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Interactive comment on "A new approach for measuring the carbon and oxygen content of atmospherically-relevant compounds and mixtures" *by* James F. Hurley et al.

Anonymous Referee #2

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This work describes the design and lab testing of a lower-cost and simplified method to determine the carbon and oxygen content of particulate matter. In this manuscript, the authors couple a NDIR CO_2 detector to a flame ionization detector to demonstrate a new approach to measure the carbon and oxygen content of atmospherically-relevant organic compounds. Three criteria need are tested through theory and fundamental validation of the approach: 1) FID combustion efficiency 2) FID response per carbon atom (i.e., measured ratio of signals, FID/CO_2) must be inversely proportional to the oxygen content of analytes and mixtures, 3) achieve high correlation amongst FID/CO_2 signal ratios, analyte O/C, and analyte FID sensitivity (rECN) within reasonable error. Field testing is not a component of this first method paper. With some minor improve-

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Discussion paper

ments, I consider this work worthy of publication.

Here are some specific comments and questions.

1. Line 71: eliminate one of the commas after "Generally"

2. Supplement: would be helpful to also list the ECN structure-activity relationship values from the Scanlon & Willis, and Jorgensen publications.

3. Figure 1: The caption should be changed to reflect that dashed line for alcohols represents the rECN calculated for a subset of alcohols, and is not structure independent like with carbonyls and carboxyls.

4. Paragraph starting at line 135: when utilizing a GC/MS system to assist in identification and relating to FID through retention time indices, were there differences in flow rate settings (constant pressure vs constant flow) utilized between the measurement methods, and if so, how was retention time matched/correlated?

5. Lines 141-142: Please clarify how closely the retention index of a given compound needed to match the NIST values.

6. Paragraph starting at line 135: It would help the reader if a more detailed instrument diagram for systems 1,2(a/b),3 were provided in supplemental information.

7. What is the complete list of supporting compressed gases required for this instrument? Helium, Hydrogen, (Nitrogen for FID?), compressed air for FID?

8. Lines 179-183: it's stated the FID/CO2 ratios measured with systems 1&2 were normalized by the ratio of the nearest-eluting alkane. However, with system 2 there was no temperature ramp. Please clarify how the normalization for samples measured by this setup occurred.

9. Figure 4: it would be helpful to have a table of compounds used in these figures within the supplement. What is the volatility range tested, range of functional groups, or some multifunctional compounds too?

10. Lines 236-237: The sentence "It is notable but probably incidental that the observed downward slopes and R2 values match closely with those of a set of alcohols, -0.58." seems ambiguously worded, and relies too heavily on the reader to have read section S2 in the supplement to understand what is meant.

11. Paragraph starting at line 243 and Figure 5: why did the authors select these specific mixtures?

12. Line 269: why would we want to determine rECN when we already have O:C from measured FID/CO2, which would be the info utilized by atmospheric scientists.

13. The technique shows good promise, it will be interesting to see how it performs on ambient mixtures in the field, relative to the existing high-cost, high-maintenance techniques.

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