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**MS/MS studies for  
the selective  
detection of isomeric  
biogenic VOCs**

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# MS/MS studies for the selective detection of isomeric biogenic VOCs using a Townsend Discharge Triple Quadrupole Tandem MS and a PTR-Linear Ion Trap MS

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## Abstract

We performed MS/MS investigations of biogenic volatile organic compounds (BVOC) using a triple quadrupole tandem mass spectrometer (QqQ-MS) equipped with a Townsend Discharge ion source and a Proton Transfer Reaction Linear Ion Trap (PTR-LIT) mass spectrometer. Both instruments use H<sub>2</sub>O chemical ionization to produce protonated molecular ions. Here we report a study of the application of these instruments to determine methyl vinyl ketone (MVK) and methacrolein (MACR) and a series of monoterpenes ( $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, limonene, myrcene, ocimene) and sesquiterpenes (humulene and farnesene). Both instruments achieved sub-ppb detection limits in the single MS mode and in the MS/MS mode for differentiating MVK and MACR. Collision induced dissociation (CID) of protonated monoterpenes and sesquiterpenes was studied under the high-energy, single-to-few collision conditions of the QqQ-MS instrument and under the low-energy, multiple collision conditions of the PTR-LIT. Differences and similarities in the breakdown curves obtained are discussed. In addition, we performed MS<sup>4</sup> of protonated limonene to illustrate the analytical power of the PTR-LIT. In spite of the progress we have made, the selective on-line mass-spectrometric detection of individual monoterpenes or sesquiterpenes in complex mixtures currently does not yet seem to be possible.

## 1 Introduction

Biogenic volatile organic compounds (BVOCs) play an important role in the production of tropospheric ozone and contribute to the formation of particulate matter, especially in continental environments (Chameides et al., 1988; Fehsenfeld et al., 1992; Meng et al., 1997; Tunved et al., 2006). While it is not surprising that BVOCs control much of the chemistry above forest environments, Biesenthal et al. (1997) found that isoprene oxidation can account for ~13% of ozone production within the Vancouver, B.C. urban environment. Sotiropoulou et al. (2004) have shown that terpenes significantly impact

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air quality in the urban environments of Athens and Marseille. Given these observations and the very large emissions of BVOCs ( $\sim 500$  Tg/Yr for isoprene,  $\sim 125$  Tg/Yr for total terpenes,  $\sim 500$  Tg/Yr other BVOCs; Guenther et al., 1995) on a global scale, it is clear that a better understanding of the temporal characteristics and magnitudes of BVOC emission rates is important to the development of better ozone and particulate matter control strategies. Furthermore, it is important to note that BVOC emission influences the photooxidation capacity of the atmosphere on a local scale, due to the large contribution BVOCs can make to the total OH, O<sub>3</sub>, and NO<sub>3</sub> reactivity in the atmosphere. The longer lived BVOC photooxidation products such as ozone and secondary organic aerosol (SOA) impact the atmosphere on a more regional scale.

These considerations result in substantial demands to improve analytical technology for in-situ BVOC measurements. BVOC concentrations are often very low, in the low ppt range, particularly for the terpenes (C<sub>10</sub>H<sub>16</sub>) and sesquiterpenes (C<sub>15</sub>H<sub>24</sub>) that are important SOA precursors (Saxton et al., 2007). Atmospheric BVOC measurements at low ppt levels are made within a highly complex mixture of volatile organics,  $\sim 10^9$  times more water vapor, and  $\sim 1000$ – $10\,000$  times more ozone. The situation is even more challenging than this, since many BVOCs and their oxidation products are structural isomers. Examples include methyl vinyl ketone (MVK) and methacrolein (MACR), which are produced from the oxidation of isoprene. There are more than 14 monoterpene isomers and more than 4 sesquiterpene isomers, respectively, present in the atmosphere (Fuentes et al., 2000), at widely varying concentrations. Thus, substantial separation power/selectivity is needed to quantitatively determine the individual species. This is important to achieve, since the chemistry and important reaction partners differ widely among these species (Atkinson and Arey, 1998).

The analytical requirements outlined above seem to imply two possibilities, either high resolution gas chromatography, or selective mass spectrometry. Isoprene has been measured extensively using an array of direct mass spectrometric techniques, e.g. PTR-MS (Stroud et al., 2002), CIMS (Colorado et al., 1998; Leibrock et al., 2003; Sellegri et al., 2005), and using a cylindrical ion trap (Edwards et al., 2007). For ter-

penes, analysis has most generally been done by capillary GC, with cartridge (Spirig et al., 2004; Kesselmeier et al., 2000) or cryogenic preconcentration (Lerdau et al., 1994). In most cases, the stationary phase was a bonded methyl silicone phase, e.g. DB-1. These chromatographic methods work well to the extent that they enable identification and determination of individual terpene species. However, they tend to be cumbersome, with marginal temporal resolution (e.g. 2–4 samples per hour).

Proton Transfer Reaction Mass Spectrometry (PTR-MS) is a powerful method for fast and sensitive determination of atmospheric VOCs (Lindinger et al., 1998). The PTR-MS technique is appealing because of its low limits of detection, and fast time response, which enables even direct VOC flux measurements (Karl et al., 2001). A PTR-TOF instrument has been recently developed combining a PTR drift tube with a high mass resolution time-of-flight MS (Müller et al., 2007). However, both conventional PTR-MS and PTR-TOF-MS can only determine total terpenes (e.g. Lee et al., 2005) and cannot distinguish between different isomers. Prazeller et al. (2003) and Warneke et al. (2005a) describe the development of PTR ion trap mass spectrometers. Both approaches utilize a 3-D ion trap as the MS analyzer, enabling collision induced dissociation (CID) based determination of isomeric VOCs. This capability was demonstrated through simultaneous determination of the isomeric compounds acetone and propanal. However, for most isomeric BVOC measurements, the instrument suffers from poor limits of detection when used in the MS/MS ( $MS^2$ ) mode. Mielke et al. (2008) have recently developed the Proton Transfer Reaction Linear Ion Trap (PTR-LIT), which utilizes a linear quadrupole ion trap mass spectrometer as the analyzer, also enabling MS/MS measurements. In principle, the PTR-LIT can achieve better limits of detection in the  $MS^n$  mode than a cylindrical ion trap because of the better trapping efficiency for injected ions. Mielke et al. (2008) demonstrated that the PTR-LIT differentiates between MVK and MACR in laboratory photochemical reaction chamber experiments.

It is still a challenge to develop selective and sensitive schemes for quantitative and fast determination of isomeric BVOCs. Here we utilize a triple quadrupole tandem mass spectrometer (QqQ-MS) and the PTR-LIT, to investigate the CID of protonated

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MVK and MACR, as well as of a series of protonated monoterpenes and sesquiterpenes. QqQ-MS based CID was conducted under high-energy, single-or-few collision conditions. CID energies are well-defined and can be varied over a high energy range. However, QqQ-MS based CID is limited to MS/MS ( $MS^2$ ). The PTR-LIT sequentially deposits a low amount of energy in multiple collisions, and It can perform multiple isolation and fragmentation steps ( $MS^n$ ).

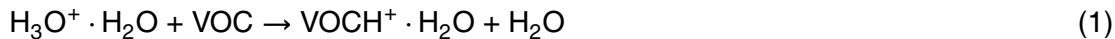
In this paper, we show ion decomposition processes in the QqQ-MS as a function of ion kinetic energy. We will compare monoterpene fragmentation patterns measured by PTR-LIT and by QqQ-MS. A PTR-LIT limonene  $MS^n$  experiment is shown for a better understanding of the fragmentation process, and to demonstrate the potential of  $MS^n$  analyses. Based on our findings we will discuss the prospects for selective atmospheric PTR-LIT and QqQ-MS determination of biogenic isomeric VOCs.

## 2 Experimental

During laboratory experiments, the  $C_4H_6O$  isomers MVK and MACR, six monoterpenes ( $C_{10}H_{16}$ ), cis-ocimene, myrcene,  $(-)-\alpha$ -pinene,  $(-)-\beta$ -pinene,  $(+)$ -3-carnene and  $R-(+)$ -limonene, and two sesquiterpenes ( $C_{15}H_{24}$ ), farnesene and  $\alpha$ -humulene, were investigated. Chemical structures of the compounds are depicted in Fig. 1. A constant gas-phase concentration of each compound was prepared using syringe pump injection of a constant flow rate of the pure liquid compound into a flow of zero air (Liquid Calibration Unit – LCU, Ionimed Analytik GbmH, Austria). Mole fractions in the ppb-to-ppm range were stable for a time period up to several hours. In addition, calibrations of the instruments were performed using a dynamic gas calibration unit (GCU, Ionimed Analytik GbmH, Austria) and a multiple-component gas cylinder (Apel Riemer Environmental Inc., Denver, CO, USA). For the monoterpene experiments the PTR-LIT and the QqQ-MS instrument were simultaneously connected either to the LCU or to the GCU using a  $60^\circ\text{C}$  heated Teflon line.

## 2.1 QqQ-MS

A modified Varian MS-320 Triple Quadrupole instrument (QqQ-MS) was used as an on-line trace gas analyzer. Protonated water and water cluster ions ( $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n, n=1-5$ ) were generated in a modified Townsend discharge running with  $\text{H}_2\text{O}$  as a source gas at 2 kV discharge voltage and 8 hPa pressure. The high proton affinity (PA) of the water clusters (PA=224.5 kcal/mol for the water trimer  $n=2$ ) prevents direct proton transfer reactions for most VOCs. Ionization is effected by ligand switching reactions, which deposit less energy into the product ion and lead to a very low degree of fragmentation.



Similar to PTR, ligand switching produces protonated analytes ( $\text{VOCH}^+$ ) in the Townsend discharge through Eqs. (1) and (2). The results of our study suggest that the structure of the analyte molecule is not altered upon protonation. Ions, extracted from the ion source by an Einzel lens system, were collimated with a hexapole guide into the first quadrupole mass filter (Q1) and guided or dissociated in a  $180^\circ$  curved collision cell quadrupole (CC) filled with  $0.4 \times 10^{-3}$ – $3.2 \times 10^{-3}$  hPa high grade argon CID gas. Finally, ions were mass filtered with the last quadrupole mass filter (Q2) and detected with an ultra-low noise detector operated in the so-called Extended Dynamic Range (EDR) mode. All lens and quadrupole settings were automatically optimized for a set of custom compounds, interpolated and dynamically adopted for every  $m/z$  ratio leading to an optimized ion transmission.

The QqQ-MS was operated in two different operation modes, the single quadrupole scan mode and the product ion scan mode. In the single quadrupole scan mode, only the first quadrupole (Q1) was used as a mass analyzer, and CC and Q2 worked as an ion guide. In the product ion scan mode, Q2 scanned for the product ions formed in the CC, when the precursor ion, selected by Q1, was fragmented by CID. Additional information on the number of collisions in CC is given as a Supplement <http://www.>

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atmos-meas-tech-discuss.net/2/1837/2009/amtd-2-1837-2009-supplement.pdf. The instrument software allows measurement of up to ten fragment ions with the highest intensities at different collision cell offset voltages ( $U_{CC}$ ), i.e. the voltage difference between Q1 and CC.  $U_{CC}$  was varied between 0 and 50 V. The selected fragment ions were measured with a dwell time of 0.1 to 10 s. To better compare fragmentation patterns, fragment ion signals were normalized to the total ion signal. As only singly-charged ions are produced, the  $m/z$  ratio is referred throughout this work as mass only, e.g. we use the notation  $m$  59 instead of  $m/z=59$  Th.

## 2.2 PTR-LIT

The PTR-LIT instrument combines a PTR source (Hansel et al., 1995; Lindinger et al., 1998) with a linear ion trap (Mielke et al., 2008). The PTR part was operated in a low E/N mode at 95 Td corresponding to 400 V drift tube voltage. This resulted in a higher sensitivity and a lowered amount of fragmentation. The ion trap was operated at a low pressure of  $1.0 \times 10^5$  hPa by adding helium as CID gas. The injection voltage between the last drift tube lens and the quadrupole rods was set at 3 V to reduce dissociation upon injection into the trap. The increased sensitivity due to a lowered amount of fragmentation allowed the reduction of the fill time to 250 ms for most experiments. A resonant ejection voltage of 500 mV was applied for 250 ms at 250 kHz dipolar excitation frequency for monoterpenes and 200 kHz for sesquiterpenes with no DC field applied to the rods.

Collision induced dissociation curves were recorded for each monoterpene and sesquiterpene by bringing ions into resonant excitation at 250 kHz, and 200 kHz dipolar excitation. The dipolar excitation voltage ( $U_{CID}$ ) was varied from 0 to 2 V while monitoring the quasimolecular ion as well as the fragment ions. A lower mass cutoff of  $m$  20 was observed for these experiments. For sensitivity and LOD analysis, 750 ms fill time was used, above which nonlinearity in the calibration curve was observed. Samples for calibration were derived from the multicomponent standard described earlier.

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### 3 Results

#### 3.1 QqQ-MS and PTR-LIT Sensitivity and LOD

The QqQ Townsend discharge produced a total primary ion signal (sum over all  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  ions) of about  $10^8$ – $10^9$  cps containing low impurities of  $\text{O}_2^+$  (0.05%) and  $\text{NO}^+$  (1.4%). At  $130^\circ\text{C}$  ion source temperature the protonated water trimer  $(\text{H}_2\text{O})_n\text{H}^+$  ( $n=3$ ) was the primary ion with a relative abundance of about 60%. Decreasing the ion volume temperature shifted the water cluster distribution towards higher  $n$ . In the PTR-LIT at 95 Td, both the monomer  $(\text{H}_2\text{O})\text{H}^+$  and the dimer  $(\text{H}_2\text{O})_2\text{H}^+$  are present as ionizing agents.

QqQ-MS and PTR-LIT sensitivities and  $2\text{-}\sigma$  LODs for three sets of selected VOCs (carbonyls, aromatics, isoprenoids) are shown in Table 1. These data represent one second integration time for the QqQ-MS running in single quadrupole mode, and 110 averages of 1 s scan time for the PTR-LIT.

The QqQ-MS instrument achieved sensitivities in the 80–340 cps/ppb regime which is comparable to the performance of a conventional High Sensitivity PTR-MS instrument. A strong mass discrimination effect was observed. From an ion chemistry point of view, the sensitivities for acetone and hexanone are expected to be similar (as it is observed in PTR-MS instruments) while we observed a sensitivity difference of a factor of 2.5. This can be explained by mass dependent ion discrimination caused by the auto-optimization of the QqQ-MS lens system. LODs were in the 0.1–0.8 ppb regime depending on the chemical background signal originating from the Townsend discharge.

The PTR-LIT sensitivity is reported as peak area per ppb in arbitrary units. The sensitivity can thus not be compared to the performance of other instruments. Relative sensitivities (normalized to acetone sensitivities) are in good agreement to what is expected from ion chemistry considerations. For MVK and MACR we expect a similar sensitivity as for acetone, but the observed relative sensitivities are somewhat low. LODs were in the 0.1–0.7 ppb regime. Mass discrimination effects become immediately

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apparent in the MS/MS mode. CID of  $\alpha$ -pinene at 0.15 V yields an  $m$  81 signal which is 1.5 greater than the original signal at  $m$  137, due to the fact that fragment ion peaks are greater than the parent peak, a greater sensitivity and a lower LOD can be obtained in the MS/MS mode.

### 5 3.2 Fragmentation of MVK and MACR

Figure 2 shows the QqQ-MS breakdown curve for MVK and MACR at  $2.3 \times 10^{-3}$  hPa CC pressure. Clear differences are visible in the relative fragmentation ratios at different CID energies, i.e. at different collision cell offset voltages. At  $U_{CC}=17$  V, protonated MVK yields a high amount of the  $m$  43 fragment ion and traces of a  $m$  41 fragment ion, with about 65% and 10% relative intensities, respectively. The fragmentation pattern of protonated MACR, on the other hand, shows a maximum  $m$  43 ion signal intensity at  $U_{CC}=10$  V and a maximum  $m$  41 signal at  $U_{CC}=17$  V, with 45% and 35% relative intensities, respectively. Both protonated MVK and protonated MACR also show a small fragment at  $m$  53 peaking at  $U_{CC}=17$  V and a relative increase of  $m$  71 and  $m$  69 towards higher CID voltages.

The relatively large  $m$  41-to- $m$  43 ratio observed for protonated MACR allows for speciated quantitation of MVK and MACR, as described for the PTR-LIT in Mielke et al. (2008). Fast on-line differentiation of MVK and MACR using the QqQ-MS will be most effective at  $U_{CC}=10$  V and  $U_{CC}=17$  V. For one second integration time, LODs of the main fragment ions  $m$  41 and  $m$  43 are 35.5 ppbv and 3.1 ppbv for MVK and 6 ppbv and 4.5 ppbv for MACR. Using Poisson statistics, an integration time of 1 min reduces product ion scan LODs to 0.4 ppbv for  $m$  43 of MVK and 0.6 ppbv for  $m$  41 of MACR. The QqQ-MS is thus also able to distinguish MVK and MACR at low ppbv concentrations. Mielke et al. (2008) have established  $2 \sigma$  LODs of 67 ppt for differentiating MVK and MACR based on CID of  $m$  71, with 1.2 min averaging times. Note that the LODs for MS/MS experiments are lower than for measurement of  $m$  71 ions for either MVK or MACR. In PTR-LIT, MVK and MACR are differentiated on the basis of the  $m$  41-to- $m$  43 which is 0.07 for MVK and 1.03 for MACR at  $U_{CID}$  of 0.55 volts. Two minor fragments

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at  $m$  53 and  $m$  39 were also detected.

### 3.3 Terpene studies

#### 3.3.1 MS/MS of monoterpenes

Three selected monoterpene fragmentation patterns are plotted in Fig. 3 to compare the CID performance of the PTR-LIT and the QqQ-MS instrument. One monoterpene with a bicyclic structure ( $\alpha$ -pinene), one with an acyclic structure (ocimene), and one with a monocyclic structure (limonene) have been chosen for illustration. Panels a, b and c show experimental results for the QqQ-MS, and panels d, e and f for the PTR-LIT. QqQ-MS data were measured at  $2.3 \times 10^{-3}$  hPa CID gas pressure, operating in a multiple collision mode with up to seven collisions for  $m$  137. Center-of-mass collision energies for  $U_{CC}=0-50$  V were in the range of 0 to 11 eV. The CID fragmentation patterns of the individual monoterpenes for both the QqQ-MS and the PTR-LIT show very little difference with regard to the fragmentation products. However, fragmentation product ratios show compound specific differences. The QqQ-MS breakdown curve can be partitioned into four different energy regimes: i) initial fragmentation at  $U_{CC}$  voltages up to 5 V, ii) primary fragmentation up to 20 V, iii) secondary fragmentation up to about 40 V and iv) tertiary fragmentation at higher  $U_{CC}$ . In the initial fragmentation regime i) the transition between a multiple collision experiment with sequentially excited ions (comparable to the fragmentation mechanism of an ion trap) to a constant low number collision experiment occurs. Therefore, fragmentation ratios at  $U_{CC}=0$  V are similar to those of  $U_{CC}=6$  V. Secondary and tertiary fragmentation is discussed in more detail in the following chapter.

Table 2 summarizes the fragmentation results for selected monoterpenes at 4 different CID voltages. While the differences in ion ratios are statistically significant, it will be difficult to selectively quantify individual monoterpenes in a complex mixture based only on small differences in the MS/MS spectra.

MS/MS of monoterpenes in the PTR-LIT produced fragment ions at  $m$  109,  $m$  95,

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*m* 81 and *m* 79. For all analyzed monoterpenes *m* 137 rapidly decreased at a dipolar excitation voltage of 0.05 V. As a tradeoff between total ion signal intensity and significant differences in the fragmentation patterns an optimum dipolar excitation voltage of 0.35 V is proposed. Table 3 summarizes the measured PTR-LIT fragmentation patterns at 0.35 V dipolar excitation voltage for selected monoterpenes. For the PTR-LIT the fragment relative intensities are very similar, although it might be possible to distinguish ocimene based on the *m* 109-to-*m* 81 ratios.

Comparing the PTR-LIT fragmentation ratios to the QqQ-MS fragmentation ratios, differences are visible, e.g. comparing the limonene *m* 95-to-*m* 81 ratios for the PTR-LIT at  $U_{CID}=0.35$  V and for the QqQ-MS at  $U_{CC}=6$  V, the ratios were 0.63 and 0.17 respectively. In addition to instrumental discrimination effects, there are significant differences in time-frames, numbers of collisions, collision energies, degrees of excitation of first generation product ions, etc., between the ion trap and triple quadrupole MS/MS experiments. Differences in product ion ratios, for this reason, are hardly surprising. Any of these differences, or a combination thereof, can give rise to differences of the magnitude noted here. For the PTR-LIT the fragment relative intensities are very similar, although it might be possible to distinguish ocimene based on the *m* 109-to-*m* 81 ratios.

To demonstrate the  $MS^n$  capabilities of the PTR-LIT, and to elucidate the breakdown pattern for comparison with the QqQ-MS, an  $MS^4$  experiment for limonene is shown in Fig. 4. Panel a shows a PTR-LIT spectrum (fill and scanout) after 0.25 s fill time of limonene. Similar to a PTR-MS, limonene signals at *m* 81, *m* 95 and *m* 137 are visible as a result of fragmentation in the drift tube with *m* 32 and *m* 37 representing  $O_2^+$  and  $(H_2O)_2H^+$  respectively (note the very low level of trimer at *m* 55). Panel b shows the isolation ability for *m* 137, protonated limonene. Isolation with very little loss of signal is possible. Panel c illustrates CID of *m* 137 with 1 V dipolar excitation voltage (second order MS spectrum,  $MS^2$ ) fragmenting to *m* 81 and *m* 95. The sum of the resulting ion signals of *m* 81 and *m* 95 is about a factor of 3 higher than the parent ion at *m* 137 suggesting a decreasing extraction and detection efficiency towards higher

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m. Dissociation of the isolated  $m$  95 ion is shown in panel d ( $MS^3$ ), yielding fragmentation products at  $m$  67 and  $m$  93. Again,  $m$  67 was isolated and dissociated yielding fragments at  $m$  41 and  $m$  39 ( $MS^4$ , panel e). Further fragmentation of either  $m$  41 or  $m$  39 did not yield fragments above the low mass cut-off of  $m$  20.  $MS^3$  fragmentation of  $m$  81 is depicted in panel f resulting in  $m$  79 and  $m$  55. Further fragmentation of  $m$  55 does not show new fragmentation products above the low mass cut-off (data not shown). The PTR-LIT capability to perform multiple MS experiments by sequential isolation and dissociation of ions ( $MS^n$ ) enables a detailed analysis of the fragmentation pathway. Figure 5 demonstrates the fragmentation pathway for limonene obtained with the PTR-LIT including the loss of neutral products.

These results allow us to better interpret the results obtained in the QqQ-MS based CID. The products observed at high  $U_{CC}$  voltages correspond to products obtained via sequential CID in the PTR-LIT. From panel C in Figs. 4 and 5 we deduce that  $m$  55 and  $m$  79 are secondary fragment ions arising from the  $m$  81 ion, and  $m$  67 is a secondary fragment ion arising from the  $m$  95 ion.

### 3.3.2 Sesquiterpenes

The relative abundances of the ten most prominent fragment ions derived from the protonated forms of farnesene and humulene are shown in Table 4. The differences in fragment ion abundances were only minor, even if an acyclic sesquiterpene was compared to a monocyclic species. For the QqQ-MS, the most significant differences in relative signal intensities were found in the  $m$  149-to- $m$  121 ratio at  $U_{CC}=12$  V and in the  $m$  93-to- $m$  81 ratio at  $U_{CC}=33$  V. The PTR-LIT produced the same 10 most abundant fragment ions. For the PTR-LIT, a  $U_{CID}=0.13$  V was used. Maximum absolute intensities were obtained at this value and ratios of the most abundant fragments did not change as a function of the dipolar excitation voltages. For both instruments the data obtained suggest that a simple mixture of farnesene and humulene in a simple binary mixture could be quantitatively determined using the  $m$  149-to- $m$  121 ratio and the

*m* 93-to-*m* 81 ratio. The analysis of a complex mixture of sesquiterpenes is, however, complicated by the similarity in the fragmentation patterns of different sesquiterpenes.

## 4 Conclusions

It has been demonstrated that the QqQ-MS instrument equipped with a Townsend Discharge H<sub>2</sub>O chemical ionization source produces similar VOC product ion spectra as a conventional PTR-MS instrument. This offers the possibility to use this instrument for structural elucidation of isomeric ions. The instrument performance was compared to that of a PTR-LIT. Single MS LODs were in the 0.1-to-0.8 ppb range for both instruments. MS/MS LODs for MVK and MACR were 0.4 ppbv and 0.6 ppbv, respectively, for the QqQ-MS instrument and 0.11 ppbv and 0.17, respectively, for PTR-LIT – all of which are suitable for ambient air measurements in some environments. Fragmentation patterns of six monoterpenes ( $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, limonene, myrcene, ocimene) were obtained for both instruments. The double-ring monoterpene  $\alpha$ -pinene showed a different fragmentation pattern than the linear monoterpene ocimene. No differences were found in structurally similar monoterpenes such as  $\alpha$ -pinene and  $\beta$ -pinene. The similarities in the fragmentation patterns of structurally similar monoterpenes complicate selective detection of individual monoterpenes in complex mixtures. The MS<sup>*n*</sup> ability of the PTR-LIT may be useful to overcome this problem – in addition to revealing sequential dissociation pathways, which cannot be observed in the QqQ-MS instrument. The sesquiterpenes humulene and farnescene could be differentiated by both QqQ-MS and PTR-LIT using the *m* 149-to-*m* 121 or *m* 93-to-*m* 81 ratio. We anticipate that selective detection of individual sesquiterpenes in complex mixtures to be problematic. Further work with the QqQ-MS will focus on the reduction of chemical background and the improvement of the long-term signal stability of the ion source. Furthermore, we will explore the potential of ion neutral reactions in the ion trap of the PTR-LIT instrument for differentiating mixtures of monoterpenes, sesquiterpenes, or other isometric compounds of interest.

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*Acknowledgements.* The PTR-LIT work was supported by the U.S. National Science Foundation under Grant CHE-0314349. The QqQ-MS was funded via the “Uni Infrastruktur III” program. Work on the QqQ-MS was funded by the Österreichische Forschungsförderungsgesellschaft mbH – Basisprogramme. Further support was provided by Ionimed Analytik GmbH, Innsbruck, Austria. We acknowledge the initial QqQ-MS work performed by Pawel Cias.

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**Table 1.** Sensitivities and LODs for selected compounds for one second integration time.

Compound	MH <sup>+</sup> [Th]	Sensitivity [cps/ppb]	QqQ-MS PTR-LIT [pk area/ppb]	Relative Sensitivity (to acetone)		LOD (ppbv)	
				QqQ-MS	PTR-LIT	QqQ-MS	PTR-LIT
acetone	59	84.9	1.20E+04	1.00	1.00	0.77	0.59
MVK	71	N/A	7.33E+03	N/A	0.61	0.40	0.11
MACR	71	N/A	5.60E+03	N/A	0.47	0.60	0.17
MEK	73	N/A	1.16E+04	N/A	0.97	N/A	0.28
hexanone	101	290.1	N/A	3.42	N/A	0.08	N/A
octanone	129	213.6	N/A	2.52	N/A	0.14	N/A
benzene	79	125.6	5.81E+03	1.48	0.48	0.22	0.24
toluene	93	261.5	1.07E+04	3.08	0.89	0.12	0.07
xylene	107	333.3	1.10E+04	3.93	0.5	0.1	0.29
trichlorobenzene	181	132.2	N/A	1.56	N/A	0.21	N/A
isoprene	69	85.3	8.00E+03	1.00	0.66	0.81	0.73
$\alpha$ -pinene	137	296.7	6.72E+03	3.49	0.56	0.16	0.11

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**Table 2.** Relative signal intensities of the main fragment ions of the analyzed monoterpenes at four different CID voltages and corresponding fragmentation ratios ( $m$  137/ $m$  81,  $m$  95/ $m$  81,  $m$  79/ $m$  67 and  $m$  81/ $m$  77).

$U_{cc}$ [V]	fragment ions $m/z$ [Th]	$\alpha$ -pinene <sup>1</sup> and $\beta$ -pinene <sup>a</sup>		3-carene		limonene		myrcene		ocimene	
		signal [%]	ratio	signal [%]	ratio	signal [%]	ratio	signal [%]	ratio	signal [%]	Ratio
3	137	45	0.91	51	1.19	43	0.84	47	1.10	53	1.38
	81	50		42		51		43		38	
11	95	13	0.17	20	0.31	13	0.17	23	0.38	22	0.36
	81	75		65		75		61		61	
32	79	31	3.53	25	1.77	29	2.79	24	1.56	25	1.77
	67	9		14		10		15		14	
50	81	27	0.89	20	0.62	26	0.89	21	0.67	19	0.63
	77	30		33		29		32		30	

<sup>a</sup> identical fragmentation patterns were observed.

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**Table 3.** PTR-LIT relative contribution of the primary fragments at  $U_{\text{CID}}=0.35$  V, ratio of  $m$  95 and  $m$  81 signal and the relative ion intensity.

$U_{\text{CID}}=0.35$ V $m/z$ [Th]	$\alpha$ -pinene	$\beta$ -pinene	3-carene	limonene	myrcene	ocimene
	relative signal [%]					
79	13	14	14	11	12	11
81	54	54	53	54	50	41
95	31	31	32	34	37	44
109	2	1	1	1	1	4
$m$ 95/ $m$ 81	0.56	0.58	0.61	0.63	0.73	1.06

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**Table 4.** Highest fragmentation ion signals for humulene and farnesene at  $U_{CC}=12$  V and 33 V and corresponding fragmentation ratios of  $m$  149/ $m$ 121 and  $m$  93/ $m/z$  81.

relative abundance [%]													
QqQ-MS Compound	$U_{CC}$ [V]	$m$ 81	$m$ 93	$m$ 95	$m$ 107	$m$ 109	$m$ 121	$m$ 123	$m$ 135	$m$ 149	$m$ 205	$m$ 149/ $m$ 121	$m$ 93/ $m$ 81
humulene	12	8	5.1	15.5	6	12.6	10.5	11.5	8.3	17.6	3.3	1.7	0.6
farnesene	12	11.3	5.5	14.5	5.8	13.6	20.4	5.3	8.5	11.4	3.3	0.6	0.5
humulene	33	33.2	17.8	10.6	8.1	3.8	3.5	1.5	1.2	1.1	0.2	0.3	0.5
farnesene	33	20.1	27.6	9.3	8.2	3.8	8.3	0.4	0.3	1.4	0.3	0.2	1.4

relative abundance [%]													
PTR-LIT compound	$U_{CID}$ [V]	$m$ 81	$m$ 93	$m$ 95	$m$ 107	$m$ 109	$m$ 121	$m$ 123	$m$ 135	$m$ 149	$m$ 205	$m$ 149/ $m$ 121	$m$ 93/ $m$ 81
humulene	0.13	2.8	0.4	16.0	2.0	14.5	5.5	7.3	14.2	34.9	2.5	6.3	0.1
farnesene	0.13	6.3	2.5	15.7	1.9	15.8	14.7	7.0	12.6	22.7	0.8	1.6	0.4

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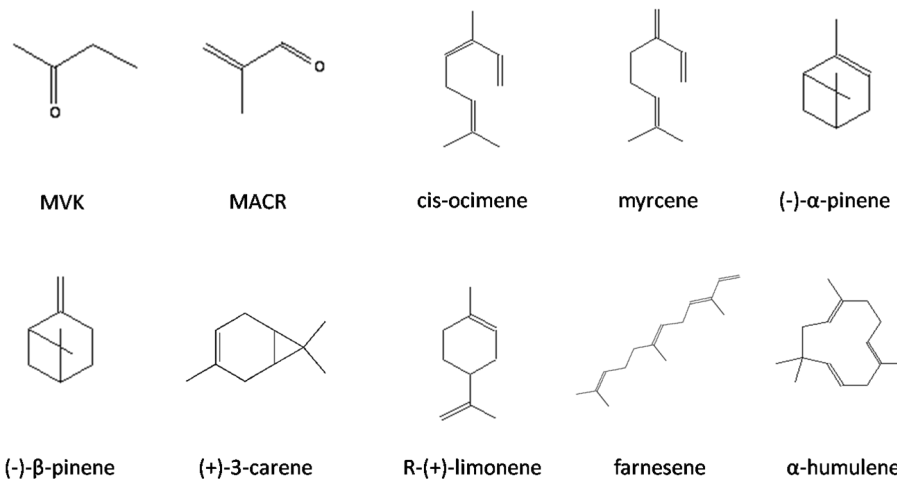
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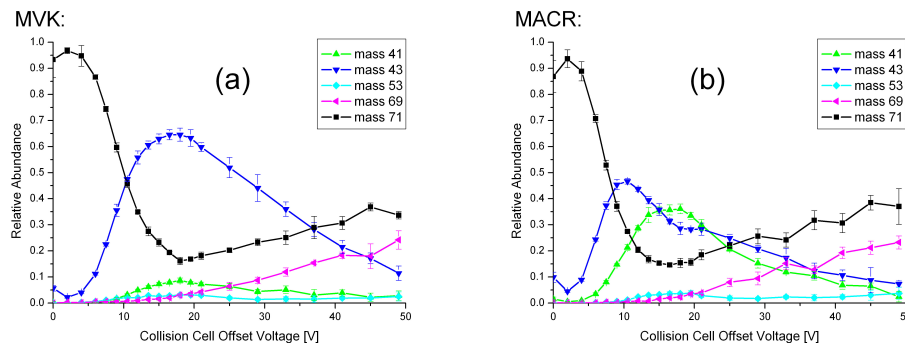


**Fig. 1.** Structures of MVK, MACR, the six monoterpene isomers and the two sesquiterpenes studied.

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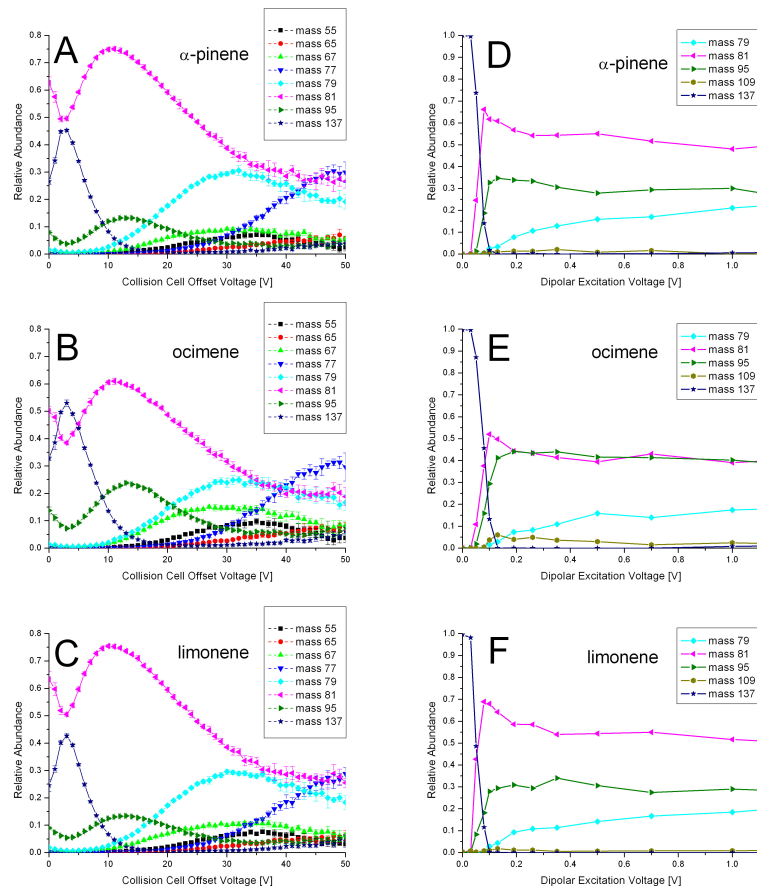


**Fig. 2.** Relative fragmentation patterns of MVK **(a)** and MACR **(b)** as a function of the collision cell offset voltage. Differences in  $m$  41 and  $m$  43 enable a quantitative separation.

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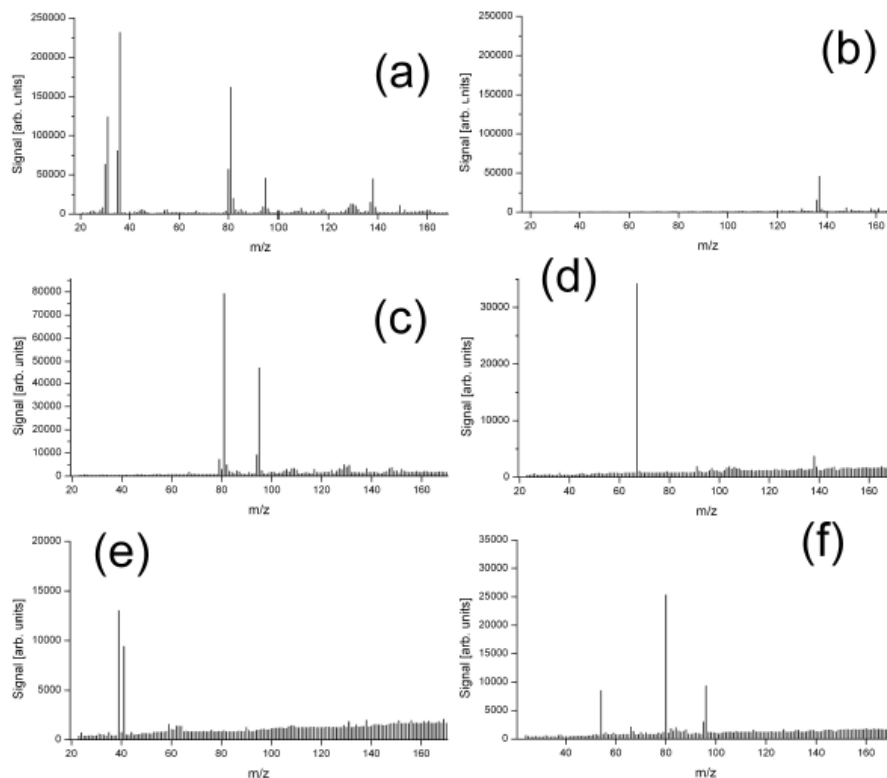


**Fig. 3.** The QqQ-MS relative fragmentation patterns as a function of the collision cell offset voltage for  $\alpha$ -pinene, ocimene and limonene are shown in (A), (B) and (C). Comparable PTR-LIT fragmentation patterns as a function of the dipolar excitation voltage are depicted in (D), (E) and (F).

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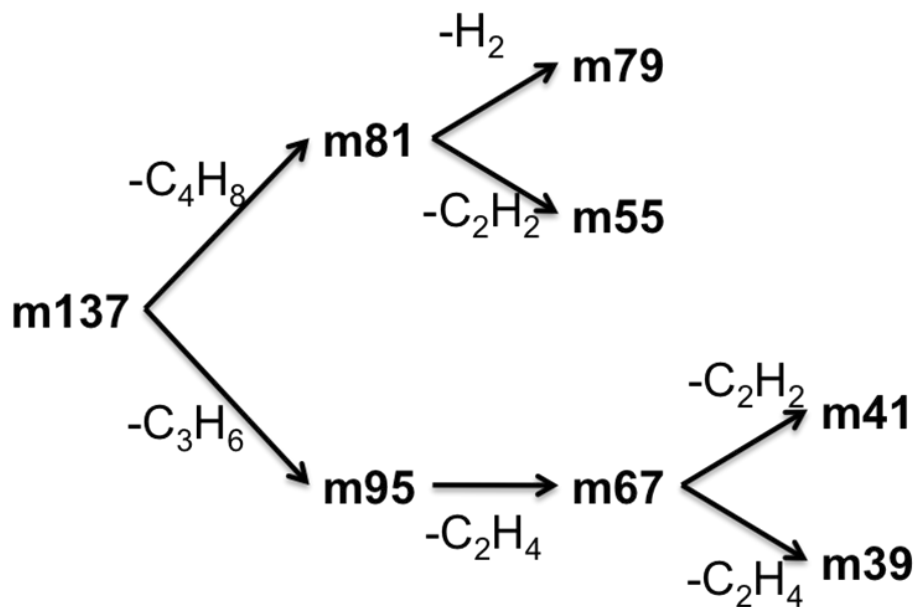
**Fig. 4.** (a) shows a PTR-LIT (fill and scanout) spectrum after 0.25 s fill time for limonene. (b) shows the isolation ability for  $m/z$  137. (c) illustrates the CID spectrum for  $m/z$  137 with 1 V dipolar excitation voltage. (d) illustrates the CID spectrum for the isolated  $m/z$  95 product, and (e) the further CID spectrum for the isolated  $m/z$  67 product. (f) depicts the CID spectrum for  $m/z$  81.

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**Fig. 5.** Fragmentation pathway of limonene obtained by a MS<sup>n</sup> PTR-LIT CID experiment.

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