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PTR-MS analysis of reference and plant-emitted volatile organic compounds

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Abstract

Proton transfer reaction-mass spectrometry (PTR-MS) was applied to the analysis of a series of volatile organic compounds (VOCs) that emit from various plants. These include a group of alcohols (methanol, ethanol and butanol), carbonyl-containing compounds (acetic acid, acetone and benzaldehyde), isoprene, acetonitrile, tetrahydrofuran (THF), pyrazine, toluene and xylene and a series of terpenes (*p*-cymene, camphene, 2-carene, limonene, β-myrcene, α-pinene, β-pinene, γ-tepinene and terpinolene) and oxygen-containing terpenes (1,8-cineole and linalool). These mass spectral data were compared to an electron ionization (EI) database identifying that not all PTR-MS fragments were common to EI. PTR-MS studies of these reference compounds were utilized to identify VOCs emitted from *Eucalyptus grandis* leaf at a temperature range of 30–100 °C. In addition to protonated molecules $(M + H)^+$, abundant proton-bound dimers or trimers were detected for alcohols, acetone, acetonitrile and THF. Abundant fragment ions attributed to the loss of water from these proton-bound clusters were also observed. The stability of butyl ($C_4H_9^+$ *m*/*z* 57) and acetyl (CH_3CO^+ *m*/*z* 43) fragment ions directed the proton-transfer reactions of butanol and acetic acid. Abundant $(M + H)^+$ ions were detected for pyrazine, THF, toluene and xylene, as well as for all terpenes except those containing oxygen. For linalool and 1,8-cineole, the loss of water generated an abundant fragment ion at *m*/*z* 137. PTR-MS fragmentation patterns for terpenes were proposed for *m*/*z* 81 ($C_6H_9^+$), 93 ($C_7H_9^+$), 95 ($C_7H_{11}^+$), 107 ($C_8H_{11}^+$), 109 ($C_8H_{13}^+$), 119 ($C_9H_{11}^+$), 121 ($C_9H_{13}^+$) and 137 (loss of water for oxygen-containing terpenes; $C_{10}H_{17}^+$). The relative abundances of $(M + H)^+$ and fragments for all terpenes (except linalool) were dependent on the drift tube voltage and the optimum voltage for detection of molecular ions was different for various terpenes.

Keywords: Proton transfer; Proton-bound dimer; Eucalyptus leaf; Terpenes; Biogenic VOCs

1. Introduction

Natural and industrial sources contribute to a group of atmospheric pollutants termed volatile organic compounds (VOCs). Considerable recent attention has been directed to biogenic VOCs arising from biological processes and their important roles in atmospheric and environmental sciences [1–4]. Biogenic VOCs include atmospheric trace gases other than carbon monoxide and dioxide, and are comprised primarily of the isoprenes and monoterpenes, as well as alcohols, esters, ethers and acids.

Plants are a major contributor of biogenic VOCs and their estimated annual emission is about 1100 tera-grams ($Tg = 10^{12}$ g) of carbon [4,5]. We are investigating the environmental effects of VOCs emitted from Australian vegetation, especially native trees in the genus *Eucalyptus*. Our studies are focused on characterizing environmental and physiological controls of VOC emissions, including the effects of plant phenology and fire. The temperatures of interest thus include those found during bushfire as well as the more commonly studied ambient range.

Mass spectrometry (MS) has played a major role in the analysis of volatile organic compounds in atmospheric and environmental sciences. The significant features of MS analysis of VOCs are detection limits on the order of parts-per-million to parts-per-trillion by volume (ppmv to pptv), and automated and detailed structural characterization of a variety of compounds.

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VOCs are routinely analyzed by either electron ionization (EI) or chemical ionization (CI). When VOCs are present at low levels, EI analysis requires that samples be pre-concentrated. This additional procedure may bias detection of some compounds due to variation in efficiency of trapping and concentrating of compounds that differ widely in vapor pressures and molecular weights. More recently, proton transfer reaction-mass spectrometry (PTR-MS) [6–8] has enabled the on-line monitoring of VOCs in air without pre-concentration. These studies include the analysis of biogenic emissions of VOCs in the Mediterranean area [9], boreal forests [10,11] and the Sierra Nevada [12] as well as laboratory measurements of biomass burning [13] and pyrolysis [14] emissions.

The selective ionization of VOCs in PTR-MS depends on proton-transfer reactions similar to chemical ionization [15] whilst utilizing water vapor with a proton affinity of 166.5 kcal/mol as the source of reagent ions (H_3O^+). Consequently, VOCs can be detected at trace concentrations without pre-concentration because the proton affinities of major components of air (O_2, N_2) are less than that of water. Atmospheric concentrations of VOCs vary from pptv to ppmv and PTR-MS provides a linear response in this range.

Here, we evaluate proton-transfer reactions for a series of reference compounds and identify their fragmentation patterns. This investigation is a necessary pre-condition for recognizing known and characterizing unknown compounds during PTR-MS analysis of VOCs from eucalypts and other native plants. Other PTR-MS studies [3,9–11] have mostly focused on correlation of specific mass-to-charge ratios (*m*/*z*) with VOCs. The present study provides detailed analysis for a group of alcohols (methanol, ethanol and butanol), carbonyl-containing compounds (acetic acid, acetone, acetylacetone and benzaldehyde), isoprene, acetonitrile, tetradydrofuran, pyrazine, toluene, xylene and a series of monoterpenes and oxygen-containing terpenes. The PTR-MS analysis of these compounds is then used to identify VOCs emitted from *Eucalyptus grandis* (F. Muell.) at temperatures ranging from 30 to 100 °C.

2. Materials and methods

2.1. Proton transfer reaction-mass spectrometry

The primary reactant/reagent ions in PTR-MS are generated from ionization of water vapor in a hollow cathode ion source. This process generates a high concentration of H_3O^+ ions as well as protonated water as dimers ($(H_2O)_2H^+$) and trimers ($(H_2O)_3H^+$) that are detected at *m*/*z* 19, 37 and 55, respectively. These reagent ions enter the drift region of the ion source for proton-transfer reactions with neutral molecules. PTR-MS contains a flow drift tube (FDT) [6,16] region where VOCs are introduced for ion–molecule reactions with reagent ions.

A high-sensitivity PTR-MS (Ionicon Analytik, Innsbruck, Austria) instrument was operated in standard conditions with inlet tubing and chamber maintained at temperatures ranging from 30 to 60 °C. The water vapor flow into the ion source was controlled at 8 ml/min and 29 kPa, corresponding to a reaction chamber pressure range of 0.18–0.21 kPa. A drift voltage of 580 V was used for all samples, and for the analysis of terpenes, drift voltages of 480 and 380 V were also examined to compare the relative abundances of fragments to their $(M + H)^+$ ions. Mass spectra were typically collected in a range of 20–350 u with a sample time of 200 ms/mass. The count rates of ions were calculated from the number of counts and the total sample time for each ion (ion counts/s). Mass spectral data were processed utilizing Microsoft Excel (Microsoft Inc.) and Origin (Microcal Software, Inc.) software. Mass spectra were plotted on a semi-logarithmic scale. Relative abundances of ions were calculated on the basis of ion counts/s.

2.2. Materials source and sample preparation

Standard reference compounds with >97% purity were obtained commercially from Ajax Fine Chemicals (Seven Hills, NSW, Australia) and Sigma–Aldrich (Castle Hill, NSW, Australia), and were used without further purification. Liquid samples of 1–2 ml portions were placed in 10 ml vials, and for the analysis of terpenes 0.25–0.5 ml portions were placed in 2 ml vials. A 30-cm tubing (0.03 in. i.d. and o.d. of 1/16 in. PEEK^{TM} (Upchurch Scientific, Oak Harbor, WA, USA)) was connected to the heated inlet tubing of PTR-MS (deactivated stainless steel (Silcosteel capillary with o.d. of 1/16 in. and i.d. of 0.04 in.)) via a union. VOCs were sampled by inserting the open end of the PEEK^{TM} tubing in the caps of the vials containing the liquid samples.

Leaves of *E. grandis* were collected fresh from trees growing on campus at UNSW and were excised to 2–3 mm square pieces before analysis. Leaf pieces were placed in a 2 ml size vial with the caps securely tightened. PEEK^{TM} tubing was inserted in the caps through a 1/16 in. hole to sample VOCs emitted from the leaf pieces. Vials were heated through heat transfer from a beaker containing sand. A thermometer was placed near the sample vials to record temperatures.

3. Results and discussion

Plants emit a wide range of volatile organic compounds into the atmosphere [1–5,9,12]. These include plant-specific isoprenoids (isoprene, terpenes and oxygen-containing terpenes) as well as more common organic compounds, such as alcohols, esters, ethers and acids. Many of these compounds are suited to PTR-MS analysis since their proton affinity is greater than that of water (166.5 kcal/mol) [6,7]. Biogenic VOCs are dominated by isoprenoids followed by alcohols and carbonyl containing compounds [5,11], and this study presents a PTR-MS analysis for these groups of compounds. In addition, PTR-MS mass spectral data are compared to an EI database in order to compare their fragmentation pathways.

3.1. PTR-MS analysis of alcohols

On-line measurements of atmospheric VOCs [3,5,9,10] and pyrolysis studies of several plant species including *Eucalyptus saligna* [14] have reported the presence of several alcohols, and methanol, ethanol and butanol were selected here for study.

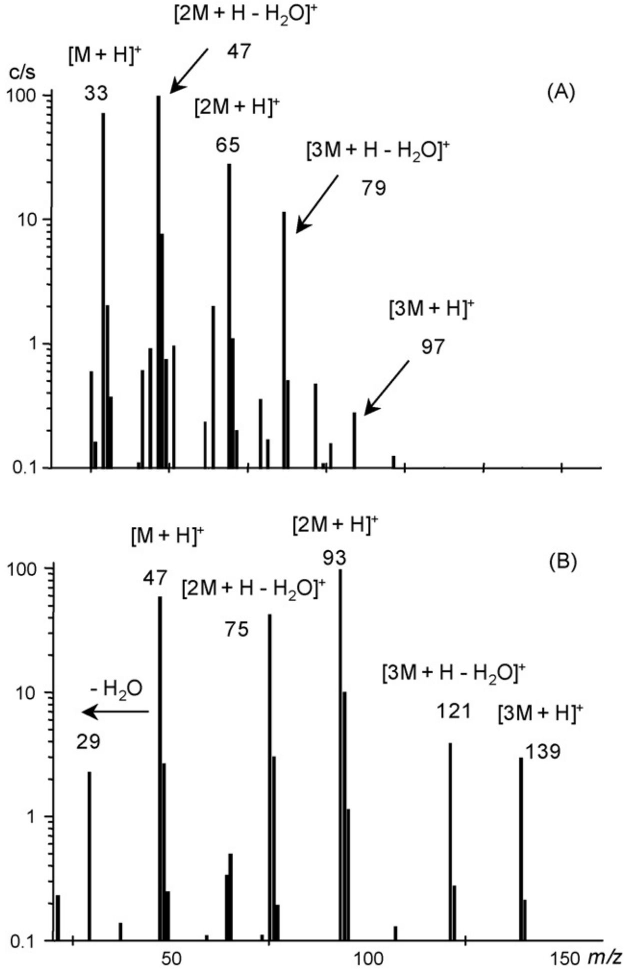


Fig. 1. PTR-MS of (A) methanol at an inlet/chamber temperature of 60 °C and (B) ethanol at an inlet/chamber temperature of 40 °C.

These low molecular weight alcohols have a proton affinity [17] range of 181.9–191.7 kcal/mol, and while their PTR-MS analysis showed dominant $(M+H)^+$ ions, the most striking feature of their mass spectral data was the presence of proton-bound clusters. For example, mass spectra of methanol and ethanol are shown in Fig. 1. As expected, $(M+H)^+$ (Fig. 1A) for methanol is observed at *m*/*z* 33, but proton-bound dimers and trimers are also observed at *m*/*z* 65 and 97, respectively. Proton-bound clusters for methanol have been studied using selected ion flow tube (SIFT) experiments [18,19]. Abundant ions of proton-bound alcohol clusters with a special stability in the gas-phase, sometimes referred to as "magic numbers", have been detected. For methanol, the proton-bound trimer ($(CH_3OH)_3H^+$) has been reported as a magic number [18], and while this trimer (<1% based on ion counts/s) is observed in this PTR-MS study, its relative abundance is far less than that of protonated methanol and the proton-bound dimer (Fig. 1A). Ions at *m*/*z* 47 and 79 are fragment ions that can be attributed to the loss of water from the proton-bound dimers and trimers. Note that the ion at *m*/*z* 47 is the most abundant ion in this mass spectrum.

For ethanol (Fig. 1B), $(M+H)^+$ is observed at *m*/*z* 47 with an abundant proton-bound dimer at *m*/*z* 93, while the trimer can be detected at *m*/*z* 139, albeit with a relative abundance of <5% (based on ion counts/s). Additionally, fragment ions due to loss of water molecules from the dimer and trimer are detected at *m*/*z* 75 and 121. Proton-bound clusters (up to trimer) of ethanol have also been reported by the SIFT method [20]. The drift tube region of the ion source in PTR-MS allows sufficient ion–molecule interactions such that proton-bound clusters similar to the SIFT method can be formed. Additionally, the drift tube region of PTR-MS instrument is not heated and condensation reactions could promote the formation of these proton-bound clusters.

Interestingly, PTR-MS analysis of VOCs emitted from *Arabidopsis* roots [21] grown under sterile conditions reported ions at *m*/*z* 47, 65 and 93. This study correlated the presence of *m*/*z* 47 to $(M+H)^+$ ion of ethanol, *m*/*z* 65 to water adducts of protonated ethanol and *m*/*z* 93 to an ethanol dimer. The same study reported the presence of *m*/*z* 75 and attributed this to an "unknown VOC". Our PTR-MS studies showed that water loss from proton-bound dimers and trimers of methanol and ethanol occurred readily and in the presence of proton-bound dimers of ethanol (i.e., *m*/*z* 93), the ion at *m*/*z* 75 (reportedly the "unknown VOC") could be correlated to fragment ions from the loss of water of proton-bound dimer of ethanol. Additionally, in our PTR-MS analysis of alcohols, water adducts of protonated alcohols were not detected at high abundance. We suggest that the *m*/*z* 65 reported in the analysis of VOCs of *Arabidopsis* roots could be due to the presence of a proton-bound dimer of methanol.

In the case of butanol, the most abundant ion was observed at *m*/*z* 57 and can be attributed to the stable butyl fragment ion ($C_4H_9^+$), while $(M+H)^+$ (*m*/*z* 75) was detected at <5%, and the protonated dimer (*m*/*z* 149) was detected at a greater relative abundance of almost 10%. In addition, a fragment ion attributed to the loss of water from the proton-bound dimer was detected at *m*/*z* 131. The special stability of the butyl fragment ion dominated over the proton-transfer reactions, and as a result, $(M+H)^+$ and proton-bound dimer were not efficiently detected.

3.2. PTR-MS analysis of carbonyl-containing compounds

A range of plants, including eucalypts have been reported to emit acetic acid and acetone [5,9,10,14]. These two compounds, and in addition acetylacetone and benzaldehyde, were selected for PTR-MS analysis.

Acetic acid has a proton affinity of 190.2 kcal/mol [6] and its $(M+H)^+$ was observed at *m*/*z* 61 but with a relative abundance of only 4%, in comparison to the very abundant fragment ion at *m*/*z* 43 (CH_3CO^+). A loss of water from protonated acetic acid directs the formation of a stable acetyl fragment ion. This fragment ion has also been reported in EI analysis of acetic acid [22] and our studies show that the fragment ion at *m*/*z* 43 is also common in proton-transfer reactions of the PTR-MS.

The two ketones, acetone (PA 194.1 kcal/mol [6]) and acetylacetone (PA 208.8 kcal/mol) [23] both showed protonated ions at *m*/*z* 59 and 101, respectively (Fig. 2). The $(M+H)^+$ of acetylacetone is the most abundant ion with the stable acetyl fragment ion observed at a relative intensity of 50% (Fig. 2A). The fragment ion at *m*/*z* 85 is attributed to the loss of a methyl group and this fragment ion is also observed in EI analysis

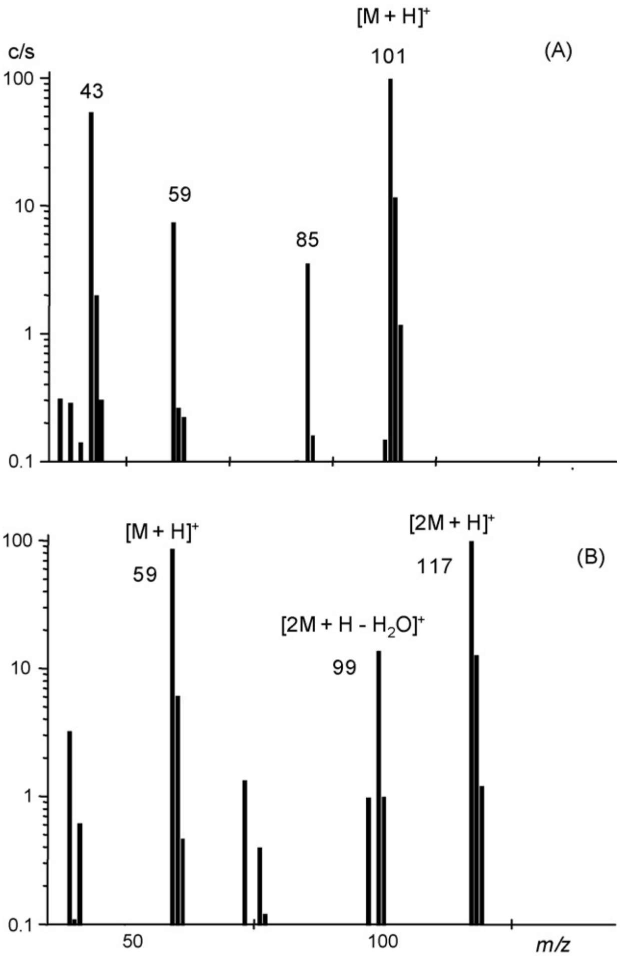


Fig. 2. PTR-MS for (A) acetylacetone at an inlet/chamber temperature of 60 °C and (B) acetone at an inlet/chamber temperature of 30 °C.

of acetylacetone [22]. The fragment ion at *m*/*z* 59 (protonated acetone) can be accounted for by loss of CH_2CO from the $(M+H)^+$ ion. This fragment ion was not observed in EI analysis of acetylacetone. For acetone (Fig. 2B) on the other hand, the abundant ion at *m*/*z* 117 is attributed to a proton-bound dimer, while loss of water from the dimer produces an ion at *m*/*z* 99. PTR-MS analysis of acetone using inlet and chamber temperatures ranging from 30 to 60 °C was used to examine thermal stability of proton-bound dimers. Our study showed that as temperature increases, the abundance of proton-bound dimer decreases compared to that of $(M+H)^+$. At inlet and chamber temperatures of 30 °C (Fig. 2B), the proton-bound dimer of acetone was the most abundant ion. The dimer declined in abundance with increasing temperature and at 40 °C, the $(M+H)^+$ and the dimer were of almost equal abundance. Above 50 °C, $(M+H)^+$ of acetone dominated. Proton-bound clusters of acetone have been reported from studies using high-pressure chemical ionization sources where acetone was used as the reagent gas [24]. These studies suggest that high concentrations of volatile compounds in the drift tube region of the PTR-MS instrument could promote formation of proton-bound clusters.

PTR-MS analysis of benzylaldehyde showed the dominance of the molecular ion at *m*/*z* 107. Nevertheless, there was an abundant fragment ion at *m*/*z* 79 (90% based on ion counts/s) that we attribute to the stable protonated phenyl ion ($C_6H_7^+$), which is also the most intense ion in the EI analysis of benzaldehyde [22].

3.3. PTR-MS analysis of other VOCs

Environmental emissions of isoprene (2-methyl-1,3-butadiene), acetonitrile, furan, pyrazine, toluene and xylene have been widely detected by gas chromatography and mass spectrometry [5,9,13,14]. These compounds were included in our studies, although tetrahydrofuran was substituted for furan due to supply availability.

PTR-MS analysis of isoprene revealed a molecular ion ($C_5H_9^+$) at *m*/*z* 69, albeit with a relative abundance of 7% while the most abundant ion was the fragment at *m*/*z* 39 that equates to loss of C_2H_6 from $(M+H)^+$. This fragment ion has also been detected in electron ionization of isoprene [22]. The proton-transfer reaction conditions can be optimized to enhance detection of $(M+H)^+$ of isoprene as described below (see Section 3.5).

Other PTR-MS studies have correlated the *m*/*z* 69 ion with emissions of furan and isoprene [13,14]. The fragment ion at *m*/*z* 39 is common in electron ionization mass spectra of these compounds [22]. The presence of this fragment ion in PTR-MS analysis of isoprene suggests that furan may also generate a fragment ion at *m*/*z* 39, and it may not be possible to differentiate these compounds based on their fragment ions.

For acetonitrile, $(M+H)^+$ was detected at *m*/*z* 42 as the most abundant ion, while the proton-bound dimer at *m*/*z* 83 was detected with a relative abundance of 20%. The mass spectrum of acetonitrile also contained an ion at *m*/*z* 56 with a relative abundance of 30% that could be accounted for by loss of HCN from the proton-bound dimer.

The dominance of $(M+H)^+$ of pyrazine (*m*/*z* 81), THF (*m*/*z* 73), toluene (*m*/*z* 93) and xylene (*m*/*z* 107) simplified their PTR-MS analysis. The mass spectrum of THF also showed the presence of proton-bound dimer at *m*/*z* 145 with a relative abundance of 20% and a fragment ion at *m*/*z* 55 (10% relative abundance) that we attribute to the loss of water from its $(M+H)^+$ ion. This fragment ion combined with the presence of the molecular ion could help in a more reliable identification of THF. For xylene, fragment ions at *m*/*z* 91 (loss of CH_4) and 79 (loss of C_2H_4) with relative abundances of approximately 30% were also detected.

3.4. PTR-MS analysis of terpenes

Terpenes are emitted by many plants including a number of eucalypt species in Australia [25–29] and gas chromatography [26] and mass spectrometry [28–30] have been utilized for their analysis. PTR-MS has been applied to quantifying atmospheric concentrations of terpenes [5,11,12]. These studies generally correlate ions at *m*/*z* 81 and 137 with the presence of monoterpenes. In order to evaluate the proton-transfer reactions of terpenes and oxygen-containing terpenes, several reference compounds (*p*-cymene, camphene, 2-carene, limonene, β-myrcene, α-pinene, β-pinene, γ-tepinene, terpinolene, 1,8-

Table 1
PTR-MS analysis of terpenes and oxygen-containing terpenes

	m/z	155	137	135	121	119	109	107	95	93	81
p-Cymene	$C_{10}H_{14}$			4.3		5.6				100.0	
Camphene	$C_{10}H_{16}$		41.0		2.2		0.3	0.5	5.7	1.0	100.0
2-Carene	$C_{10}H_{16}$		69.3		0.6				4.9	1.1	100.0
Limonene	$C_{10}H_{16}$		26.5		0.6			0.6	9.5	1.4	100.0
β-Myrcene	$C_{10}H_{16}$		44.0		0.7		1.6		35.0	1.3	100.0
α-Pinene	$C_{10}H_{16}$		44.0		1.5		0.4	1.0	7.2	21.7	100.0
β-Pinene	$C_{10}H_{16}$		30.0		1.0		0.4		10.5	1.4	100.0
γ-Terpinene	$C_{10}H_{16}$		38.7						2.2	3.7	100.0
Terpinolene	$C_{10}H_{16}$		100.0		1.5				4.8	0.5	82.3
1,8-Cineole	$C_{10}H_{18}O$	0.3	70.0						7.8		100.0
linalool	$C_{10}H_{18}O$	0.7	36.6						2.4	0.9	100.0
p-Cymene[a]	$C_{10}H_{14}$			55.2		1.1				100.0	
p-Cymene[b]	$C_{10}H_{14}$			100		0.8				2.5	
1,8-Cineole[a]	$C_{10}H_{18}O$	1.3	100						3.1		85.1
1,8-Cineole[b]	$C_{10}H_{18}O$	53.5	100						3.9		4.0

Relative abundance of ions calculated on the basis of ion counts/s (ions listed with relative abundances of >0.3%). The ionization source conditions were kept constant for these compounds, and a drift tube voltage of 580 V was applied except where noted.

[a] Drift tube voltage of 480 V.

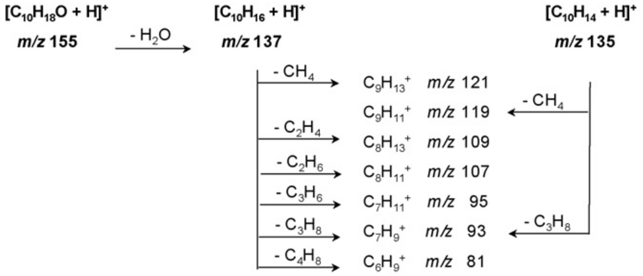
[b] Drift tube voltage of 380 V.

cineole and linalool) were assessed. Mass spectral data recorded under similar ionization conditions for these compounds are summarized in Table 1.

For *p*-cymene, $(M+H)^+$ was observed at *m/z* 135, but with a relative abundance of 4.3% (Table 1). The most abundant ion was observed at *m/z* 93 and results from the loss of $C(CH_3)_2$ leading to the stable $C_7H_9^+$ fragment ion. The combined loss of a methyl group and a hydrogen (i.e., loss of CH_4) results in the fragment ion at *m/z* 119. The proposed fragmentation patterns for terpenes are presented in Scheme 1.

The $(M+H)^+$ at *m/z* 137 is observed for camphene, 2-carene, limonene, β-myrcene, α-pinene, β-pinene, γ-tepinene and terpinolene. In contrast $(M+H)^+$ of the oxygen containing terpenes (linalool and 1,8-cineole) were present only at <1%. For these oxygen-containing terpenes, loss of water from their protonated molecules produces abundant fragment ions at *m/z* 137. Note that these terpenes were analyzed under similar ionization conditions and at a drift tube voltage of 580 V.

With the exception of *p*-cymene, all terpenes show an abundant fragment ion at *m/z* 81 (Table 1). Electron ionization mass spectral fragmentation patterns of naturally occurring monoterpene esters report a stable fragment ion $(C_6H_8)^+$ at *m/z* 80 [30]. PTR-MS analysis shows that the fragment ion at *m/z* 81 is common to monoterpenes including the oxygen-containing terpenes. The data suggests a similar structure $(C_6H_9^+)$ for a fragment ion at *m/z* 81. With the exception of *p*-cymene, all terpenes show a fragment ion at *m/z* 95 (Table 1) and, similarly, all terpenes except 1,8-cineole show a fragment ion at *m/z* 93 of (Table 1). This latter fragment is the most abundant ion in PTR-MS analysis of *p*-cymene and is also abundant (21.7%) in PTR-MS analysis of α-pinene. EI analysis of terpenes [22] also report these fragment ions and on the basis of these observations, the fragment ion at *m/z* 93 could be attributed to $(C_7H_9^+)$ and *m/z* 95 to $(C_7H_{11}^+)$. Other fragments at *m/z* 121, 109 and 107 are also common to non-oxygen containing terpenes (Table 1). In general, we attribute these fragment ions to the loss of CH_4, C_2H_4 and C_2H_6 as depicted in Scheme 1.



Scheme 1. PTR-MS fragmentation pattern for terpenes and oxygen-containing terpenes.

The results of our analysis of reference terpenes show that PTR-MS data could not differentiate various types of terpenes and their isomers as ions of *m/z* 81, 93, 95 and 137 are commonly observed irrespective of terpene. Recent PTR-MS analysis of Mediterranean oak species [9] correlated the ion at *m/z* 93 to the presence of toluene and *m/z* 95 to the presence of vinylfuran/phenol. These studies also purportedly detected the presence of monoterpenes. Our PTR-MS studies show that numerous terpenes have common fragment ions at *m/z* 93 and 95 and that the total ion current for *m/z* 93 and 95 should not be directly correlated to the presence of toluene and vinylfuran/phenol.

3.5. Effect of drift tube voltage on relative abundances of protonated molecules and fragments of isoprene and terpenes

Pseudo first-order kinetics applies to proton-transfer reactions in the drift tube region of the PTR-MS based on a high concentration of reactant/reagent ions and a maximum drift tube voltage (600 V) that minimizes the ion residence time. Proton-transfer reactions of VOCs can be affected by the type of primary reactant/reagent ions and by the drift tube voltage [8,31,32]. In our studies, water vapor conditions were kept constant and the drift tube voltage was varied in order to determine optimum voltage for detection of $(M+H)^+$ ions of isoprene and terpenes. As the drift tube voltage is reduced, the residence time of ions increases resulting in greater numbers of ion-molecule interactions and increasing diversity of ion-molecule reactions (i.e., reactions that are not strictly first-order). The kinetic energy of ions decreases as a function of the lower drift tube voltage resulting in less effective collisions (i.e., less fragmentation).

PTR-MS analysis of isoprene at a near maximum drift tube voltage of 580 V was dominated by the abundant fragment ion *m/z* 39. Reducing drift tube voltage to 380 V, reduced the abundance of this fragment ion to <1% allowing the protonated molecule at *m/z* 69 to dominate. Similarly, analysis of *p*-cymene and oxygen-containing terpenes (1,8-cineole and linalool) at a drift tube voltage of 580 V showed a minor peak for their protonated molecules. For *p*-cymene, reducing drift voltage from 580 to 480 V increased the abundance of protonated molecules from <5 to 55% (Table 1). The same reduction in voltage increased the relative abundance of $(M+H)^+$ (*m/z* 155) for 1,8-cineole to 1.3% (when compared to a drift tube voltage of 580 V), and a drift tube voltage of 380 V increased the relative abundance of the protonated molecule to 54%.

In the case of *p*-cymene, the total count for $(M+H)^+$ and fragments was not affected by reducing drift tube voltage and $(M+H)^+$ completely dominated (relative abundance close to 100%) at a drift tube voltage of 380 V (Table 1). The total ion counts for $(M+H)^+$ and fragments of 1,8-cineole did not differ between drift tube voltages of 480 and 580 V. At a voltage of 380 V, the total ion counts for $(M+H)^+$ and fragments of 1,8-cineole fell three-fold. This loss of total ion count could be correlated to scattering of ions and an increase in ion–molecule interactions. Reduced drift tube voltages did not increase the abundance of $(M+H)^+$ ions of linalool. Losses of water from this acyclic compound could promote the more stable fragment ion (*m/z* 137) over the protonated molecule.

Our results suggest that it is essential to perform PTR-MS measurements of VOCs from environmental sources at a range of drift tube voltages in order to improve the reliability and detection of low levels of terpenes. The effects of various drift tube voltages are particularly important for the identification of new compounds that could arise from photochemical or degradation reactions of terpenes in the atmosphere.

3.6. *Temperature dependence of VOC emissions from Eucalyptus grandis*

VOCs are continuously emitted from many plants during growth [3,4]. Atmospheric concentrations of VOCs change seasonally and as a function of daily temperature and sunlight [33]. Evidence to date suggests isoprene and terpenes dominate VOC emissions from eucalypts, and rates of emission of these compounds vary greatly across Australia and among species [26,27].

Monoterpenes emitted from Australian eucalyptus have been reported to include α-pinene, β-pinene, 1,8-cineole (eucalyptol) and limonene [25–29]. Our studies of reference compounds (Table 1) suggests that PTR-MS analysis cannot be simply used to distinguish specific terpenes since the ions at *m/z* 81, 93, 95 and 137 are common to several. Abundances of these ions could be the result of collective fragmentation of numerous terpenes. For example, PTR-MS analysis of volatile organic compounds from *E. grandis* leaf (Fig. 3) shows abundant ions at *m/z* 81, 93, 95 and 137.

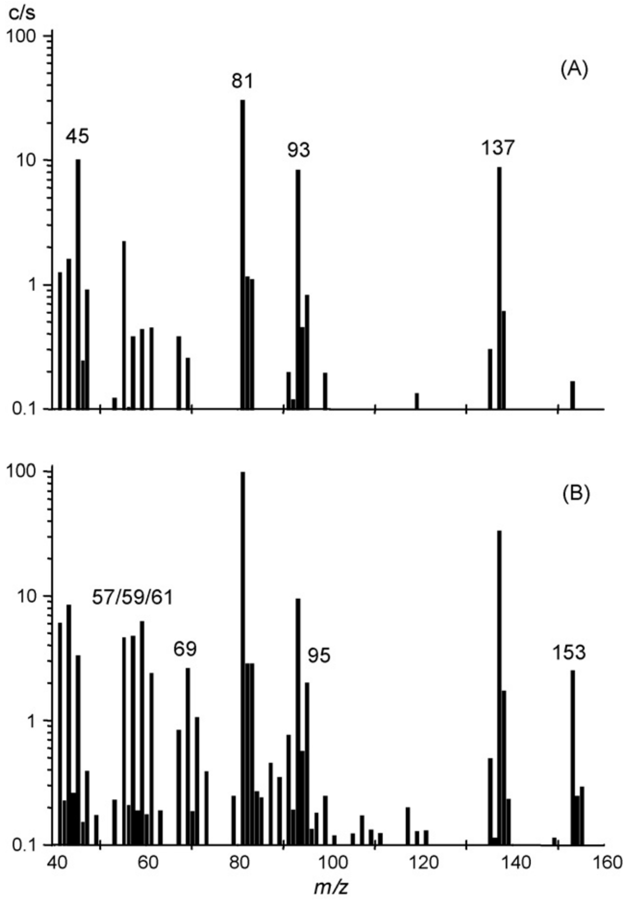


Fig. 3. PTR-MS of VOCs emitted from heating *Eucalyptus grandis* leaf at (A) 35 °C and (B) 100 °C.

Emissions of VOCs from leaves of *E. grandis* was examined as a function of temperature, and spectra for 35 and 100 °C are presented in Fig. 3A and B, respectively. These results show that abundances of ions at *m/z* 81 and 137 increased approximately five-fold as temperature increased from 35 to 100 °C. The ion at *m/z* 81 could be correlated to $(M+H)^+$ of pyrazine ($C_4H_5N_2^+$) or the $C_6H_9^+$ fragment of terpenes. These ions differ by 0.03 u and accurate mass measurements are required for their unambiguous identification. A mass analyzer with a resolving power of 3k is sufficient to distinguish their presence but this was beyond the capability of the instrument used here. We suggest caution needs be applied to inferences that increase in abundance of ions of *m/z* 81 correlated with increased abundance of specific terpenes. Temperature profile data (Fig. 3) showed dramatic increases (15 fold) in abundance of ions at *m/z* 153 and 155. The ion at *m/z* 153 is likely the $(M+H)^+$ ion of oxygen-containing terpenes

($C_{10}H_{16}O$), such as camphor, while the ion at m/z 155 is probably 1,8-cineole (eucalyptol).

The ion at m/z 69 (Fig. 3B) can be correlated to the presence of isoprene ($C_5H_9^+$) or furan ($C_4H_5O^+$). These compounds can be distinguished by accurate mass measurements on instruments with greater resolving power (>1500). Temperature profile studies showed a 10-fold increase in the ion current at m/z 69. Ions with m/z 61 and 43 are likely the $(M+H)^+$ ions of acetic acid and acetyl fragments, respectively. Our analysis of acetic acid (see above) showed that the CH_3CO^+ fragment is abundant in proton-transfer reactions. In this direct analysis without a gas chromatography step, we speculated and attributed the ion m/z 45 to protonated molecular acetaldehyde and the m/z 59 to acetone. These compounds have previously been reported in PTR-MS analysis of plant tissues from *E. saligna* [14]. The ions m/z 57 could possibly represent $C_4H_9^+$ that was observed in our analysis of butanol (see above PTR-MS analysis of alcohols). This ion could also be correlated to other compounds, such as protonated acrolein or the fragment corresponding to water loss from protonated propanoic acid. Our future studies will combine GC with PTR-MS analysis in order to better identify isobaric compounds. Such studies will also be required to elucidate contributions of wound-induced VOCs to total emissions. For example, m/z 57, 69, 81, 83 and 87 (Fig. 3) have been correlated with fragment ions from a series of C5 and C6 VOCs released after leaf wounding [33].

4. Conclusion

Analysis of reference compounds revealed that proton-transfer reactions within the ionization source of the PTR-MS were not specific to simple exchange reactions resulting $(M+H)^+$ ions—abundant proton-bound clusters (dimers and trimers) as well as fragment ions were generated. The presence of abundant fragment ions suggests that the majority of PTR-MS reaction pathways have similar energies to EI reactions. This information is important in the analysis of VOCs when a chromatographic step is not used and when the identification of compounds is based solely on the observation of mass-to-charge (m/z) values.

For the series of reference compounds in this study, abundant proton-bound dimers or trimers were detected for methanol, ethanol, butanol, acetone and acetonitrile. Fragments attributed to the loss of water from proton-bound dimers and trimers were also observed. The relative abundances of proton-bound clusters were greatly reduced by increasing the chamber temperature to >50 °C. Other PTR-MS studies of plant emitted VOCs [21] have suggested the presence of ethanol dimers and correlated the presence of m/z 75 to an unknown compound, while our studies show the presence of proton-bound dimers for a series of compounds and suggest that loss of water from proton-bound dimers of ethanol could easily account for m/z 75 especially when its proton-bound dimer was reportedly observed at m/z 93 [21].

The stability of fragment ions directed the proton-transfer reactions. For example, butyl (m/z 57) and acetyl (m/z 43) fragments were observed as the most abundant ions in PTR-MS analysis of butanol and acetic acid. The presence of these specific fragments and $(M+H)^+$ can be used to improve reliability of identification of these compounds. Analysis of the atmosphere above boreal forest by PTR-MS correlated the presence of m/z 75 to butanol and m/z 57 was considered a fragment of hexanal [10]. Our results suggest that m/z 57 can be attributed to $C_4H_9^+$ fragments that can arise from a number of compounds. The same study [10] related the m/z 43 to the presence of propene, and our studies show that this ion can be attributed to the acetyl group that is commonly present in a number of compounds. Additionally, the m/z 79 was correlated with the presence of benzene when xylene was detected at m/z 107. Our studies show that m/z 79 can be attributed to a fragment ion of xylene from the loss of C_2H_4. For the identification of VOCs from environmental sources, the possibility of fragmentation overlap must be considered. Cross comparison of PTR-MS analysis with other analytical methods (gas chromatography and spectroscopy) is necessary for reliable identification of VOCs present in the atmosphere [13].

PTR-MS analysis showed $(M+H)^+$ for a series of terpenes (Table 1). Detection of $(M+H)^+$ for *p*-cymene and 1,8-cineole were more dependent on the drift tube voltage (Table 1), and a protonated molecule was detected at <1% for linalool. Several ions at m/z 81, 93, 95 and 137 were common to PTR-MS analysis of terpenes. These results show that PTR-MS data is not sufficient to distinguish various types of terpenes. Other PTR-MS studies of VOCs emitted from plants have related the presence of m/z 93 and 95 to toluene and vinylfuran/phenol, respectively [9,10]. Our studies showed that these ions are stable fragment ions of several terpenes (Table 1). For example, m/z 93 was an abundant ion in the PTR-MS analysis of α-pinene. Additional studies are required to verify the presence of toluene and vinylfuran/phenol as VOCs emitted from plants.

Our PTR-MS analysis of VOCs from eucalyptus leaf suggests the presence of acetaldehyde, acetone, acetic acid, isoprene/furan and terpenes including their oxygen-containing terpenes. We are currently continuing our temperature profile emission studies of VOCs from various eucalypts species by PTR-MS and extending our studies to other plant tissues and to a higher temperature range (>300 °C). Our future studies will also expand to analysis of the composition of smoke under various combustion conditions to further analyze VOCs and smoke and their potential environmental effects.

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