Supplement for: Evidence for pyrazine-based chromophores in cloudwater mimics containing methylglyoxal and ammonium sulfate

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Spectrum RT 27.80 - 28.26 (27 scans) - Background Subtracted 8.43 - 10.55 2017 10 <u>9 9 41</u> 28 is1.datx 2017.10.09 09:54:28 Hawkins lab - MG+AS pH varied samples; APCI + Max: 4.3E8 Intensity



Spectrum RT 29.47 - 30.43 (55 scans) - Background Subtracted 8.43 - 10.55 2017 10_9_9_41_28_jst.datx 2017.10.09 09:54:28 Hawkins lab - MG+AS pH varied samples; APCI + Max: 66E8 Intensity



Intensity

Spectrum RT 33.88 - 35.39 (86 scans) - Background Subtracted 8.43 - 10.55 2017_10_9_9_41_28_is1.datx 2017.10.09 09:54:28 Hawkins lab - MG+AS pH varied samples; APCI + Max: 4.1E8



Figure S1. Under initial condition of pH 5, from top to bottom subfigures are: ¹⁴N AS capped sample, ¹⁵N AS capped sample, ¹⁴N AS dried sample, ¹⁵N AS dried sample.

 Spectrum RT 37.51 - 37.85 (20 scans) - Background Subtracted 8.43 - 10.55

 2017_10_9_9_41_28_is1.datx 2017.10.09 09:54:28 Hawkins lab - MG+AS pH varied samples;

 Intensity
 APCI + Max: 1.1E8



 Spectrum RT 38.72 - 39.52 (46 scans) - Background Subtracted 8.43 - 10.55

 2017 10 - 9 - 41 . 28 is1.datx 2017.10.09 09:54:28 Hawkins lab - MG+AS pH varied samples;

 APCI + Max: 3.6E8



 Spectrum RT 42.42 - 43.91 (85 scans) - Background Subtracted 8.43 - 10.55

 2017 - 10.9.9.41_28.jst.datx 2017.10.09 09:54:28 Hawkins lab - MG+AS pH varied samples;

 Intensity
 APCI + Max: 5.4E8







Figure S2. Under initial condition of pH 7, from top to bottom subfigures are: ¹⁴N AS capped sample, ¹⁵N AS capped sample, ¹⁴N AS dried sample, ¹⁵N AS dried sample.





 Spectrum RT 52.07 - 52.46 (23 scans) - Background Subtracted 8.43 - 10.55

 2017 10.9.9_41 28 (st.datx 2017.10.09 09:54:28 Hawkins lab - MG+AS pH varied samples; PPCI + Max: 19.58







Figure S3. Under initial condition of pH 9, from top to bottom subfigures are: ¹⁴N AS capped sample, ¹⁵N AS capped sample, ¹⁴N AS dried sample, ¹⁵N AS dried sample.

File :D:\MassHunter\GCMS\1\data\LNH\171012_pH2b.D Operator : Acquired : 12 Oct 2017 15:10 using AcqMethod pyrazineSearch.M Instrument : 5975 GCMS Sample Name: pH2 Misc Info : Vial Number: 2

Figure S4. Top: Total ion chromatogram for the ethyl acetate extract of a dried pH 2 sample. Middle: sum of all ions selected for SIM showing a peak at 4.175 min corresponding to the pyrazine internal standard and a second peak at 6.572 min corresponding to 2,5-dimethylpyrazine. Bottom: Electron impact spectrum acquired at retention time 6.560 (during 2,5-DMP elution) with prominent fragments at m/z 108, 42, and 81.

Figure S5. Top: spectrum obtained during elution of (proposed) 2,5-DMP peak from column. Bottom: NIST reference spectrum for electron impact ionization of 2,5-DMP.

Figure S6. Image taken after 24 hours of reaction time between methylglyoxal and AS in capped samples. A pH dependence on absorbance is immediately visible.