Comparison of Analytical Derivatization Methods for Polar Organic Aerosol Speciation

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Background

•GC/MS semi-volatile polar organic compound (SVPOC) characterization is often done by derivatization of polar functional groups to reduce molecular polarity.

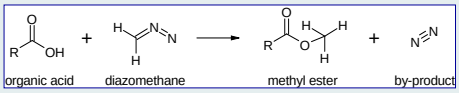
•Derivatization can be done using methylation & silylation methods to produce methyl esters and TMS esters, respectively.

•Ambient samples dominated by biomass combustion are used to provide a comparison between methylation and silylation derivatization methods for quantitation.

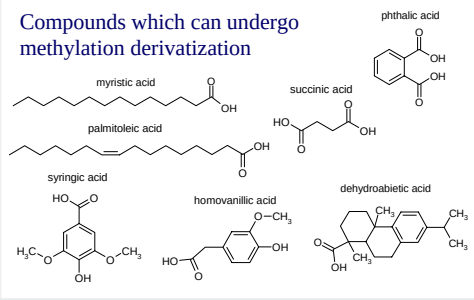
•Most biomass combustion molecular markers used for receptor source apportionment are SVPOCs, including levoglucosan, guaiacol, syringol, dehydroabietic acid, etc.

Derivatization Reactions for Polar Molecular Tracers for GC/MS Analysis

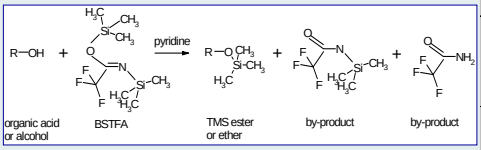
Methylation Derivatization Reaction



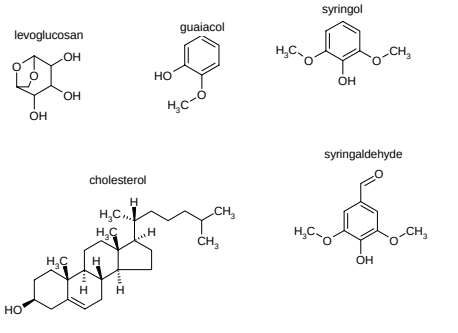
Compounds which can undergo methylation derivatization



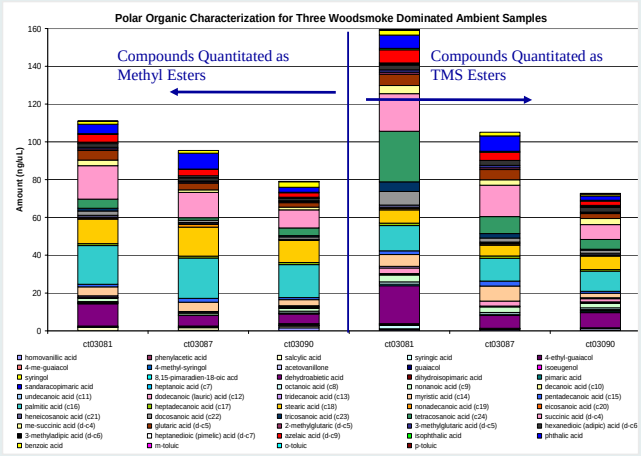
Silylation Derivatization Reaction



Compounds which cannot undergo methylation derivatization



Biomass Combustion Dominated Ambient Sample Characterization for TMS Esters & Methyl Esters



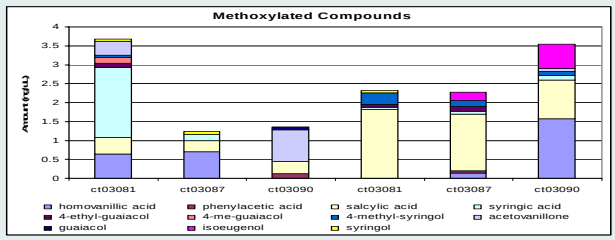
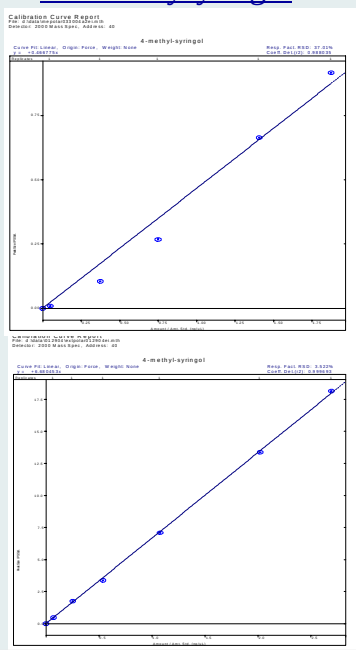


Table of Results for TMS Esters & Methyl Esters with the Corresponding % Differences

	Results for TMS Esters			Results for Methyl Esters			Percent Difference		
	ct03081	ct03087	ct03090	ct03081	ct03087	ct03090	%Diff = (TMSE-ME)/(TMSE+ME)/2*100		
Compound Name	Amt(ng/uL)	Amt(ng/uL)	Amt(ng/uL)	Amt(ng/uL)	Amt(ng/uL)	Amt(ng/uL)	Values above 20% in Red		
homovanillic acid	0.637	0.699			0.139	1.573		33	
phenylacetic acid			0.121		0.061			-50	
salcylic acid	0.449	0.297	0.318	1.819	1.492	1.028	-30	-33	-26
syringic acid	1.846	0.169		0.058	0.076	0.11	47	19	
4-ethyl-guaiacol	0.109			0.078	0.13		8		
4-me-guaiacol	0.153								
4-methyl-syringol	0.056			0.304	0.165	0.115	-34		
acetovanillone	0.372		0.849			0.075			42
guaiacol			0.078						
isoeugenol					0.205	0.641			
syringol	0.05	0.069		0.054			-2		
							Std Dev % Difference		34
8,15-pimaradien-18-oic acd	0.105	0.07	0.208	0.212	0.227	0.231	-17	-26	-3
dehydroabietic acid	20.075	6.811	8.057	11.726	5.634	5.164	13	5	11
dihydroisopimaric acid			0.093	0.171	0.242	0.152			-12
pimaric acid			0.756	0.344					
sandaracopimaric acid			0.266	0.413		0.298			-3
							Std Dev % Difference		14
octanoic acid (c8)	1.181	0.941	0.885	0.255		0.941	32		-2
nonanoic acid (c9)	3.638	2.951	2.496	1.753	0.984	1.527	17	25	12
decanoic acid (c10)	0.292	0.172	0.22	0.284	0.238	0.303	1	-8	-8
undecanoic acid (c11)	0.419	0.25	0.407	0.134	0.163	0.519	26	11	-6
dodecanoic (lauric) acid (c12)	2.98	2.642	1.731	0.216		0.061	43		47
tridecanoic acid (c13)	0.891		0.502	0.692	0.458	0.476	6		1
myristic acid (c14)	6.332	7.991	2.399	4.706	4.906	3.26	7	12	-8
pentadecanoic acid (c15)	1.921	2.6	0.989	1.295	1.988	1.053	10	7	-2
palmitic acid (c16)	13.333	11.997	10.655	20.554	21.385	17.45	-11	-14	-12
heptadecanoic acid (c17)	1.226	1.292	0.881	1.044	0.988	1.095	4	7	-5
stearic acid (c18)	7.115	5.699	7.079	12.892	15.325	11.744	-14	-23	-12
nonadecanoic acid (c19)	0.637	0.694	0.367	0.508	1.516		6	-19	
eicosanoic acid (c20)	0.724	0.474	0.325	0.536	0.315	0.412	7	10	-6
heneicosanoic acid (c21)	1.169	0.466	0.791	1.07	0.682	0.172	2	-9	32
docosanoic acid (c22)	7.161	2.171	1.659	2.213	1.125	1.189	26	16	8
tricosanoic acid (c23)	5.097	2.368	0.52	1.431		0.691	28		-7
tetracosanoic acid (c24)	26.756	8.975	5.193	4.831	1.39	4.102	35	37	6
							Std Dev % Difference		17
succinic acid (d-c4)	19.94	16.611	7.86	17.709	13.364	9.551	3	5	-5
me-succinic acid (d-c4)	4.314	2.843	3.195	3.031	1.343	1.493	9	18	18
glutaric acid (d-c5)	5.943	5.486	2.638	5.047	3.577	2.388	4	11	2
2-methylglutaric (d-c5)	1.081	0.885	0.454	0.829	0.655	0.597	7	7	-7
3-methylglutaric acid (d-c5)	1.232	1.282	0.285	0.857	0.46	0.347	9	24	-5
hexanedioic (adipic) acid (d-c6)	2.565	2.636	2.438	1.991	1.684	1.27	6	11	16
3-methyladipic acid (d-c6)	0.607		0.491	0.205	0.374	0.246	25		17
heptanedioic (pimelic) acid (d-c7)	0.539		0.62	0.483	0.777	0.359	3		13
azelaic acid (d-c9)	6.925	4.311	2.326	4.181	3.317	2.386	12	7	-1
isophthalic acid	0.786	0.517	0.44	0.326	0.156	0.272	21	27	12
phthalic acid	6.996	8.141	2.29	5.006	8.398	2.636	8	-1	-4
							Std Dev % Difference		9

- Methoxy phenols and methoxy acids have very different quantitation results in this comparison.
- These compounds benefit from BSTFA + 1%TMCS derivatization due molecular hydroxyl groups which highly interact with stationary phase of GC column.
- Calibration curves using the same set of calibration mixtures provide evidence of column interactions. The top calibration curve with underivatized 4-methylsyringol appears to be linear with an r^2 value of 0.988, while the bottom calibration curve shows an excellent linear fit with an r^2 value equal to 0.999 for a range of 0.28 to 10.6 ng/uL.

Calibration Curves for 4-methoxysyringol



Conclusion

- Quantitation of SVPOC depend greatly upon the derivatization methods used for analysis.
- Both derivatization methods provide a similar SVPOC data pattern as seen in the stacked bar chart with some variation in quantitation.
- Increasing molecular polarity from hydroxyl functional groups hinder quantitation due to increasing affinity for stationary phase interactions.
- Highest quantitation differences were found for methoxylated acids and phenols followed by alkanoic acids, while differences in quantitation for resin acids and dialkanoic acids were smaller.