

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 #3

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I am puzzled by the disconnect between what the paper says is a main goal – to develop a fast/easy/inexpensive way to measure organic carbon and O/C in particulate matter, and the fact that the authors present no measurements of particulate samples. The paper does describe a method for measuring the carbon and oxygen content of organic compounds that could potentially be used for particulate samples, but how that application would work is not explained and certainly not demonstrated. The method involves a combination of flame ionization (FID) and carbon dioxide (CO₂) detection schemes, and the ratio of FID to CO₂ response is used to estimate the O/C ratio of organic species. The paper describes a potentially interesting and useful technique, but there are major issues with the paper, and it will need considerable work before it

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is acceptable for publication. I have the following general and specific comments that need to be dealt with.

General Comments:

No particle-phase, or particulate-like samples were analyzed in this work. If the authors were to try to emulate particle organic carbon (POC) they would realize they should also be working with compounds like oxalic acid and glyoxal, which have O/C ratios of 2 and 1, but probably no FID response. There is potentially a lot of oxalic acid/oxalate – which would represent a large deviation from the clusters of points that are presented by the compounds studied in this work. There needs to be some discussion of how such compounds would affect what is actually observed for POC. In addition, organic nitrates and organo-sulfates should also be explored if the authors really want to demonstrate that this technique works for POC. The only hetero-atom (i.e. non-O atom) containing species, Musk ketone (apparently a di-nitro compound) was excluded from the analysis – because it did not conform. This does not bode well for the technique. What was the nature of the problem that led to this disqualification, and how does that bear on whether the technique can work for nitro-aromatics for example?

The LI-COR instruments used for CO₂ measurements have distinct characteristics: the LI-COR 6262 is an older model and has an inherently non-linear response to CO₂ that must be calibrated throughout the useful range with multi-point calibrations, and the LI-COR 7000 has a linearized response. The specifics of how these two different instruments were calibrated need to be presented. In addition, these detectors are concentration-sensitive and therefore the systems, at least as far as I can understand them from the diagram, require an accurate knowledge of the flow rates and pressures in the systems. The details of how these were determined need to be presented in this work.

Inherent uncertainty in O/C is simply an unavoidable feature of the technique, but we

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don't have any substantive discussion that places this in context. How do the uncertainties in O/C ratios from this technique compare to uncertainties from AMS measurements of O/C? Does this technique really represent an advance in this area or is its' main feature that it is less expensive and easier to field?

Specific Comments:

Page 4, Lines 119-120. This statement needs much more context given that the slopes of rECN to O/C can vary between -1 and -0.5. Is this really good enough for the purposes of what we'd like to do with POC data?

Page 5. The instrument diagrams and associated descriptions are not nearly adequate to explain what was done, where uncertainties could be introduced, and how POC sampling and analysis would work. Doesn't the TAG cell have a filter in it? Was that part of the configuration, if not, how would that change how the system would operate?

Page 6. Lines 165-166, and Figure 2b. It seems clear that there was incomplete separation in the GC peaks, especially for the CO₂ detector. How were these analyzed and how did that impact the results e.g. accuracy and precision?

Page 6, Line 183. Doesn't normalizing to the nearest n-alkane create problems and uncertainties? It seems like some oxygenates might be in a completely different retention time range than the number of carbons it has. The carbon count could easily be off by one or more carbons.

Page 7. Section 3.1 I have a hard time believing that FIDs are not 100% efficient in converting carbon compounds to CO₂: isn't this known? There are errors in both quantities plotted in Figure 3. Those need to be shown for the data points and other possible sources of systematic error should be discussed. For example, the CO₂ instruments are concentration sensitive, so flow rates and pressures need to be known accurately and/or controlled so that they don't change as the experiments are being conducted.

Page 7 Line 224. I had to read this several times to decide I basically disagree with this

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statement. Figure 1 suggests there will be considerable uncertainty in the relationship between rECN and O/C but it doesn't imply anything about FID/CO₂. The extension to FID/CO₂ is really because both carbonyl and carboxyl carbons have no FID response.

Page 8., Line 229. Is this $\pm 4\%$ from the fit to the data?

Page 8., Line 258- Page 9, Line 259. This statement doesn't seem correct, especially when one considers compounds like oxalates, glyoxal, glycolic acid and the like. There is an inherent $\pm 25\%$ built into the technique.

Page 11. The Chow et al., reference has an error. Page 11., Line 336. Should be "Association" Page 11., Line 344. Should this be 'GC'? Page 14., Line 442. Correct the typo.

Figure 4 – Please give the uncertainties in the fit parameters, i.e. slope, intercept

Conclusions; The authors have failed to do the necessary work to demonstrate that this technique works for analyzing POC. The whole paper needs to be re-cast to focus on gas phase species, or a considerable amount of additional work needs to be done on actual particle samples and the species that we already know they contain: N- and S- containing organic compounds. As far as the built-in $\pm 25\%$ uncertainty in O/C, the authors need to make a case that their measurement can still be useful in spite of this feature.

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