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The Effect of Solvent on the Analysis of Secondary Organic Aerosol Using Electrospray Ionization Mass Spectrometry

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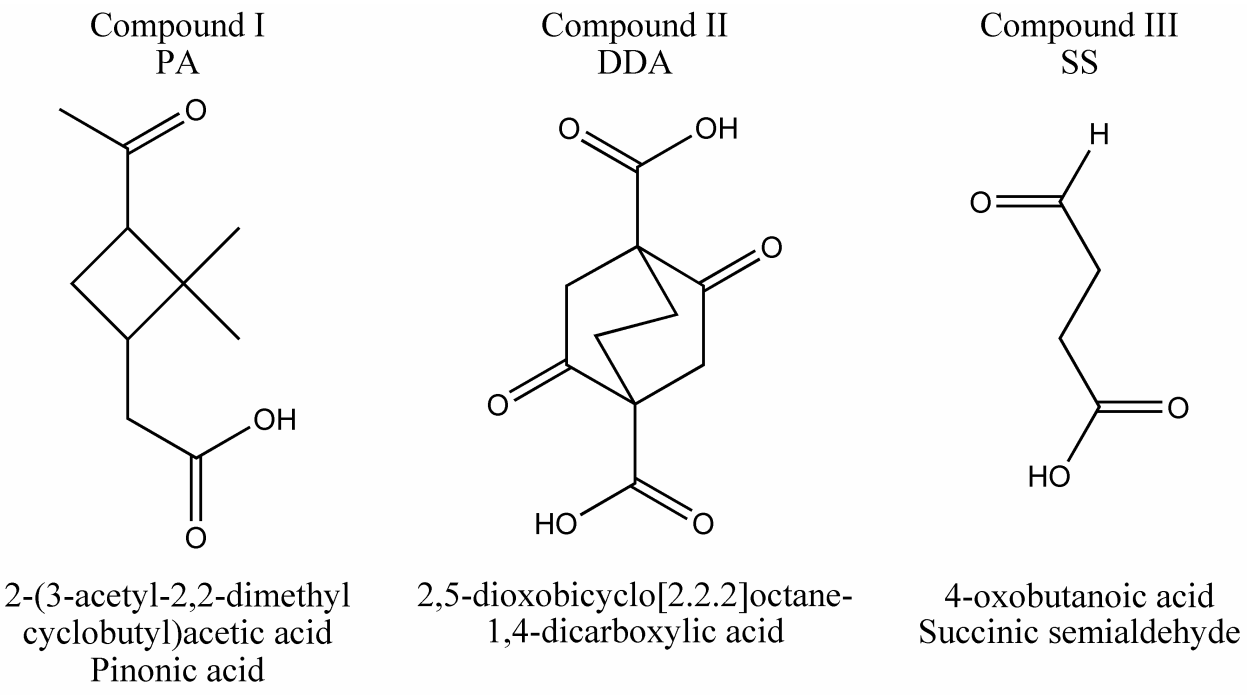
1. Sources and purity of chemicals used in this work

The following chemicals were acquired and used without further purification.

- *d*-limonene (98%, Acros Organics, Inc.)
- methanol (HPLC grade, Fisher Scientific, Inc.)
- d_3-methanol (99.8 atom% D, Sigma-Aldrich, Inc.)
- d_4-methanol (99.8 atom% D, Sigma-Aldrich, Inc.)
- acetonitrile (HPLC grade, Fisher Scientific, Inc.)
- d_3-acetonitrile (99.8 atom% D, Sigma-Aldrich, Inc.)
- cis-pinonic acid (98 %, Sigma-Aldrich, Inc.)
- succinic semialdehyde (4-oxobutanoic acid, 15% solution in water, Thermo-Fisher, Inc.)
- 2,5-dioxobicyclo[2.2.2]octane-1,4-dicarboxylic acid (>90 %, Maybridge Scientific, Inc.)

2. Supporting figures

Figure S1. Structures, acronyms (used throughout this paper), IUPAC names, and common names of test organic compounds used to investigate the rate and extent of solvent-analyte reactions.



Compound I
PA

2-(3-acetyl-2,2-dimethyl cyclobutyl)acetic acid
Pinonic acid

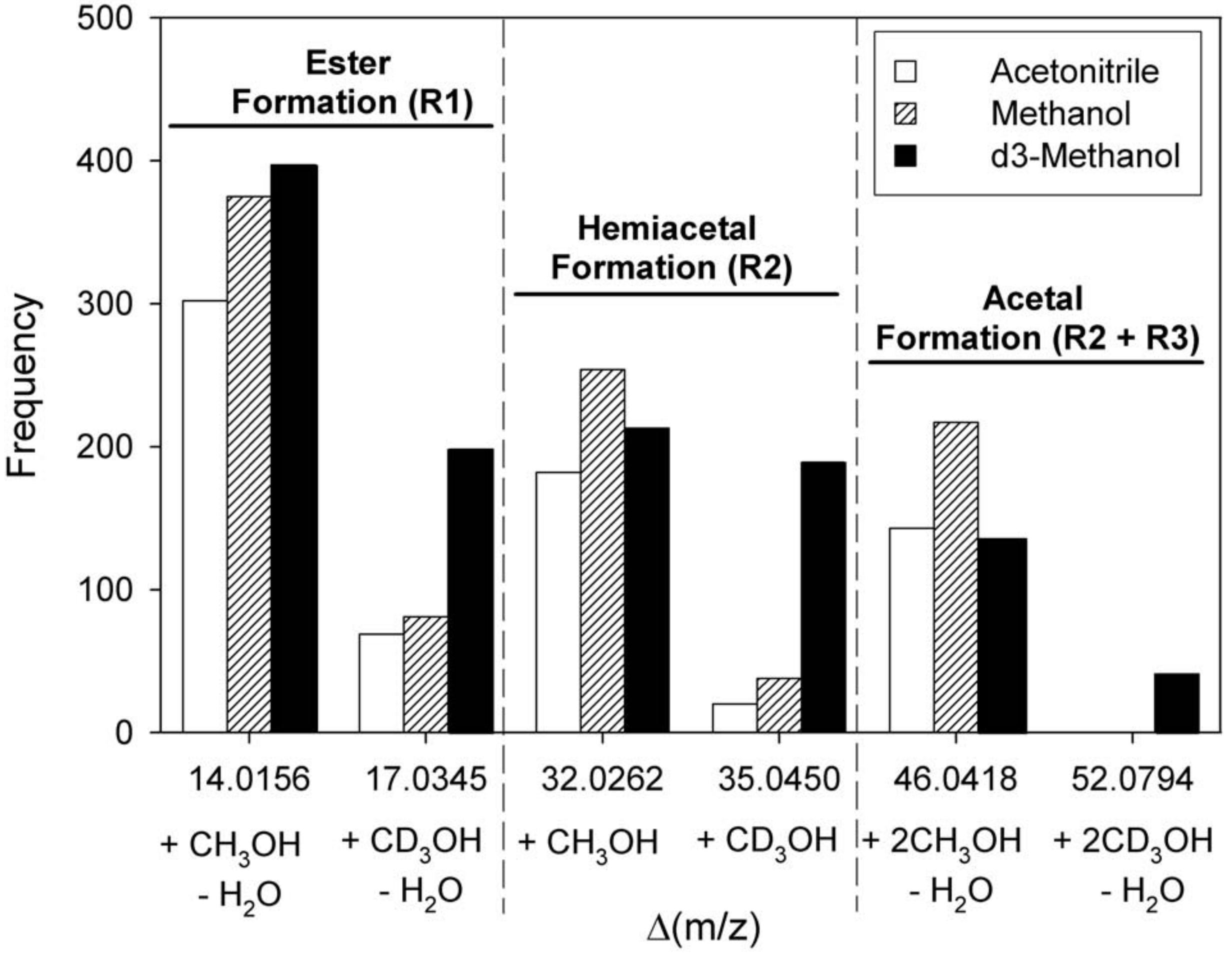
Compound II
DDA

2,5-dioxobicyclo[2.2.2]octane-1,4-dicarboxylic acid

Compound III
SS

4-oxobutanoic acid
Succinic semialdehyde

Figure S2. Frequency of occurrence of selected Δ(m/z) differences between peak positions in *d*-limonene SOA positive ion mode mass spectra recorded in acetonitrile, methanol and d_3-methanol in m/z range of 150-500.



Note: As expected, Δ(m/z) values corresponding to the CH_3OH reactions (32.0262 and 46.0419 m/z) occur more frequently in methanol, and those corresponding to the CD_3OH reactions (17.0345, 35.0450, and 52.0794 m/z) are dominant in d_3-methanol spectra. All Δ(m/z) frequencies increase in methanol and d_3-methanol mass spectra because they contain more peaks than the acetonitrile mass spectrum. This explains why the observed frequencies for Δ(m/z) = 14.0156 (CH_2 group) in methanol and d_3-methanol are somewhat higher than in acetonitrile. The presence of odd Δ(m/z) values that correspond to CD_3OH reactions in the acetonitrile and methanol based spectra can be explained by the interference from ^{13}C peaks in all mass spectra, allowing for odd Δ(m/z) values from all spectra. In addition, this can result in double counting of peaks corresponding to compounds capable of solvent-analyte reactions.

3. Supporting tables

Table S1: Relative abundance of ESI MS peaks after 24 hours of storage in methanol in the presence of variable amounts of acetic acid (AA) normalized to the corresponding precursor peaks (e.g., $[M+Na]^+$ and $[M-H]^-$ the positive and negative ion modes, respectively).

	Acetal Positive Mode	Acetal Negative Mode	Hemiacetal Positive Mode	Hemiacetal Negative Mode	Ester Positive Mode
PA / No AA added	1.27×10^{-4}	3.40×10^{-4}	1.03×10^{-4}	5.65×10^{-5}	3.45×10^{-4}
PA / 16 μM AA	5.54×10^{-5}	3.38×10^{-4}	5.51×10^{-5}	1.57×10^{-5}	2.84×10^{-4}
PA / 1.6 mM AA	1.53×10^{-4}	2.26×10^{-3}	1.72×10^{-5}	2.31×10^{-5}	1.27×10^{-3}
PA / 16 mM AA	1.37×10^{-4}	2.03×10^{-3}	5.82×10^{-5}	3.66×10^{-5}	2.08×10^{-3}
DDA / No AA added	2.55×10^{-3}	6.89×10^{-5}	7.31×10^{-1}	1.24×10^{-3}	1.95×10^{-2}
DDA / 16 μM AA	3.00×10^{-3}	6.47×10^{-5}	7.12×10^{-1}	1.11×10^{-3}	1.77×10^{-2}
DDA / 1.6 mM AA	2.71×10^{-3}	6.32×10^{-5}	6.62×10^{-1}	1.19×10^{-3}	1.94×10^{-2}
DDA / 16 mM AA	2.65×10^{-3}	5.54×10^{-5}	6.81×10^{-1}	6.71×10^{-4}	1.89×10^{-2}
SS / No AA added	2.70×10^{-2}	9.80×10^{-5}	9.79	1.34×10^{-2}	5.55
SS / 16 μM AA	2.41×10^{-2}	1.31×10^{-4}	7.55	1.38×10^{-2}	5.71
SS / 1.6 mM AA	4.01×10^{-2}	4.68×10^{-4}	6.43	1.26×10^{-2}	5.51
SS / 16 mM AA	7.45×10^{-2}	9.76×10^{-4}	4.89	6.27×10^{-3}	4.94

Note: The relative concentrations cannot be obtained from this data set because of the unknown differences in ionization and detection efficiencies of reactants and products. Indeed, the product/reactant ratios obtained from the mass spectra recorded in the positive and negative mode are quite different (Table 1S). The detection sensitivity is especially affected when a carboxylic group is esterified; this strongly influences the ionization pathways in ESI by reducing the efficiency of deprotonation in the negative ion mode, and changing the affinity of the molecule to Na^+ in the positive ion mode. As a result of the poor negative ion yield from esters (with the exception of the ester of dicarboxylic acid DDA), Table 1S only reports the positive ion product/reactant ratios for the esterification reactions.

Table S2: The largest peaks observed in the positive ion mode ESI mass spectrum of d-limonene SOA in acetonitrile, methanol, and d_3-methanol. Relative abundance is given in parentheses next to m/z values in *italic*. Peak labeled "*100*" has the largest intensity in a given mass spectrum. The table includes hemiacetal peaks resulting from addition of one methanol or d_3-methanol molecule to the precursor molecule. The corresponding neutrals are classified as aldehydes or ketones based on the relative abundance of the hemiacetal peak.

m/z (abundance) acetonitrile	m/z (abundance) methanol	m/z (abundance) d_3-methanol	Non-ionized composition	Likely classification
209.0785 *(100)*	209.0785 *(54)*	209.0784 *(63)*	$C_9H_{14}O_4$	Ketone
-	241.1047 *(30)*	-		
-	-	244.1236 *(16)*		
207.0992 *(88)*	207.0992 *(41)*	207.0992 *(50)*	$C_{10}H_{16}O_3$	Aldehyde
-	239.1255 *(100)*	-		
-	-	242.1444 *(100)*		
223.0942 *(94)*	223.0942 *(57)*	223.0942 *(64)*	$C_{10}H_{16}O_4$	Ketone
-	255.1203 *(10)*	-		
-	-	258.1391 *(8)*		
193.0835 *(30)*	193.0835 *(29)*	193.0835 *(35)*	$C_9H_{14}O_3$	Aldehyde
-	225.1098 *(62)*	-		
-	-	228.1286 *(49)*		
191.1043 *(23)*	191.1042 *(11)*	191.1043 *(23)*	$C_{10}H_{16}O_2$	Aldehyde
-	223.1305 *(47)*	-		
-	-	226.1494 *(52)*		

Note: All of these molecules definitively contain a carbonyl functional group based on the fact that they all produce hemiacetals. Furthermore, peaks at m/z 207.0992, 193.0835, and 191.1043 are accompanied by the corresponding hemiacetal peaks that are stronger than their precursors suggesting the presence of at least one aldehyde group in these molecules. This is consistent with our previous assignments of 191.1043 m/z peak to limononaldehyde (*Walser et al*, *PCCP*, **2008**, *10*, 1009-1022). On the contrary, peaks at 209.0785 and 223.0942 m/z have much weaker hemiacetal peaks, and likely correspond to ketones. This is consistent with assignments of these peaks to keto-limononic and 7OH-limononic acids, respectively (*Walser et al*, *PCCP*, **2008**, *10*, 1009-1022).

4. Mass spectra of SOA extracted in d_4-methanol

For SOA samples extracted into d_4-methanol, peaks corresponding to addition of CD_3OD and CD_3OH to precursor ions are both visible. This is expected because of the facile isotopic exchange of the hydroxyl D-atom in CD_3OD with H-atoms from SOA constituents followed by reactions of SOA species with both CD_3OD and CD_3OH. Because mass spectra recorded in d_4-methanol do not provide additional information compared to methanol- and d_3-methanol-based mass spectra, their analysis is not presented in this manuscript.

5. Assignment of ^{13}C peaks in mass spectra

Peaks with even nominal m/z values observed in acetonitrile and methanol based mass spectra were attributed to compounds containing one ^{13}C atom. In d_3-methanol based mass spectra, compounds that reacted with d_3-methanol to form esters or hemiacetals also resulted in even m/z peaks. In most cases, the peaks attributed to formation of d_3-methanol adducts could be distinguished from the ^{13}C peaks by their relative intensities, i.e., the relative intensity for ^{13}C isotope substitution peaks can be predicted by the number of carbon atoms and the isotopic abundance of ^{13}C. Most peaks attributed to d_3-methanol derivatives had relative intensities far greater than those expected for ^{13}C peaks.

Figure 2S includes all $\Delta(m/z)$ values, even differences from compounds containing ^{13}C atoms. Figure 3 of the manuscript includes all peaks present in acetonitrile-based mass spectra on the upper portion of the graph. The lower portion of the graph includes only peaks attributed to compounds that formed a hemiacetal adduct with either methanol or d_3-methanol.