

S1 Estimated CO₂ produced in the FID combustion of atmospheric particles

In order to estimate the feasibility of measuring bulk 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, a detector train 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 actually some 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.

<i>Assumptions:</i>	High signal case	Low signal case
Total flow of all FID gases (cm ³ /min)	250	400
Organic aerosol concentration (µg/m ³)	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
<i>Calculations:</i>		
Sampled carbon (ng)	1286	5
Carbon reaching FID (ng/s)	257	0.225
Concentration of carbon in FID outflow (ng/cm ³)	62	0.03
Concentration of carbon in FID outflow (ppb)	123,840	68

S2 Determination of rECN

- 20 Relative ECN values were calculated based on the method of Scanlon and Willis, 1985, Table 1. These authors credit Sternberg et al. (1962, Gas Chromatography, Academic Press, pp.231-267) for their values (Scanlon and Willis, 1985). Tables S2 below gives the relevant ECNs used in our work.

Table S2. Assignments of ECNs as described by Scanlon and Willis, 1985.

<u>Atom</u>	<u>Type</u>	<u>ECN contribution</u>
C	Aliphatic	1
C	Aromatic	1
C	Olefinic	0.95
C	Carbonyl	0
C	Carboxyl	0
O	Ether	-1.0
O	Primary Alcohol	-0.5
O	Secondary Alcohol	-0.75
O	Tertiary Alcohol	-0.25

- 25 Example calculation

Consider linalool, 3,7-dimethyl-1,6-octadien-3-ol ($C_{10}H_{18}O$). There are two alkene functionalities and therefore four olefinic carbons. There are six aliphatic carbons. There is also a tertiary alcohol.

$$6 \text{ (aliphatic C)} + 4 \text{ (olefinic C)} + 1 \text{ (tertiary alcohol O)} = 6(1) + 4(0.95) + 1(-0.25) = 9.55$$

30

The ECN of linalool is therefore 9.55

$$\text{The rECN of linalool} = \frac{ECN}{Total Carbon Number} = \frac{9.55}{10} = 0.955$$

35

For multifunctional aromatics, the method of Jorgensen et al, 1990, Table IX was used (Jorgensen et al., 1990). Table S3 below gives the relevant reductions used in our work.

Table S3. Reductions in ECN described by Jorgensen,1990, for substituent groups on aromatics.

<u>Functionality on aromatic compound</u>	<u>Reduction</u>
Ketone	0.80
Ether	0.78
Phenol	0.64

40

Example calculation

Consider vanillin, C₈H₈O₃. The aromatic ring has hydroxy (phenol), methoxy (ether) and aldehyde (treat as ketone) substituents.

In this method, the ECN is determined by applying the reductions to the total carbon number.

45 Total carbon # - reductions = 8 – phenol - ether - aldehyde = 8 - 0.80 - 0.78 - 0.64 = 5.78

ECN of vanillin = 5.78

$$\text{rECN vanillin} = \frac{\text{ECN}}{\text{Total Carbon Number}} = \frac{5.78}{8} = 0.7225$$

50

S3 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 S4 ($R^2 = 0.93$). 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).

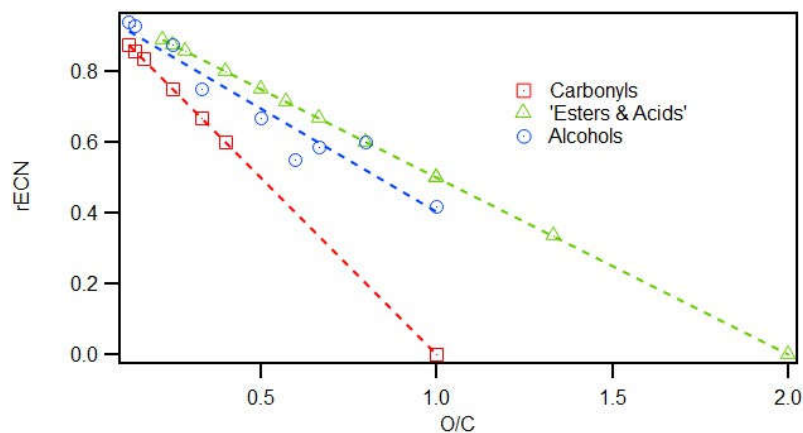


Figure S1: Plots of calculated relative ECN (rECN) versus O/C for compounds comprised exclusively of different functional groups.

Table S4. 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	C ₆ H ₁₄ O ₃	0.5	0.667
2,3,4-Pentanetriol	C ₅ H ₁₂ O ₃	0.6	0.55
Propylene glycol	C ₃ H ₈ O ₂	0.667	0.583
Pentaerythritol	C ₅ H ₁₂ O ₄	0.8	0.6
Glycerol	C ₃ H ₈ O ₃	1	0.417
1-Butanol	C ₄ H ₁₀ O	0.25	0.875
1-Octanol	C ₈ H ₁₈ O	0.125	0.938
Isopropanol	C ₃ H ₈ O	0.333	0.75
Benzyl alcohol	C ₇ H ₈ O	0.143	0.929

S4 Summary list of the 89 analytes with their functionalities and vapor pressure

65 Table S5 gives the functional groups and vapor pressures (via EPI Suite database,(US EPA, 2019)).

Of the 89 total compounds, 20 were n-alkanes. Of the remaining 69 compounds, 46 were multifunctional (marked with an asterisk*). The overall counts of compounds containing a functionality were: 20 alkanes, 18 alkenes, 29 aromatics, 13 ethers, 29 esters, 6 aldehydes, 8 ketones, 35 alcohols, 1 acid, 1 epoxide, 2 lactones (also counted as esters) and 2 polycyclic aromatics (also counted as aromatics). Therefore, pentaerythritol counts as 1 alcohol, whereas hydroxyacetone is counted as
70 both an ester and an alcohol.

The volatility range (through EPI) was 3.38 E-6 to 8120 Pa (pentaerythritol to ethanol).

Table S5. Functional groups present and vapor pressures for the 89 analytes. An asterisk* denotes a multifunctional compound.

<u>#</u>	<u>Compound</u>	<u>Functional groups</u>	<u>VP (Pa)</u>
1	Heptane	alkane	6120
2	Octane	alkane	1980
3	Nonane	alkane	661
4	Decane	alkane	231
5	Undecane	alkane	83.8
6	Dodecane	alkane	31.5
7	Tridecane	alkane	12.3
8	Tetradecane	alkane	4.92
9	Pentadecane	alkane	2.03
10	Hexadecane	alkane	0.929
11	Heptadecane	alkane	0.432
12	Octadecane	alkane	0.195
13	Nonadecane	alkane	0.0897
14	Icosane	alkane	0.0413
15	Henicosane	alkane	0.0189
16	Docosane	alkane	0.00923
17	Tricosane	alkane	0.00473

18	Tetracosane	alkane	0.00226
19	Pentacosane	alkane	0.00128
20	Limonene	alkene	207
21	1,2,4-Trimethylbenzene	aromatic	215
22	Naphthalene	polycyclic aromatic	5.38
23	Isophytol*	alkene, alcohol	0.00188
24	Patchouli alcohol	alcohol	0.0328
25	Butylated hydroxytoluene*	aromatic, alcohol	0.236
26	alpha-Cetone*	dialkene, ketone	1.3
27	Methyl ionone*	dialkene, ketone	0.868
28	2-Dodecanol	alcohol	0.381
29	Phytol acetate*	alkene, ester	0.0048
30	Linalool*	dialkene, alcohol	11.1
31	alpha-Terpineol*	alkene, alcohol	5.64
32	Citronellal*	alkene, alcohol	5.88
33	2-Naphthol*	polycyclic aromatic, alcohol	0.0218
34	2-Nonanone	ketone	86.2
35	1-Octanol	alcohol	13.2
36	Phenylethyl alcohol*	aromatic, alcohol	3.24
37	Tetradecanoic acid ethyl ester	ester	0.339
38	2-Hydroxycyclopentadecanone*	ketone, alcohol	0.0000602
39	1,1,-Dimethyl-2-Phenyl ester butanoic acid*	aromatic, ester	0.343
40	Benzyl benzoate*	aromatic (two rings), ester	0.0741
41	2-Heptanone	ketone	655
42	Methyl laurate	ester	1.45
43	4-Tertbutyl cyclohexyl acetate	ester	9.13
44	Benzene ethanol, alpha, alpha-dimethyl acetate*	aromatic, ester	3.17
45	Linalyl acetate*	dialkene, ester	17.5
46	Hexanal	aldehyde	1280

47	Peach lactone	lactone (ester)	0.545
48	meta-Eugenol*	alkene, aromatic, ether, alcohol	0.311
49	3,5,5- Trimethyl hexyl acetate	ester	50.9
50	Safrole*	alkene, aromatic, diether	0.24
51	Eugenol*	alkene, aromatic, ether, alcohol	1.26
52	Allyl heptanoate*	alkene, ester	30.2
53	2-Methoxy-3-(2-Propenyl) phenol*	alkene, aromatic, ether, alcohol	0.311
54	Hydroxy-citronellal*	aldehyde, alcohol	0.773
55	Benzene methanol alpha-methyl acetate*	aromatic, ester	14.9
56	Benzyl salicylate*	aromatic (two rings), ester, alcohol	0.0024
57	Benzyl acetate*	aromatic, ester	25
58	Hexanoic acid, propenyl ester*	alkene, ester	96.1
59	Hedione*	ketone, ester	0.158
60	2-Phenoxyethyl isobutyrate*	aromatic, ether, ester	0.701
61	2-Hydroxy-2-Methylbutyl ester benzoic acid*	aromatic, ester, alcohol	0.0174
62	Isoamyl salicylate*	aromatic, ester, alcohol	0.0868
63	Acetic acid, Hexyl ester	ester	194
64	Strawberry aldehyde*	aromatic, ester, epoxide	0.423
65	Indan-1,3-Monopropionate*	aromatic, ester, alcohol	0.0129
66	1-Butanol	alcohol	1040
67	Ethylene brassylate*	dilactone (diester)	0.0000585
68	Myristicin*	alkene, aromatic, triether	0.861
69	Indan-1,3-Diol monoacetate*	aromatic, ester, alcohol	0.0398
70	Prenyl acetate*	alkene, ester	556
71	Isopropanol	alcohol	6610
72	1-Propanol	alcohol	3090
73	Diethyl phthalate*	aromatic, diester	0.339
74	Ethyl vanillin*	aromatic, aldehyde, ether, alcohol	0.039
75	Vanillin*	aromatic, aldehyde, ether, alcohol	0.0595

76	Piperonal*	aromatic, aldehyde, diether	1.41
77	Isopropyl acetate	ester	8110
78	Syringaldehyde*	aromatic, aldehyde, diether, alcohol	0.00865
79	Maltol*	aromatic (pyrone), ketone, alcohol	0.00571
80	1-Methoxy-2-Propanol*	ether, alcohol	984
81	Ethyl acetoacetate ethylene ketal*	diether, ester	18.1
82	5-Hydroxymethyl-2-(Dimethoxymethyl)furan*	aromatic(furan), diether, alcohol	0.168
83	HEM (Hydroxyethyl methacrylate)*	alkene, ester, alcohol	10.6
84	Ethanol	alcohol	8120
85	Propylene glycol	di-alcohol	14.8
86	Hydroxyacetone*	ketone, alcohol	232
87	Pentaerythritol	tetra-alcohol	3.38E-06
88	Acetic acid	acid	2290
89	Glycerol	tri-alcohol	0.0106

S5 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 $2.1\% \pm 1.8\%$, with a maximum relative error of 6.6%. The range of errors for all 14 compounds is shown in Figure S2.

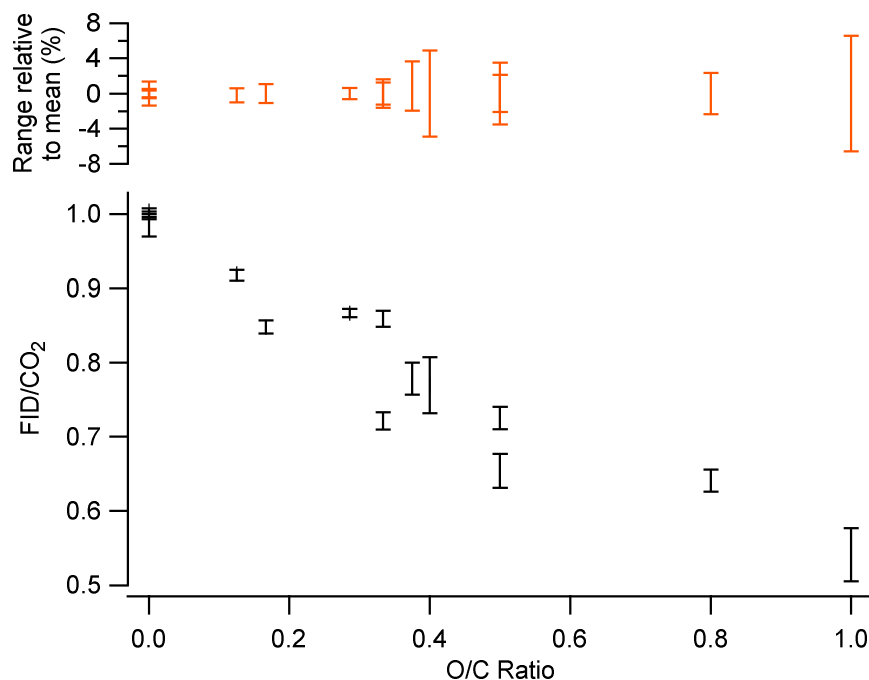


Figure S2: FID/CO₂ versus O/C for the 14 compounds analysed in multiple instrument configurations. Error bars show minimum and maximum value measured for each compound. Relative error shown on top as the ratio of the extrema to the mean. For the 11 compounds run on only two configurations, the extrema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

90 **S6 Error in Complete Combustion Experiments**

The data for the complete combustion experiments are presented in Table S6. As described in Section 3.1, squalene and diethyl phthalate were dissolved in dichloromethane, whereas hydroxyethyl methacrylate (HEM) and propylene glycol were dissolved in water. See also Figure 3 of the text.

95 **Table S6. Results for the complete combustion experiments**

<u>Compound</u>	<u>Number of injections</u>	<u>Mean % yield ± Std Dev</u>
Squalene	23	95.2 ± 5.5
Diethyl Phthalate	23	95.7 ± 5.3
HEM	21	100.2 ± 12.8
Propylene Glycol	33	87.2 ± 7.4
<i>All points</i>		93.7 ± 9.5

S7 Uncertainty in the correlations between rECN, O/C and FID/CO₂

Uncertainties for the slope and intercept of the three plots of Figure 4 are given in Table S7.

Table S7. Correlation parameters and uncertainties for Figure 4 plots

<u>Figure</u>	<u>Plot</u>	<u>Slope± error</u>	<u>% error</u>	<u>Intercept ± error</u>	<u>% error</u>
4a	FID/CO ₂ vs O/C	-0.54 ± 0.02	3.7	0.98 ± 0.01	0.6
4b	FID/CO ₂ vs rECN	0.85 ± 0.03	3.8	0.14 ± 0.03	21.5
4c	rECN vs O/C	-0.60 ± 0.02	3.1	0.99 ± 0.01	0.6

References

- 105 Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U. and Jimenez, J. L.: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, *Environ. Sci. Technol.*, 42(12), 4478–4485, doi:10.1021/es703009q, 2008.
- 110 Jorgensen, A. D., Picel, K. C. and Stamoudis, V. C.: Prediction of Gas Chromatography Flame Ionization Detector Response Factors from Molecular Structures, *Anal. Chem.*, 62(7), 683–689, doi:10.1021/ac00206a007, 1990.
- Scanlon, J. T. and Willis, D. E.: Calculation using effective carbon number, *J. Chromatogr. Sci.*, 23, 333–340, doi:10.1093/chromsci/23.8.333, 1985.
- US EPA: Estimation Programs Interface Suite for Microsoft Windows, 2019.