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The effect of relative humidity on the detection of pyrrole by PTR-MS for OH reactivity measurements

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ABSTRACT

The hydroxyl radical (OH) is the most important atmospheric oxidant. Recently Sinha et al. [V. Sinha, J. Williams, J.N. Crowley, J. Lelieveld, Atmos. Chem. Phys. 8 (2008) 2213] developed a new method to measure the total OH reactivity of ambient air (OH sink) employing a proton transfer reaction mass spectrometer (PTR-MS) as a detector. The new method uses pyrrole (C_4H_4NH) as a reagent and for an OH reactivity measurement this species must be measured under both dry (~0% RH) and humid air (>30% RH). Here, we investigate the sensitivity dependence of the PTR-MS for pyrrole, as a function of relative humidity in the sampled air. Various normalizations with respect to the H_3O^+ ion and its different hydrated cluster ions $H_3O^+(H_2O)_{n=1,2,3}$ are compared. It is shown that both the primary ion signal (H_3O^+ ion $m/z = 19$) and the first water cluster ion $H_3O^+(H_2O)$ ($m/z = 37$) should be used for pyrrole quantification. However, in spite of using this normalization, the PTR-MS sensitivity for pyrrole changes by as much as 16% between dry (~0% RH) and humid air (above 30% RH), with higher sensitivity when the sampled air is humid. Thus, for accurate quantification of pyrrole using a PTR-MS, calibration factors appropriate to dry and humid air should be employed. We recommend that humidity dependence of the PTR-MS be taken into account when reactivity measurements are performed using the pyrrole based comparative reactivity method (CRM).

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1. Introduction

Hydroxyl radicals maintain the self-cleansing capacity of the atmosphere [2]. Measurements of the atmospheric sink of the hydroxyl radical (also referred to as the total OH reactivity of ambient air) are necessary for understanding and constraining the budget of the hydroxyl radical. In combination with ambient air measurements of the hydroxyl radical and its production processes (e.g., $O^1D + H_2O$), OH reactivity measurements provide a test for the accuracy of photochemical models [3,4]. Moreover direct measurements of the total OH reactivity allow quantification of the "missing" OH reactivity, as shown by Di Carlo et al. [5].

Sinha et al. [1] recently developed a new technique to directly measure the total OH reactivity of ambient air called the comparative reactivity method (CRM). Compared to existing OH reactivity measurement techniques which rely on accurate measurement of OH, by for example laser induced fluorescence, the new CRM technique is more economical, portable and applicable to many detector systems and other measurement groups have already started applying the CRM method for atmospheric measurements [6]. The CRM method as described by Sinha et al. employs pyrrole as the reagent molecule and a proton transfer reaction mass spectrometer (PTR-MS) as a detector. The PTR-MS technique was first applied for atmospheric measurements by Lindinger et al. in 1998 [7] and over the last decade has been used extensively for quantification of volatile organic compounds (VOCs) in the earth's atmosphere from aircraft, ships and ground based stations [8–10]. While the influence of humidity on the PTR-MS sensitivity for typical ambient air VOCs, such as methanol, acetone, isoprene, benzene, toluene and monoterpenes has been reported previously [8,11,12], no study regarding the humidity influence on the PTR-MS sensitivity for pyrrole exists. The humidity of sampled air affects the partitioning of the primary ion signal within the PTR-MS between the hydronium ion (H_3O^+; $m/z = 19$) and the hydrated hydronium ion water clusters ($H_3O^+(H_2O)_n$; $n = 1, 2, 3$). This in turn leads to a change in the PTR-MS sensitivity for VOCs that have different rates of reaction with the H_3O^+ ion and the hydrated water cluster ions such as $(H_2O)H_3O^+$ ($m/z = 37$). Accurately accounting for the humidity dependence of pyrrole detection in the PTR-MS is necessary for correct determination of OH reactivity using the new method developed by Sinha et al. [1].

Here, we investigate the influence of relative humidity, on the sensitivity of the PTR-MS system to pyrrole, under conditions preva-

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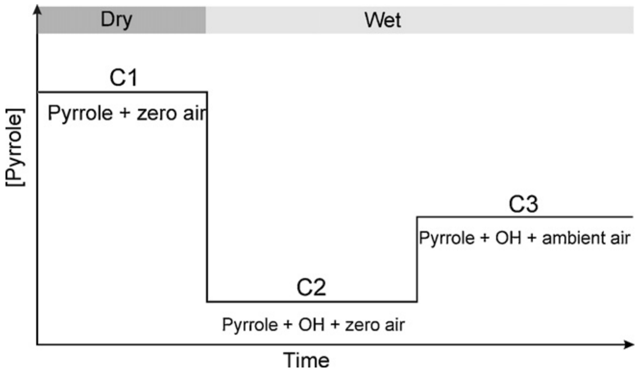

Fig. 1. Schematic illustrating concept of the comparative reactivity method with shaded regions showing the prevalent humidity regimes.

lent during typical CRM OH reactivity measurements. We also examine the impact of using different normalization procedures to obtain the PTR-MS sensitivity for pyrrole and recommend a calibration method for the specific application of conducting OH reactivity measurements using a PTR-MS.

2. Experimental

At the outset, it is worthwhile to reiterate the stages of a typical comparative reactivity measurement bearing in mind the prevalent humidity regimes.

2.1. The comparative reactivity method

Fig. 1 illustrates the general concept of the comparative reactivity method. This discussion is confined to those parts that are relevant for studying the sensitivity dependence of the PTR-MS for pyrrole under different humidity regimes. For a more detailed description of the method the reader is referred to Sinha et al. [1].

Pyrrole (C_4H_5N; M.W.: 67 g/mol) is introduced into a glass reactor and its concentration $C1$ is monitored with a PTR-MS, in the air exiting the reactor. Note that at this point the air matrix entering the PTR-MS is dry, as the OH source has not been switched on. After some time when $C1$ is well determined, synthetically generated OH radicals (OH < [Pyrrole]) are introduced into the reactor at a constant rate to react with pyrrole. At this point the humidity in the glass reactor changes significantly as OH is generated by the photolysis of water vapour, carried into the glass reactor by nitrogen passed over a water bubbler. $C1$, the initial concentration of pyrrole now decreases to $C2$, due to the reaction of pyrrole with the OH radicals. The decrease in the monitored concentration of pyrrole (from $C1$ to $C2$) gives the initial concentration of the OH radicals, as all the OH is completely titrated by pyrrole. Next, an air sample containing OH reactants is introduced into the glass reactor. At this point the humidity regime in the reactor is almost the same as the humidity of the introduced ambient air. The various OH reactants present in ambient air then compete with pyrrole for the available OH radicals, so that the concentration of pyrrole in the air exiting the reactor increases to $C3$. Comparing the amount of pyrrole exiting the reactor without ($C2$) and with the ambient air ($C3$) allows the introduced air sample's OH reactivity to be determined in a quantitative manner, provided the system is suitably calibrated. Knowing the rate coefficient of pyrrole with the hydroxyl radical ($k_p = 1.2 \pm 0.15 \times 10^{-10}$ molecules $\mathrm{cm^{-3}\,s^{-1}}$), the measured signals can be converted to the OH reactivity of the introduced air sample using the following equation:

$$R_{\mathrm{air}} = \frac{(C3 - C2)}{(C1 - C3)} \cdot k_p C1 \qquad (1)$$

2.2. Humidity experiments with the PTR-MS

Details about the PTR-MS system used, including its mass identifications, sensitivity and detection limits are given elsewhere [13,14]. Hence only a brief description is provided here. The entire inlet system of the PTR-MS including switching valves is made of Teflon. The instrument was operated at a drift tube pressure of 2.2 mbar, drift tube voltage of 600 V and drift tube temperature of 318 K, in the selected ion monitoring mode with a dwell time of 1 s for $m/z = 68$ (protonated mass of pyrrole). Within the instrument, organic species with a proton affinity greater than water are chemically ionised by proton transfer reactions with H_3O^+ ions and the products are detected using a quadrupole mass spectrometer [7]. Pyrrole is detectable by the PTR-MS since its proton affinity ($209.2\ \mathrm{kcal\,mol^{-1}}$) is higher than that of water ($165.2\ \mathrm{kcal\,mol^{-1}}$) and the signal is observed without fragmentation at $m/z = 68$ ($C_4H_5NH^+$). There are no other known species in ambient air that could interfere at $m/z = 68$ within the PTR-MS, and most ambient air species detectable by PTR-MS (e.g., methanol, acetone, acetaldehyde and isoprene) are detected at odd masses after protonation. While this description of chemical ionization in the PTR-MS is inherently attractive in its simplicity, water clusters of the form $H_3O^+(H_2O)_n$ (with $n \geq 1$) are also, at least transiently, present in the drift tube in a distribution dependent on the number density of water molecules entering the drift tube and the energetic conditions therein [12]. Many chemicals also react with higher water clusters of the hydronium ion (e.g., ammonia). The unique distribution of water clusters $H_3O^+(H_2O)_n$ in combination with variable reactivity of analyte chemicals with these clusters gives rise to a humidity dependence for detection with the PTR-MS technique.

In order to ascertain how the PTR-MS signal sensitivity for pyrrole, changes as a function of the relative humidity, five different mixing ratios of pyrrole were measured with the PTR-MS (range = 10–100 $\mathrm{nmol\,mol^{-1}}$; the typical pyrrole mixing ratio range during a CRM experiment), and at each of these mixing ratios, the relative humidity of the introduced air sample was varied between circa 0% RH, 30% RH, 50% RH, 70% RH and 90% RH, respectively.

Humidification of the dry zero air (Synthetic air, Westfalen A.G., Germany, 99.999% purity, <0.5 $\mathrm{\mu mol\,mol^{-1}}$ THC) was accomplished using a commercial humidifier (Bronkhorst, Germany). The humidifier consists of three basic units: the first unit is a heated water tank which leads through a digital μ-flow meter (μ-flow 0–1.2 $\mathrm{g\,h^{-1}}$ range, Bronkhorst, Germany) into the second unit, which is a controlled evaporation mixer system (CEM, Bronkhorst, Germany). The third unit of the humidifier is a zero air mass flow controller (EL-Flow, Bronkhorst, Germany) which regulates how much of the zero air mixes with the water vapour. The flows and temperature of the CEM are controlled using a digital panel (Bronkhorst, Germany).

At the start of the experiments, the Teflon lines were flushed with a mixture of dry synthetic air ($1146 \pm 2\ \mathrm{cm^3\,min^{-1}}$) and pyrrole ($3.36 \pm 0.01\ \mathrm{cm^3\,min^{-1}}$) for more than an hour to condition the lines and stabilize wall effects. Thereafter, different flows of pyrrole (Westfalen A.G., Germany, stated uncertainty 5%; 10 $\mathrm{\mu mol\,mol^{-1}}$ in N_2) were diluted using a constant dry or humidified zero air stream of 1146 $\mathrm{cm^3\,min^{-1}}$ to yield pyrrole mixing ratios of circa 10 $\mathrm{nmol\,mol^{-1}}$, 30 $\mathrm{nmol\,mol^{-1}}$, 50 $\mathrm{nmol\,mol^{-1}}$, 70 $\mathrm{nmol\,mol^{-1}}$ and 100 $\mathrm{nmol\,mol^{-1}}$, before being introduced into the PTR-MS inlet via a Teflon T-connector. Forty measurement cycles (2 × 20 cycles; ~0.3 Hz measurement frequency) were taken at each of the five pyrrole dilutions (circa 10, 30, 50, 70 and 100 $\mathrm{nmol\,mol^{-1}}$) and relative humidity set points (0%, 30%, 50%, 70%, and 90% RH). All the flows were verified both before and after the experiments using a bubble flow meter (Gillian Inst. Corp., Sensidyne, USA).

3. Results and discussion

In order to determine the sensitivity (calibration factor) for converting the measured PTR-MS signal in counts per second (cps) to nmol mol^{-1} (or ppb) of pyrrole, the measured signals at $m/z = 68$ are normalized using the concurrently measured primary ion signals due to H_3O^+ and $H_3O^+(H_2O)_n$ ($n = 1, 2, 3$). Normalizing the signal to the total number of parent ions aids in intercomparison of instruments having variable reaction conditions and can partially account for varying reactivity of a chemical with respect to the variety of distributions of parent ions produced as humidity varies over time. Expressing the measured signals in normalized counts per second (ncps) also ensures that slight fluctuations in the amount of primary ions, the drift tube pressure and the drift tube temperature, do not add to the noise of the measured signals at $m/z = 68$. The measured signals in cps were normalized to a drift tube pressure of 2 mbar, drift tube temperature of 298.15 K, and a total of one million parent ions employing the following combinations Case (1) only $m/z = 19$; Case (2) the sum of $m/z = 19$ and $m/z = 37$; Case (3) the sum of $m/z = 19$, $m/z = 37$ and $m/z = 55$; Case (4) the sum of $m/z = 19$, $m/z = 37$, $m/z = 55$ and $m/z = 73$.

Expressed as an equation this is

$$\mathrm{NCPS} = \frac{I(\mathrm{RH}^+) \times 10^6}{\sum_{n=1}^{x} I(\mathrm{H_3O^+(H_2O)}_{n-1})} \times \frac{2}{P_{\mathrm{drift}}} \times \frac{T_{\mathrm{drift}}}{298.15} \qquad (2)$$

where $x = 1, 2, 3$ and 4 in Eq. (2) for Case 1, Case 2, Case 3 and Case 4, respectively. $I(\mathrm{RH}^+)$, $I(\mathrm{H_3O^+})(\mathrm{H_2O})_{n-1}$ are the ion signals of the protonated pyrrole ion, and the hydrated water reagent ions, P_{drift} is the measured drift tube pressure (~2.2 mbar) and T_{drift} is the measured drift tube temperature (~318.15 K), respectively. NCPS is the total ion signal of the protonated pyrrole ion normalized to 10^6 cps of reagent ions for 2 mbar drift tube pressure (P_{drift}) and 298.15 K. Eq. (2) is identical in form to the normalization equation used by Tani et al. [11] except for the additional temperature normalization term.

To avoid overloading the SEM ion counter within the detector, we monitored $m/z = 21$ ($H_3{}^{18}O^+$ ion) instead of $m/z = 19$ (H_3O^+ ion), a standard practice in PTR-MS studies. The natural abundance ratio of the oxygen isotopes ^{16}O to ^{18}O is 500:1. Thus, by multiplying the measured $m/z = 21$ ion signal by 500 we obtained the primary ion signal for $m/z = 19$ (H_3O^+ ion). The hydrated water ions $(H_2O)H_3O^+$, $(H_2O)_2H_3O^+$, $(H_2O)_3H_3O^+$, correspond to $m/z = 37$, $m/z = 55$ and $m/z = 73$, respectively. Typically, the primary ion signal including all water clusters is of the order of 10 million or higher and varies on the order of a few percent during an experimental session.

For the instrumental background at $m/z = 68$, we took the background signal due to zero air at this m/z ratio, as the single platinum catalyst was unable to completely oxidize higher mixing ratios of pyrrole (>30 nmol mol^{-1}). Note that the usual method of obtaining the background signal during PTR-MS studies of ambient air is by using a platinum catalyst scrubber that completely oxidizes carbon containing organics to CO_2, but for this particular application such an approach was found to be unsuitable.

Fig. 2 shows the pyrrole signal ($m/z = 68$) normalized using various combinations of primary ions on the vertical axis against the mixing ratio of pyrrole introduced into the PTR-MS under dry (0% RH) and humid conditions (70% RH) on the horizontal axis. While it is the absolute humidity of the sample air that affects the partitioning between the H_3O^+ ion and the water cluster ions $H_3O^+(H_2O)_n$ ($n = 1, 2, 3$), here we use relative humidity as it is a convenient index of ambient air humidity. This example demonstrates the linearity of the PTR-MS signal over the range of pyrrole mixing ratios used (10–100 nmol mol^{-1}). The slope of a linear fit to the calibration data defines the sensitivity, which is given in units of ncps/ppbv. For data shown in Fig. 2, normalizations were performed with respect to the primary ion signal at $m/z = 19$ and the first water cluster ion ($m/z = 37$; $H_3O^+(H_2O)$). The horizontal error bars represent the total uncertainty of the pyrrole mixing ratio, comprising of the uncertainty in the measured flows and the inherent uncertainty of the pyrrole standard (5%), while the vertical error bars represent the overall statistical noise of the measured signal. While excellent linearity ($r = 0.99$) is observed for both the dry and humid air conditions, it can also be seen that there is a clear difference in sensitivity for the two cases.

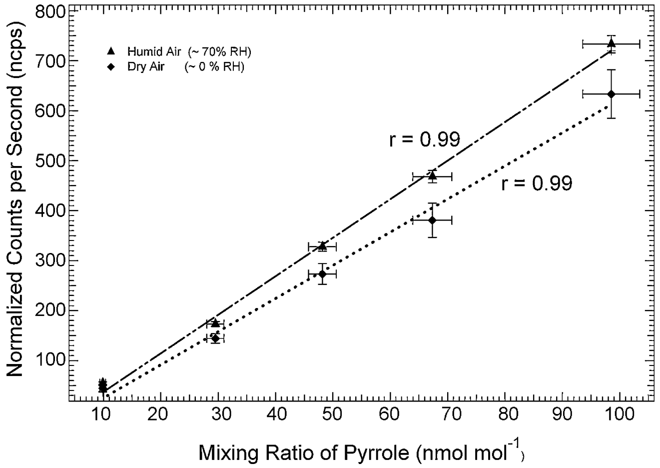

Fig. 2. Plot showing the linearity of the PTR-MS signal under both dry (~0% RH) and humid air (~70% RH) conditions.

Fig. 3 summarizes the results of all the experiments. The sensitivities obtained using different normalizations, expressed in normalized counts per second per nmol mol^{-1} of pyrrole (ncps/ppbV), is plotted on the vertical axis against the relative humidity (%) of the sampled air, on the horizontal axis. Note that the result of normalizing the measured pyrrole signals with respect to $m/z = 19$ and $m/z = 37$, is the same as the result obtained by normalizing it using these two ions and the subsequent water cluster ions (namely $m/z = 55$; $m/z = 73$). The sensitivity trend after 50% RH, for normalization performed using both the H_3O^+ and the $H_3O^+(H_2O)$ ions ($m/z = 19$ and $m/z = 37$, respectively) hardly changes, while the sensitivity trend for normalization employing only the H_3O^+ ion seems to increase slightly after 50% RH. The most noteworthy feature, however, is the significant increase

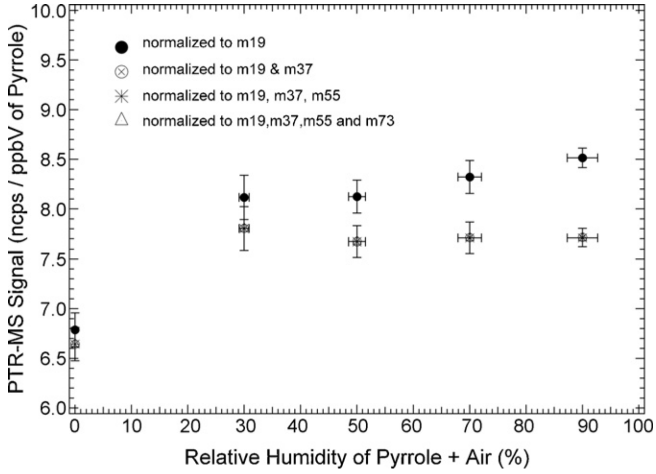

Fig. 3. Summary of all the results showing the sensitivity obtained using different normalizations (vertical axis; markers) against the relative humidity of sampled air (horizontal axis).

in sensitivity between dry air conditions (0% RH) and humid air conditions (30% RH and higher), with the increase being higher for the case where the normalization is done only with respect to the H_3O^+ ion (∼21%) compared to the other normalizations (∼16%). Note also that above 30% RH the sensitivity change for all normalization procedures involving two or more water clusters is statistically insignificant. The higher sensitivity under humid conditions (above 30% RH) is related to the increased fraction of the water cluster ions such as $m/z = 37$ and $m/z = 55$ in the drift tube of the PTR-MS with respect to the primary ion signal ($m/z = 19$) [12]. Pyrrole has a proton affinity (209.2 kcal mol^{-1}) comparable to that of ammonia (P.A. = 203.1 kcal mol^{-1}) and isoprene (P.A. = 200.4 kcal mol^{-1}), but significantly higher than aromatics such as benzene (P.A. = 181.3 kcal mol^{-1}) and toluene (P.A. = 189.8 kcal mol^{-1}. Spanel and Smith [15] have previously reported that because of the exceptionally high proton affinity of isoprene (C_5H_9), it can react with the monohydrate $H_3O^+(H_2O)$ ion to form the weakly bound $C_5H_9{}^+$ H_2O ion, which later thermally dissociates (2.4 kcal mol^{-1}) to form $C_5H_9{}^+$ (before reaching the detector). Due to its even higher proton affinity, it is very likely that pyrrole undergoes similar reactions resulting in higher PTR-MS sensitivity for pyrrole under humid conditions. Although Warneke et al. [12] investigated the humidity dependence of the PTR-MS sensitivity for isoprene at a drift tube pressure of 2.3 mbar (close to the operating drift tube pressure of 2.2 mbar used in this study) and reported no significant change in sensitivity, it should be borne in mind that the humidity range covered in that study was 20% RH or higher. In fact in the present study also no statistically significant change was observed for PTR-MS sensitivity to pyrrole at 30% RH or higher. It is also possible that ligand switching reactions with the $H_3O^+(H_2O)$ ion, similar to that for ammonia (P.A. = 203.1 kcal mol^{-1}) [15], give rise to the enhanced PTR-MS sensitivity for pyrrole under humid conditions. Both possibilities are consistent with the fact that normalizations involving one or more of the $H_3O^+(H_2O)_{n=1,2 \text{ and } 3}$ ions yield the same results. The humidity dependence of PTR-MS sensitivity is chemical specific and has been investigated for a number of species, although not yet for pyrrole [11,12,15]. For some species, the sensitivity decreases with increasing humidity. Benzene and toluene, with proton affinities of 181.3 kcal mol^{-1} and 189.8 kcal mol^{-1}, respectively, are examples of this trend. The $H_3O^+(H_2O)$ ion has an estimated proton affinity of 193 kcal mol^{-1} making reaction of either benzene or toluene with this ion energetically unfavourable [12,15]. For pyrrole (P.A. = 209 kcal mol^{-1}) reaction with the hydrated water ion $H_3O^+(H_2O)$ ion (P.A. = 193 kcal mol^{-1}) is energetically feasible and the most likely cause for increased sensitivity between dry air (∼RH of 0%) and humid air (>30% RH) conditions within the PTR-MS.

The implications of these new results are quite significant for CRM OH reactivity measurements performed using a PTR-MS. As shown in Fig. 1, $C1$ (the initial pyrrole mixing amount available for reaction with OH) is measured under dry conditions and so the dry calibration factor should be applied for converting the ncps of $C1$ to nmol mol^{-1}. From the presented results in Fig. 3, it is also clear that normalization of the measured pyrrole signals should be performed using both the $m/z = 19$ and $m/z = 37$ ions. Moreover, wet calibration factors should be used to convert the measured $C2$ and $C3$ signals (see Fig. 3) from ncps to nmol mol^{-1}. This will ensure accurate quantification of the measured OH reactivity, which is obtained using Eq. (1). Note also that according to Eq. (1), the sensitivity change of the PTR-MS between dry and wet air conditions for pyrrole causes the measured OH reactivity to scale non-linearly and hence a linear correction factor based on only the dry or wet calibration factor should not be applied to the measured OH reactivity.

4. Conclusion

A detailed study of the PTR-MS sensitivity to pyrrole as a function of humidity under typical CRM OH reactivity measurement conditions has been carried out. The results show that the sensitivity changes by as much as 16% between dry (∼0% RH) and humid air (above 30% RH) conditions, with higher sensitivity when the sampled air is humid. Normalizations using both the primary ion signal due to the H_3O^+ ion ($m/z = 19$) and the first water cluster ion $H_3O^+(H_2O)$ ($m/z = 37$) should be employed for the calculations. Furthermore, the appropriate dry or wet calibration factors should be applied for converting the measured pyrrole signals ($C1$, $C2$ and $C3$) to mixing ratios by measurement groups that have already started using the CRM method for OH reactivity measurements. As ambient air humidity is typically higher than 30% RH in most natural environments we recommend the use of the wet calibration factor for even ambient air measurements of pyrrole. Other applications that involve PTR-MS measurements of a particular reagent molecule under both humid and dry conditions should be similarly tested for humidity dependence of the PTR-MS sensitivity.

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