

Interactive comment on “Ground-based intercomparison of two isoprene measurement techniques” by E. Leibrock et al.

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This paper presents results on an intercomparison between in-situ gas chromatography and a new technique for the direct measurement of isoprene in air by chemical ionization mass spectrometry using benzene cation as a reagent ion. These results are of interest to the atmospheric chemistry measurement community as the CIMS technique may be a viable fast isoprene sensor. The paper is the first presentation of field measurements by this particular CIMS method and draws important conclusions about potential interferences from VOCs emitted from urban sources. Overall the paper is clear and the conclusions drawn are sound. Since the topic of the paper is an intercomparison of methods I would like the authors to add some more detail on the experimental method, as noted below in my specific comments, and discuss in more detail the factor of 3 differences between the GC and CIMS measurements on one of

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the intercomparison days.

Does one of the reagent ions reacted more rapidly with isoprene than the other so that variations in the monomer to dimer ratio would affect the calibration factor? What were the calibration levels? You specify this for the GC but not for the CIMS instrument.

What types of VOCs are these reagents likely to react with? Can a mass spectrum of Denver air be shown? Does water vapor cluster with the reagent and analyte ions in this technique?

How often were background and standard additions to the CIMS performed during the intercomparison? If the background from synthetic zero air was between 100 and 200 Hz then this would be a large fraction of your signal for the Sept 30 and Oct 1 data. If this background varies throughout the day then frequent background checks would be necessary. Some more discussion on how the backgrounds were calculated (interpolated between zero air additions?) and how background variations may influence the intercomparison results is necessary. Is there an influence of humidity on the zero levels?

If at all possible it would help if Figures 2 and 4 were made larger. In Figure 2 it is difficult to see the difference between the red, green and blue symbols. I suggest changing them to different marker types (circles, squares, triangles) to help distinguish them.

In Figures 4 and 5 you argue that the normalized differences are best correlated with wind direction. While Figure 5 clearly displays a positive CIMS bias when wind is from the south, there is a similar level of discrepancy at other wind directions. For example the sector around 350 degrees shows normalized differences between +1.5 and -1.5. What is the cause of the wide range of variability for the other wind directions?

In Figure 2 the CIMS and GC data from Sept 18 are in excellent agreement. On Sept 29 the isoprene levels are similar to Sept 18 but now the agreement is poor - CIMS

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data are a factor of 3 greater than the GC data at several time periods. It would help the discussion if the obvious differences on Sept 29 could be traced to pollution, wind direction, etc that you try to illustrate in Figure 4, 5 and 6. The other days displayed in Figure 2 (Sept 30 and Oct 1) have isoprene levels at 100 pptv or less and thus near the DL of the CIMS where knowing the exact background level will be critical for comparing with the GC. The agreement for these days is reasonable given the isoprene levels and how the CIMS background was determined. The real story about CIMS interferences is contained in the contrast between Sept 18 and Sept 29 and this should be the focus of more discussion.

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 905, 2002.

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