

## ***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.***

**P.T. Palmer (Referee)**

palmer@sfsu.edu

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The authors collectively represent a broad array of expertise in MS/MS, PTR-MS, and atmospheric chemistry, and this paper is the result of a successful and productive collaboration on a very intractable problem - obtaining real-time measurements of closely related VOCs at sub-ppb levels. The paper is well written, provides relevant history of instrumentation used for this application, the appropriate context and details, a good comparison between two different types of PTR-MS like instruments, and some worthwhile (if not exactly the desired) results.

C537

I have only a few substantive comments on the scientific work. Some of this relates to past work (unpublished, of course) that I and my students had done in 1996 on differentiating monoterpene isomers via MS/MS. In our case, we likewise used CI and tried a number of different reagent gases including methane, isobutane, oxygen, and dimethyl disulfide. Our idea was at to maximize the intensity  $[M+H]^+$  ion and to see if the latter two gases could possibly add across the terpene double bonds so as to hopefully maintain differences in the various structures that could be evidenced in different fragmentation patterns. Just as in this paper, our work failed to show any significant differences in the product ion spectra. In researching this further, I noted that McLafferty explained this in his classic MS Interpretation text by noting that "monoterpene hydrocarbons exhibit spectra which are consistent with initial isomerization to a cyclohexane structure plus other rearrangements such as methyl migration". Perhaps this manuscript could benefit from the addition of this comment along. 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? The authors make a few comments on this in the introduction, but perhaps further elaboration, especially with respect to the issues I've raised, are warranted. 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. 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. Perhaps the authors would be interested in citing a recent paper discussing the use of DART for monitoring terpene emissions (RCMS, 2009, 23, 2241).

A few minor comments and suggestions regarding terminology. I'm sure David Sparkman would disapprove of the term "quasimolecular ion" and perhaps more specific terminology could be used here. In the abstract and body of the manuscript, the triple quad CID process is referred to as a high energy process. Perhaps the qualifier "relatively" should be added here, as high energy CID usually refers to the keV collision energies

C538

used in sector and hybrid instruments. The manuscript also takes some liberty in the use of significant figures for reporting LODs. By definition, LODs have 33% or 50% RSD (corresponding to the 3 or 2 sigma definitions). The manuscript is inconsistent in reporting computed LODs in the results section and the table, and uses anywhere between 1 and 3 sig figs. This should be corrected and all LODs should be reported to at most 2 sig figs.

A couple type-o's:

Start of results section line 11, "... are show(n) in Table 1."

Results section on terpenes: "monocyc(l)ic" and line 22: "following (section)" not chapter

p. 1847 line 1-7: missing several commas here

Table 1 header "QqQ-MS PTR LIT pk area/ppb" is confusing - please clarify which instrument this metric refers to?

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