surface that the dry nitrogen contacted as it flowed down its length. The water vapor in the nitrogen was assumed to be at thermodynamic equilibrium within the flow ranges through the glass tube (0 – 1000 sccm). The assumption was verified by comparing the water vapor concentration in the

glass tube to the water vapor concentration calculated from an inline Vaisala relative humidity sensor. The humidity sensor had a reported accuracy of  $\pm$  3% RH and  $\pm$  0.6 °C. The temperature of the glass tube was measured with an Omega hand held digital thermometer (model HH501BJK) using a type K thermocouple with a stated accuracy of 0.1%. The water vapor concentration in the tube was calculated using Antoine's constants and the measured tube temperature, assuming the temperature of the water was the same as the tube surface. It was then compared to water vapor concentrations inferred from the humidity sensor. The two calculated water vapor concentrations showed strong agreement, demonstrating that water vapor concentrations exiting the glass tube were at thermodynamic equilibrium with water in the tube and at ~100% RH.

#### 2.3. Dehumidifier Design: Peltier Cooler

The initial design for a dehumidifier was to construct a device that could cool a  $\frac{1}{4}$ " OD tube down to -30 °C or lower temperatures. Moist air flowing through the tube would loose its water content and be dried to a dew point equivalent to the tube temperature. A prototype cooler was constructed from an aluminum block sandwiched between four Peltier thermoelectric modules. The Peltier thermoelectric modules (TE technology, INC, model HP – 127-1.0- 0.8) cooled the block to ~ -30 °C at full power and a linear power supply was used to drive the Peltier thermoelectric modules by controlling the voltage across the modules. The adjustable output voltage of the linear power supply (0 - 15 volts) was scaled by a 0-5 volt input signal from a Watlow SD6 temperature controller sensing the temperature of the aluminum block. Two  $\frac{1}{4}$ " stainless steel tubes coated with amorphous silicon (Silonite coating, Restek Inc.) were mounted through the aluminum

block. The tubes were resistively heated using polyamide coated nichrome wire with a resistance of 65 ohms (California Fine Wire Corp). Two additional Watlow SD6 temperature controllers monitored and controlled the two tube temperatures through on/off solenoid control. The warm sides of the Peltier thermoelectric modules were cooled using forced air heat sinks implementing 12 volt fans. For the dehumidifier to operate properly, the aluminum block had to have an operating temperature of -30 °C or colder. Through initial heat transfer model calculations, the feasibility of the implementation of Peltier thermoelectric modules for cooling seemed probable, but after initial testing, the aluminum block temperature never fell below -23 °C. With every thermodynamic property being optimal, the Peltier thermoelectric module at full power could reach a  $\Delta$ Temperature of 67 °C, resulting in an aluminum block temperature of ~ 27 °C with a hot side temperature of ~ 40 °C. The thermoelectric cooled dehumidifier was abandoned in favor of a dehumidifier design which implemented an immersion cooler with operating temperatures of ~ -50 °C.

#### 2.4. Dehumidifier Design: Immersion Cooler

The dehumidifier assembly consisted of two 6" x  $\frac{1}{4}$ " OD stainless steel tubes coated with amorphous silicon (Silonite coating, Restek Inc.) mounted inside a block of aluminum that was cooled by an immersion cooler probe (FTP Systems). The probes were in loose thermal contact with the block, with an air gap of 1/16" between the tube wall and the block. The immersion cooler probe cooled the block to between -45 °C and -55 °C depending on the ambient temperature, cooling the tubes as well. The tubes were resistively heated using polyamide coated nichrome wire with a resistance of ~ 95 ohms

(California Fine Wire Corp.) that was coiled around the tubes. The temperature of the individual tubes was controlled by a pair of Watlow SD6 temperature controllers with solid state relay control. Tube temperature was controlled by resistive heating. Tube temperature was monitored using an ungrounded thermocouple probe in contact with the inner tube wall. The thermocouple was inserted through a septum mounted on a Silonite coated (Restek) <sup>1</sup>/<sub>4</sub>" tee on the upstream side of the tube.

The dehumidifier was constructed with two tubes to ensure continuous measurements at the cold temperature over long time periods. Each tube of the dehumidifier was operated in one of three states; sample, condition, and back flush. While one tube is removing water from the sample stream, the other tube is heated and back flushed with dry nitrogen to remove ice accumulated in the tube during the last sample cycle and then cooled and conditioned with ambient air prior to sampling to ensure a seamless transition between tube measurement cycles. Upon initial introduction of VOC's and water to a clean tube, a conditioning period took place where some mass of VOC's is loss to the tube wall. The conditioning state ensures that the VOC's have come to equilibrium with the ice covered tube wall before being switched over to the sample state. All flows through the tubes in the dehumidifier were directed by six 3-way PFA solenoid valves (Entegris). The valves were arranged so that one tube can be in the sample mode, while the other tube can be operated in the back flush or conditioning state. While a tube is in the sample state, flow through the tube is determined by the PTR-MS inlet flow. Back flush and conditioning flows are regulated by two separate rotameters.



**Figure 2.3.** The operational flow diagram of dehumidifier system illustrates the dehumidifier, valves, flow controlling devices, calibration devices, and the calibration/zero electronic box. NO denotes normally open position of valves.

## 2.5. Software Control

Data acquisition and control of the sample preparation and dehumidifier apparatus was done using a LabJack U3-LV USB data acquisition device and DaqFactory Standard software. The LabJack U3-LV provided control voltages for all valves and solenoids and the electronic architecture to read digital and analog signals. DaqFactory provided the user interface and drivers to communicate with the LabJack U3-LV and Watlow SD6 temperature controllers. DaqFactory communicated with the LabJack U3-LV using
supplied USB drivers. DaqFactory communicated with the Watlow SD6 temperature controllers through a serial 485 interface with MODBUS RTU reverse word protocol.

#### **CHAPTER 3: RESULTS AND DISCUSSION**

#### 3.1. The Kinetics of Formaldehyde detection by the PTR-MS

Formaldehyde has been proven difficult to measure with the PTR-MS due to poor sensitivity from water interference. The proton affinity of formaldehyde (713 kJ) is only slightly greater than that of water (697 KJ), so the exothermicity of R 1.1is small. Within the drift tube, the kinetic energies of the ions are large enough that the endothermicity of the reverse reaction can be overcome, and the rate of the reverse reaction can be significant.

$$CH_2OH^+ + H_2O \rightarrow CH_2O + H_3O^+$$
 R 3. 1

The rate constant for R 3.1 increases with drift field intensity (Hansel et al., 1997). Table 3.1 lists forward and reverse rate constants for the  $H_3O^+$  + HCHO reaction at different drift field intensities. The reverse reaction rate constants for formaldehyde were taken from Hansel et al., 1997. The forward reaction was calculated for Hansel et al. 1997 drift field intensities using a capture rate constant parameterization that accounts for the effective temperature of the reaction (Su & Chesnavich, 1982). The effective temperature is a metric to account for the kinetic energy associated with the ion moving under the influence of an electric field. The kinetic energy of the ion was calculated following the procedure described by Lindinger et al. Table 3.1 shows that at higher field strengths the forward rate constant decreases and the reverse rate constant increases. To minimize the influence of the reverse reaction the drift should be operated at the lowest field strength possible.

Table 3.1 Forward  $(k_{cap f})$  and Reverse  $(k_r)$  Rate Constants for the  $H_3O^+$  + HCHO reaction listed with drift tube field intensity and mean kinetic energy (KE<sub>cm</sub>) between formaldehyde and  $H_3O^+$ .

Field Intensity (Td)	$\mathrm{KE}_{\mathrm{cm}}\left(\mathrm{eV}\right)^{a}$	$k_{cap f} (10^{-9} \text{ cm}^3 \text{ s}^{-1})^b$	$k_r (10^{-11} \text{ cm}^3 \text{ s}^{-1})^a$
75	0.08	2.29	0.6
85	0.09	2.19	1.0
120	0.14	1.86	1.5
150	0.20	1.66	3.5
190	0.28	1.51	7.5

*a* Obtained from Figure 2 of Hansel et al., 1997

*b* Calculated parameterization from Su & Chesnavich, 1982

Figures 3.2, 3.3, 3.4, and 3.5 illustrate the influence of drift field strength and water vapor concentration on  $H_3O^+$  count rates,  $H^+(H_2O)_2$ , and the normalized sensitivity of formaldehyde, acetaldehyde, and benzene. The drift tube was operated at a temperature of 60 °C and a pressure of 2.1 mbar. The voltage applied to the drift tube was adjusted to yield the following drift field intensities: 108, 120, 140, 162 Td. At the highest drift field intensity of 162 Td, the relative abundance of the  $H^+(H_2O)_n$  (n=1, 2, 3) water cluster distribution is unchanged with increasing water vapor mixing ratio. Likewise, the normalized sensitivity of acetaldehyde and benzene is unchanged. Formaldehyde, however, displayed more than a factor of 5 decrease in normalized sensitivity over the water vapor mixing ratio range from 1 mmol / mol (0.1 %) to 24 mmol/ mol (2.4%). This is caused by the increase in the reverse reaction rate (R3.1) as water vapor concentration increases.

Three trends are apparent as the Townsend number was decreased by lowering the electric field. The first trend is the change in the relative abundance of the  $H^+(H_2O)_n$  clusters. At the lower drift field intensities, the  $H_3O^+$  ion signal clearly decreases, while those of the water clusters increases, as water vapor increases. At 108 Td and 24 mmol/mol water vapor, the first water cluster  $H^+(H_2O)$  is as abundant as  $H_3O^+$ . The factor of 3 decrease in  $H_3O^+$  ion count rates over this water vapor range should cause a corresponding and undesirable reduction in RH<sup>+</sup> ion count rates. Interestingly this is indeed observed for some species (aromatics) but not for others as discussed below.

The second trend is the increase in formaldehyde normalized sensitivity (ncps) for the driest conditions as the field intensity is reduced. The ncps for formaldehyde increased from 10.7 Hz/ppbV at 162 Td to 24.6 Hz/ppbV at 108 Td. The trend is consistent with the reduction in the reverse rate constant at lower field intensities (Table 3.1). Formaldehyde sensitivity still displayed a strong decrease with increasing water vapor for all field intensities. The ncps values of acetaldehyde and benzene also increased with decreasing field intensities. For example the ncps of benzene at a water vapor mixing ratio ~ 1 mmol/mol increased by 80% from 4.6 Hz/ppbV at 162 Td to 7.2 Hz/ppbV at 108 Td.

The third trend observed is that the ncps for acetaldehyde displays an increasing dependence on the water vapor mixing ratio for lower drift field intensities. At 108 Td the ncps for acetaldehyde changes by a factor of 1.7 over the 1 mmol/mol to 24 mmol/mol water vapor mixing ratio range. If acetaldehyde was only protonated by  $H_3O^+$ 

29

as is implied in equation 1.6, the neps values should not change with changes in  $H_3O^+$ count rates due to neps being normalized to  $H_3O^+$ . An explanation for the acetaldehyde trend is that acetaldehyde is reacting with protonated water clusters such as  $H^+(H_2O)_2$ . Since the proton affinity of acetaldehyde is lower than that of the water dimer, the likely mechanism is a ligand switching reaction with the first water cluster and subsequent dissociation to produce protonated acetaldehyde. Other polar organics tested but not shown in the figures, such as acetonitrile, acetone, methyl ethyl ketone, and methacrolein, also displayed significant water vapor dependence. Table 3.2 lists the polarizability, dipole moment and solubility of VOC's present in the calibration mixture.

In contrast to acetladehyde, the ncps of benzene did not display such a pronounced dependence on water vapor. Ligand switching reactions appear to be fast only if the organic has a large dipole moment. The dipole moment of benzene is zero, and indeed no ligand switching reactions have been observed with benzene (Spanel and Smith, 1995). Therefore, it was expected that benzene and other aromatics with low dipole moments would display no change in ncps as water vapor increases. However, close inspection of the 108 Td experiment shows the ncps of benzene increased from 7.2 Hz/ppbV at the driest condition to 8.5 Hz/ppbV at the most humid, an 18% increase. Other aromatics such as toluene and p-xylene displayed similar increases in ncps. No definitive explanation can be given at this point for the apparent increase in ncps for the aromatics. There are two possibilities. The first is a change in the drift tube kinetics, whereby the mobility of  $H_3O^+$  decreases with increases in humidity, leading to an increase in reaction times. The second is that the increase is a result of an ion sampling artifact caused by

 $H_3O^+$  clustering with water vapor in the ion sampling section after the drift tube. The vacuum interface immediately after the drift has a section that operates at a pressure of ~ 0.15 mbar and the nose cone voltage in this section must be adjusted to match the field intensity of this region to that of the drift.

**Table 3.2** The dipole moment  $(\mu_D)$ , polarizability  $(\alpha)$ , and Henry's constant  $(k_H)$  of VOC's found in the calibration mixture

Substance	$\mu_{\mathbf{D}}\left(\mathbf{D}\right)^{a}$	a $(10^{-24} \text{ cm}^3)^a$	$k_{\rm H} (M \text{ atm}^{-1})$
Formaldehyde	2.183	2.41	3.1 X 10 <sup>3</sup> b
Methanol	1.662	2.67	$2.2 \times 10^{2}$ <sup>c</sup>
Acetonitrile	3.828	4.29	5.3 X 10 <sup>1 d</sup>
Acetaldehyde	2.648	4.30	$1.3 \ge 10^{1}$
Acetone	2.289	6.09	2.7 X 10 <sup>-1</sup> d
Isoprene	0.250	10.22	$1.3 \ge 10^{-2} e^{-2}$
Methacrolein	2.800	8.41	4.3 <sup>f</sup>
MEK	2.764	7.90	$2.0 \times 10^{1} g$
Benzene	0.000	10.78	1.6 X 10 <sup>-1</sup> g
Toluene	0.343	12.90	1.5 X 10 <sup>-1</sup> g
Styrene	0.186	15.86	3.8 X 10 <sup>-1 h</sup>
<i>p</i> -Xylene	0.081	15.08	1.3 X 10 <sup>-1</sup> g
1,3,4-trimethylbenzene	0.291	17.16	1.7 X 10 <sup>-1</sup> <sup>e</sup>
α-pinene	0.149	18.07	4.9 X 10 <sup>-2</sup> <i>i</i>

*a* Zhao and Zhang, 2004

 $b\,$  Zhou and Mopper, 1990

c Snider and Dawson, 1985

d Benkelberg et al., 1995

e Mackay and Shiu, 1981

f Allen et al., 1998

g Staudinger and Roberts, 1996

h USEPA, 1982

I Sanders, 1999

From these experiments we conclude that formaldehyde normalized sensitivity can be significantly increased by drying the sample air. Drying the sample would have the added benefit of being able to operate the drift tube at lower field intensities, thereby further increasing the normalized sensitivity to all compounds. An additional benefit of drying the sample to some constant dew point is that the normalized sensitivities would be independent of ambient air humidity. This would simplify the calibration of the instrument by eliminating the addition of a correction factor to sensitivity humidity dependence observed in formaldehyde.



**Figure 3.1** Normalized sensitivity vs. water vapor mixing ratio for Td = 108.



**Figure 3.2** Normalized sensitivity vs. water vapor mixing ratio for Td = 120.



Figure 3.3 Normalized sensitivity vs. water vapor mixing ratio for Td = 140.



**Figure 3.4** Normalized sensitivity vs. water vapor mixing ratio for Td = 162.

## 3.2. Influence of Dehumidifier Temperature on Formaldehyde Sensitivity

Proper operation of the dehumidifier depends on many variables, with temperature the most important variable. It influences many operating dynamics, such as tube conditioning time, dehumidifier transmission efficiency, and overall sensitivity gain of the PTR-MS to formaldehyde. The operating temperature must be chosen carefully to minimize losses of VOC's in the sample stream to the ice surface of the dehumidifier while maximizing the sensitivity of the PTR-MS to formaldehyde.

Water is removed from the sample stream by passing the sample stream through a cold tube where it condenses and freezes onto the tube surface, effectively lowering the dew point temperature of the sample stream to the tube surface temperature. Figure 3.5 demonstrates the response of the PTR-MS formaldehyde sensitivity to dehumidifier temperature at a flow rate of 500 sccm. The sensitivity increases with lower tube temperatures due to a decrease of water vapor entering the PTR-MS drift tube. The lower water vapor concentration reduces the reaction rate of the reverse reaction between protonated formaldehyde and water vapor. Figure 3.5 suggests that the dehumidifier should be operated at the lowest possible temperature to maximize PTR-MS sensitivity to formaldehyde.

35



**Figure 3.5** Formaldehyde normalized sensitivity versus sample dew point at 2.4 mbar drift pressure and 120 Td illustrating an abrupt change in sensitivity between -30 °C and - 25 °C.

Before the tubes in the dehumidifier are used for sample collection, the tubes must be conditioned to ensure no sample is lost to the tube walls. When sample gas is first introduced to the cold tube, the VOC's in the sample gas adsorb to the tube walls. Figure 3.6 demonstrates the adsorption of formaldehyde flowing through a cold amorphous silicon tube at a temperature of -67 °C. The gas flow was 100 sccm. The time series was smoothed to better illustrate the trend (binomial smooth function over 3 data points). The experiment was conducted as follows. Initially the PTR-MS was sampling diluted calibration mixture without going through the dehumidifier. The PTR-MS sampled the species at a dwell time of 0.2 seconds and a drift tube field intensity of 120 Td. The

calibration mixture contains 13 species at a nominal mixing ratio of 20 ppbV and formaldehyde at a nominal mixing ratio of 40 ppbV in dry N<sub>2</sub>. The figure shows the formaldehyde signal. At time = 125 seconds a solenoid valve was actuated and the sample was directed through the cold tube. The immediate effect was a large decrease in the formaldehyde count rate which recovered after about 25 seconds. The initial loss in signal when the sample is first passed through the dehumidifier is likely due to a physisorption to the cold tube walls, whereby formaldehyde molecules form a layer on the surface of the tube wall until an equilibrium is reached. Equilibrium occurs when all available sites for adsorption on the tube surface are filled and formaldehyde molecules deposit on the tube wall at the same rate as formaldehyde molecules leave the tube surface. Once in equilibrium with the tube surface, formaldehyde is transmitted through the tube and exits at the same concentration as it entered the tube. The time it takes to recover the signal is called the conditioning time. The area under the dashed line relates to the total mass of formaldehyde lost to the tube wall. From the incoming mixing ratio and flow rate through the tube, the mass of formaldehyde lost to the tube was calculated to be  $\sim 10$  nanograms. With water vapor in the calibration system, the system behaves similarly. Some mass of the compounds is lost to the tube walls during a conditioning period, but ultimately, the compound reaches an equilibrium condition between ice surface and the compound concentration in the gas phase.

37



**Figure 3.6** Formaldehyde ion count rates versus time showing adsorption loss to a cold Restek tube when dry sample air containing 40 ppbV formaldehyde was directed through the dehumidifier at a temperature of -67 °C. Solid line is smoothed data.

Figure 3.7 illustrates the impact of the dehumidifier on a 20 ppbV calibration mixture sample flow at a relative humidity of 50% at 23 °C. It shows the dehumidifier operating at a dew point of -40 °C. There are three identifiable ion signal levels: A) ion signal at ambient temperature, B) a conditioning period when the sample first flows through the cold tube, and C) equilibrium signal level at the cold tube temperature.



**Figure 3.7** Ion signal versus time showing the impact of the dehumidifier at -40 °C when the sample stream is diverted through the dehumidifier. Label A, ambient conditions RH=50%. Label B represents a conditioning period as sample flows through dehumidifier. Label C, sample has achieved equilibrium through dehumidifier.

In state A, the sample gas is passed through a tube at room temperature (T = 23 °C) to serve as a reference measurement to compare to the dehumidified sample. In this state, water vapor in the sample contributes to a decrease in formaldehyde sensitivity and a lower observed count rate. The sample gas was then redirected by a series of valves into a cold tube at the given temperature where tube conditioning began, as indicated by label B. In the conditioning state, the formaldehyde signal increased due to the sharp decrease of water vapor in the drift tube, After ~ 7 minutes, the formaldehyde signal is reasonably stable at ~3800 Hz. At this point the formaldehyde is in equilibrium with the cold ice surface, as indicated by label C. Water vapor leaving the dehumidifier is low, as indicated by the large change in water cluster count rates, from  $\sim 450,000$  Hz at room temperature to  $\sim 3800$  Hz at -40 °C. For the -40 °C tube temperature the formaldehyde signal has increased a factor of 5 above the ambient conditions at 50% RH and 23 °C.



**Figure 3.8** Ion signal versus time for six different dehumidifier temperatures. The formaldehyde signal changes significantly when sample air is diverted through the trap.

Figure 3.8 demonstrates a relationship between temperature and total time to tube equilibrium. As expected, water vapor concentrations leaving the dehumidifier decreased as tube temperature was decreased, and observed formaldehyde counts increased due to less water vapor present in the PTR-MS drift tube. An unexpected finding was that colder dehumidifier temperatures decreased the time it took for formaldehyde to reach

equilibrium. Interestingly, the formaldehyde normalized sensitivity showed a steep increase between -20 °C and -30 °C as shown previously in Figure 3.8.

Figure 3.9 illustrates the steep increase in normalized sensitivity in more detail. At temperatures less than -30 °C, the tube conditioning process behaved as described above (Point A on Figure 3.9), but at temperatures -25 °C and greater, the conditioning process showed very little increase of formaldehyde sensitivity (Point B on Figure 3.9).



**Figure 3.9** Ion signal versus time for 2 different dehumidifier temperatures illustrating a significant loss of methanol and formaldehyde to the trap at -25 °C compared to -30 °C. This loss may be due to a liquid water film on the ice at -25 °C.

It is postulated that this is due to absorption effects to a disordered quasi liquid layer that exists on ice crystals (Beaglehole & Nason, 1979). The layer forms at temperatures greater than -25 °C and reaches nearly 100 angstroms thick at the water freezing point (Beaglehole & Nason, 1979). Formaldehyde is very soluble with a Henry's law coefficient at -20 °C of 1.8 x 10<sup>5</sup> M atm<sup>-1</sup> (Staudinger and Roberts, 1996). Formaldehyde would thus partition into the liquid water layer, resulting in a loss of formaldehyde from the sample stream. From Figure 3.8, it can be seen that at a tube temperature of -25 °C, less formaldehyde makes it through the tube than the ambient RH condition, despite the lower water vapor concentration in the drift tube and the inherently greater normalized sensitivity. This absorption effect was also observed for methanol but not for other gases in the test mixture such as acetaldehyde, acetone, and methacrolein. At -20 °C these species have a Henry's Law coefficient at least a factor of 10 less than that of methanol and partitioning into the liquid phase is not as significant (Table 3.2). Thus two effects determine the transmission efficiency through the cold tube: 1) physical adsorption of VOC's to ice or the Restek tubing surface 2) absorption of soluble VOC's into a quasi liquid layer of water on the ice surface.

The operating temperature of the dehumidifier is an important consideration. The operating temperature must be set to a point where it is sufficiently cold to remove water vapor from the sample stream, but not too cold where conditioning times and transmission efficiencies are compromised, resulting in poor measurements. Many species require more time to reach equilibrium at colder temperatures, with large aromatic hydrocarbons and organic acids having the longest conditioning periods. At an

42

operating temperature of -30 °C, there appears to be no effect of absorption into a quasi liquid layer and sufficient water vapor is removed from the sample to increase the PTR-MS sensitivity to formaldehyde.

### **3.3.** Sample Flow through the Dehumidifier

Sample flow through he dehumidifier had an effect on sensitivity as indicated by Figure 3.10. Formaldehyde sensitivity decreased at flows above 500 sccm. The decreased sensitivity at higher flows was due to decreased efficiency of the dehumidifier. At the larger flow rates, less water vapor was frozen out of the sample stream, resulting in more water vapor reaching the drift tube and lower formaldehyde sensitivities.

Flow through the dehumidifier also plays a role in the length of the conditioning period. Increased flow rates pass a greater amount of mass across the tube surface per unit of time resulting in the ice surface coming to equilibrium more quickly and shorter conditioning periods. Flow through the dehumidifier should be adjusted to a point where water vapor in the sample is efficiently removed for maximum sensitivity of formaldehyde and minimum loss of VOC's to the dehumidifier while maintaining a short conditioning period. For an operating temperature of -30 °C, a flow of ~ 250 sccm satisfied these conditions.

43



**Figure 3.10** The normalized sensitivity of formaldehyde versus sample flow rate at 50% RH through the dehumidifier operated at -30 °C. At the high flow rates the dehumidifier operates at less than 100% efficiency.

# **3.4. Drift Tube Optimization**

The PTR-MS drift tube is routinely tuned for maximum sensitivity and minimum interference from water clusters to reduce the water vapor dependence observed in many polar ions. Water clusters are minimized by increasing the drift tube electric field resulting in greater ion velocity and greater energy in ion collisions. The energy at the given electric field results in a fraction of water clusters broken apart by collisional disassociation. The downside of increased velocity of the ions in the drift tube is reduced sensitivity due to decreased reaction time.

With the dehumidifier in line, water vapor entering the drift tube from the sample is small. The ion source is the major contributor of water vapor, which is regulated and constant. With a constant water vapor source, the drift tube can be tuned to maximize reaction time with little concern for variability due to water clusters in the drift tube. The water clusters present provide an additional stable source of ions, which protonate VOC's that participate in ligand switching reactions and direct proton transfer from the second water cluster, increasing the overall sensitivity of the VOC's.



**Figure 3.11** Normalized sensitivity versus reaction times. Reduced drift tube field intensities result in longer reaction times and increased normalized sensitivities for many species. Polar species, such as acetaldehyde, have a strong positive correlation with reduced drift tube field intensities due to the rapid formation of water clusters in the drift tube and polar species participating in ligand switching reactions.

Figure 3.11 shows an increase in sensitivity of all VOC's with longer reaction times. Typically, the sensitivity of ions will increase linearly with reaction time and follows equation 3.1

$$kt = \frac{[H_3O^+][R]}{[RH^+]} = \frac{ncps}{ppbV}$$
 3.1

where k is the rate constant of the proton transfer reaction, t is the reaction time,  $H_3O^+$  is the reagent ion, R is the sample VOC,  $RH^+$  is the ionized VOC, and ncps/ppbV is the normalized sensitivity. Formaldehyde and benzene follow the reaction kinetics, but acetaldehyde displays nonlinear behavior due to it's interaction with water clusters in the drift tube. The kinetic behavior of polar compounds is better represented by equation 3.2.

$$RH^{+} = k_{1}t[H_{3}O^{+}] + k_{2}t[H^{+}(H_{2}O)_{2}] + k_{n}t[H^{+}(H_{2}O)_{n}]$$
 3.2

where  $H^+(H_2O)_2$  is the first water cluster,  $H_n(H_2O)_n$  is any water cluster from  $n = 3 \rightarrow \infty$ , and  $k_n$  is the rate constant for the respective water cluster. Typically, the first and second water clusters are present when the electric field of the drift tube is tuned to normal operating conditions. Larger water clusters ( $n \ge 3$ ) are present, but at concentrations that have a minimal impact on the drift tube kinetics. When the drift tube electric field is tuned for longer reaction times, the larger water clusters increase exponentially and are present in concentrations at a level where they play a role in the drift tube kinetics. With the dehumidifier inline, the water clusters formed in the drift tube are constant due to steady incoming water vapor concentrations resulting in increased stable sensitivities of polar compounds.

# **3.5. Houston Experiment**

From April 15, 2009 to May 30, 2009, an urban air shed study was conducted in and around Houston, Texas named A Study of Houston Atmospheric Radical Precursor (SHARP). The purpose of the study was to quantify the radical precursors budget, such as formaldehyde and HONO, and to provide more accurate inputs to atmospheric models to better estimate tropospheric ozone concentrations in the Houston district. The PTR-MS, with the dehumidifier inline, was implemented as a method to identify specific sources of oxygenated VOC's from atop the Moody Towers at the University of Houston. A source apportionment study will be conducted with the data to determine if the measured formaldehyde originates from direct emissions, such as oil refineries and automobile traffic, or from secondary sources, such as the photoxidation of regional VOC's. The PTR-MS was operated continuously for the length of the campaign with a sample taken every  $\sim$  73 seconds. For the first two weeks, tube 1 and tube 2 temperatures were operated at 30 °C and -30 °C, respectively at a drift field intensity of 120 Td, a drift tube pressure of 2.1 mbar, and a drift tube temperature of 60 °C. The sample was switched between the two tubes at 25 minute intervals resulting in periodic measurements at ambient dew points and a dew point of -30 °C.



**Figure 3.12** Data collected during the 2009 SHARP campaign in Houston, Texas illustrates the effect of water vapor on the PTR-MS response to formaldehyde. The uncorrected formaldehyde time series (bottom) shows a strong dependence to changes in water vapor in the drift tube (top). Using a calibration curve of normalized sensitivity a dew point of -30 °C fit to the first water cluster, the formaldehyde measurements influenced by water vapor interferences were corrected (middle).

Figure 3.12 displays the second water cluster count rate (top), corrected formaldehyde mixing ratio (middle), and uncorrected formaldehyde mixing ratio (bottom) for a three day period taken from the two week data set. Examination of the water cluster time series illustrates the operation of the dehumidifier. At ambient humidity, the water cluster signal shows variability, which results in humidity dependent measurements of formaldehyde. With the dehumidifier operating at a dew point of -30 C, the magnitude of

the water clusters was decreased and the variability eliminated, resulting in a constant response to formaldehyde. In the uncorrected time series, the improvement in formaldehyde response implementing the dehumidifier at a dew point of -30 °C can be observed. The high values reveal the response of the PTR-MS to formaldehyde measurements with very little water vapor present in the drift tube and little contribution to drift tube reaction kinetics from the reverse reaction.



Figure 3.13 Several calibrated points of normalized formaldehyde count rate at an ambient dew point was fit to varying  $H^+(H_2O)_2$  count rates to account for the water vapor dependent sensitivity of formaldehyde.

The normalized sensitivities for ambient dew point measurements were corrected using a best fit calibration curve of normalized formaldehyde count rate at an ambient dew point

fit to the first water cluster. Due to the limited number of calibration points, the regression did not model the water vapor dependent sensitivity of the PTR-MS perfectly and the corrected formaldehyde plot displayed variability due to water vapor (Figure 3.12). In particular, few calibration points were collected at low water vapor mixing ratios resulting in poor correction of formaldehyde measurements taken at dry ambient dew points. More data points at dry conditions are needed to model the strong water vapor dependence at low water vapor mixing ratios.

The transmission efficiency of VOC's through the dehumidifier operating at a temperature of -30 °C was analyzed to quantify losses of VOC's to the ice covered tube walls. Data from thirteen calibration periods between the 19<sup>th</sup> and 26<sup>th</sup> of April 2009 were used to compare transmission of several VOC's through a cold tube at -30 °C and a warm tube at 30 °C. Figure 3.14 is an example of a calibration period of formaldehyde and the first water cluster.



**Figure 3.14** Thirteen VOC's in the calibration mixture were sampled every 12 hours at both ambient dew point and a dew point of -30 °C. The calibration transition from ambient dew points to a dew point of -30 °C was characterized by a sharp decrease in water cluster count rates indicating a drop in water vapor. Formaldehyde count rates rose sharply due to the drop in water vapor.

At the beginning of the calibration sequence, the PTR-MS is sampling zero air through a warm tube at 30 °C. Initially, ~ 7 zero air data points are collected before calibration gas at a mixing ratio of ~ 20 ppbV is combined with the zero air, where approximately, 8 calibration data points are collected through the warm tube. Then the sample flow is switched over to the cold tube as indicated by the sharp decrease in  $H^+(H_2O)_2$ . Approximately 8 more calibration data points through the cold tube are then collected. The calibration period concludes with a final zero period through the cold tube. The

sharp increase in the formaldehyde count rate through the cold tube is due to removal of water and an increase in sensitivity to formaldehyde. Many of the species showed very little change in the detection signal when the sample path was switched from an ambient dew point to a dew point of -30 ° C. Figure 3.15 represents the average ratios of 13 calibration periods and the error bars represent the standard deviation (1 $\sigma$ ) of the averaged ratios. The ratio is the average normalized VOC count rate at the cold tube temperature (T2) divided by the average normalized VOC count rate at ambient conditions (T1). A ratio greater than 1 indicates greater transmission of the VOC species through the dehumidifier and a ratio below 1 indicates decreased transmission of the VOC through the trap. All VOC's had transmission efficiencies greater than 90 % with MVK having the worst transmission efficiency at 94 %. Some VOC's had improved transmission efficiency through the dehumidifier. Acetaldehyde demonstrated the greatest increase in transmission efficiency with transmission improved by 5 % when the sample was dehumidified to a dew point of -30 °C.



**Figure 3.15** The ratio represents the transmission of the VOC's through the dehumidifier. A ratio greater than one indicates increased transmission through the dehumidifier and a ratio below one indicates reduced transmission through the dehumidifier.

During the month of May, both tubes of the dehumidifier were operated at -30 °C. Also, the drift tube field intensity was varied. The drift tube field intensity from May 1, 2009 to May 22, 2009 was 120 Td and the drift tube field intensity from May 23, 2009 to the end of the month was 80 Td. Figure 3.16 shows a time series of formaldehyde for the month of May, 2009. The time series is split into one plot from May 1, 2009 through May 15, 2009 (top) and a second plot from May 16, 2009 through May 31, 2009 (bottom). The time period is characterized by a strong diel cycle of formaldehyde during

the first half of the month and influenced by heavy pollution during the last two weeks of the month.



**Figure 3.16.** Formaldehyde measurements of the SHARP campaign for May, 2009 are displayed in the time series. The formaldehyde time series for the first two weeks of May (top) displays a strong diel cycle, while the last two weeks of May (bottom) are heavily influenced by strong pollution episodes.

The diurnal cycle and strong pollution episodes displayed by formaldehyde are consistent with other measurements taken in the Houston area. Chen et al. (2004) monitored ambient formaldehyde concentrations during July and August, 2002 at Deer Park, Texas. The site was near a ship channel adjacent to Houston and is often exposed to formaldehyde source plumes originating from industry within the ship channel. Chen et al. used a laser spectrometer technique based on difference frequency generation to measure formaldehyde. The formaldehyde measurements displayed diurnal variation with peaks typically less than ~20 ppbV and intense peaks as high as ~ 30 ppbV. Karl et al. (2003) and Dasgupta et al. (2005) also measured formaldehyde during a study named The Texas Air Quality Study 2000 conducted from August 15, 2000 to September 14, 2000. Both groups were situated near the ship channel, Karl et al. in La Porte, Texas and Dasgupta et al. at the Houston Regional Monitoring Network EPA site 48-201-0803. Karl et al. reported mean formaldehyde concentrations of ~6 ppb with a maximum peak of ~ 40 ppbV, while Dasgupta et al. reported similar values with a mean mixing ratio of 3.3 ppbV and maximum peaks greater than 47 ppbV. The measurements outlined in Figure 3.16 also agree well with formaldehyde measurements of other campaigns, but at lower mixing ratios. The mean mixing ratio for the time series is ~ 2 ppbV with peaks reaching mixing ratio magnitudes as high as 12 ppbV.

Upon visual inspection, the time series at 80 Td appears to demonstrate improved signal to noise over the time series with a drift tube field intensity of 120 Td. Figure 3.17 is an expanded view of formaldehyde, acetaldehyde, and isoprene time series for the drift tube field intensities of 120 Td (left) and 80 Td (right). Small pollution episodes displayed by acetaldehyde are apparent in the formaldehyde measurement at the lower drift tube field intensity, where they are much more difficult to make out in a drift tube intensity of 120 Td. Also, the signal to noise ratio of formaldehyde and isoprene near the detection limit appears to decrease at a drift tube intensity of 80 Td. According to equation 1.6, the

55

reaction time (equation 1.5). The precision and resolution will increase as a result of increased sensitivity. The detection limits, precision, and resolution will be investigated in the following sections.



**Figure 3.17** The formaldehyde, acetaldehyde, and isoprene time series were collected during the month of May at the 2009 SHARP project in Houston, Texas and displays diurnal variation and pollution events characteristic of the region. The drift tube field intensity of the time series on the left and right are 120 Td and 80 Td, respectively.

# **3.6. Detection Limits**

Detection limits with a confidence level greater than 95 % are reported using Poissonian statistics for compounds with a mean count rate below 9 Hz and detection limits using a

Gaussian distribution with  $2\sigma$  of the mean distribution and a confidence interval of ~ 95.4 % are reported for compounds with a mean greater than 9 Hz. For the Gaussian distribution, the standard deviation was calculated as the square root of the mean count rate (de Gouw & Warneke, 2007). Poisson statistics were used to determine the detection limits of the PTR-MS at count rates less than 9 Hz due to the operating characteristics of the instrument detector. The detector of the PTR-MS is a secondary electron multiplier (SEM) and operates by creating a current through collisions of ions with the detector. A collision that results in current that exceeds some threshold results in a count. Counting detectors, such as the SEM have been shown to correlate well to Poissonian statistics (Hayward et al., 2002, de Gouw and Warneke, 2007).

Poissonian statistics fail at count rates greater than 9 Hz. Poissonian statistics assume an event is rare and the assumption is only true at low count rates (Event < 9 Hz). Gaussian statistics assume a common distribution of events (Event > 9 Hz). Studies have found that Poissonian systems, with mean count rates greater than 9 Hz, are represented well by the Gaussian distribution with error less than 2 % (Hayward et al., 2002). For Poissonian distributions, the standard deviation is the square root of the mean count rate. Hayward et al., 2002 found less than a 1 % difference between the standard deviation of the detector noise assuming a Gaussian distribution and a Poissonian distribution.

Detection limits were calculated for both moist sample air and dry sample air at a drift tube intensity of 120 Td. Data was collected over a two week period from April 14, 2009 to April 30, 2009, where the sample stream was alternated between a cold channel of the dehumidifier at a dew point of -30 °C and warm channel at ambient dew point. The ambient dew point varied between 20 °C to 30 °C. During the two week period, zero air was introduced to the PTR-MS through the sample line via the dehumidifier at 6 hour intervals, alternating between the cold channel and the warm channel. 54 zero periods were collected and each period had ~8 data points collected at ~ 73 second intervals. All data were averaged resulting in a single value that is assumed to represent the minimum detection capabilities of the instrument. The count rate for each zero period varied over the two week period and the detection limits calculated for the two week span likely overestimate the actual detection limit of the instrument.

Detection limits were also calculated for a dry air sample at a dew point of -30 °C and a drift tube intensity of 80 Td. For the experiment, zero air was sampled over a  $\sim$ 3 hour period on May 30, 2009 during the 2009 SHARP campaign in Houston Texas. A total of 139 data points were collected at a  $\sim$  73 second interval. The data points were averaged and detection limits were calculated as described above using the average count rate. In this experiment, zero air was passed through the dehumidifier and tubing for  $\sim$  3 hours ensuring ample time to condition and remove VOC contamination from the zero air delivery system to the PTR-MS. The PTR-MS drift tube operating conditions for both the 2 week period starting April 14, 2009 and the three hour period on May 30, 2009 are listed in Table 3.3.

PTR-MS Drift Tube Configuration					
	April 14, 2009	May 30, 2009			
Drift Field Intensity (Td)	119	80			
P <sub>drift</sub> (mbar)	2.1	2.1			
U <sub>drift</sub> (Volts)	500	260			
T <sub>drift</sub> (°C)	60	45			

Table 3.3 The PTR-MS drift tube configurations for the two detection limit experiments.

For the April 14<sup>th</sup> experiment, all zero data for both the warm channel and the cold channel were separately averaged for the two week period resulting in a mean ( $\lambda$ ) count rate for each of the channels. For the May 30<sup>th</sup> experiment, the three hour zero period was averaged resulting in a mean count rate. If the mean count rate was greater than 9 Hz, then the detection limit was assumed to be two standard deviations above the mean. If the mean count rate was 9 Hz or less, the mean count rate was applied to the probability mass function (pmf) for the Poissonian distribution to calculate the minimum count rate (k) greater than the mean where a measurement is greater than 95 % of the confidence interval of the mean of the zero periods. The pmf of the Poissonian distribution is represented as

$$f(k;\lambda) = \frac{\lambda^k e^{-\lambda}}{k!}$$
3.3

where  $f(k; \lambda)$  is the fraction of occurrences that occur outside the distribution. The confidence interval (CI) is represented as

$$CI = 1 - f(k;\lambda) \tag{3.4}$$

The minimum count rate greater than 95 % of the CI was converted to mixing ratios using the averaged normalized sensitivity and averaged reagent ion count rate as described in de Gouw and Warneke, (2007).

Table 3.4 outlines the calculated detection limits at a confidence interval greater than 95 % for all three measurement conditions.

	Dwell	Dew Point: 25 °C		Dew Point: -30 °C		Dew Point: -30 °C	
Compound	Time	Drift Intensi	ty: 120 Td	Drift Intensity: 120 Td		Drift Intensity: 80 Td	
	(seconds)	DL (pptv)	CI (%)	DL (pptv)	CI (%)	DL (pptv)	CI (%)
Formaldehyde	5	716	95.4	244	95.4	105	95.4
Methanol	1	383	95.4	426	95.4	221	95.4
Acetonitrile	2	72	97.4	82	97.7	30	97.0
Propene	2	332	95.4	378	95.4	83	95.4
Acetaldehyde	2	198	95.4	225	95.4	84	95.4
Formic Acid	2	703	95.4	798	95.4	905	95.4
Methylperoxide	2	103	96.4	115	96.4	64	97.4
Acrylonitrile	2	84	97.7	80	96.4	42	96.4
Acrolein/Butenes	2	278	95.4	318	95.4	165	95.4
Acetone	2	99	95.4	113	95.4	54	95.4
Acetic Acid	2	191	95.4	218	95.4	72	95.4
Isoprene	2	128	97.4	149	97.4	42	96.4
MVK	2	149	97.0	175	97.4	71	97.7
MEK	2	85	95.4	77	97.4	39	95.4
Glyoxic Acid	2	67	97.0	77	97.7	91	95.4
PAN	2	1543	96.4	1683	97.0	270	96.4
Benzene	2	131	97.4	145	97.4	69	97.4
Toluene	2	129	97.7	121	96.4	55	96.4
Phenol	2	110	97.7	103	96.4	42	97.8
Styrene	2	102	96.4	115	96.4	43	96.4
C2 Benzene	2	116	96.4	133	96.4	48	96.4
Cresols	2	126	97.7	120	97.0	37	96.4
C3 Benzene	2	150	97.7	143	96.4	65	96.4
Naphthalene	2	139	97.7	133	96.4	65	97.0
C3 Benzene	2	133	96.4	155	96.4	59	96.4
Monoterpene	2	340	96.4	392	97.0	111	96.4

Table 3.4. Detection limits of the PTR-MS measuring at ambient dew point and dew point = -30  $^{\circ}$ C.

Many of the compounds had higher detection limits at a dew point of -30 ° C and a drift tube intensity of 120 Td than at an ambient dew point and a drift tube intensity of 120 Td.
All detection limits decreased at a dew point of -30 ° C and a drift tube field intensity of 120 Td. Figure 3.18 shows the trend with the noticeable exception of formaldehyde



**Figure 3.18.** The detection limits were the lowest at a dew point of -30 ° C and a drift tube field intensity of 80 Td. The large decrease in detection limits for all species at drift tube intensity of 80 Td is due to an increase in normalized sensitivity.

Zero count rates are lower for the low dew point channel due to small amounts of sample being lost to the ice covered tube wall of the dehumidifier resulting in lower calculated sensitivities and higher detection limits. The detection limit of formaldehyde is greatly increased at low dew points due to the removal of water vapor from the sample stream and a large increase in sensitivity.

	$T_d = 25$ °C	$T_{d} = -3$	$T_d = -30 \ ^{\circ}C$	
VOC Ions	120 Td	120 Td	80 Td	
Formaldehyde	3.5	11.3	26.1	
Methanol	10.4	10.2	19.1	
Acetonitrile	18.1	17.3	34.2	
Propene*	6.3	6.1	19.1	
Acetaldehyde	14.2	13.6	25.8	
Formic Acid*	8.7	8.3	19.1	
Methylperoxide*	10.4	10.2	19.1	
Acrylonitrile*	15.3	14.7	19.1	
Acrolein/Butenes*	9.2	8.8	19.1	
Acetone	15.3	14.7	29.0	
Acetic Acid*	11.5	11.0	29.0	
Isoprene	10.1	9.5	19.1	
MVK	8.7	8.1	17.2	
MEK	19.3	18.4	36.5	
Glyoxic Acid*	19.3	18.4	17.2	
PAN*	0.7	0.7	2.1	
Benzene	9.9	9.8	17.7	
Monoterpene Fragment	4.9	4.8	6.9	
Toluene	10.1	9.8	18.5	
Phenol	11.8	11.4	24.0	
Styrene	10.6	10.3	18.9	
C2-Benzene	9.3	8.9	17.0	
Cresols*	10.3	9.8	22.2	
C3-Benzene	8.6	8.2	15.7	
Naphthalene*	9.3	8.9	15.7	
C4-Benzene	8.1	7.6	13.7	
Monoterpene	3.2	3.0	7.3	

**Table 3.5.** The normalized sensitivities at two dehumidifier temperatures and two drift tube intensities.

Formaldehyde had over a seven fold increase in sensitivity from a dew point of 25 and a drift tube intensity of 120 Td to a dew point of  $-30 \degree$  C and drift tube field intensity of 80 Td (Table 3.5). At a drift tube intensity of 80 Td, all compounds had the lowest detection limits due to a large increase in sensitivity. The normalized sensitivity at a dry dew point of  $-30 \degree$ C and a drift tube field intensity of 120 Td for formaldehyde increased from  $\sim 11$ 

Hz/ppbV to  $\sim 26$  Hz/ppbV resulting in a decrease of the detection limit from 244 to 105 pptv, respectively.

## 3.7. Precision

Upon initial inspection of formaldehyde time series measured during the Houston 2009 SHARP campaign, the precision of the measurements appeared to be improved over ambient dew point measurements when the sample was dried to a dew point of -30 °C and an investigation of the differences of the precision was carried out. For a two week period, the sample stream was switched on a 30 minute cycle between an ambient dew point sample path and a dry sample path set at a dew point of -30 °C. The ambient dew point ranged between 20 to 30 °C during the measurement period. A ~ 12 hour period from the data set representing ambient background formaldehyde measurements was chosen from the data to quantify measurement precision for both the dry and humid sample paths. The formaldehyde mixing ratios held constant at ~ 1 ppbV for the 12 hour period.

For each sample path, a Gaussian distribution was fit to a discrete probability function (DPF) of formaldehyde concentration verses number of occurrences for a range of concentrations assuming the measurement noise fit a Gaussian distribution. The resolution (RS) of the DPF was calculated using the following equation:

$$Rs = \frac{1Hz}{\overline{S}_{Formaldehyde} * \left(\frac{\overline{H_3O^+}}{10^6}\right)}$$
3.5

where 1Hz is a 1 ion measurement by the detector accounting for the smallest detectable change by the PTR-MS for a particular ion,  $\overline{S}$  is the averaged normalized sensitivity for the 12 hour period, and  $\overline{H_3O^+}$  is the average reagent ion count for the 12 hour period. A resolution was calculated for each sample path due to the humidity dependence of the PTR-MS sensitivity. The average normalized sensitivity of the sample path at ambient dew point was 2.9 Hz/(ppbV \* per million H<sub>3</sub>O<sup>+</sup>) with a corresponding resolution of 70 pptV. The normalized sensitivity and resolution was greatly improved at a dew point of -30 °C with an averaged normalized sensitivity of 9. 7 Hz/(ppbV \* per million H<sub>3</sub>O<sup>+</sup>) resulting in a resolution of 20 pptV. Although measurements by the PTR-MS are often better represented by a Poissonian distribution, the detection limits of formaldehyde for the measurement period were at a level where a Gaussian distribution accurately represents measurements with error less than 2 % (Hayward et al., 2002).

Quantification of the precision for both sample paths demonstrated that the dry measurements had better precision over measurements conducted at ambient dew points. Figure 3.19 demonstrates the difference in precision of the two sample paths with the top histogram representing the measurement distribution of ambient dew point measurements and the bottom histogram representing the distribution of dry measurements.



**Figure 3.19** The precision of the 1 ppbV formaldehyde concentration at a drift tube field intensity of 120 Td and a dew point of 30 °C increased by  $\sim$  30% when at a dew point of -30 °C.

Because both sample paths were measuring from the same source over the 12 hour period, one would expect the median concentration to agree. The median concentrations for the two measurements at different dew points are nearly identical. The median concentration were  $1.0 \pm 0.14$  ppbV and  $0.99 \pm 0.0083$  ppbV for the ambient dew point measurement and the measurement at a dew point of -30 °C, respectively. The difference is likely due to small losses of formaldehyde in the sample stream to the sample path.

The measurements made from the sample path with a -30 °C dew point showed an increase in precision of nearly 30 % over measurements taken at the ambient dew point.

The improvement in precision is due to the large increase in sensitivity. A greater abundance of formaldehyde ions are produced in the drift tube at the low dew point resulting in a higher count rate and improved precision. The overall precision of formaldehyde measured by the PTR-MS is strongly influenced by the detector. The precision of the detector follows a Poissonian distribution and the standard deviation scales as the square of the measurement count rate (de Gouw & Warneke, 2007). Therefore, higher PTR-MS sensitivity to formaldehyde at a dew point of -30 °C results in better precision.

## **CHAPTER 4: SUMMARY AND FUTURE WORK**

In this experiment, water vapor was removed from the inlet sample to a PTR-MS using a constructed dehumidifier to increase the sensitivity of formaldehyde and eliminate the water dependent sensitivities of other polar compounds. With the dehumidifier in place, water vapor in the sample line was controlled to a dew point equal to the tube temperature resulting in increased sensitivity of the PTR-MS to formaldehyde and near removal of water vapor dependent sensitivity of several measureable volatile organic compounds (VOC's), including formaldehyde and acetaldehyde. Through laboratory testing of the dehumidifier, the optimal operating tube temperature and flow through the tube were determined to be -30 °C and ~ 250 sccm respectfully.

At normal operating conditions (drift tube field intensity = 120 Td), the normalized sensitivity increased by 5 fold with a decrease in water vapor at a dew point of 11 °C to a dew point of -30 °C. With the water vapor removed, the natural variability of humidity in the atmosphere was removed, resulting in water vapor independent VOC sensitivities. The drift tube field intensity could be operated in an uncharacteristic regimen (drift tube field intensity = 80 Td) where water clusters would normally dominate the drift tube kinetics. At this operating regimen, the normalized sensitivity of all compounds in the calibration mixture increased, resulting in lower detection limits. Also, the precision of formaldehyde was observed and quantified when water vapor was removed from the drift tube. The precision of a 1 ppbV formaldehyde signal at a dew point of -30 °C was increased by 30 % over a 1 ppbV signal at ambient dew point of  $\sim 25$  °C.

Work still remains to better understand the dehumidifier. The transmission of compounds through the dehumidifier is still not completely understood. The trends of the data suggest that the transmission efficiency of soluble compounds, such as methanol, is primarily impacted by the presence of a disordered quasi liquid layer present at dehumidifier temperatures greater than -30 °C and the transmission efficiencies of larger compounds, such as  $\alpha$ -pinene, decrease with colder dehumidifier temperatures. Transmission tests at a fixed sample humidity and variable trap temperatures should be performed to better understand the impact of absorption of soluble gases and adsorption of low vapor pressure compounds. The data collected for formaldehyde sensitivity as a function of dehumidifier temperature proved difficult to duplicate using the first generation dehumidifier. The first generation dehumidifier had the tube temperature sensor located on the outside of the tube and the measured temperature with that configuration was unreliable due to voltage interferences from the resistive heating wire. For the current generation of dehumidifiers, an ungrounded thermal probe is placed against the inside tube wall. Because the thermocouple probe is ungrounded, it is isolated from any voltage leakage from the resistive heating wire and no voltage interference from the heating wire is possible. Operation of the dehumidifier using the ungrounded thermocouples has proven reliable. The experiment should be repeated using the current dehumidifier configuration to more accurately characterize the formaldehyde sensitivity as it relates to dehumidifier temperature.

Several interferences impact formaldehyde measurements. Inomata et al., (2008) identified methyl hydroperoxide, methanol, and ethanol as positive interferences with interference ion to parent ion ratios of  $0.92 \pm 0.06$ ,  $0.0073 \pm 0.0002$ , and  $0.045 \pm 0.004$ , respectively. The reported values for Inomata et al. are instrument specific and the values must be quantified for individual PTR-MS instruments and specific drift tube operating conditions. To quantify the interferences, each interference species must be scanned separately and a mass scan spectrum produced to indentify the ratio of the interference ion to the parent ion.

Organic acids, such as formic acid and acetic acid proved to be difficult to measure though the dehumidifier. While attempting to quantify the normalized sensitivities of the two species, it was discovered that the conditioning periods for the compounds are excessive. For a 100 ppbV test mix of the acids to come to equilibrium with the tube walls at -30 °C and a flow ~250 sccm, formic acid required ~ 25 minutes and acetic acid required ~ 35 minutes. For seamless operation of the dehumidifier system, the tube cycles between a conditioning/back flush mode and sampling mode. One tube conditions and back flushes while the other tube samples. The time required for a tube to become plugged by ice during the sample period determines the total time of the cycle. At ambient humidity, the cycle time is typically shorter than the required time for the acids to come to equilibrium with the tube surface resulting in inaccurate measurements of the acids. To measure the acids with this dehumidification configuration would require an equipment alteration in order to lengthen the time before an ice plug forms. Also, the

smearing effects of variable acid concentrations through the dehumidifier would have to be quantified to determine the impact on precision and accuracy.

Finally, detection limits should be analyzed in further detail. The detection limits at a drift tube field intensity of 120 Td were calculated using data points during introduction of zero air (Figure 3.14) created from a VOC oxidizing catalyst. The zero periods do not reflect the true detection limit of the instrument, but reflect the detection limit of the calibration system (Figure 2.3) and PTR-MS conditioned to current VOC ambient concentrations. The VOC background of the PTR-MS varies with changing ambient VOC concentrations. To capture the true detection limit of the instrument only, the calibration system and PTR-MS must be conditioned with clean zero air for many hours removing VOC's adsorbed to the surfaces of the calibration system and PTR-MS. Also, the zero air generator output gas must be compared to a certified zero air standard to ensure that the zero air generator is producing zero air containing no VOC's.

The system offers many additional benefits other than increased sensitivity of formaldehyde. It could be used to measure and quantify the mixing ratio of other compounds, such as HCN and hydrogen sulfide, which are impacted by the negative effects on normalized sensitivity due to ambient water vapor content. HCN is a useful biomass tracer and is also emitted from automobiles (Knighton et al., 2009). Hydrogen sulfide is emitted from mainly plants on the continents and makes a large part of the marine system sulfur budget (Watts, 2000). In addition, the system could be implemented to measure formaldehyde fluxes out of both urban and rural atmospheres to

better understand the contribution of formaldehyde to the overall VOC budget and the oxidative capacity of the atmosphere. Finally, the system could be used to better understand ice-VOC interactions. The interactions of ice with VOC's in the extreme northern and southern latitudes drive much of the regions tropospheric chemistry (Dominè and Shepson, 2002). Langmuir isotherms could be calculated with smart application of the dehumidifier. A thin layer of pure ice could be deposited on the tube walls and then a VOC gas at a known concentration and flow rate pushed through the tube. The gas would deposit on the ice until a monolayer forms and the gas depositing on the ice comes to equilibrium with the gas flowing through the tube. The mass per surface area of ice could be calculated using the PTR-MS response to the gas and knowing the surface area of the ice coating on the tube. The described procedure could be done using trace levels of gas, much like atmospheric conditions.

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