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Atmospheric Measurement Techniques Discussions

Interactive comment on "Development of a thermal desorption-gas chromatography-mass spectrometry method for the analysis of monoterpenoids, sesquiterpenoids and diterpenoids" *by* Aku Helin et al.

Anonymous Referee #1

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The manuscript of the development of a thermal desorption gas chromatography mass spectrometry method for the analysis of monoterpenoids, sesquiterpenoids and diterpenoids is a useful contribution to AMT, but it needs to undergo major revisions before it is published.

There are three main issues 1- The method has already been validated for monoterpenoids and sesquiterpenoids, so all the information in the paper about these compounds is not necessary. Furthermore, there is a strong mix up in the text between monoterpenoids, terepenes and terpenoids which is highly confusing. Since I recom-

mend to use only diterpenoids, this problem will be solved.

2- The ambient measurements are not representative. You will never get 60°C in a boreal environment. Additionally, there is no blank for these measurements, making the experiments quite doubtful. Please discuss why such high increases of temperature are representative for boreal environments, and how likely is for such compounds to really be emitted from this ecosystem.

3- Method development. The paper needs definitions on method development and validation. Please explain how this is different from previous studies. Furthermore, please discuss while you develop a method for quantification but at the end, for real samples you use a different system and you only give semi-quantitative information.

Specific comments: Page 1 Line 14: Despite I think ozone reactivity of diterpenes is important and should be stated in the paper, it is really not introduced in the text. . . how these measurements add to your method validations. It must be better introduced here in abstract and in text.

Page 1 line 19: I do not understand why heating up to 60°C is representative of anything natural, you will never get these temperatures in boreal ecosystems. In which way these diterpenes will then be emitted to ambient air?

Page 1 Line 20: five what?

Page 1 Line 20: it is really not acceptable that you provide a method validation to then deliver semi-quantitatively.

Page 2 Line 41. The way you express monoterpenoids (as well as sesquiterpenoids and diterpenois) is really confusing. By omitting mt and sqt this problem will be solved. But please do explain what do you mean by monoterpene and monoterpenoid. . . for instance, is p-cymene not a monoterpenoid? And it is only C10H14. . ..In fact, you could name them in Table 1, S4,S5.

Page 2 line 62. This is confusing, please state which branch enclosure you are referring

and which ambient studies? Do you mean you experiments or the previously reported studies?

Page 2 Line 63. If you are going to say this, you need to explain what do you mean by method validation. Do you need two different analytical systems to prove your concentrations? And what do you mean by performance parameters? GC and sampling settings? In is normally well mentioned in the methods of each study? Please state why you method is 1) better than previously mentioned for DT measurements, and 2) how you truly validate the method rather than say your method is good because I do not loose DT in the lines. . .

Page 3 Line 69-78. In your objectives are somehow confusing. First you talk about the applicability of sorbent tubes and GCMS for mt, sqt and dt. I do not know what is new here. This has been shown in the past, plus this is no objective, but rather telling what you did. Later you say the method was incorporated from previous studies for sqt and mt. Thus there is no novelty on sqt and mt, so this builds my point of removing mts and sqt from the text. Then you say you do a method development for dt, and it is not clear to me what is the actual development (not just simply that you have calculated the LOD. . .. But rather than the lod is lower than using this other method. . ..) as compared to mt and sqt analysis. It is also very strange to me that you offer a validated method and then you report only semi-quantitative values. Thus the whole objectives section must be rewritten. Please bear in mind to put what do you intent to do and why.

Page 3 Line 83: If one of the dt standard is not analytically valid, then you have to skip it.

Page 3 Line 84-86. Delete sentence

Page 3 Line 88: Please state why do you dilute the standards in methanol and not other solvent such as hexane.

Page 3 line 88 and 90. You can't report such a large range in concentrations for analyte

solutions. You must be certain of the concentration of your solution, and this is why you use calibrated pipettes. So please change accordingly. If you have a range of concentrations due to different compounds, then state them in a table.

Page 3 line 91. Why do you store solutions in the dark at 4°C?

Page 4 line 103-104. I do not understand this sentence. Please rephrase thinking what is the point of this statement to the objective of the paper.

Page 5 Line 130: why you changed the method (different final state) for TDGCMS2?

Page 5 Line 136-140: I think this information is useless, either rephrase or remove.

Page 5 Line 146: please state how many tubes were stored.

Page 6 line 186: please state which are the guidelines so the reader doesn't need to go somewhere else to find it. You can do it in SI if you don't want this info in the text.

Page 7 line 206: at what temperature did you store it? Then you freeze the material? is not clear how you did it.

Page 7 line 214: what do you mean as a proof-of-concept type of experiment? And please state if the branch enclosure was just a branch or it also had needles in.

Page 7 line 215: What do you mean but shrank?

Page 7 line 217: state reason for copper tube.

Page 7 line 219: what is the reason of artificially promote BVOC emissions? Why would you do this if it is not realistic to the ecosystem of interest.

Page 7 application to real samples. I do not see any blank measurements, please include them. If you have not taken blank measurements then I ask how do you exclude contamination effects.

Page 8 line 231: what is the sufficient confidence?

Page 8 line 233-5: if you can't identify the compounds then remove them from identified compounds.

Page 8 line 241: What is C1?

Page 8 line 348-9. Remove this sentence, it does not contribute anything to the ms.

Page 9 line 250: what is the desorption efficiency of TDGCMS2?

Page 9 line 251: what do you mean by carryover?

Page 9 line 269: why did you choose 60 and not 70 or 50C? How did you know all liquid goes into the gas phase?

Page 9 line 271: how did you observe that diterpenes were sticking into walls and not decomposing some other way?

Page 9 line 273-279: This is a very serious statement which I think is wrong. It is fine that you did not find any losses with you inlet line, but this will be highly dependent upon the ambient temperature that the line will be subjected to. For instance 15 m non heated Teflon line for outdoor sqt monitoring in a boreal ecosystem during winter HAS to be heated!. Please remove statement about not heating the Teflon tube, it is totally misleading.

Page 9-10 lines 280-297: I wonder what will be the effect of transpiration inside a cuvette. This must be really important for diterpenes as you mention, so I think it is wise to let people know that inside cuvette humidity monitoring is essential.

Page 10 line 288-290: why do you think there is a longer residence time in the cuvette for diterpenes? I think this whole paragraph needs to be rewritten. You simply say that you may not be volatilizing well your diterpenes, thus, you can't be really validating the method if you are not sure you can't get all your diterpenes into the gas phase. Please rephrase by 1) taking away the mt and sqt info (because as you say it is explained in other studies) 2) you think account for this HUGE limitation and how this affects your

method validation. In fact, somewhere in the text you must state why you are truly validating a method here with these limitations.

Page 10 line 299. I do not understand how you say first that you can't really be sure of 3MA and then you actually show LOQ values. How is this possible?. Please explain.

Page 10 line 300: please state that RSD means relative standard error. I wonder why you did not show any repeatability among different systems. This will really validate your method!

Page 10 line 306: What do you mean by assuming sampling volume? You must know this.

Page 11 line 327-9: I do not understand this sentence. Please rephrase.

Page 12 line 375. Please expand on why heated stainless steel better than other ozone removal mechanisms.

Page 13 line 380. I think it would be wise and enriching the ms if you add this data.

Page 13 section 3.2.1. Please explain why you heat needles and twigs.

Page 13 line 389. If you could only identify 5 how can you report 11?

Page 13 line 406: what do you mean by coefficients? Please explain.

Page 15 line 460: what do you mean by good? This is very vague, good as compared to what. Please expand.

Editting comments Page 2 Line 34. OH must go before hydroxyl not before radical.

Page 2 line 35: You must explain what VOC is, you only said BVOC before.

Page 7 line 219: put a before temperature and I suppose you mean that you place the temp sensor in the cuvette not the logger itself, right?

Page 9 line 268: replace "with" with "for". And state which compounds you refer to.