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Effect of water vapour pressure on monoterpene measurements using proton transfer reaction-mass spectrometry (PTR-MS)

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Abstract

The effects of water vapour pressure (WVP) on the fragmentation of seven monoterpene and related C_{10} volatile organic compounds (VOCs) in the drift tube of a proton transfer reaction-mass spectrometer (PTR-MS) were investigated. In addition, the combined effects of varying WVP and the ratios of electric field strength to number density of the buffer gas (E/N) were investigated in detail for three of these compounds, the monoterpenes α-pinene and sabinene plus the related C_{10} VOC *p*-cymene.

Under normal operating conditions (E/N = 124 Td), WVP affected the fragment patterns of all compounds with the exception of β-pinene and the three oxygenated C_{10} VOCs. WVP had a significant effect on the fragment patterns of α-pinene and sabinene at the lower E/N ratios (around 80 Td) but had little effect on fragmentation towards the higher E/N ratios used here (∼142 Td). On the other hand, *p*-cymene fragmentation was most affected by WVP under normal operating conditions.

PTR-MS sensitivity towards the three compounds was also considered under three conditions where reaction was assumed with (1) H_3O^+ only; (2) H_3O^+ and $H_3O^+H_2O$; and (3) H_3O^+, $H_3O^+H_2O$ and $H_3O^+(H_2O)_2$. Our results indicate that α-pinene and sabinene react not only with H_3O^+ and $H_3O^+H_2O$ via direct proton transfer but also with $H_3O^+(H_2O)_2$ via ligand switching. *p*-Cymene seems to react only with H_3O^+ via direct proton transfer and with $H_3O^+H_2O$ via ligand switching. It is speculated that the WVP effect on fragmentation results from the differing abundances of hydrated reagent ions which causes different frequencies of individual reactions to occur, thus, determining how ‘soft’ the overall reaction is. These results also indicate that under normal conditions, a correction should be made for WVP if the concentration of *p*-cymene in air samples is to be determined from the single ion signal of either protonated molecular ions or the most dominant fragment ions.

Keywords: Water vapour; Monoterpene measurements; PTR-MS; Volatile organic compounds; Fragmentation

1. Introduction

Many compounds in the monoterpene family ($C_{10}H_{16}$) are produced by tree species and emitted into the atmosphere as a result of their high volatilities. They represent a significant fraction of the total volatile organic compound (VOC) flux from the biosphere to the atmosphere. Their mechanisms of formation and rates of emission, plus their roles in atmospheric chemistry, are reviewed extensively by Fall [1] and Fehsenfeld et al. [2] respectively, and elsewhere.

Measurement of the atmospheric concentrations and biogenic emission rates of the monoterpenes and related VOCs are necessary if their roles in plant biochemistry, plant physiology and atmospheric chemistry are to be understood and quantified. However, the low emission rates and atmospheric concentrations of these compounds render their analysis difficult. Until recently, their determination has relied upon pre-concentration with subsequent off-line analysis by gas chromatography with, typically, flame ionisation or mass

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spectrometric detection. Recently, proton transfer reaction mass spectrometry (PTR-MS), using protonated water (H_3O^+) as the primary ionising reactant, has been developed, allowing the on-line monitoring of VOCs, including the monoterpenes and related compounds [3]. The transfer of protons from H_3O^+ to neutral entities can be regarded as 'soft' ionisation and, under 'normal' PTR-MS operating conditions (detailed below), many VOCs are detected as their molecular mass plus one. However, the monoterpenes have been observed to undergo some degree of fragmentation within the instrument [4–6].

In a previous paper [6], we investigated their fragment patterns in detail and showed that the monoterpenes α- and β-pinene, 3-carene and limonene produced fragment ions of masses 67, 81 and 95, while the related VOC *p*-cymene ($C_{10}H_{14}$) produced ions of masses 41, 91, 93 and 119. The fragment patterns were observed to vary as a function of E/N (where E is the electric field strength and N the buffer gas number density in the drift tube). We also showed that water vapour pressure (WVP) in the inlet air affected the fragment pattern for *p*-cymene, limonene and 3-carene at E/N of 120 Td (Td: Townsend; 1 Townsend = 10^{-17} V cm^2). In particular, we showed that for *p*-cymene, the relative abundance of the protonated non-isotopic molecular ion (mass 135) increased from 23 to 31% following a relative WVP (RH) change from 26 to 100% at 21 °C. This result indicates that in order to measure monoterpene concentrations as precisely as possible, the effect of WVP on the monoterpene fragment patterns at different E/N values should be investigated and the cause of this fragment pattern change addressed.

In the present study, we use a diffusion system to maintain constant vapour concentrations of monoterpenes and related compounds across various WVP ranges. The fragment patterns of two compounds in the monoterpene family (α-pinene and sabinene ($C_{10}H_{16}$)), plus one compound related to the monoterpenes (*p*-cymene ($C_{10}H_{14}$)) are investigated at different WVPs and E/N ratios. For other monoterpene compounds, the effect of WVP on the fragment patterns are measured at normal measurement conditions and the importance of WVP correction is emphasised for specific measurement conditions.

2. Experimental methods

2.1. PTR-MS instrumentation

The PTR-MS (Ionicon GmbH, Innsbruck) has been described in detail elsewhere [3,7], as has its operational characteristics [8]; therefore, only the points relevant to this paper are given here. The PTR-MS consists of three parts: an ion source, a drift tube (reaction chamber) and an ion separation/detection system. H_3O^+ ions formed in the hollow cathode ion source react with neutrals (R) in the drift tube, undergoing proton transfer reactions, if the proton affinity (PA) of the neutral R is higher than that of water. On the other hand, the major components of air undergo non-reactive collisions with H_3O^+ ions because of their lower proton affinities. The resultant product ions (RH^+) are separated by a quadrupole mass spectrometer (Balzers QMG421) and detected as ion counts per second (cps) by a secondary electron multiplier. The signals are corrected for instrumental mass discrimination coefficients.

H_3O^+ ions may also become hydrated to produce $H_3O^+(H_2O)_n$ cluster ions, although under the 'normal' operating conditions described herein (RH of 20–30%, an ambient temperature of 21 ± 1 °C, and a drift tube E/N of 122–124 Td), the ratio of the densities of $H_3O^+H_2O$ to H_3O^+ in the drift tube is usually less than 3%. The E/N range between 120 and 140 Td has been regarded as a compromise between minimising water cluster ion formation, which could obscure the mass spectra, and suppression of product ion fragmentation which would complicate the identification of the target analytes [3]. Since the density of H_3O^+ ions, $[H_3O^+]$, is high in the drift tube, and only a small fraction of the H_3O^+ ions reacts with the neutrals, $[H_3O^+]$ remains constant and pseudo-first order reaction kinetics are maintained. Under these conditions, the density of product ions $[RH^+]$ is given by:

$$[RH^+] \approx [H_3O^+][R]kt \qquad (1)$$

where $[H_3O^+]$ is the density of H_3O^+, [R] the molecular ion density of trace component R, k the reaction rate coefficient for the proton transfer reaction between R and H_3O^+ and t is the time taken for H_3O^+ ions to traverse the drift tube. The k values the reactions between monoterpenes and H_3O^+ ions were experimentally determined to be $(2.2 - 2.5) \times 10^{-9}$ cm^3 s^{-1} and that of *p*-cymene was 2.5×10^{-9} cm^3 s^{-1}. The application of PTR-MS to measurements of relevance to environmental science has recently been reviewed by Hewitt et al. [9].

2.2. Standard preparation and water vapour pressure (WVP) control

In order to investigate the effects of WVP of the inlet air and of the values of E/N on these fragment patterns, a diffusion system was constructed. A range of nominal gaseous concentrations can be produced with this system (Fig. 1). An air stream, dried by $CaSO_4$ and purified by charcoal fil-

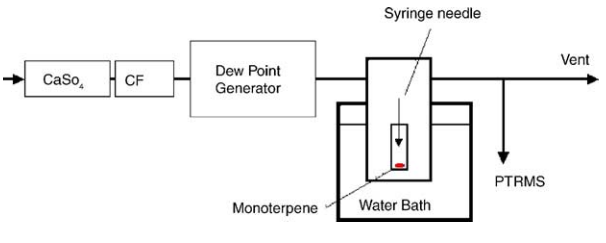

Fig. 1. Schematic diagram of a diffusion system for preparing standard atmospheres, CF: charcoal filter.

tration, was passed through a dew point generator (LI-610, LI-COR, USA) and a temperature controlled (293–358 K, with an accuracy of ±0.1 K) monoterpene diffusion system. The air flow through the system was maintained by a pump built into the dew point generator, and regulated with the mass flow controller at a flow rate of 0.9 L min^{-1}, before being diverted through the diffusion chamber and introduced to the PTR-MS inlet. Water vapour pressure of the air was varied from 0.59 to 2.4 kPa, which is equivalent to a relative humidity of 28–98%. The diffusion system consisted of a glass chamber (~100 mL) housing a sealed vial (1.5 mL) containing 10–20 μL of a pure monoterpene standard. The septum of the vial was pierced by a syringe, enabling monoterpene vapour to diffuse out at a constant nominal rate into the air stream. The resultant air stream was sampled by PTR-MS. Monoterpene concentrations of 10^2–10^3 ppbv were achieved by manipulation of the water bath temperature.

The purities of the α-pinene (Aldrich, UK), sabinene (R.C. Treatt, UK) and *p*-cymene (Fluka, UK) liquid standards were 98, >70 and 95%, respectively. Their respective purities in the vapour phase were quantified by GC-FID and found to be 99, 90 and 98%, respectively, which is higher than their purities in the liquid phase due to vapour pressure differences. Ions derived from both standards and impurities were carefully identified by three methods described previously [6]. Their concentrations in the vapour phase used for this experiment were in the range 350–550 ppbv.

2.3. PTR-MS operation

Sample air containing constant concentrations of monoterpenes was introduced to the PTR-MS drift tube via a ~1 m length of 1/8 in. o.d. PFA tubing at a flow rate of 9.6 or 11.8 mL min^{-1}. To assess fragment patterns, the E/N of the drift tube was increased to 142 Td and decreased to 82 Td from the normal value of 124 Td by altering the drift tube voltage (400–600 V) and pressure (0.18–0.21 kPa), respectively. The water vapour flow into the ion source was controlled at 7 mL min^{-1}. The mean relative center-of-mass kinetic energies, KE_{ion}, calculated from ion mobility data [10] were found to be 0.09, 0.22 and 0.31 eV for E/N values of 82, 124 and 142 Td, respectively.

Water vapour pressure was found to be linearly correlated with the ion signal of mass 37 ($H_3O^+\ H_2O$) at an E/N of 124 Td and with the ion signal of mass 55 ($H_3O^+(H_2O)_2$) at an E/N of 82 Td. These masses were therefore monitored continuously. Even at zero RH in the inlet air, a small amount of water exists in the drift tube from the ion source [7]. By extrapolating the linear relationships to the points where the $H_3O^+H_2O$ signal was zero, the water vapour density entering from the ion source was calculated to be equivalent to 20% relative WVP when the sample air temperature was 294 K.

2.4. Sensitivity calculation

The PTR-MS sensitivity is expressed as:

$$\text{Sensitivity} = \frac{\text{SCPS}}{\{\mathrm{R_c}\}} \qquad (2)$$

where $\{\mathrm{R_c}\}$ is the concentration of the target compound and determined with GC-FID method [6] in this experiment. SCPS is the total ion signal of the relevant ions standardised to 10^6 cps of reagent ions and for 2 kPa drift tube pressure, and defined as follows

$$\text{SCPS} = \frac{\sum i(\text{RI}) \times 10^6}{\sum_{n=1}^{3} i(H_3O^+(H_2O)_{n-1})} \times \frac{2}{p_{\text{drift}}} \qquad (3)$$

where p_{drift} is the drift tube pressure. The sensitivities for the three compounds were obtained from Eqs. (2) and (3).

3. Results

3.1. Changes in ion signals during measurement

Fig. 2 shows the ion count rates of masses 81 and 137 derived from α-pinene at different drift tube E/N ratios under various water vapour pressures in the inlet air. Integration time for the measurements of ions originating from the target compounds and from the reagent ions was 2–5 s each and therefore the total measurement interval was 20–30 s. Individual data sets at each given water vapour pressure and E/N ratio showed that the ion signals of masses 81 and 137 were almost constant and had small standard deviations. Although the measurements were carried out at almost constant concentrations of the standard monoterpene vapours, the concentrations were observed to slightly increase or decrease with time. All the data sets were corrected for these slight changes in the ion signals.

3.2. Fragment patterns affected by WVP at different values of E/N

Since we have shown in our previous paper [6] that the dominant fragment ions for α-pinene and sabinene were masses 67, 81 and 95 and for *p*-cymene were masses 41, 91, 93 and 119, signals for these ions and their ^{13}C mono-substituted ions were monitored, as well as the non-isotopic and ^{13}C mono-substituted protonated molecular ions, at differing WVP and collisional energy conditions. The major non-isotopic ion signals are presented in Fig. 3 as percentages of the total ion signal of all ions that originated from the target compounds.

The relative abundance of the protonated molecular ion (mass 137) for α-pinene, measured at E/N of 103 Td, increased from 61 to 67% when the water vapour pressure was increased from 0.59 to 2.40 kPa. On the other hand, the fraction of mass 81 decreased from 29 to 23% across this WVP

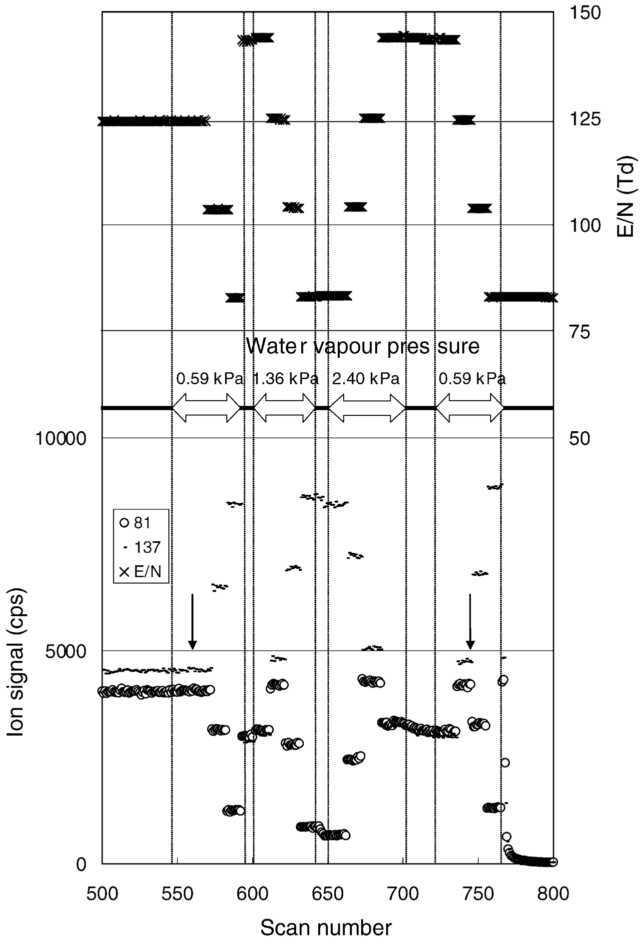

Fig. 2. Change in ion signals of mass 81 and 137 derived from α-pinene resulting from different drift tube *E*/*N* ratios and water vapour pressures. *E*/*N* ratio was changed by varying the electric field strength *E* (41.7–62.5 V cm^{-1}) and drift tube pressure (0.18–0.21 kPa). An *E*/*N* ratio less than 124 Td was, in many cases, achieved at 0.21 kPa, but, in some cases, achieved at 0.18 kPa, by changing *E*, accordingly. For example, an *E*/*N* ratio of ∼124 Td could be achieved at two parameter sets: 62.5 V cm^{-1} and 0.21 kPa, and 52.1 V cm^{-1} and 0.18 kPa. In this paper, however, only the data obtained at 62.5 V cm^{-1} *E* were used for fragment pattern analysis at *E*/*N* ratios less than 125 Td. Arrows show the signals at *E*/*N* ratio of 124 Td which were used for signal correction, assuming the change was linear.

range. The effect of WVP on the α-pinene fragment patterns was more pronounced at a lower *E*/*N* range (82–103 Td), but the sum of the relative abundances of the two dominant ions (81 + 137) was not affected by WVP.

Although the relative abundances of masses 81 and 137 for sabinene were different from those of α-pinene, the effect of WVP on the sabinene fragment patterns was similar to that on α-pinene. The vapour resulting from the sabinene standard was found to include 10% impurities, most of which were other monoterpenes (determined by GC-FID and GC-MS analyses). Since the other monoterpenes produce fragment ions which are similar to those for either sabinene or α-pinene [6], and show similar fragment patterns (35–50% for mass 81 at *E*/*N* of 124 Td), the 10% of impurity in the vapour phase of the sabinene stan-

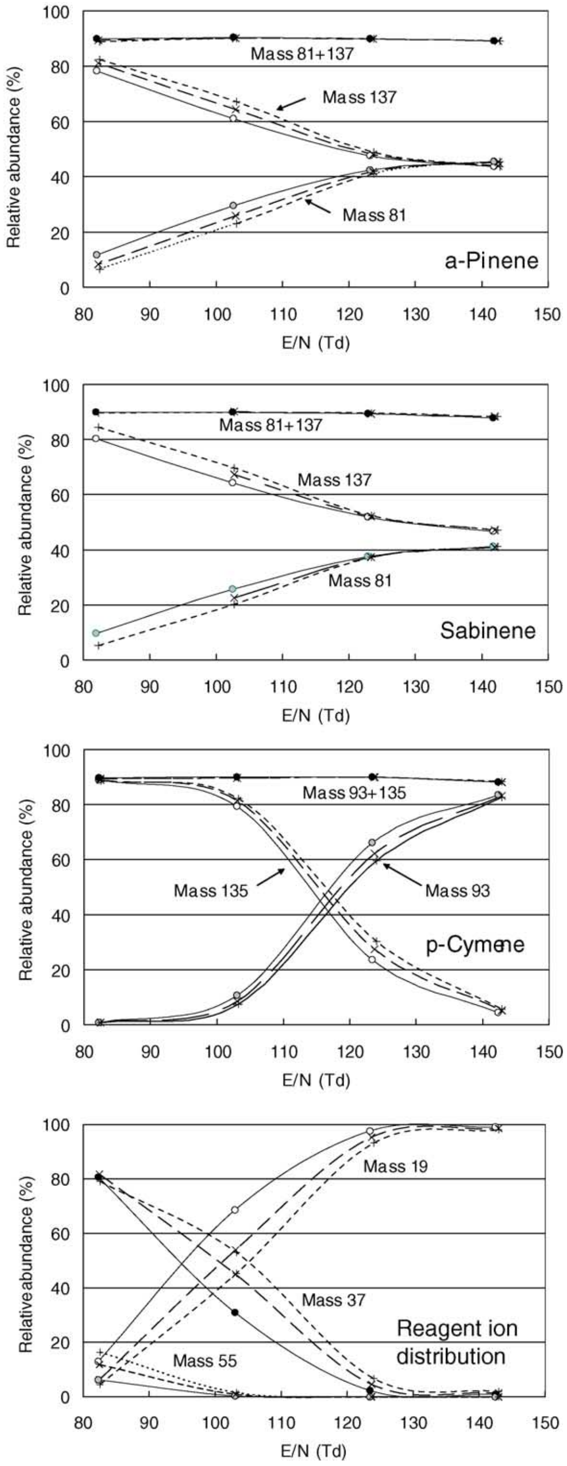

Fig. 3. Fragment patterns of major ions derived from α-pinene, sabinene and *p*-cymene and the reagent ion distribution as affected by *E*/*N* and water vapour pressure of the inlet air. Solid, broken and dotted lines indicate the data measured at water vapour pressure of 0.59, 1.36 and 2.40 kPa, respectively. Ions originating from α-pinene and sabinene are masses 67, 81, 95 and 137. Ions originating from *p*-cymene are masses 41, 91, 93, 119 and 135. The relative abundance of the major ions is expressed as their percentage relative to the total signal of all the ion products. The reagent ion distribution was the same in the three experiments.

dard did not significantly alter the fragment ion distribution.

As shown in our previous paper [6], *p*-cymene had an abundant fragment ion at mass 93, the ion signal of which was much higher than that of mass 135 at high *E*/*N* (124–142 Td). The effect of WVP was most pronounced at *E*/*N* of 124 Td and least evident at the highest (142 Td) and lowest (82 Td) *E*/*N* ratios. The relative abundance of the sum of masses 93 + 135 was not, however, affected by WVP across the WVP range.

3.3. Ratio of protonated molecular ion signals to dominant fragment ion signals

Table 1 shows the ratio of the protonated molecular ion signal to the dominant fragment ion signal (mass 81 for α-pinene and sabinene and mass 93 for *p*-cymene) for the three compounds. Switching the *E*/*N* ratio during measurement gives some information on the identity of the individual compounds [6]. Since *p*-cymene is often the dominant or sole C_{10} benzene compound emitted by vegetation, the ion signal ratio of mass 135–93 at more than two different *E*/*N* ratios can be used to confirm the molecular origin of the observed signals at masses 93 and 135. The ratio of masses 135–93 showed considerable variation between *E*/*N* ratios and showed the highest humidity dependency at an *E*/*N* of 103 Td. If the ion count ratio of mass 135–93 at a given *E*/*N* ratio is outside of the ranges shown in Table 1, it may suggest that some fraction of masses 93 and/or 135 originate from other volatile compounds present in the sample. This method might be useful for distinguishing *p*-cymene in the presence of other compounds such as the oxygenated monoterpene thujone, which produces mass 93 and 135 as fragment ions, but gives a different ratio for masses 135:93 [Tani et al., unpublished work]. For the two monoterpene species considered here, the ratio of protonated molecular ion to major fragment ion increased as *E*/*N* was decreased, and showed most WVP dependence at lower *E*/*N* values. Since many monoterpene emitting plants typically release 10 or more monoterpene species, additional measurements for the other monoterpene species are required.

3.4. The effect of humidity on PTR-MS sensitivity

By assessing instrumental sensitivitiy to monoterpene vapours at different vapour pressures and drift tube *E*/*N* ratios, it is possible to obtain information on the viability of reaction between monoterpenes and the different reagent ions (unhydrated, mono-hydrated and di-hydrated). Fig. 4 shows the sensitivity of the PTR-MS with varying water vapour pressure towards measurements obtained with three monoterpenes (A) α-pinene, (B) sabinene and (C) *p*-cymene. In each case, three hypothetical reaction scenarios are considered. The left, centre and right panels show the sensitivity of the monoterpene reactions with the ion cluster $H_3O^+(H_2O)_{n-1}$, where $n = 1$, 1 or 2 and 1, 2 or 3, respectively. The sensitivity for the three monoterpenes in the H_3O^+ reaction (left panels) was unrealistically sensitive to WVP, indicating that they react not only with H_3O^+ ion but also with the hydrates. The centre and right panels show that sensitivities for the three compounds did not seem to be affected by WVP within the *E*/*N* range 103–142 Td, whether they react with the $H_3O^+(H_2O)_2$ ion or not. At an *E*/*N* ratio of 82 Td, however, the measured sensitivity for *p*-cymene decreased with an increase in WVP for both reagent ion cluster groups (centre and right panels). In the α-pinene and sabinene measurements at the *E*/*N* ratio of 82 Td, the sensitivity was almost constant when all three reagent ion cluster groups acted as reagent ions (Fig. 4B and C, right hand panels), but slightly increased as WVP was increased in the case where only H_3O^+ and $H_3O^+H_2O$ ion cluster groups reacted (Fig. 4B and C, centre panels).

4. Discussion

4.1. Reactions of $H_3O^+(H_2O)_n$ ions with monoterpenes

The sensitivities for the three compounds did not seem to be affected by WVP within the *E*/*N* range 103–142 Td. This can be explained in the following way:

Reactions of hydrated hydronium ions, $H_3O^+(H_2O)_{n-1}$, (n = 2 and 3), with hydrocarbons could proceed either by direct proton transfer, e.g.:

$$H_3O^+H_2O + VOC \rightarrow VOCH^+ + (H_2O)_2 \qquad (4)$$

or via ligand switching reactions, e.g.:

$$H_3O^+H_2O + VOC \rightarrow VOCH^+H_2O + H_2O \qquad (5)$$

followed by dissociation of the weakly bound $VOCH^+–H_2O$ cluster in the drift tube to produce $VOCH^+$. Direct proton transfer from the monohydrate hydronium ion is only ener-

Table 1

Ion signal ratio of non-isotopic protonated molecular ion to major fragment ion derived from the three compounds (mass 81 for α-pinene and sabinene and mass 93 for *p*-cymene) as affected by *E*/*N* and water vapour pressure of the inlet air

E/*N* (Td)	α-Pinene			Sabinene			*p*-Cymene		
	0.59 kPa	1.36 kPa	2.40 kPa	0.59 kPa	1.36 kPa	2.40 kPa	0.59 kPa	1.36 kPa	2.40 kPa
82	6.7	9.9	12.5	8.4	–	15.9	112	131	126
103	2.1	2.5	2.9	2.5	3.0	3.5	7.5	9.6	10.8
124	1.1	1.1	1.2	1.4	1.4	1.4	0.4	0.4	0.5
142	1.0	1.0	1.0	1.1	1.2	1.2	0.1	0.1	0.1

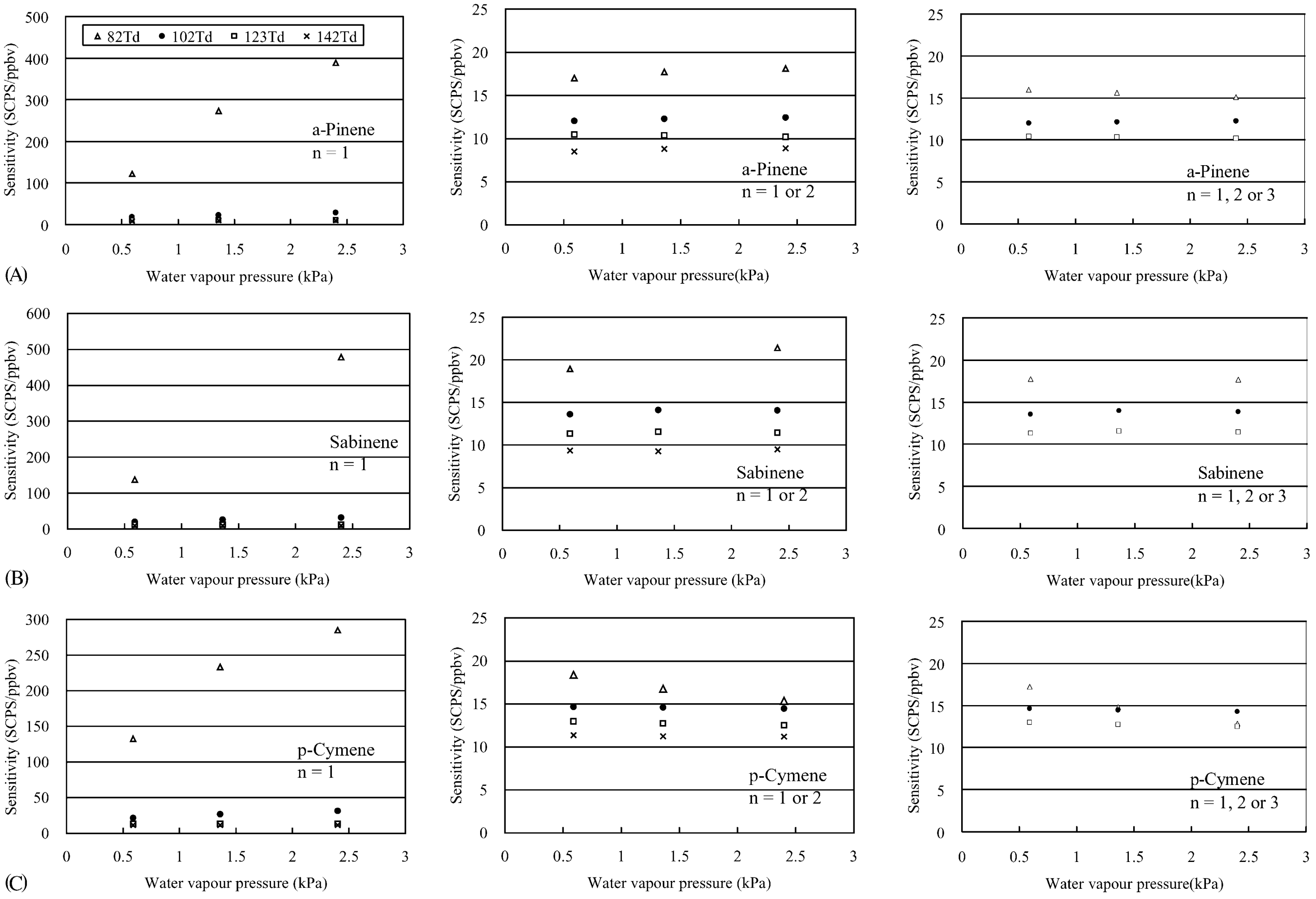

Fig. 4. Change in sensitivities for α-pinene (A), sabinene (B) and *p*-cymene (C). The left, centre and right hand panels show the sensitivities for reaction with the ion cluster $H_3O^+(H_2O)_{n-1}$, where *n* = 1, 1 or 2 and 1, 2 or 3, respectively.

getically possible if the proton affinity of the respective VOC is greater than the PA (H_2O) plus the H_3O^+–(H_2O) bond energy. Thus, for direct proton transfer to become exothermic a hydrocarbon needs to have a PA which is greater than 810 kJ/mol for $H_3O^+(H_2O)$ reaction. This value was calculated using the following binding energies of the most weakly bound H_2O molecule BE (H_3O^+–H_2O) = 134 kJ/mol [11], BE (H_2O–H_2O) = 15 kJ/mol [12] and PA (H_2O) = 691 kJ/mol [13].

The only reagent ions which could contribute to product ion formation at *E*/*N* ratios above 100 Td are H_3O^+ and the monohydrate $H_3O^+H_2O$ (Fig. 3). The second and higher hydrates of the hydronium ion are not present in substantial amounts in the drift tube due to the elevated collision energy condition which favours dissociation rather than stabilization of higher hydrates in collisions with the air buffer gas (Fig. 3). Proton affinities are known only for α-pinene (PA (α-pinene)) <854 kJ/mol [14] and for limonene (PA (limonene)) =875 kJ/mol [15]. These proton affinity values are well above 810 kJ/mol, which is the energetic limit for direct proton transfer to become exothermic from the monohydrate. Thus, we might expect that even direct proton transfer is exothermic and hence fast for α-pinene and the other monoterpenes in collisions with $H_3O^+H_2O$. This is directly supported by the experimental observation that changing the water vapour pressure in the inlet air from 0.59 to 2.4 kPa, which causes a doubling of the relative abundance of $H_3O^+H_2O$ reagent ions from 25 to 50% at 103 Td, does not alter the sensitivities for α-pinene, sabinene and *p*-cymene, respectively.

At an *E*/*N* ratio of 82 Td, however, the measured sensitivity for *p*-cymene decreased with increasing WVP in contrast to the sensitivities of α-pinene and sabinene which stayed almost constant, independent of WVP. As can be seen from Fig. 3 the dominant reagent ion at 82 Td is the monohydrate $H_3O^+H_2O$ with a relative abundance of 80% independent of WVP. The abundance of the second hydrate $H_3O^+(H_2O)_2$ changes from 5 to 15% and H_3O^+ changes counter-wise from 15 to 5% as the water vapour pressure is increased from 0.59 to 2.4 kPa. This dramatic change in $H_3O^+(H_2O)_2$ reagent ion concentration should affect the sensitivity of those compounds, which do not react rapidly with the second hydrate but do react rapidly with H_3O^+ and $H_3O^+H_2O$. As mentioned before only *p*-cymene reveal a reduction in sensitivity as the relative amount of $H_3O^+(H_2O)_2$ ions is increased.

Monohydrate ions of protonated α-pinene and sabinene ($C_{10}H_{16}\cdot H^+\cdot H_2O$) were produced at the lowest *E*/*N* (Fig. 5).

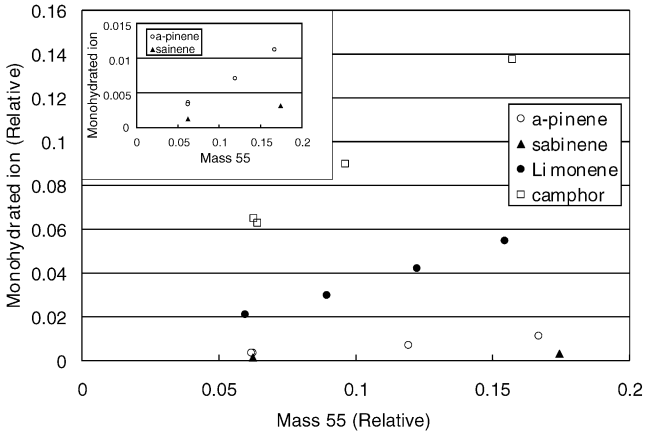

Fig. 5. Relationship between mass 55 and $C_{10}H_{17}{}^{+}H_2O$ signals, at *E*/*N* of 82 Td. Mass 55 signal is expressed as signal abundance relative to total signal of reagent ions (19 + 37 + 55). $C_{10}H_{17}{}^{+}H_2O$ signal is expressed as signal abundance relative to total signal of all ions originated from the respective monoterpene compounds.

The data for limonene and camphor shown in the previous paper [6] are also plotted in Fig. 5. The relative abundances of the monohydrate molecular ions of the four monoterpene compounds were closely correlated with the relative abundance of $H_3O^+(H_2O)_2$, suggesting that they are produced via ligand switching reactions between monoterpenes and $H_3O^+(H_2O)_2$. The fact that the monohydrate ion was observed in greater abundance for camphor and limonene than for α-pinene in Fig. 5 might be attributed to the difference in their dipole moment values [16]. The dipole moments for limonene and camphor are 1.57 and 3.1 D, while the value for α-pinene is 0.6 D. Therefore, we conclude that α-pinene and sabinene react rapidly with the second hydrate and *p*-cymene does not. Further support for this conclusion comes from energetic considerations:

The proton affinity of *p*-cymene is not known, but that of 1-methylethylbenzene, which has a structural formula similar to that of *p*-cymene, is low (792 kJ/mol) [13], indicating that direct proton transfer from *p*-cymene to $H_3O^+H_2O$ and $H_3O^+(H_2O)_2$ is energetically impossible. However, a ligand switching reaction might occur. For ligand switching to become exothermic the former calculated proton affinities of a hypothetical hydrocarbon can be further reduced, namely by the $VOCH^+–H_2O$ bond energy. Few bond energies of protonated hydrocarbons with water molecules are reported in the literature, but typical values for small hydrocarbons are BE ($VOCH^+–H_2O$) ∼70 kJ/mol and BE ($VOCH^+H_2O–H_2O$) ∼35 kJ/mol [17].

Assuming the proton affinity of *p*-cymene is the same as that of 1-methylethylbenzene, the low proton affinity would put a lower limit for the bond energies of the protonated *p*-cymene monohydrate and second hydrate clusters of 34 and 118 kJ/mol to make ligand switching from $H_3O^+H_2O$ to $H_3O^+(H_2O)_2$, respectively, exothermic.

Thus, comparing the minimum bond energy of 34 kJ/mol which is necessary for the $H_3O^+H_2O$ *p*-cymene reaction to become exothermic, with typical bond energies of small hydrocarbons BE ($VOCH^+–H_2O$) ∼l70 kJ/mol we see that this is clearly met. The opposite is the case for the $H_3O^+(H_2O)_2$ *p*-cymene reaction. The necessary bond energy of 118 kJ/mol is far too high compared to typical BE ($VOCH^+H_2O–H_2O$) ∼35 kJ/mol of small hydrocarbons. In short, the small proton affinity of *p*-cymene restricts exothermic reactions between hydrated hydronium ions and *p*-cymene to the monohydrate only.

4.2. *Product ion distribution as a function of E/N and water vapour pressure (WVP)*

As can be seen from Fig. 3, reactions of $H_3O^+(H_2O)_n$ ions with α-pinene, sabinene and *p*-cymene produce intact protonated molecular ions as well as fragment ions. Major fragment ions are $C_6H_9{}^+$ (mass 81) in the case of α-pinene and sabinene, and $C_7H_9{}^+$ (mass 93) for *p*-cymene. The degree of fragmentation is strongly reduced as *E*/*N* is changed from 142 to 82 Td. This can be explained in the following way: at high *E*/*N* (*E*/*N* > 120 Td) the prevailing reagent ion leading to product formation is H_3O^+. Since proton transfer from H_3O^+ to α-pinene, sabinene and *p*-cymene is expected to be exothermic by >100 kJ/mol, the protonated molecular ions are highly excited. This is also true for other monoterpenes due to their high proton affinity. The internal excitation of the product ions is close enough to their respective dissociation limits to cause immediate fragmentation or collision induced fragmentation after collisions with the buffer gas (air) molecules. Thus the yield of fragmentation depends critically on the transferred energy expressed as the reaction enthalpy and the collision energy. At low *E*/*N* values (82 Td) the major reagent ion is $H_3O^+(H_2O)$, which reacts either by direct proton transfer or by ligand switching. In any case the transferred energy, and therefore, the internal excitation of the product ions is less. Ionisation under these low collision energy and reduced exothermicity conditions are more “soft”. Direct proton transfer from, e.g. $H_3O^+H_2O$ to α-pinene is exothermic by <30 kJ/mol which is substantially less as compared to the H_3O^+ case (<160 kJ/mol). Thus, internal excitation of product ions formed in $H_3O^+H_2O$ collisions is insufficient to cause fragmentation. But still a substantial fraction of product ions formed in H_3O^+ collisions undergo fragmentation even at the lower collision energy conditions (82 Td). In fact this can be seen by the following observation: the relative abundance of $C_6H_9{}^+$ fragment ions at 82 Td for α-pinene and sabinene reactions is reduced from approximately 10% to less than 5% as the water vapour pressure is increased from 0.59 to 2.4 kPa. As can be seen from Fig. 3 (reagent ion distribution panel), the relative abundance of H_3O^+ reagent ions is reduced accordingly from 15 to 5%. There is clearly a correlation between the degree of fragmentation and the distribution of reagent ions, hence shifting the distribution towards hydrated hydronium ions leads to “softer” ionisation and less fragmentation of the monoterpenes. This shift can be caused most efficiently by reducing *E*/*N* or to a lesser ex-

Table 2
Effect of water vapour pressure on relative compounds in monoterpene family, at *E*/*N* abundance of protonated non-isotopic molecular ion of ratio of 122–124 Td

Molecule		Protonated molecular ion	Relative abundance, $f(x)$		
			Equation (x = water vapour prjessure (kPa))	At 0%RH	At 100%RH
α-Pinene	$C_{10}H_{16}$	137	$f(x) = 0.005x + 0.472$	0.47	0.48
β-Pinene[a]	$C_{10}H_{16}$	137	$f(x) = 0.486$	0.49	0.49
δ-Limonene[a]	$C_{10}H_{16}$	137	$f(x) = 0.017x + 0.419$	0.42	0.46
3-Carene[a]	$C_{10}H_{16}$	137	$f(x) = 0.01\ 1x + 0.565$	0.56	0.59
Sabinene	$C_{10}H_{16}$	137	$f(x) = 0.003x + 0.516$	0.52	0.52
α-Phellandrene	$C_{10}H_{16}$	137	$f(x) = 0.005x + 0.484$	0.48	0.50
α-Terpinene	$C_{10}H_{16}$	137	$f(x) = 0.009x + 0.530$	0.53	0.55
p-Cymene	$C_{10}H_{14}$	135	$f(x) = 0.038x + 0.214$	0.21	0.31
Cineole	$C_{10}H_{18}O$	137[b]	$f(x) = 0.522$	0.52	0.52
Linalool	$C_{10}H_{18}O$	137[b]	$f(x) = 0.414$	0.41	0.41
Camphor[a]	$C_{10}H_{16}$	153	$f(x) = 0.899$	0.90	0.90

[a] Previous data (6).

[b] Most dominant fragment ion, Ambient temperature: 21 °C not protonated ion.

tend by keeping *E*/*N* constant and increasing the water vapour pressure in the inlet air.

4.3. Atmospheric relevance

One of the major applications of PTR-MS has been in the study of volatile organic compound emissions from plants. From Figs. 3 and 4, it is clear that the sum of the relative abundances of the most dominant fragment ions and protonated molecular ions can give reasonable estimates of the concentrations of the standard monoterpene atmospheres, independent of the varying water vapour pressure conditions. However, in some circumstances this procedure may not be appropriate. For example, when plants are physically damaged they emit (*z*)- *and*(*E*)-hexenal, which have dominant fragment ions of mass 81 [18]. In such cases where 'wound' compound interference might be expected, mass 137 alone may give a better estimate of the total monoterpene concentration than the sum of mass 137 and mass 81. In addition, since mass 93 is also the protonated molecular ion of toluene, it may be unwise to use this mass to quantify *p*-cymene concentrations. In cases where toluene contamination might be expected, quantification using the ion signal of mass 135 alone might be a more appropriate means of providing an estimate for the *p*-cymene concentration.

To determine total monoterpene concentrations from the protonated molecular ion signal only, a high *E*/*N* ratio should be used (∼140 Td) in order to inhibit the effect of WVP on fragmentation. It has been shown earlier that the ion signal of mass 137 is consistent (±0.5%) across the WVP range. On the other hand, the relative abundance of the protonated molecular ion of *p*-cymene at an *E*/*N* ratio of 142 Td is too low (<8%) to give a reliable estimate of concentration. At an *E*/*N* ratio of 124 Td a relatively high signal of mass 135 is produced but a correction for WVP is then needed.

Table 2 shows the relative abundance of the protonated molecular ions of monoterpenes, *p*-cymene and oxygenated monoterpenes at *E*/*N* of 124 Td. No WVP effect was observed for the oxygenated monoterpenes. A slight effect was observed for some individual monoterpene species such as limonene and 3-carene and differences in the relative abundance of mass 137 for monoterpenes at 0 and 100%RH are less than 10%.

5. Conclusion

Sensitivity analysis indicates that α-pinene and sabinene react not only with H_3O^+ and $H_3O^+H_2O$ via direct proton transfer but also with $H_3O^+(H_2O)_2$ via ligand switching. *p*-

Table 3
The effects of humidity on the error in calculated monoterpenes and *p*-cymene concentrations

	α-Pinene/sabinene			*p*-Cymene		
	E/*N* = 82 Td	*E*/*N* = 103–124 Td	*E*/*N* = 142 Td	*E*/*N* = 82 Td	*E*/*N* = 103–124 Td	*E*/*N* = 142 Td
$\sum i$ (RI) calculated[a]						
From mass 137 + 81 or mass 135 + 93	No effect	No effect	No effect	No effect	No effect	No effect
From mass 137 or 135	Slight effect	Slight effect	No effect	No effect	Large effect	Slight effect
Sensitivity[b]	No effect	No effect	No effect But lowest sensitivity	Large effect	No effect	No effect But lowest sensitivity

No effect 0–5%, Slight effect 5–15%, Large effect 15–30%, Σi (RI) is the sum of the relevant ions (see Eq. (2)). For sensitivity analysis, proton donor species are assumed to be H_3O^+, $H_3O^+(H_2O)$ and $H_3O^+(H_2O)_2$ ions for α-pinene and sabinene and H_3O^+ and $H_3O^+(H_2O)$ ions for *p*-cymene.

[a] The effects are evaluated from the data in Fig. 3.

[b] The effects are evaluated from the data in Fig. 4.

Cymene seems to react with H_3O^+ via direct proton transfer and $H_3O^+H_2O$ via ligand switching. Here it is found that all compounds which produce fragment ions, regardless of their reagent ion species (n = 1 and 2 or 1–3), are susceptible to the effects of WVP. This is due to different abundances of reagent hydrated ions which result in different frequencies of individual reactions and characterize how soft the overall reaction is.

The effects of WVP on monoterpenes and *p*-cymene measurements at different E/N ratios are summarized in Table 3 and it can be seen that, at some conditions of E/N, ignoring the WVP effect can result in error of up to 30% in calculated concentrations.

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