



Supplement of

On-line derivatization for hourly measurements of gas- and particle-phase Semi-Volatile oxygenated organic compounds by Thermal desorption Aerosol Gas chromatography (SV-TAG)

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S1. Derivatization efficiency tests

As discussed in the text, derivatization efficiency is tested using repeated injection of a mixture including 43 oxygenated compounds. In Table S1, names of the compounds injected and their molecular formulas and number of OH groups are shown, as well as the retention index of the derivatized compound. For every OH group, the derivatized compound eluted contains a trimethylsilyl group, adding C_3H_8Si to the formula of the observed peak. Relative retention times are shown as a Kovats-like (Kovats, 1958) retention index relative to *n*-alkanes, with i.e. *n*-pentacosane (C_{15}) having an index of 1500. Compounds span a retention time of approximately tridecane to tetratriacontane, but most (38 compounds) elute earlier than pentacosane.

Table S1. Compounds injected to assess derivatization efficiency: name, molecular formula, number of OH groups, and retention index of the derivatized peak relative to an *n*-alkane series.

Injected Compound Name	Molecular Formula	Number OH Groups	Derivatized Retention Index
Glyceric acid	$C_3H_6O_4$	3	1323
2,6-Dimethoxyphenol (Syringol)	$C_8H_{10}O_3$	1	1398
3,3-Dimethylglutaric acid	$C_7H_{12}O_4$	2	1433
<i>n</i> -Decanoic acid	$C_{10}H_{20}O_2$	1	1453
Threitol	$C_4H_{10}O_4$	4	1493
Erythritol	$C_4H_{10}O_4$	4	1501
Ketopinic acid	$C_{10}H_{14}O_3$	1	1507
<i>cis</i> -Pinonic acid	$C_{10}H_{16}O_3$	1	1526
3-Methoxy-4-hydroxybenzaldehyde (Vanillin)	$C_8H_8O_3$	1	1537
2-Methoxy-4-propenylphenol (Isoeugenol)	$C_8H_{10}O_3$	1	1568
Diethyltoluamide	$C_{12}H_{17}NO$	0	1582
Benzophenone	$C_{13}H_{10}O$	0	1645
<i>cis</i> -Pinic acid	$C_9H_{14}O_4$	2	1663
γ -Dodecalactone	$C_{12}H_{22}O_2$	0	1688
Levoglucosan	$C_6H_{10}O_5$	3	1698
α -Bisabolol	$C_{15}H_{26}O$	1	1742
<i>n</i> -Tridecanoic acid	$C_{13}H_{26}O_2$	1	1746
1,9-Nonadioic acid	$C_9H_{16}O_4$	2	1791
1,10-Decadioic acid	$C_{10}H_{18}O_4$	2	1887
Methyl palmitate	$C_{17}H_{34}O_2$	0	1924
<i>n</i> -Hexadecanol	$C_{16}H_{34}O$	1	1956
<i>cis</i> -9-Hexadecenoic acid	$C_{16}H_{30}O_2$	1	2022
Homosalate	$C_{16}H_{22}O_3$	1	2025
<i>n</i> -Hexadecanoic acid	$C_{16}H_{32}O_2$	1	2041
1,12-Dodecadioic acid	$C_{12}H_{22}O_4$	2	2082
Methyl stearate	$C_{19}H_{38}O_2$	0	2125

<i>n</i> -Heptanoic acid	C ₁₇ H ₃₄ O ₂	1	2139
<i>n</i> -Octadecanol	C ₁₈ H ₃₈ O	1	2154
<i>cis,cis</i> -9,12-Octadecadienoic acid	C ₁₈ H ₃₂ O ₂	1	2206
<i>cis</i> -9-Octadecenoic acid	C ₁₈ H ₃₄ O ₂	1	2213
<i>cis</i> -11-Octadecenoic acid	C ₁₈ H ₃₄ O ₂	1	2220
<i>n</i> -Octadecanoic acid	C ₁₈ H ₃₆ O ₂	1	2240
1,14-Tetradecanoic acid	C ₁₄ H ₂₆ O ₄	2	2275
<i>n</i> -Eicosanol	C ₂₀ H ₄₂ O	1	2349
Isopimaric acid	C ₂₀ H ₃₀ O ₂	1	2353
16-Hydroxyhexadecanoic acid	C ₁₆ H ₃₂ O ₃	2	2385
12-Hydroxyoctadecanoic acid	C ₁₈ H ₃₆ O ₃	2	2423
Abietic acid	C ₂₀ H ₃₀ O ₂	1	2433
Deoxycholic Acid	C ₂₄ H ₄₀ O ₄	3	3065
Cholesterol	C ₂₇ H ₄₆ O	1	3166
β -Stigmasterol	C ₂₉ H ₄₈ O	1	3297
β -Sitosterol	C ₂₉ H ₅₀ O	1	3360
Lupeol	C ₃₀ H ₅₀ O	1	3441

S2. Derivatization reproducibility tests

When correcting analytes for run-to-run variability using internal standards, an internal standard must be selected to use for the correction. Several possible selection criteria are available for correction of oxygenated compounds. Table 1 in the main text lists the schemes tested for correction of all oxygenates with hydroxyl groups and the error of each scenario, measured as the relative standard deviation from the average ratio of one internal standard to another one selected based on the criteria of the scenario. Figure S1 shows the cumulative error distribution for a subset of the test scenarios selected to apply to most, if not all, operating conditions. Correcting for compounds using an internal oxygenated standard of only similar volatility (i.e. in the case of analytes of unknown structure or a functionally similar internal standard is unavailable) is modeled by correcting all oxygenates to the nearest *n*-acid in volatility, of which there are 4 of various volatility in the standard used (Fig. S1a). The error present in correcting for only general changes in derivatization efficiency is quantified by correcting all oxygenates using a single, relatively stable oxygenate, *n*-octadecanoic acid-d₃₅ (Fig. S1b). Under operating conditions requiring minimal internal standards or maximizing standard stability by not including oxygenates, oxygenates can be corrected for variability in transfer efficiency and detector sensitivity using only alkanes of similar volatility, but this results in large errors with a relatively non-Gaussian distribution (Fig. S1c). Due in part to operational

improvements after the SOAS field campaign, Study 2 has lower error in all cases shown in Fig. S1 owing to more reproducible measurements of multi-functional acids.

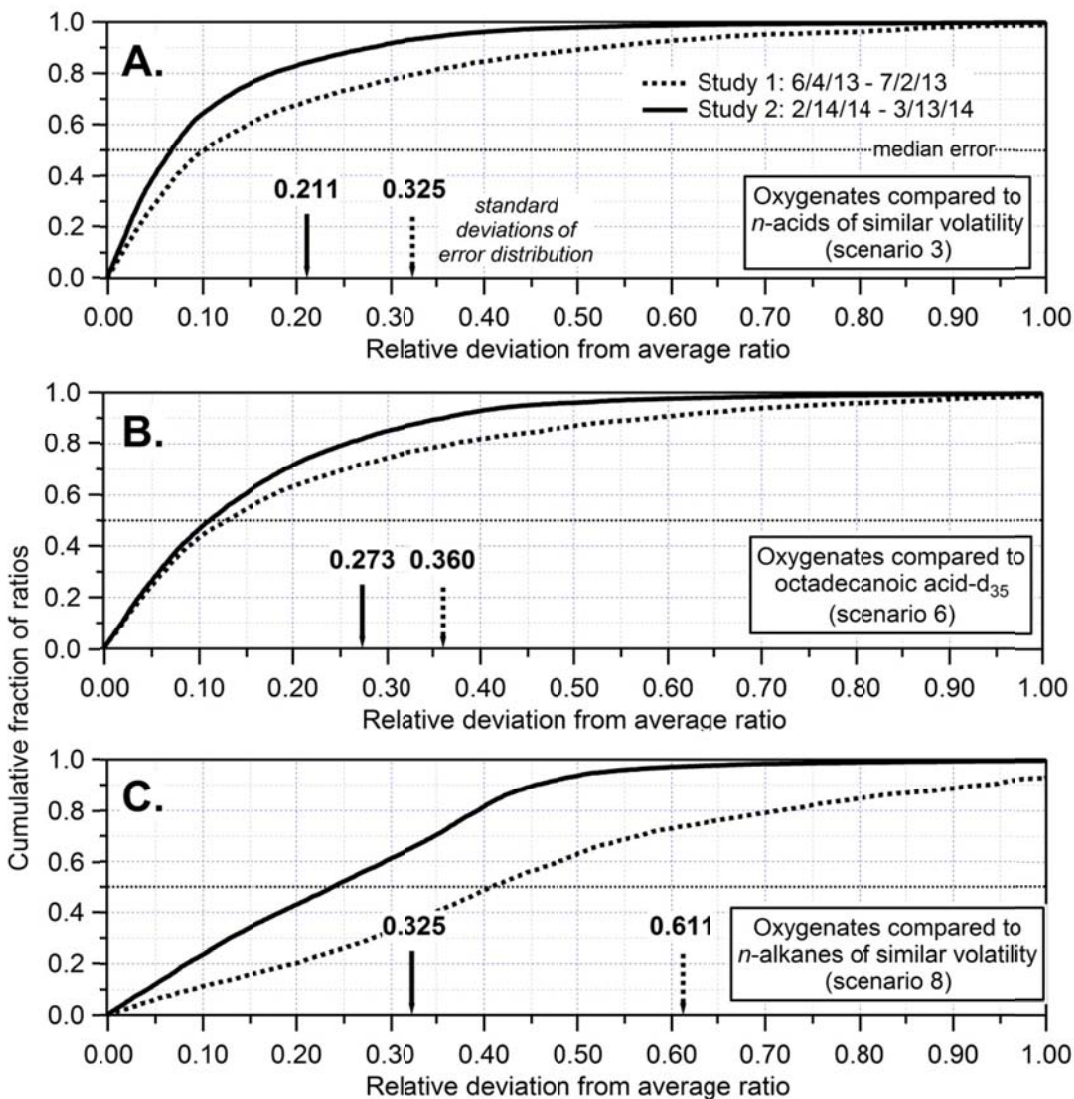


Figure S1. Cumulative distribution of error in correction of oxygenates for run-to-run variability in derivatization efficiency and instrument response measured as relative deviation of two internal standards from their average ratio. Boxes and Sect. S2 describe each correction scenario, which are numbered corresponding to Table 1 in the main text. Arrows show relative standard deviation for each study. Dotted line is median error (50% of points have less than this error).

41 **References**

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