

Interactive comment on “An intercomparison of GC-FID and PTR-MS toluene measurements in ambient air under conditions of enhanced monoterpene loading” by J. L. Ambrose et al.

Anonymous Referee #2

Received and published: 24 February 2010

Summary. The authors present an analysis of toluene and monoterpene data collected at a rural eastern US site in summer of 2004 to determine if PTR-MS based measurements of toluene are biased high because of interferences from other compounds such as monoterpenes. The motivation for the paper is that the regression analysis of the PTR-MS toluene data versus GC-FID toluene yielded a slope of 1.13 and there are reports that some monoterpenes undergo dissociative fragmentation in the PTR-MS to produce an ion at $m/z=93$, the ion corresponding to toluene. Thus, the authors question if low level (< 0.5 ppbv) toluene measurements by PTR-MS can be trusted in environments with abundant monoterpenes. The authors provide a rather exhaustive analysis of the compounds that could produce a positive PTR-MS bias (monoterpenes,

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monoterpene photoproducts, chloroacetone, etc) but found that the difference can't be accounted for and conclude the differences may be due to calibration or quantifying the PTR-MS background. The ending conclusion statement is that the PTR-MS measurements have been validated.

The measurements appear to be of high quality but I think the reasoning and construction of the paper could be significantly improved. If the point is to compare toluene measurements then the first order of business is to establish that the instrument's calibrations were consistent. There is no clear statement in the experimental section of how the GC-FID and PTR-MS were calibrated for toluene – we are left to assume they were calibrated using the same compressed gas standard. If the same standard was used how can they state on page 17 and conclude on page 29 that the 13% differences may be due to calibration? The calibration and background issues mentioned on page 17 are not explained in the paper. An examination of these basic issues is required before all the additional analysis of potential interferences. To put the 13% difference in perspective, this amounts to 50 pptv at the upper end of the measured toluene data (400 pptv), and would correspond to about a 3 Hz ion count rate in the PTR-MS data. Such a small ion count rate might be due to variations in background count rates as a function of ambient toluene levels. The authors need to at least discuss this.

The ending statement is that the PTR-MS measurements have been validated. This begs the question of why all the bother to calculate (estimate) potential interferences if the 13% difference is deemed good enough in the end and leaves the reader wondering about the purpose of the paper.

One important omission in the experimental section was quantifying the impact of humidity on the PTR-MS sensitivity to toluene. Water vapor dependent sensitivities are widely known, and can be significant depending on the operating conditions of the PTR-MS. I note that the highest toluene mixing ratios occurred at night. Understanding the toluene and monoterpene reaction kinetics with $H_3O^+(H_2O)$ is an important factor but not discussed at all.

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Another weakness in the paper is that monoterpene fragmentation yields from other studies were used to estimate the level of interference for their PTR-MS instrument. Why not empirically establish the fragmentation yields for the PTR-MS used in the study? That would be much more quantitative and simple enough to do.

Specific Comments:

Title: Are you performing an “intercomparison” or a “comparison”?

Abstract. Please be more quantitative in the abstract – what was the level of agreement between GC-FID and PTR-MS.

P6. GC operation. Was ozone removed? Could ozone reactions be the reason that some of the other monoterpenes were not observed?

P8. Calibration. How close in agreement were the response factors for C10 compounds and monoterpenes - can you be more quantitative. To what degree of certainty do we know that tertiary carbons and cyclic alkene compounds yield the same per carbon atom response as n-alkanes? How was the FID response to toluene calibrated? How often was the PTR-MS calibrated?

P8. What 24 ions were monitored by the PTR-MS – weren't monoterpenes measured at $m/z=137$ or $m/z=81$? Some more information on the operation of the PTR-MS would be useful. What was the H_3O^+ ion count rate? What was your normalized sensitivity to toluene? What were the background count rates for $m/z=93$? What does the 13% difference represent in terms of $m/z=93$ count rates? Was the $m/z=93$ background count rate a function of the toluene mixing ratio?

P10. Equation 8 and 9 are incorrect. The sentence above equation 8 is confusing. The transmission efficiency of an ion is a function of m/z and ion optic voltages, detector voltages, and pressure in the mass spectrometer. What you want to account for is the difference in ion transmission efficiencies for your reagent and analyte ions to calculate a mixing ratio from measured ion count rates and ion-molecule kinetics. You don't

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have to know the ion transmission efficiency if you determine the instrument sensitivity empirically.

Page 11. “ values of F are obtained ...”. What are the sources of this information? How valid are the rate constant data and yield data for $m/z=93$ from the literature since most of the studies (SIFT-MS) are done at thermal neutral conditions?

P13. I found the reference to Roberts et al., 1985 odd. Is Colorado vegetation relevant to your site?

P15. How was the precision of the GC-FID and PTR-MS determined as a function of mixing ratio? What is the measurement precision of the PTR-MS and GC-FID at 85 pptv – the median toluene mixing ratio? Usually precision is determined by replicate analysis – trickier to determine with GC systems at low mixing ratios.

P17. You state the 13% bias may be due to calibration or background issues in the PTR-MS. You need to fully explain and eliminate these as factors before spending so much effort investigating interferences.

P18. Since monoterpenes can also react with the first water cluster $H_3O^+(H_2O)$ in the PTR-MS, the yields of $m/z=93$ for this reaction must also be examined or at least discussed. Was $H_3O^+(H_2O)$ an important reagent ion in your system?

P26. Section 3.5 is a bit of a stretch. Proton bound ethanol dimers are only going to be found at unrealistically high mixing ratios of ethanol and chloroacetone is a “specialty” photoproduct. Since you don't estimate an interference level for chloroacetone anyway I would suggest removing section 3.5 from the paper to shorten the paper.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 1, 2010.

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