

## ***Interactive comment on “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” by M. Müller et al.***

**M. Müller et al.**

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The authors thank the reviewers for their good comments and suggestions that helped to improve the quality of the manuscript. In the following we respond to the individual comments and describe their realization.

Comments on the review by Referee 1 (P.T. Palmer)

Comment: In researching this further, I noted that McLafferty explained this in his classic MS Interpretation text by noting that "monoterpene hydrocarbons exhibit spectra

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which are consistent with initial isomerization to a cyclohexane structure plus other rearrangements such as methyl migration".

Reply: Following comment was added to section 3.3.1: "McLafferty (1993) noted that monoterpene hydrocarbons containing a cyclohexane ring (e.g. limonene and  $\alpha$ -pinene) exhibit spectra which are consistent with initial isomerization to a cyclohexane structure, plus other rearrangements, such as methyl migration. Therefore, the similar fragmentation patterns suggest isomerization due to ionization, even caused by the soft proton transfer reaction."

Comment: This also begs the question that if the chemistry of the fragmentation of these monoterpenes are so similar, then would not their atmospheric chemistry likewise be similar and hence would not a measurement of TOTAL monoterpene concentration suffice?

Reply: Indeed, photo-oxidation studies (smog chamber experiments) show, that monoterpenes show only slightly different photo-oxidation products and product ratios (Hallquist et al., 2009). Nevertheless, the authors think that measuring the total monoterpene concentration might not be sufficient to answer certain atmospheric relevant questions, as:

(1) the analyzed monoterpenes show different atmospheric lifetimes. As an example, the OH lifetime of  $\alpha$ -pinene,  $\beta$ -pinene and limonene are reported to be 2.6 h, 1.8 h and 50 min, respectively (Atkinson and Arey, 1998).

(2) different monoterpenes are emitted by different sources. For example, Ruuskanen et al., 2005, demonstrated by GC-MS analysis, that Scots pine predominantly emit 3-carene and  $\alpha$ -pinene, 71

Comment: The manuscript would also benefit from a critical comparison of their reported LODs to other PTR-MS work - I recall one manuscript in which single ppt LODs were achieved with a quad mass analyzer.

Reply: Indeed, reported commercial PTR-MS (Ionicon Analytik, Austria), LODs achieve

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LODs of about 10 pptv per m/z and second integration time. Following comment was added to section 3.1 to clarify the superiority of a PTR-MS for monitoring purposes: “Nevertheless, the reported  $2\sigma$ -LODs of the QqQ-MS and the PTR-LIT are still a magnitude higher compared to the performance of a commercial PTR-MS (Ionicon Analytik, Austria), reaching  $2\sigma$ -LODs down to 10 pptv per m/z for one second integration time.”

Comment: One often finds that LODs are typically better in MS/MS vs MS mode due to lower background (noise) levels. This is not the case here and perhaps some explanation is warranted.

Reply: In the MS mode, the QqQ-MS is operated without CID gas. As a result of the higher transmission, sensitivities are about a magnitude higher. Therefore, although the BG Intensity is higher in the MS mode, the increased sensitivity causes a lower LOD compared to the MS/MS mode. Therefore following comment was added to section 3.2: “As a result of the decreased ion signal intensities caused by collisions with the added CID gas, QqQ-MS LODs for MS/MS experiments are higher compared to single MS measurements.”

Comment: The manuscript also takes some liberty in the use of significant figures for reporting LODs.

Reply: The whole manuscript was clarified to show only  $2\sigma$ -LODs

Comments about terminology:

Reply:

“quasimolecular ion” was changed to “protonated molecule”

“high energy CID” was changed to “relatively high energy CID”

Technical corrections:

Reply:

P1844, L11: are SHOWN in Table 1.

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P1846, L7: with a MONOCYCLIC structure

P1846, L22: in the following SECTION

P1853, Table 1 header: Table header was shifted due to Word to TeX conversion

Comments on the review by Referee 2 (M. Claeys)

Comment: Most comments relate to standard definitions of terms relating to mass spectrometry, which can be found in the following publication: “Standard definitions of terms relating to mass spectrometry (IUPAC Recommendations 2006)” by Murray et al. (<http://old.iupac.org/reports/provisional/abstract06/murray<sub>pr</sub>s.pdf>)

Reply: Thank you very much for that comment. Accordingly, the manuscript has been updated to the standard definitions of terms relating to mass spectrometry recommended by IUPAC.

P1838, L6 and following: “quasimolecular ion” was changed to “protonated molecule”

P1843, L8 and following: for the whole manuscript “m” is changed to “m/z”

P1847, L24: the term “parent ion” is changed to “precursor ion”

Comment: I suggest to refer early on in the introduction to the recent comprehensive review article on the current status of secondary organic aerosol from the oxidation of BVOCs: Hallquist et al., The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155-5236, 2009.

Reply: The citation was added after P1839, L10: “The current status of knowledge of formation, properties and impact of SOA was recently reviewed by Hallquist et al. (2009).”

Comment: As already pointed out by another reviewer (P. Palmer), I also do not consider the CID regime applied in QqQ-MS as high-energy but rather as low-energy, because the energy deposited in the ions is in the eV range and lower than 25 eV. The

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latter energy can only be achieved with laboratory frame energies in the keV range, which is not the case here.

Reply: Indeed, the collision energies obtained with the QqQ-MS are much lower than 25 eV. Therefore, and to point out, that the CID energy is higher compared to the PTR-LIT, "high energy" was changed to "relatively high energy" for the whole manuscript.

Comment: The abbreviations "E/N" and "Td" need to be defined.

Reply: P1843, L12 has been updated to "The PTR part was operated in a low E/N (E represents the electric field strength, N the gas particle number) mode at 95 Townsend (1 Td = 10<sup>-17</sup> V cm<sup>2</sup>) corresponding to 400 V drift tube voltage."

Technical corrections:

Reply:

P1840, L16: Both approaches utilize a 3D ion trap as the MASS ANALYZER

P1841, L5: . . . , and IT can perform. . .

P1841, L13: . . .(-)- $\alpha$ -pinene, (-)- $\beta$ -pinene, (+)-3-CARENE and. . .

P1841, L19: . . . AT a constant flow rate . . .

P1844, L11: . . . are SHOWN in . . .

P1846, L7: . . . a MONOCYCLIC structure . . .

P1849, L27: . . . other ISOMERIC compounds . . .

P1856, Table 4: Highest FRAGMENT ion signals . . .

References:

Atkinson R., and Arey J.: Atmospheric chemistry of biogenic organic compounds, *Acc. Chem. Res.*, 31, 574-583, 1998.

Hallquist et al.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155-5235, 2009.

T.M. Ruuskanen et al.: On-line field measurements of monoterpene emissions from

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Scots pine by proton-transfer-reaction mass spectrometry, *Bor. Environ. Res.* 10 (2005), p. 553.

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Interactive comment on *Atmos. Meas. Tech. Discuss.*, 2, 1837, 2009.

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