Supplemental information for:

Coupling Liquid Chromatography with Aerosol Mass Spectrometry to Enhance Chemically Resolved Aerosol Analysis

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S1. IC-AMS Background Subtraction

Throughout this work, we utilize SP-AMS data obtained from the chopper open position, resulting in signal related to the instrument background. Additionally, organic signal related to the IC eluent was also measured by the AMS. An example of the HR-MS measured by the SP-AMS during the IC analysis of a water blank is shown in Figure S1. Of particular note are the $C_xH_yO_zS^+$ ions, with the most prominent fragments being $CHSO^+$ (*m/z* 61), $CH_3SO_2^+$ (*m/z* 79), and $CH_4SO_3^+$ (*m/z* 95). Although $CH_3SO_2^+$ and $CH_4SO_3^+$ are signatures for methanesulfonic acid (MSA; CH_4SO_3), these fragments do not appear when the IC system is bypassed and the sample is directly injected into the nebulizer. Furthermore, $CHSO^+$ does not appear in the AMS spectra of pure MSA (Huang et al., 2015). It is suspected that this background may be an artifact related to the use of the suppressor, which uses 0.1M H_2SO_4 during the regeneration process, or possibly another unknown source from within the IC system. Based on typical ambient AMS spectra, the contribution from $C_xH_yO_zS^+$ ions are expected to be minor even for pure organosulfate compounds (Huang et al., 2015). Therefore, these fragments, along with fragments with similar molecular mass that were heavily influenced by the $C_xH_yO_zS^+$ ions, were removed from further analysis.

A number of other fragments have a stable but elevated background signal, with the most prominent being CO_2^+, likely formed due to the Na_2CO_3 present in the anion eluent. There was also a minor but persistent influence from $C_xH_yN^+$ fragments, including CH_3N^+ (*m/z* 29), C_2HN^+ (*m/z* 39) and $C_2H_6N^+$ (*m/z* 44). These may result from bleeding or degradation of the ammonium groups on the columns stationary phase. To correct the concentration of these species, the background contribution of each fragment was determined as the average concentration during the first 60 seconds of the IC run, following the sample injection but prior to the elution of any compounds. This value was then subtracted from the respective fragments time series. This process was repeated separately for each IC run. All time series and spectra reported show the background corrected results.

For the cation analysis, there was minimal background signal except from NO_x fragments, likely resulting from the high concentration of HNO_3 in the eluent. As nitrate is not expected to be relevant for analysis of cations, no background subtraction was performed.

S2. Quantification of Isotopically Labeled Ammonium Sulfate

For accurate quantification of offline samples, isotopically labeled ammonium sulfate with ^{34}S ($A^{34}S$) was used as an internal standard. Throughout this analysis, all $H_y{}^{34}SO_x{}^+$ fragments were allowed to be fit independent of parent peak concentration. To determine the total $^{34}SO_4$ concentration, a new species was created within the high resolution "fragmentation table" (Allan et al., 2004). The fragmentation pattern of $A^{34}S$ was assumed to be identical to standard ammonium sulfate (AS) and the fragmentation table entries for $A^{34}S$, including the formation of H_yO^+ ions, were kept the same. The fragmentation table entries for both $A^{34}S$ and AS were modified for the naturally occurring ^{34}S in AS. This was done by scaling all major $H_y{}^{32}SO_x$ fragments by the isotopic abundance of ^{34}S while simultaneously removing this value from the respective fragment in $A^{34}S$ family.

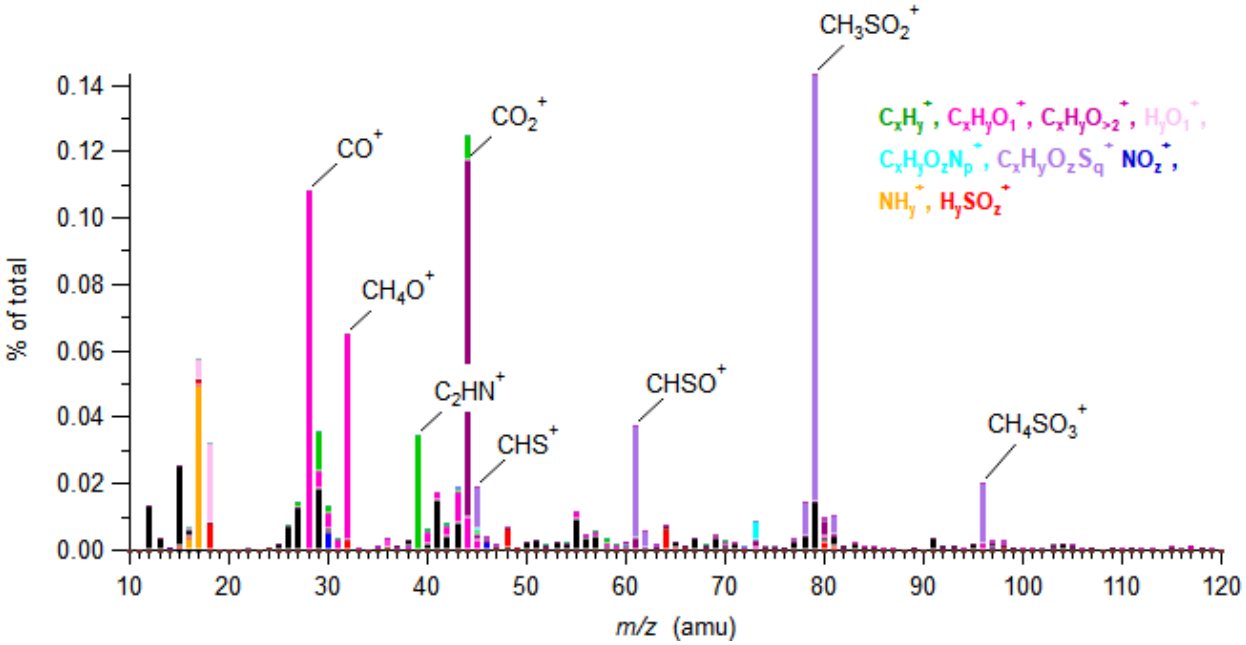

Figure S1: Average HR-MS of eluent background measured during Milli-Q blank

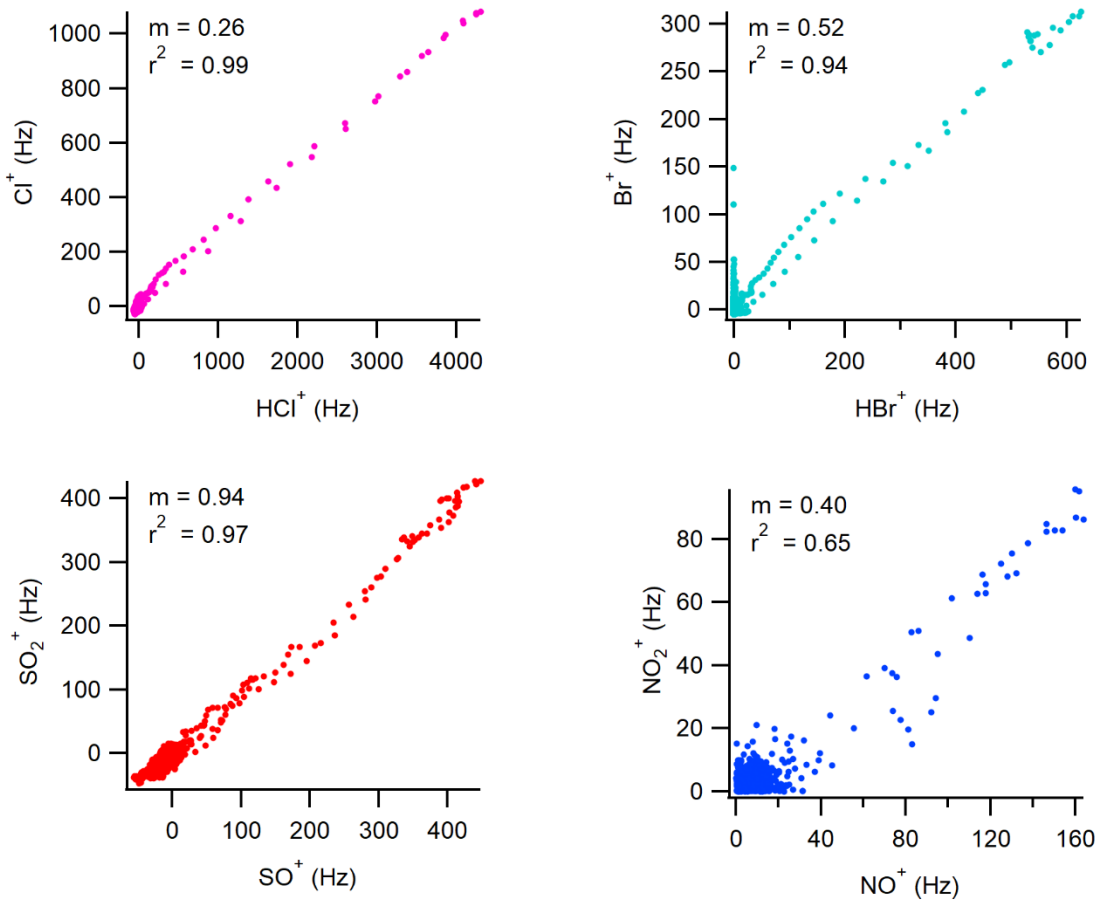

Figure S2: Correlation between major (a) chloride (b) Bromine (c) sulfate, (d) nitrate fragments measured during the anion standard.

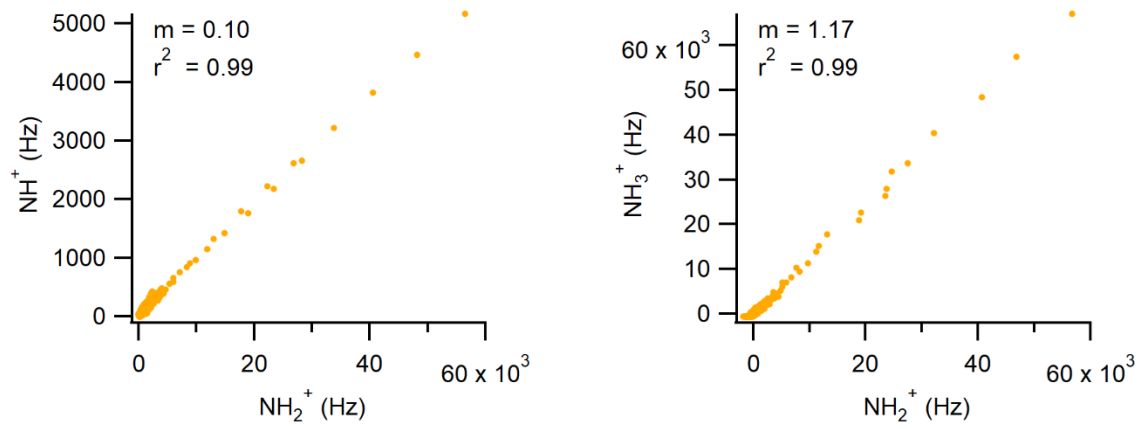

Figure S3: Correlation between ammonium fragments measured during the cation standard.

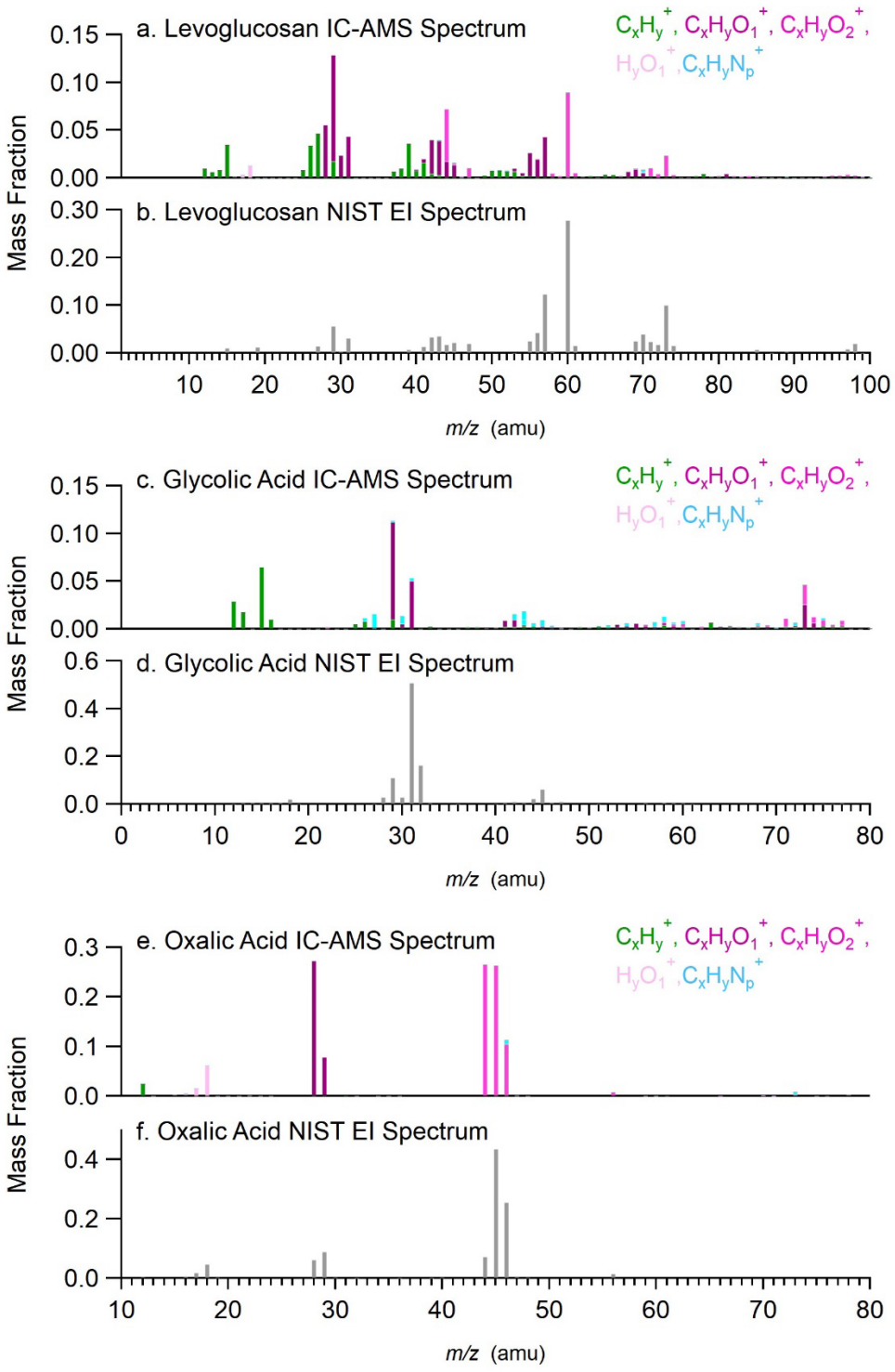

Figure S4: Average high resolution mass spectrum during the elution of (a) Levoglucosan, (c) glycolic acid, (e) oxalic acid measured by IC-AMS. Reference mass spectrum from NIST Mass Spectral Library for (b) levoglucosan, (d) glycolic acid and (f) oxalic acid.

References

Huang, D. D., Li, Y. J., Lee, B. P., and Chan, C. K.: Analysis of organic sulfur compounds in atmospheric aerosols at the HKUST supersite in Hong Kong using HR-ToF-AMS, Environ Sci Technol, 49, 3672-3679, 10.1021/es5056269, 2015.