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Atmospheric Measurement Techniques Discussions

Interactive comment on "Addition of a fast GC to SIFT-MS for analyses of individual monoterpenes in mixtures" *by* Michal Lacko et al.

Anonymous Referee #1

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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 (NO+, H3O+) were used in the SIFT-MS system to aid in compound identification.

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 papers describing fast GC coupled with other chemical ionization mass spectrometry (CIMS) systems, in particular PTR-MS (Materic et al 2015, Pallozzi et al 2016). 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:

1) 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.

2) The first reported use of NO+ reagent ions in a fast GC - CIMS set-up.

However, additional additions/revisions are required for substantial conclusions to be reached regarding the performance and potential applications of fast-GC-SIFT-MS for quantification of monoterpene isomers. Specifically, more quantitative information is required on the detection limits, sensitivity and procedures for the quantification of species concentrations- see specific comments below.

Specific comments

Detection limit - p 17 Line 15 states "The present experiments indicate that using the fast GC-SIFT-MS combination, it is possible to achieve only qualitative analysis of the monoterpene mixture with a limit of the detection of about 100 ppb." Detection limits of 100 ppb is a major limitation for the application of fastGC-SIFTMS to measurements

of individual monoterpenes in ambient air where concentrations are typically orders of magnitude lower (1 -10 ppb). The manuscript must include descriptions of:

1) How the stated detection limit of ∼100 ppb was determined?

2) Why is this detection limit so high?

3) Potential improvements to the instrumental set-up that would reduce the detection limit to a range that would allow its application to measurements of ambient air (< 1 ppb).

Without these additions the application of this measurement technique for atmospheric measurements is limited making the relevance of this work to AMT highly questionable.

Quantification - The abstract, p 1 Line 18 states "Thus, it is possible to quantify components of a monoterpene mixture in less than 45 s by the MXT-1 column and to separate them in less 180 s by the MXT Volatiles column."

Concentrations of monoterpenes are not quantified in this work and this claim is contradicted in the text p 17 Line 15 (as shown above) "it is possible to achieve only qualitative analysis of the monoterpene mixture". There are other similar contradictory statements in the manuscript which must be addressed.

Calibration – What is the sensitivity of this method? Was the system calibrated with certified gas standards containing one or more monoterpenes, and an empirical calibration factor determined?

Absolute quantification - In lieu of an empirical calibration factor, the well-defined conditions in the SIFT-MS permit calculation of the concentrations of monoterpenes based on the raw signals of reagent and analyte ions (ie [m/z 137] as defined in section 3.2 of the manuscript), known reaction rates, and branching ratiosand instrument parameters as described in the SIFT-MS literature (e.g. Smith and Spanel 2005, Mass Spectrom. Reviews, 24, 661 – 700).

Direct measurement via SIFT-MS - Was direct quantification via SIFT-MS (without GC column) performed? Few comparisons of NO+ and H3O+ measurements of monoterpenes are available in the published literature and would be a valuable contribution.

Both the detection limit and the sensitivity of the method are critical to understanding the application of this method for measurements of monoterpenes in the atmosphere and in laboratory studies. Neither are adequately described here making the relevance of this work to AMT highly questionable.

Relative abundance - In lieu of quantitative determination of individual monoterpene isomers, can the peak areas be used to estimate the relative abundance of each monoterpene species in the samples (mixtures and leaf headspace samples) ? Understanding the rel. abundance of monoterpenes is key to determining accurate calibration factors (see deGouw et al. (2003) JGR-Atmospheres 108, D21), and more importantly understanding the OH reactivity of BVOC dominated atmospheres. Suggest including NO+ and H3O+ reaction rates in Table 1 to demonstrate the importance of understanding the monoterpene composition to the accuracy of CIMS monoterpene measurements based on a single m/z, and adding a table of OH and O3 reaction rates for each monoterpene isomer identified and their relative abundance in leaf samples as well as some discussion regarding the potential contribution of different monoterpenes in the oxidation budgets of atmospheres dominated by emissions from these plant species. Overall, the measurement system and its operation are sufficiently explained however, inadequate information of the performance of this method in terms of detection limit and sensitivity are provided and potential future developments to improve performance are not adequately covered. Without this additional information the manuscript does not provide a substantial enough contribution to development of atmospheric measurement techniques for publication in AMT.

A key issue with CIMS instruments such as SIFT-MS and PTR-MS is essentially we know how much there is but we don't know what it is? Adding pre-separation techniques attempts to overcome this however, the data presented in this paper essentially

reverses the challenge- we know what there is but not how much ? The manuscript requires a clear procedure for the quantification of monoterpene concentrations and/or the relative abundance of monoterpene isomers from the raw data in order to demonstrate the usefulness of this method over direct measurements with SIFT-MS. Quantification has been demonstrated in related instruments (Jones et al 2014, Materic et al 2015, Pallozzi et al 2016).and it is unclear why it was not part of this work.

If these additions/revisions can be made, the following technical comments should also be considered.

Technical comments

Whole manuscript– replace SCI-MS with CIMS, the term chemical ionisation mass spectrometry (CIMS) is an established mass spectrometry term for analytical systems including SIFT-MS, PTR-MS etc

Abstract p1 line 18, change “quantify” to "qualitatively identify”

Abstract – add a couple of sentences at the end -what is the practical significance of this work? what is the theoretical significance?

P2 line 3, change “The analytical ion-molecule reactions” to “ The chemical ionisation reactions”

P2, line 13, suggest addition of a new paragraph discussing the fact that due to issues with stability of monoterpene mixtures in certified gas standards, CIMS instruments employed in ambient air studies are often calibrated with certified gas standards containing only one or two monoterpenes, (typically a-pinene). However the instrument response differs between isomers due to differences in their ionization reaction rates and branching ratios. To determine an accurate (weighted) instrument sensitivity value for monoterpenes, the relative abundance of monoterpene isomers must be known (see deGouw et al. (2003) JGR-Atmospheres 108, D21).

P2 paragraph lines 13 – 21 – these concepts need to be re-visited in discussion and

summary to demonstrate the usefulness of these techniques.

P2 line 21, move these two sentences into subsequent paragraph “Gas chromatography mass spectrometry (GC-MS) coupled with pre-concentration techniques has been developed to successfully identify and quantify different atmospheric monoterpenes (Janson, 1993; Räisänen et al., 2009; Song et al., 2015). However, the requirements of pre-concentration and long cycle time (more than 1h) are obviously unsuitable for real-time measurements.”

P4, “It is interesting to note that the flow of sampled air, established by the pressure difference between ambient atmosphere and the low pressure of the SIFT-MS flow tube, changes with the column temperature due to the variation of the dynamic viscosity of the air (see Fig. 2).” – Does this affect flow tube residence time (reaction time, t) important in SIFT-MS quantification calculations?

P4, line 16, Can measurements by the SIFT-MS when the GC set-up is in “normal mode” be considered an instrument zero (SIFT-MS instrument background)? Can you use this data to calculate the detection limit and subtract from “sampling mode” measurements?

P5, line 16- “Sampling was repeated several times to improve sensitivity.” No data for sensitivity is presented.

P5 Section 3- insert details on the time it takes to switch between reagent ions and to achieve stable ion signals- this is crucial if NO+ and H3O+ are to be used for compound identification. What was the intensity and purity of the reagent ion signals?

P7 insert section (after section 3.2) describing quantification procedure (as discussed in specific comments above) either using empirically derived calibration factors or via absolute quantification procedure based on [m/z 137] for H3O+ mode; and [m/z 136] for NO+ mode.

P8 Section 4.1 Comparison of columns: MXT-1 vs MXT-volatiles. The comparison of

these two columns is valid given the use of the MXT-1 column in related instruments presented in the published literature (Jone et al 2014, Pallozzi et al 2016, Materic et al 2015 etc).

P8 paragraph line 12 -18 – Your approach needs to be more clearly articulated – for instance, firstly the instrument response to individual monoterpene species, in terms of retention time, and product ion ratios, was characterized via analysis of a series of prepared standards with both the MXT1 and MXT volatile columns and when H3O+ and NO+ were employed as the primary reagent ion in the SIFT-MS. Secondly, the separation of monoterpenes isomers using two columns, and the two reagent ions (NO+, H3O+) was demonstrated through analysis of prepared mixtures containing 8 monoterpenes. Lastly, the application of the GC-SIFT-MS for the separation (and quantification?) of monoterpene isomers in a real-world analysis is presented in a series of leaf headspace analyses.

Section 3.3, Note it is unclear whether the same individual standards and mixtures of monoterpene were analysed by both NO+ and H3O+ in the same analysis runs?

P8 line 22 – "Whilst the retention times for individual monoterpenes are different, they are not sufficiently stable (fluctuate by > 1 s, see Table 1) in the present fast GC device for analyses based on retention time only to be reliable." Suggested improvements to instrument design?

P8 line 28, the following statement is unclear "the peak shapes cannot be compared directly but the peak width (FWHM) increased only two times for the MXT-Volatiles column". Also define FWHM.

P9, Table 1 – add columns for reaction rates of monoterpenes with NO+ and H3O+ - consider landscape page layout (see comment above re Relative Abundance)

P11 Section 4.1 – Discussion of response to individual monoterpene standards. Insert Figure S2 and a corresponding plot for the MXT-volatiles column into section 4.1.

These are very helpful when interpreting subsequent Figures 3 and 4. What conclusions can be reached from the tests of individual monoterpene standards – based on these tests what peaks are likely to co-elute, and what peaks are likely to be able to be separated in analysis of an unknown mixture? These tests provide the fundamental information for interpretation of the data from mixtures and leaf samples and should be included in the main text.

P10 line 10 "As observed for both columns, separation can be improved by decreasing the column temperature (see Fig. S3 in the Supplement), however this may increase the chromatogram width and thus decrease the sensitivity of the technique. Additional sensitivity can be achieved by increasing the injection time, which will, however, increase the peak width." – this discussion is not quantitative, no explicit sensitivity data is presented.

The discussion in Section 4.1 regarding analysis of mixtures needs to be restructured.:

1) provide a direct comparison between MXT-1 and MXT-volatiles at the same conditions. ($\sim$40- 45C). Figures 3 and 4 – Figure 3 is actually a comparison of H3O+ and NO+ and the data from the MXT1 and MXT-volatiles column are not compared side-by-side. Format a page in landscape orientation, combine figures 3 and 4 (three panels) and present them in a compatible format (ie same formatting and labelling etc).

2)Discuss challenges and potential improvements ie stability in retention times, improved separation via decreasing column temp, improved sensitivity by increasing injection times.

3)Present MXT-volatiles column data under optimized conditions – ie "The MXT-Volatiles column facilitates identification of all monoterpenes present in the mixture for temperatures close to room temperature (see Fig. S3 in the Supplement)." – the top panel in the S3 plot is key to demonstrating the achievable separation of the MXT-volatiles column - move it from the supplement to the main body. The additional species identifiable using this technique compared to the MXT-1 set-up need to be more clearly

summarised.

P12 Paragraph lines 8 – 17- needs to be moved to later in the discussion or into section 4.5 to show that aside from potentially better selectivity other co-benefits of employing the NO+ reagent ion in CIMS measurements of BVOCs, in particular in measurements of isoprene (See Karl et al 2012 ACP 12:11877 – 11884, and Karl et al 2014 Int J. Mass Spectrom. 365-366:15-19). There are many more species which interfere with quantification of isoprene in H3O+ reagent ion mode such as furan, 2,3,2-MBO, C5 aldehydes.

P12 line 19 " However, the ratios obtained for α-pinene and myrcene are somewhat variable between the FS and MIM data and they also differ somewhat from the literature values." – be quantitative ie state % variability. Is the variability a result of changes in the reagent ion intensity (consider using normalised intensity), or composition (eg % reagent ion impurities of H3O+(H2O), O2+, NO+)?

P14 Section 4.3 –For this method to be useful in atmospheric research the concentrations of monoterpene isomers or an estimate of their relative abundance must be quantified from the data and presented here and section 4.4(see specific comments above re quantification).

P14 Section 4.4- be consistent – use dot point format as for previous section. Why is the data from non-optimized conditions (40C) presented? Was the analysis done at the optimal temperature (5V) for separation? If so, should be presented.

P14 line 14, " The signal increase in the third region may indicates trace presence of (R)-(+)-limonene." – the m/z81 signal or the ion intensity?- not clear.

P15 Section 4.4- need to state that similar experiments but on a different series of conifer samples were also conducted using the MXT-volatiles column.

P15 Figure 5- consistent units (normalised intensity) should be used for all figures (3-6), label peaks in both H3O+ and NO+ chromatograms (both Fig 5&6). Query the signal

to noise ratio of some of the identified peaks e.g. H3O+ spruce 3-carene / limonene peak. Re-iterates importance of quantifying method LoD.

P17 Section 4.4 – This section should conclude with a table of the relative abundance of each monoterpene isomer in the leaf samples and their reaction rates with OH and O3 with associated discussion.

P17 Section 4.5 – "The present experiments indicate that using the fast GC-SIFT-MS combination, it is possible to achieve only qualitative analysis of the monoterpene mixture with a limit of the detection of about 100 ppb. This is inferior to the previously described fastGC-PTR-MS systems (Materić et al., 2015; Pallozzi et al., 2016), which achieved full separation with limit of the detection up to 1-2 ppt." – list the reasons for the difference in performance and potential future developments of the GC-SIFT-MS method to improve performance. This statement must be addressed in more detail as these significant limitations preclude the application of this method to ambient studies and make the inclusion of this work in AMT questionable.

P17 line 17 – start new paragraph at "However, one advantage of SIFT-MS is the facility to use two reagent ions, and the analysis of product ion ratios provides additional information. Thus, the combination of the data from the two reagent ions together with the analyses of the product ion signal ratios ri can be shown to improve the identification of monoterpenes." – be more specific, what additional compounds were identified using the reagent ion chemistry. Suggest insert discussion from 4.2, on usefulness of NO+ reagent ion for identification of other BVOCs here. As a side note, switchable reagent capability has been developed for PTR-MS and other CIMS and is not unique to SIFT-MS.

P17 line 20 – "The results obtained from the present study agree well with the literature reports." Be more specific, suggest – the results obtained from the analysis of leaf headspace samples agree well other studies in the published literature. Suggest authors present comparisons by tree species as a table with following columns-

plant species name; monoterpenes identified; rel. abundance where available; measurement method; time resolution; and where available: LoD & sensitivity; and literature reference. Focus discussion on number and rel. abundance of monoterpenes identified and the methods used, not on geographical variability or variability between species beyond the scope of this work. What is the potential advantage of this method over others? Time resolution?

P18 Section 5- "A new method has been developed that allows quantitative analyses of individual monoterpenes in mixtures using SIFT-MS enhanced by chromatographic preseparation." As previously stated this is not correct and contradicts the first line of the previous section (4.5) "The present experiments indicate that using the fast GC-SIFT-MS combination, it is possible to achieve only qualitative analysis of the monoterpene mixture with a limit of the detection of about 100 ppb."

P18 line 16 start new paragraph at "A weakness of the current fast GC setup is the relatively poor temperature stability caused by a strong dependence on the laboratory ambient temperature. . .."

P18 line 18 "It has been shown that a clear advantage of SIFT-MS is the facility to use different reagent ions and to utilize the ratios of the specific product ions of their reactions with the various monoterpene isomers at the same retention time to improve the identification of the monoterpenes." Belongs in previous paragraph (P18, line 10).

P18 line 23 – "This novel idea of a fast GC-SIFT-MS combination could broaden the application of SIFT-MS to in situ trace gas analyses of complex mixtures such as ambient air and exhaled breath.". There are several issues with this statement:

1) SIFT-MS is already used for in situ ambient air and breath analysis- this technique GC-SIFTMS does not broaden its application. The practical significance of this work is that it aims to address the challenge of quantifying isomers in CIMS measurements of complex mixtures.

2) Also, need to preface this statement "With improved limits of detection and sensitivity, this novel fastGC-SIFT-MS could. . .. . .." currently its application in ambient air analysis is limited due to high LoD and lack of data about its sensitivity.

What is the theoretical significance of this work- what will an improved understanding of the complex mixture of monoterpenes contribute to our understanding of atmospheric chemistry? Ie estimates of total OH reactivity etc.

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