

Interactive comment on “Measurements of I/SVOCs in biomass-burning smoke using solid-phase extraction disks and two-dimensional gas chromatograph” by Lindsay E. Hatch et al.

Anonymous Referee #2

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This manuscript describes the analytical methodology associated with a relatively novel sampling strategy, analyte extraction/recovery, and analysis by two-dimensional gas chromatography for biomass combustion aerosol sampled at the Fire Science Laboratory. The authors have apparently studied a wide number of samples using a new analytical method without sufficient preliminary validation to understand the potential method errors associated with intermediate- and semi-volatile organic compounds (I/SVOC). For example, samples were dried under N₂ to exchange solvents one or two times and the authors noted sample losses during storage. These are very significant errors leading to incorrect quantities of I/SVOC components. Some of these errors are discussed, but the associated limitations in the results interpretation is not suffi-

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cient. Overall, the paper is quite long including 3 major goals: (1) test the application of untargeted analysis to the new sampling strategy, (2) compare the I/SVOC speciation profiles, and (3) assess the accuracy of the measurements. Unfortunately, I did not understand how the accuracy was assessed.

Considering the method errors, it is very difficult to have a meaningful discussion of the I/SVOC profiles, which I thought was the main point of this paper. I think the authors could do a better job of eliminating the analytes most susceptible to evaporative losses, and then proceed with the comparison of the profiles and their correlation. I would like to see the paper strongly revised with careful attention to the limitations associated with the method errors/assumption. At the same time, I think the paper should be substantially shortened to focus on the most valuable results.

Specific comments:

- 1) Please specify how the blank subtraction was performed.
- 2) MeOH extraction was performed prior to BSTFA derivatization and BSTFA derivatizes hydroxyl groups. Unfortunately, this can lead to unexpected variations in the amount of BSTFA that is available for reaction with the analytes, since the relative reaction rates are expected to be much slower for carboxylic acids compared to primary alcohols. This limitation should be noted.
- 3) Drying extracts leads to substantial losses of components depending on their specific volatility and can increase the possibility of solvent reaction artifacts (e.g., ester and hemiacetal formation). This limitation must be made clear along with appropriate caveats in the interpretation of the results.
- 4) An interesting point of discussion that could be elaborated here relates to the meaning of untargeted and targeted analysis. What is the actual certainty associated with the NIST library matches? I would expect them to have variations, especially with consideration to derivatized components. What happens to the analyte signals without

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library matches? What fraction of the overall signal do they represent?

5) Extraction efficiency tests include a test named PTFE test, but this test doesn't have anything to do with the PTFE filter. Please rename the tests. See also figure 1, where PTFE recovery is used to assess the SPE recovery. What is the slope of the fit? What are the outliers in the plot with red symbols?

6) Please discuss the possibility of positive and negative sampling artifacts with respect to your sampling scheme.

7) The threshold for poor recovery is quite low at 20%; I recommend raising it toward 50% for the discussion.

8) Several specific compounds were poorly recovered from the SPE tests. To what degree are these recovery issues related to the various method errors (solvent evaporation steps, sampling artifacts, or derivatization artifacts).

9) Extracts for I/SVOC analysis should never be allowed to dry. Practically speaking, there are variations in the N₂ flow rate and there are sample matrix differences that affect the rate of solvent evaporation. The two practical considerations contribute to variations in time the dried solute is exposed to the N₂ thus varying the extent of analyte losses. This is a very important limitation that is poorly addressed.

10) Were any internal standards used to monitor analyte losses?

11) Considering the method limitations, please justify how the analyte recovery from the SPE filters was determined to be satisfactory? For which analytes?

12) Again, the assessment of diversity in the I/SVOC is dependent on the assumption that the samples did not have losses associated with the sample preparation. What if some of the variation you see is due to solvent evaporation during storage or during the solvent exchange steps?

13) Please define what is meant by composite chromatograms?

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14) Please define the RI values \sim 1200-2100.

15) References on page 8 did not simply use PUF for SVOC collection. XAD has been frequently used and XAD is an SPE material.

16) Figure 4 is quite complex. The effect of levoglucosan on the correlation is quite strong. Since levoglucosan is non-volatile, it could suggest that the more volatile components were more highly variable even between replicate burns. But, is this related to the sampling strategy, sample prep, or actual burn conditions? This makes me curious about other volatility bins and their correlations.

17) What is the purpose/significance of figure 5?

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