Response to reviewers for
“Quantifying Functional Group Compositions of Household Fuel Burning Emissions” by Li et al. (amt-2023-90)

Reviewer 1

The manuscript entitled “Quantifying Functional Group Compositions of Household Fuel Burning Emissions” describes the application of FTIR analysis for the identification of organic functional group (OFG) in particulate matter emitted during combustion of different fuels by household appliances. In addition, different combustion phases are investigated. The results obtained by FTIR analysis are compared to those obtained from traditional analytical techniques, including thermal-optical analysis (for total OC determination) and GC-MS (for the quantification of PAHs).

The manuscript presents new data on OFG composition of primary emissions and describes the value of FTIR measurements to investigate the aromatic aerosol component, which is extremely relevant for defining the impact of combustion aerosols on human health. Some more discussion would be useful to understand the discrepancies between thermal optical OC and FTIR OC.

The manuscript is clear and well written. I recommend its publication after minor revision.

We thank the reviewer for the encouraging evaluation.

Specific comments.

1. Section 2.1 Can the authors add any details about the dilution ratio of the sampled emissions and the temperature at sampling point?

   The following text has been included:

   “Volumetric flow rates were \(\sim 4.0 \text{ m}^3\text{ min}^{-1}\) and \(\sim 26.8 \text{ m}^3\text{ min}^{-1}\) in the primary (6”) and secondary (10”) dilution tunnels, respectively. With the steady flow dilution tunnel system, dilution ratios vary as cookstove emissions fluctuate during testing. Temperatures at the filter sampling locations varied between \((24–50^\circ\text{C})\) and \((21–26^\circ\text{C})\) for the primary and secondary dilution tunnels, respectively.”

2. Line 78 What is the ratio between the OC quartz back filter and the OC measured on the Qf collected in parallel?

   The following text has been added:

   “The ratio between OC on Qf back and front filters ranged between 0.06–1.79.”

   This ratio is known to range widely, with lower ratios for increased loading as the filter saturates.

3. Line 198: As suggested by the authors, one of the reason for the underestimation of FTIR-OC compared to TOT-OC is the "operationally defined EC-OC separation". Do the authors observed a link between the OC underestimation and the pyrolytic carbon quantified by thermal-optical analysis?
The bias between FTIR OC and TOT OC over remains indiscernable (within a wide range of variation) above pyrolitic carbon (PyC) loadings of 5 $\mu$g/cm$^2$, while PyC to TOT OC ratio by 10% on average over this same range. At low PyC concentrations, PM loadings are low overall and FTIR OC likely exhibits a high relative bias due to PTFE interferences, though this variation does not preclude effects of pyrolysis.

It may be that the optical transmittance correction captures and corrects for the relative trend in pyrolyzed organic fraction, leading to a consistent relationship between FTIR OC and TOT OC. Another perspective on the bias of TOT OC measurements due to the operational definition in EC-OC separation is provided through comparison with thermal optical reectance (TOR) in other studies. For instance, Chiappini et al. (2014) report that OC estimates can diverge between these two methods, with TOT OC systematically higher than TOR OC. A more comprehensive discussion in the text is included in response to Reviewer 2, Comment #3.


4. In addition, is it possible that the sensitivity of FTIR is reduced by the signal attenuation due to high EC loading? The agreement between TOC-OC and FTIR-OC is generally higher in ambient samples, where I assume the OC to EC ratio is higher. Do you see a link between the underestimation of FTIR OC and the OC to EC ratio?

High EC loading does not lead to substantial attenuation of the signal since the electronic transition is small compared to the scattering contribution from PTFE (McClenney et al., 1985; Parks et al., 2021) and absorption bands of graphitic carbon defects (below 1600 cm$^{-1}$) apparent in the infrared spectrum are relatively weak (discussed by Friedel and Carlson, 1971; Takahama et al., 2019).
5. Line 209-202: Can the authors comment on the potential artefact of soot/graphitic carbon/EC on the aromatic CH signal? (Fig. S12) The conclusion about the contribution of multiple PAH, in addition to those quantified by GC-MS is convincing. Nevertheless, one of the strongest points of the manuscript is the ability of FTIR measurements to describe the totality of the aromatic component. So it would be good if the authors could say something about the potential artefacts on the PAH quantification due to EC.

The out-of-plane (OOP) aromatic CH is specific to the C=C-H bonds in PAHs, which are absent in graphitic carbon. Graphitic carbon and PAHs exhibit weak intensity bands near 1600-1500 cm$^{-1}$ for C=C bond stretching which have been used previously for EC quantification (also now discussed in the main text in response to Reviewer 2, Comment #1), but we do not use this band in this work. Soot and EC are thought to contain low-volatility organic compounds (e.g., Chow et al., 2004; Lack et al., 2014), but this OOP aromatic CH band is distinct from other organic bands such as aliphatic or alkene CH and oxygenated groups.


Technical corrections

1. Several citations are reported without leaving a space before the brackets. For ex. lines 13 and 15.

2. Line 194: S12 should be S13

   We have corrected the Supplement so that Figure S11 has been removed and this error is corrected.

3. Line 197: I guess the term "variability" would be more accurate than "uncertainty"

   The reviewer is correct in that there is variability in absorption coefficients for the same functional group in different molecules that can lead to biases in our quantification. However, we do mean “uncertainty” in the sense that we do not know what the value for the (effective) absorption coefficient that is most appropriate for these particular samples.
4. Line 208: S11 should be S12

We have corrected the Supplement so that Figure S11 has been removed and this error is corrected.

5. Fig S11 and fig 7 looks the same. Please remove one of them

We thank the error for catching this error. We have corrected the Supplement so that Figure S11 has been removed.

Reviewer 2

The manuscript titled "Quantifying Functional Group Compositions of Household Fuel Burning Emissions" by Li et al. discusses the utilization of Fourier transform infrared spectroscopy (FTIR) to analyze fine particulate emissions originating from various cookstoves. The study presents source profiles of functional groups derived from different fuel types and cookstoves. Quantitative outcomes were achieved by comparing the results with OC/EC and GC-MS measurements. Overall, the manuscript is well-written and aligns with the scope of AMT. I recommend its publication after some minor revisions.

We thank the reviewer for the encouraging evaluation.

Minor aspects

1. The authors need to clearly state how the baseline is determined. Which is to say whether the baseline is defined by individual Teflon filters before sampling, or a unified baseline is used. It would be important for the researchers who would like to follow this method.

We have rewritten the section on baseline correction (2.3.1) and added a section to the supplement (S3) with illustrations.

2. It would greatly benefit readers to include an example plot in the supplementary information illustrating the subtraction process of both blank baseline and EC-influenced baseline.

We have rewritten the section on baseline correction (2.3.1) and added a section to the supplement (S3) with illustrations.

3. Line 149, it would be valuable to provide insights into the factors contributing to the substantial variability observed in charcoal combustion tests. Possible connections with temperature or other combustion conditions could be explored and explained.

We have added this discussion in the main text:

"Variability in results was observed in charcoal combustion tests due to non-uniform fuel and differences in combustion conditions. Lump charcoal (not briquettes) was used for testing because it was representative of fuel usually used in low- to middle-income countries. Charcoal had non-uniform size and shape, and it was screened between 2.5 and 5.0 cm. Variation in the fuel bed packing due to the non-uniform pieces and variation in the carbonization of the charcoal can affect combustion and emissions. Kerosene was used as an accelerant to ignite the charcoal for all cold-start test phases, with a small amount of wood kindling used for the EcoZoom stove only, where red oak was ~9% of total fuel mass consumed. No accelerant was used during hot-start or simmer test phases. Different combustion characteristics between stoves strongly influences emissions. For example, turbulence/mixing within the combustion chamber of a traditional charcoal stove is a key factor in devolatilization of fuel and formation of organic PM (Lea-Langton et al., 2019). Field testing of traditional charcoal stoves finds relatively steady emissions of CO (and hence modified combustion efficiency) during the entire test period, while contributions of PM\textsubscript{2.5}, black carbon (BC), and light scattering (Bsp, $\lambda =$
635 nm, an optical-based proxy for EC largely occur during the ignition period (e.g., 62% and 67% of BC and Bsp respectively occurred during the first 20% of testing) (Champion and Grieshop, 2019). Therefore, both particle composition and emission rate change drastically during charcoal ignition, indicative of the highly variable process."

4. Line 196, it’s reasonable to assume that the volatilization of organic compounds might lead to lower concentrations on PTFE filters, contrasting the adsorption of VOCs on quartz filters. While a 40% underprediction compared to TOT OC is acceptable, the authors should provide more comprehensive reasoning behind this discrepancy.

We have provided this explanation:

“This underprediction can be attributed to imperfect correction of quartz adsorption artifacts, volatilization of compounds from particles on PTFE filters, uncharacterized FGs, uncertainty in FG absorption coefficients, underprediction of the fractional carbon associated with each FG, and the operationally-defined EC and OC separation threshold for TOT. Volatilization losses off filters (following a denuder) for urban ambient samples have been reported to be on the order of 10% (Subramanian et al., 2004), though the amount may be different for fresh emissions that can contain substances that can revolatilize (Robinson et al., 2007). Underprediction in OC due to uncharacterized FGs is reported to be on the order of 8–20% considering the range of structures in compounds expected in OM (Takahama and Ruggeri, 2017). OC estimates by TOT have been reported to be higher than that by reflectance correction by 0–35% due to charring profile through the filter (Chow et al., 2004; Chiappini et al., 2014). The magnitude of each contribution across samples can vary substantially. A combination of these factors can lead to the overall discrepancy observed in this study, which is on the higher end relative to comparisons of FTIR OC or OM to different techniques in previous studies (e.g., Liu et al., 2009; Russell et al., 2009; Hawkins and Russell, 2010; Takahama et al., 2011; Corrigan et al., 2013; Liu et al., 2018; Regente et al., 2019). Nonetheless, the consistent mass recovery permits us to make systematic comparisons regarding the OM composition using FG analysis.”


5. Line 229-240, consistently elevated OM/OC ratios (1.6-1.8) were observed in the cookstove test utilizing the FTIR method, a value that appears to surpass the OM/OC ratio derived from the AMS method (ranging from 1.3 to 1.5 for primary emissions, as reported by (Canagaratna et al., 2015)). It is advisable for the authors to discuss further on this aspect, providing in-depth discussions and explanations concerning this disparity.

Reference


We have included this discussion in the main text:

“There is a dearth of estimates of OM/OC ratios from cookstove emissions for direct comparison. The similarity in the range of OM/OC ratios (1.6-1.8) between fossil fuel and red oak combustion in this work stand in slight contrast to differences observed in a previous study comparing primary primary OM from coal combustion and wood burning in furnaces where
average OM/OC ratios were 1.4 and 1.6, respectively, which were similar to AMS (Yazdani et al., 2021). The current values are higher than reported by AMS for submicron HOA (1.3–1.5), though closer to the range of laboratory-generated and inverse-modeled BBOA (>1.5) Canagaratna et al., 2015. OM/OC estimates from FTIR can be biased high if some unfunctionalized carbon is not considered in the calculation (Takahama and Ruggeri, 2017; Reggente et al., 2019); in that case the OM/OC would reflect the ratio for polyfunctional carbon atoms that are extracted by our current FTIR calibrations. In the study by Yazdani et al. (2022), the FTIR OM was estimated to be 30% higher than AMS measurements without collection efficiency correction, while FTIR OC is underestimated by about 40% compared to TOT OC in this work. Bürki et al. (2020) proposed an approach to find parameters for estimation of FTIR OC (including calibration coefficients and undetected carbon fraction) that were most consistent with the observed TOR OC concentrations in collocated ambient measurements. These model parameters were then used to obtain an revised estimates of OM/OC, which resulted in lower OM/OC estimates as the original FTIR OC estimates underpredicted the TOR OC concentrations by approximately 40%. Such an approach can also be considered for further investigation of cookstove primary emissions. Nonetheless, the bias of TOT OC is systematically similar across fuel types in this work, so the relative differences among them reported here are likely to be consistent with respect to this source of bias. Differences in absorptivities for the same functional group found in different compounds across sources may exist, but are not accounted for in this study. More studies in this area are warranted given the difficulty in quantifying OM/OC using various techniques, and lack of definitive reference methods. Molecular methods sample a small subset of molecules present (Rogge et al., 1993), AMS relies on calibrations to a set of selected representative compounds to adjust for ionization losses (Aiken et al., 2007; Canagaratna et al., 2015), reconstructed fine mass regression are subject to compounding analytical errors (Hand et al., 2019), and estimation of OM through thermo-gravimetric analysis (Polidori et al., 2008) is prohibitively labor-intensive (and is also subject to compounding analytical errors).”


6. I recommend including a table summarizing the functional group abundances alongside their corresponding typical wavenumbers from source profiles of different cookstoves. This addition will be immensely helpful for future researchers interested in employing the same method.

We have included such a table in the new Section S10.