Supplementary Information: A new approach for measuring the carbon and oxygen content of atmospherically-relevant compounds and mixtures

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# S1 Estimated CO2 produced in the FID combustion of atmospheric particles

In order to estimate the feasibility of measuring atmospheric particles by combusting them in an FID and measuring the CO2 produced, operating conditions for a theoretical instrument are examined here. In this instrument, particles would be sampled and thermally desorbed to an FID, with CO2 detected downstream, similar to the instrument used in this work. Table S1 provides assumptions and resulting measured values of such an instrument, with the basis of these assumptions discussed here. Total flow rate of FID gases (hydrogen and air) is in the range of 250 to 400 sccm based on typical instrument operating conditions. The instrument is assumed to sample at flows of 0.3 to 1.5 lpm, as these are typical operating conditions for aerosol instrumentation, with a time resolution of one to two hours (roughly 60-120 minutes of sampling time, though actuallysome turnaround time would be necessary). The duration of the desorption process is estimated at 5 to 20 seconds, which impacts the relative sharpness (and thus height) of the signal observed. Two scenarios are tested to bound the operating conditions. In a low signal case, all parameters are set to minimize signal, particle concentrations are assumed to be low (0.5 μg/m3), and the fraction of that mass that is carbon is assumed to be on the low end of typical ambient conditions (OM/OC = 2) (Aiken et al., 2008). In a high signal case, all parameters are set to maximize signal, particle concentrations are assumed to be moderate (10 μg/m3), and the fraction of that mass that is carbon is assumed to be on the high end of typical ambient conditions (OM/OC = 1.4).

Table S1. Assumptions and calculations to estimate amount of CO2 produced in the combustion of atmospherically-relevant concentrations of organic aerosol.

|  |  |  |
| --- | --- | --- |
| Assumptions: | High signal case | Low signal case |
| Total flow of all FID gases (cm3/min) | 250 | 400 |
| Organic aerosol concentration (ug/m3) | 10 | 0.5 |
| Organic mass/organic carbon (OM/OC) | 1.4 | 2 |
| Instrument sample flow rate (l/min) | 1.5 | 0.3 |
| Sample interval (min) | 120 | 60 |
| Duration of desorption (sec) | 5 | 20 |
|  |  |  |
| Calculations: |  |  |
| Sampled carbon (ng) | 1286 | 5 |
| Carbon reaching FID (ng/s) | 257 | 0.225 |
| Concentration of carbon in FID outflow (ng/cm3) | 62 | 0.03 |
| Concentration of carbon in FID outflow (ppb) | 123,840 | 68 |

# S2 Theoretical slopes of rECN

A plot of relative ECN versus O/C for three different categories of functional groups is shown in Figure S1. The impact of carbonyls and carboxyls (esters/acids) are independent of chemical structure, so rECN decreases with O/C at slopes of exactly -1.0 and -0.5, respectively. The impact of hydroxyl groups on rECN varies depending on whether the alcohol is primary, secondary, or tertiary, so the average slope is structurally dependent. A representative slope (-0.58) is shown based on the estimated rECN of the alcohols provided in Table S1 (R2 = 0.93). Relative ECN values were calculated based on the method determining ECN of Scanlon and Willis (1985). For all three categories, at least one aromatic and one multifunctional compound were chosen (e.g. benzaldehyde and glyoxal were chosen as carbonyls).

A close up of a map

Description automatically generated

Figure S1: Plots of calculated relative ECN (rECN) versus O/C for compounds comprised exclusively of different functional groups.

Table S2: List of the compounds used to generate the slope of the relationship between rECN and O/C plot for alcohols.

|  |  |  |  |
| --- | --- | --- | --- |
| Compound | Formula | O/C | Relative ECN |
| 1,3,5-Hexanetriol | C6H14O3 | 0.5 | 0.667 |
| 2,3,4-Pentanetriol | C5H12O3 | 0.6 | 0.55 |
| Propylene glycol | C3H8O2 | 0.667 | 0.583 |
| Pentaerythritol | C5H12O4 | 0.8 | 0.6 |
| Glycerol | C3H8O3 | 1 | 0.417 |
| 1-Butanol | C4H10O | 0.25 | 0.875 |
| 1-Octanol | C8H18O | 0.125 | 0.938 |
| Isopropanol | C3H8O | 0.333 | 0.75 |
| Benzyl alcohol | C7H8O | 0.143 | 0.929 |

# S3 Comparison of FID/CO2 across Systems 1, 2, and 3

To test the reproducibility of measured FID/CO2, 14 compounds were run on more than one instrumental configuration. Of these 14 compounds, 11 were run on two configurations. The relative error of the FID/CO2 measured for each system was calculated as the difference between the measured value and the mean of FID/CO2 measured for that compound for all systems tested, relative to the mean. The average relative error is 2.1% ± 1.8%, with a maximum relative error of 6.6%. The range of errors for all 14 compounds is shown in Figure S2.



Figure S2: FID/CO2 versus O/C for the 14 compounds analysed in multiple instrument configurations. Error bars show minimum and maximum value measured for each compound. Relative error shown on top as the ratio of the extrema to the mean. For the 11 compounds run on only two configurations, the extrema are symmetric about zero.

# References

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