

Interactive comment on “Mapping and quantifying isomer sets of hydrocarbons ($\geq C_{12}$) in diesel fuel, lubricating oil and diesel exhaust samples using GC \times GC-ToFMS” by Mohammed S. Alam et al.

Anonymous Referee #1

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In this work, the authors Alam et al. present a novel method to characterize the composition of organic mixtures, especially those from fossil fuel combustion sources. This is an important topic for atmospheric sciences, as many of these mixtures can react in the atmosphere and form oxygenated compounds and organic aerosol. This work uses a similar approach as work by Zimmerman et al. and Goldstein et al., and combines low energy ionization with multidimensional chromatography to separate and identify aliphatic and aromatic isomers. This work is of clear interest to the field, and is within the scope of AMT. Overall, the work here is quite solid. I suggest a few more discussion points that would advance the understanding of the technique, so that the technique is more likely to be adopted by researchers in this field.

1. Ionization temperature plays an important role in the fragmentation of the molecule. The thermal energy can lead to substantial fragmentation, e.g. Isaacman et al. show that lowering ion source temperature from 300C to 150C reduces fragmentation temperature significantly. Amirav et al. (2008) uses a supersonic molecular beam to achieve cold electron impact ionization, and was able to reduce fragmentation substantially. Have the authors tried to lower ionization source temperature?

2. Is isomer-level differentiation/quantification necessary? There is some debate whether or not the isomers are different enough to warrant detailed characterization. I suggest the authors look at Tkacik et al. (2012) and Goodman-Rendall et al. (2016). In other words, it might be sufficient for process level understanding of hydrocarbon composition (e.g. volatility basis set approach or 2-product Odum model) to predict oxidation characteristics and volatility changes. I think this is an important point: the authors will first need to identify the need to perform this level of chemical characterization before they will be able to convince the field that this technique is useful.

3. Can the authors explain why the total ion current is so similar between different compound types? Ion sensitivity is a strong function of electron absorption cross section, and at lower energies, there is significant differences in cross section. Aromatic compounds, for example, would absorb much more effectively than aliphatic compounds, and cyclic compounds (six- and five-carbon ring) would also absorb more than cyclic compounds. I understand that the authors are just showing their results, but they seem a little counter-intuitive to me.

4. While this technique would be ideal for investigating fossil fuel sources (e.g. motor vehicles, oil extraction activities), how would this work for atmospheric mixture where there will be many other types of compounds and sources? In urban areas, the HOA factor from aerosol mass spectrometer studies accounts for around 20% of total OA, so the majority will be oxygenated. What happens when an urban aerosol sample is analyzed using this technique? Will the “contamination” by oxygenated compounds limit the ability to measure the hydrocarbons?

5. Given that this is an atmospheric journal, the writing should reflect the focus on atmospheric applications. For example, the discussion about other environmental mixtures in the conclusions may not be necessary and seem to detract from the main point.

Minor comments:

1. Samples from the diesel exhaust are obtained from extraction using dichloromethane. What is the extraction efficiency for oxygenated compounds using DCM as a solvent?

2. Lines 231-233: How reproducible are the retention times in both dimensions? In other words, are the polygons drawn to separate different compound types consistent from one run to another, one column set to another (assuming the same type of columns), one day to another?

3. Line 310: Carboxylic acids are very difficult to be detected by GC/MS without prior derivatization. If they are detected, their quantities might be highly uncertain. It might be difficult to say whether they are truly minor, or it is just a limitation of GC/MS.

4. Line 274: aren't saturated cyclic alkanes also alkanes?

References:

Goodman-Rendall, K.A., Zhuang, Y. R., Amirav, A., Chan, A. W. H., 2016. Resolving detailed molecular structures in complex organic mixtures and modeling their secondary organic aerosol formation. *Atmos. Env.* 128, 276-285.

Tkacik, D.S., Presto, A.A., Donahue, N.M., Robinson, A.L., 2012. Secondary organic aerosol formation from intermediate-volatility organic compounds: cyclic, linear, and branched alkanes. *Environ. Sci. Technol.* 46, 8773-8781.

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Discussion paper

