

# *Referee report on Addition of fast GC to SIFT-MS for separation and analysis of monoterpene isomers*

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## **General Comments**

This work describes a GC-CIMS measurement technique developed to improve understanding of the composition of monoterpenes in the atmosphere which is an active area of interest in the atmospheric chemistry community due to key their roles in processes leading to formation of ozone and secondary organic aerosol (SOA) and is therefore highly relevant to the scope of AMT.

A series of experiments on individual standards of monoterpene isomers, monoterpene standard mixtures and the headspace of conifer foliage samples using a bespoke fast GC system coupled with a SIFT-MS is presented to demonstrate the potential application of fast GC-SIFT-MS for the separation and analysis of monoterpenes and other isomers in atmospheric and laboratory studies that is not currently achievable with SIFT-MS alone. The performance of two different GC columns in the fast GC SIFT-MS system was assessed - a generic (MXT-1) GC column and an application specific GC column (MXT-Volatiles). In addition, two reagent ions ( $\text{NO}^+$ ,  $\text{H}_3\text{O}^+$ ) were used in the SIFT-MS system to aid in compound identification. The methods and assumptions described in the manuscript are valid, clearly outlined and reproducible.

This work represents one of the first, if not the first, reported trial of a fast GC coupled with an SIFT-MS system which has a considerable user group worldwide. As noted in the manuscript introduction, this is an area of active development with previous work describing fast GC coupled with other chemical ionization mass spectrometry (CIMS) systems, in particular PTR-MS (Materic et al 2015, Pallozzi et al 2016) are properly acknowledged in the manuscript.

Given the similarities between SIFT-MS and PTR-MS it could be considered that this paper does not represent a substantially novel development.

The original contributions to atmospheric measurement practice are:

- The comparison of two GC columns - a generic (MXT-1) GC column (as used in previous fast-GC and GC-PTR-MS studies) and an application specific GC column (MXT-Volatiles) – this has relevance to the wider fast GC applications (SIFT-MS, PTR-MS, other CIMS, fast GC-FID...) in which MXT-1 column has been used.
- The first reported use of  $\text{NO}^+$  reagent ions in a fast GC - CIMS set-up.

The presentation is generally well structured however the language is at times unclear and the manuscript requires significant copy editing prior to final submission. Furthermore, specific comments below should also be addressed.

## Specific Comments

- **P1 lines 24 - 26** – suggest re-write “The system can thus be used for direct rapid monitoring of monoterpenes above 20 ppbv, such as applications in laboratory studies of monoterpene standards and leaf headspace analysis. Limitation of the sensitivity due to the total sample flow can be improved using a multicolumn pre-separation.”.
- **P2 lines 12 – 14** – “ However, chemically similar molecules with the same atomic composition (structural isomers) usually produce identical analyte ions with similar branching ratios and therefore the neutral analyte molecules cannot be easily differentiated using SCI-MS alone (Smith et al., 2012)”. *Suggest addition* - As a result, standard SCI-MS techniques such as SIFT-MS and PTR-MS are limited to reporting concentrations of the sum of monoterpenes present in the sample, and the composition of monoterpenes present cannot be determined.
- **P2 lines 19 – 27** – move paragraph to start of Introduction, then follow on with introductory discussion of measurement of monoterpenes.
- **P4 line 1** – what were the findings of the discussion in Pallozi et al relevant to this section? The relevant limitations?
- **P4 lines 4 – 7** – suggest re-write “In the present article, we report method development results aimed to ~~selective analyses of~~ selectively analyse individual monoterpenes in mixtures in air using a bespoke fast GC/SIFT-MS combination with H<sub>3</sub>O<sup>+</sup> and NO<sup>+</sup> reagent ions..”
- **P6 line 11** – “This effect can to be estimated and have to be included to a quantification calculation.” *Rewrite* – This effect can be estimated and has to be included in the quantification calculation”. *Further detail needed for reproducibility of results– the effect is estimated how? And how is the estimation included in the quantification calculation described in section 3.3?*
- **Section 3.1** – Why is exothermicity relevant? – The stability of the product ion molecules depends on their internal energy which in turn depends on the exothermicity of the chemical ionisation reactions. The exothermicity of NO<sup>+</sup> reactions is discussed, but not the exothermicity of PTR from H<sub>3</sub>O<sup>+</sup>. The exothermicity of proton transfer from H<sub>3</sub>O<sup>+</sup> is given by the proton affinity (PA) of the H<sub>2</sub>O (165 kcal mol<sup>-1</sup>) minus the PA of the analyte.  
“The interaction of the primary ions with monoterpenes may be affected by presence of neutral water molecules and thus by different humidity of the sample”. In the case of H<sub>3</sub>O<sup>+</sup> this is due to the presence of H<sub>3</sub>O<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub> reagent ion clusters which also undergo PTR with monoterpenes and have a higher PA than that of H<sub>2</sub>O (PA (H<sub>2</sub>O.H<sub>2</sub>O) = 195 kcal mol<sup>-1</sup>) and the PTR reaction is less exothermic thus reducing fragmentation.
- **Section 3.3** – add detail of temperature effect mentioned previously on P6 (see above).
- **P10 lines 12 – 15** – In the present experiment ~~we used heated columns~~ both columns were heated isothermally to the temperature app. 40 °C due to the behaviour of the MXT-1 column selected to optimise both temperature stability and chromatographic separation (see Fig S4 in supplement). For higher temperatures, the monoterpene chromatogram peaks coalesced while for lower temperatures a significant influence of the lab air temperature fluctuations was apparent. However, even At these

optimised conditions for MXT-1 column, monoterpenes are not fully separated and thus, fast GC with MXT-1 column alone (at 40 °C) provides only qualitative analysis.

- **P16 lines 13 – 16** – clarify “The second region of a small peak 0.38 (H<sub>3</sub>O<sup>+</sup>) and 0.14 (NO<sup>+</sup>).”
- **Section 4.4** – As we do not know the composition of the monoterpenes in the leaf samples and are comparing to only 8 standards, consider less definitive language in places e.g. for Spruce: “The tailing edge of the first peak shows a decrease of  $r_w$  (0.29 for H<sub>3</sub>O<sup>+</sup>, 0.14 for NO<sup>+</sup>) ~~due to~~ attributed to a small contribution by camphene.
- **P22 lines 4 – 9** – The description of LOD determination and results should come earlier - move to section 3.3 re-name the section “Fast GC SIFT-MS limits of detection and quantification”. Only comparison with LOD of other similar techniques (e.g. GC-PTR-MS) - why are they different?, as well as proposed developments to improve LOD of this system should be discussed here in section 4.5.
- **P22 lines 21 – 24** - *re-write* “Aside from potentially better selectivity, a benefit of employing the NO<sup>+</sup> reagent ions in atmospheric analysis is quantification of isoprene, which for H<sub>3</sub>O<sup>+</sup> reagent ion mode, suffers mass interference from product ions of other biogenic species including ~~ions interferes with~~ furan, C<sub>5</sub> aldehydes and 2-methyl-3-buten-2-ol (Karl et al., 2012; Karl et al., 2014), ~~and overlapping with as well as~~ the second hydrate of methanol that is also emitted by plants (12% of global BVOC emissions) (Španěl et al., 1999).
- **P23 line 28** – *suggest adding-* The major limitation of the GC-SIFT-MS system described here is the high limits of detection (~16 ppb) which currently preclude its application in measurements of monoterpenes in typical ambient concentrations.
- **P23 lines 26 – 27** – *This statement is unclear, consider re-writing* “The fast GC SIFT-MS combination can thus be a step towards atmospheric analyses of monoterpenes that should resolve individual compounds due to their different reactivity with the OH radicals.” – due to their different OH reactivities, the ability to distinguish individual monoterpenes at high time resolution with fast GC SIFT-MS has the potential to improve our understanding of the contribution of individual monoterpenes in atmospheric chemistry processes such as formation of tropospheric ozone and SOA.

