

## ***Interactive comment on “Deployment of a ground-based CIMS apparatus for the detection of organic gases in the boreal forest during the QUEST campaign” by K. Sellegri et al.***

### **Anonymous Referee #2**

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The manuscript describes the deployment of a CIMS instrument for the detection of various volatile organic compounds in the boreal coniferous forest with some of the reported species being important players in secondary organic aerosol formation. As such, it is certainly very valuable to the ACP community and, in principle, suitable for publication in this journal. I have, however, serious doubts on the quantitativity and specificity of the novel analytical method proposed. The authors extend the well-established CIMS technique developed in their lab for on-line analysis of acetone to a large set of volatile organic compounds. As a novel analytical method is presented, more emphasis should be placed on method validation. For most of the reported compounds the novel technique remains poorly characterized in terms of sensitivity and specificity. In atmospheric pressure chemical ionization mass spectrometry (and also

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at the somehow lower pressures used for this work) it is essential to carry out rigorous calibrations to determine humidity-dependent calibration factors and changes in the product ion distribution. This is particularly true if the kinetics of the involved ion-molecule reactions and the influence of hydration on ligand-switching reactions and reaction equilibria is not known in detail. I thus believe that mixing ratios reported for uncalibrated species are highly speculative. Specificity also seems to be problematic for most of the reported compounds. I share the concerns expressed by T. Karl (see interactive comment from July 12) on the interference between methanol hydrates and isoprene. In addition the authors should investigate whether the occurrence of electron transfer reactions from the primarily generated  $O_2^+$  ions could give rise to some of the reported even-numbered products. Acetonitrile measurement clearly suffer from some unknown interferences. Also it is questionable whether the presence of  $NO_2^+$  at  $m/z=46$  (deriving from nitric acid or nitro-organic compounds) can be excluded as interferant to protonated DMA.  $m/z=83$  and  $m/z=101$  can certainly not be unambiguously attributed to ethanol/formic acid with hexenol, hexanal and many others being potential interferants. Generally, the proposed CIMS technique seems to suffer from a lack of specificity due to extensive hydrate formation. Scepticism is increased by the fact that some of the obtained results are counterintuitive (see interactive comment T. Karl, July 12) My conclusion is that the presented results are too speculative to make the current manuscript suitable for publication in ACP.

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Interactive comment on Atmos. Chem. Phys. Discuss., 4, 3835, 2004.

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