



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

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Abstract.

We present a novel analytical method that couples liquid chromatography with aerosol mass spectrometry (LC-AMS) to separate and chemically characterize soluble constituents in atmospheric samples. This method is demonstrated here using ion chromatography (IC) to resolve ionic species prior to AMS detection. As the IC effluent is analyzed by the AMS, quantitative ion signals and reproducible mass spectra are obtained throughout the chromatographic run. These chromatographically resolved AMS data provide both quantitative information and chemical signatures for individual and partially overlapping chromatographic features. Method performance was evaluated using standard mixtures of inorganic anions and cations, as well as atmospherically relevant organic compounds (e.g., levoglucosan and organic acids). The IC-AMS chromatograms exhibited stable background signals, allowing the peak areas of AMS-derived ions to be integrated reliably for quantification. Isotopically labeled ammonium sulfate ($(\text{NH}_4)_2^{34}\text{SO}_4$) was used as an internal standard to correct for variations in aerosol generation efficiency and AMS sensitivity. Recoveries were near unity for low-volatility compounds such as ammonium sulfate and sucrose. Application to an ambient aerosol sample collected during a wildfire event demonstrated that LC-AMS can extract significantly richer chemical information from the complex aerosol mixtures than that bulk AMS analysis alone. The enhanced chemical resolution provided by LC-AMS can improve characterization of aerosol sources, atmospheric processing, and climate- and health-relevant properties.

1 Introduction

Atmospheric aerosol particles are complex mixtures of organic and inorganic components that are either directly emitted or formed through secondary atmospheric processes, with their composition continuing to evolve during aging. Organic aerosol (OA) is a major fraction of fine particulate matter ($\text{PM}_{2.5}$), often accounting for 50-90% of its mass (Jimenez et al., 2009; Zhang et al., 2007). OA is composed of thousands of compounds whose identities and abundances vary with emission source contributions and atmospheric processing (Goldstein and Galbally, 2007). Inorganic ions, including NO_3^- , SO_4^{2-} , Cl^- , NH_4^+ , Na^+ , and K^+ , also contribute substantially to $\text{PM}_{2.5}$ mass. Because aerosol composition reflects its emission



sources and atmospheric aging processes and strongly influences its impacts on radiative forcing, cloud processes, and human health (Bates et al., 2019; Laskin et al., 2015; Park et al., 2018), analytical methods that better resolve the chemical complexity of ambient aerosols are needed.

Liquid chromatography (LC) coupled with mass spectrometry (MS) is well suited to address this need because LC
35 separates complex mixtures before MS detection. Because LC separation is based on differences in analyte physicochemical properties, such as polarity, charge, and interactions with the stationary and mobile phases, it helps distinguish species that might otherwise appear convoluted in MS detection. Different LC techniques, including ion exchange, reversed-phase, and hydrophilic interaction chromatography (HILIC), may enable the separation of a wide range of compounds in atmospheric aqueous samples, including aerosol extracts, cloud and fog waters, and precipitation. These compounds range from inorganic
40 ions to diverse organic species with different functional groups, polarity, and hygroscopicity (Hettiyadura et al., 2015; Bros et al., 2025; Cui et al., 2018; Brent et al., 2014; Mazzoleni et al., 2010).

Ion chromatography (IC), a form of LC based on ion-exchange interactions, is widely used to analyze ionic species, which include both inorganic ions (e.g., Cl^- , NO_3^- , SO_4^{2-} , Br^- , NH_4^+ , Na^+ , and K^+) and organic acids and bases (Brent et al., 2014; Parworth et al., 2017). Anion IC has been frequently applied to quantify mono- and dicarboxylic acids (e.g., formate
45 and oxalate) in ambient and laboratory-generated aerosol. Many of these water-soluble species are products of atmospheric oxidation of volatile organic compounds (VOCs) (Yatavelli et al., 2015; Ervens et al., 2011; Charbouillot et al., 2012). Cation IC has also been used to quantify alkylamines (Ge et al., 2014; Parworth et al., 2017; Huang et al., 2014), which play important roles in aerosol formation and growth (Ge et al., 2011).

IC is typically coupled with a conductivity detector, which provides sensitive and near-universal response to
50 charged species but lacks chemical specificity. As a result, identification of unknown peaks generally requires comparison of retention times with authentic standards. Coupling IC with MS has been explored to improve chemical identification (Huang et al., 2014; Brent et al., 2014; Kwiezinski et al., 2021), most often using soft ionization techniques such as electrospray ionization (ESI). While ESI enables molecular-level information, quantitative analysis can be complicated by compound-dependent and highly variable ionization efficiencies.

In contrast, aerosol mass spectrometry (AMS) utilizes thermal vaporization followed by electron impact (EI)
55 ionization. This produces reproducible fragmentation patterns and enables quantitative analysis using relatively consistent ionization efficiencies for major aerosol components, including organics, nitrate, sulfate, chloride, and ammonium (Allan et al., 2003; Jimenez et al., 2016; Jimenez et al., 2003). Although ionization efficiencies for organics can vary with composition, this variability is generally much lower than that observed with soft ionization techniques (Nault et al., 2023; Jimenez et al., 2003). However, AMS is most commonly used for stand-alone measurements of bulk, ensemble-averaged
60 aerosol composition. In this mode, extensive EI fragmentation limits direct identification of individual compounds in complex mixtures (Canagaratna et al., 2007).

To address these limitations, we couple IC with a high-resolution aerosol mass spectrometer (IC-AMS) to enable more chemically resolved analysis of solvent-extractable aerosol components. IC distributes compounds across



65 chromatographic retention time according to properties such as charge, polarity, and ion-exchange affinity. As the IC
effluent is analyzed by the AMS, the AMS provides quantitative ion signals and mass spectral signatures through the
chromatographic run. This combined approach added chromatographic resolution to AMS analysis while reducing reliance
on compound-specific standards. In this study, the IC-AMS method was characterized using mixtures of inorganic and
organic compounds to assess recovery and quantification performance. The method was then applied to an ambient PM
70 sample impacted by aged biomass burning emissions. Although IC was utilized here to target ionic and highly polar species,
the broader LC-AMS framework can be extended to other LC modes (e.g., reversed-phase LC and HILIC) to broaden
chemical coverage based on analyte properties.

2. Experimental Methods

2.1 Chemicals

75 All standards were prepared using MilliQ water (resistivity of 18.2 MΩ cm). Ammonium nitrate (>98%),
ammonium sulfate (>99%), ³⁴S isotopically labeled ammonium sulfate (>98% ³⁴S), oxalic acid (> 99%), and glycolic acid
(>99%) were purchased from Sigma-Aldrich. Levoglucosan (1,6-Anhydro-β-D-glucose; > 99.0%) was purchased from TCI
Chemicals. Sucrose (ACS grade) was purchased from Fischer Scientific. Commercial Inorganic standards included Dionex
Seven Anion Standard II and Dionex Combined Six Cation Standard (Thermo Fisher Scientific).

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2.2 PM Sample Extraction and Preparation

The ambient filter sample presented here was collected on a Teflon filter at the Mt. Bachelor Observatory (MBO)
during the 2013 Biomass Burning Observation Project (Zhou et al., 2017). MBO is a remote, mountaintop site located in
central Oregon, USA, with minimal anthropogenic emissions. During the sampling period (8/9/2013–8/10/2013), aerosol
85 composition was dominated by aged biomass burning organic aerosols (BBOA), with additional influence from biogenic
SOA as described in Zhou et al. (2017) and Collier et al. (2016). Sampling was conducted at 14 L min⁻¹ resulting in 3.5μm
size cutoff. Filters were stored at -20°C prior to analysis. Based on the measurements of the collocated HR-AMS, the PM
extract is estimated to contain 23 mg/L of soluble organic matter.

The filter sample was extracted using a solution containing 25% methanol and 75% Milli-Q water. Isotopically
90 labeled ammonium sulfate (A³⁴S) was added to the extract at 500 ppb ³⁴SO₄ as an internal standard. The sample was
sonicated in an ice bath for 30 minutes, and the resulting extract was filtered through a 0.45μm PTFE syringe filter prior to
analysis.

2.3 Coupling Ion Chromatography with Aerosol Mass Spectrometry

An overview of the IC-AMS sampling setup is shown in Figure 1. Chromatographic separation was performed
95 using a Metrohm 881 Compact IC Pro system (Metrohm AG, Switzerland) equipped with a conductivity detector and a UV-



Vis diode array detector (Model 887). For anion analysis, a Metrosep A Supp 7 (250 × 4.0) column with a polyvinyl alcohol stationary phase functionalized with quaternary ammonium groups was used. The column was operated at 45°C with 5.0 mM Na₂CO₃ eluent at a flow rate of 0.8 mL min⁻¹. An anion suppressor module was employed to enhance the sensitivity of conductivity detection. For cation analysis, a Metrosep C4 (250 × 2.0) column containing carboxyl groups was used, with a column temperature of 30°C and 4.5 mM HNO₃ at 0.25 mL min⁻¹ as the eluent. Cation eluents are often modified using an organic compound, such as 1.7 mM dipicolinic acid (Ge et al., 2014), however this resulted in excessive AMS organic background signal; therefore, only HNO₃ was used.

Following chromatographic separation, the eluent was introduced into a micro nebulizer system similar to what is described in Niedek et al. (2023). The liquid eluent flow intersected a flow of high-purity N₂ (>99.99%) to generate aerosols. The aerosol stream passed through a heated glass cyclone to remove large droplets and prevent condensation. Both the carrier N₂ gas and the transfer lines were heated to 40 °C, and the flow was subsequently dried using a silica desiccant dryer prior to introduction into a high-resolution soot-particle aerosol mass spectrometer (SP-AMS; Aerodyne Inc).

The SP-AMS operation principles have been described in detail elsewhere (Onasch et al., 2012). Briefly, particles are focused using an aerodynamic lens with a size cutoff of 1 μm vacuum aerodynamic diameter and vaporized using a tungsten thermal vaporizer resistively heated to 600°C. This results in the flash vaporization of non-refractory (NR) PM, including nitrate, sulfate, chloride, ammonium and most organic species. The SP-AMS also includes a 1064 nm intracavity laser vaporizer to vaporize particles containing refractory black carbon (rBC). The SP-AMS was operated in dual-vaporizer mode with both the thermal vaporizer and laser vaporizer operating simultaneously (Avery et al., 2020). Vaporized species are ionized by 70 eV electron impact and detected using a high-resolution time-of-flight mass spectrometer operated in V-mode ($m/\Delta m \sim 2500$ at m/z 28) over m/z 12–480 amu. In this study, the SP-AMS was operated in “fast mode” with a time resolution of 1 Hz.

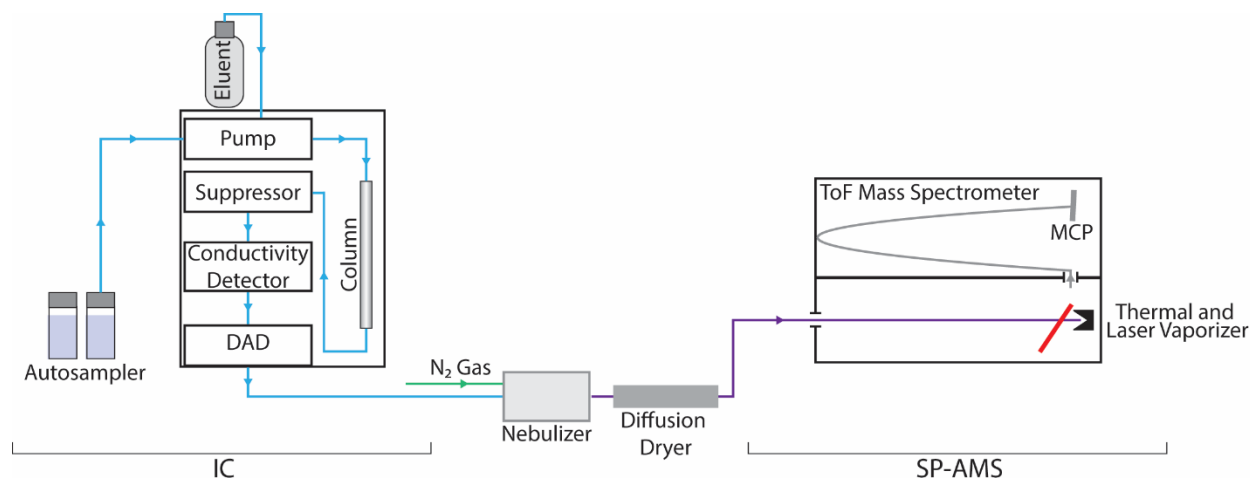


Figure 1: Schematic of IC-AMS setup. Blue lines indicate liquid flow, green lines indicate gas flow, and purple lines indicate aerosol flow. DAD stands for diode array detector.



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2.4. Data Analysis

Chromatograms from the conductivity detector and Diode array detector (DAD) within the IC system were exported directly from the MagIC Net software. AMS chromatograms were created by isolating the run period and converting the recorded AMS timestamps to retention time based on the IC injection time. An approximately 10 second lag between the IC and AMS signals, due to dead volume between the two instruments, was corrected by aligning the peaks of the A³⁴S internal standard. The SP-AMS was operated at 1 Hz, while the conductivity and DAD acquired data at 10 Hz and 3 Hz, respectively. However, as the chromatographic peaks typically spanned 20 - 60 seconds, these acquisition rates were sufficient for peak characterization.

SP-AMS data were analyzed using the Squirrel (1.65B) and PIKA (1.25B) toolkits in Igor Pro 8 (Wavemetrics Inc). Due to potential background signal drift over the duration of each chromatographic run, we utilize spectra from the chopper-open mode. A background correction was then applied to remove contributions from both the instrument background and IC eluent. Specifically, the average intensity of each ion during the first minute after IC injection was calculated and subtracted from the corresponding ion time series. Additional details of this correction are provided in SI Section S1.

For quantification, default relative ionization efficiency (RIE) values were applied for nitrate (1.05), chloride (1.3), sulfate (1.2), ammonium (4.0), and rBC (0.2). For sucrose, an RIE of 2.50 was determined based on analysis of sucrose and ammonium sulfate mixtures of known composition. As the amount of aerosol generated and transmitted to the SP-AMS is dependent on the nebulizer conditions, individual ion chromatograms are reported as ion count rates in units of Hz.

To determine the liquid-phase concentration of analytes measured by IC-AMS, peak areas were first calculated from the background-corrected AMS chromatograms for the analyte of interest (*X*), and for ³⁴SO₄ internal standard. The liquid concentration of *X* was then calculated using the following relationship:

$$[X]_{Liquid} = \frac{A_x}{A_{^{34}SO_4}} [^{34}SO_4]_{Liquid} \quad (1)$$

Where $[X]_{Liquid}$ is the calculated concentration of species *X* in the liquid sample in ppb, A_x and $A_{^{34}SO_4}$ are the peak areas of species *X* and ³⁴SO₄, respectively, from the AMS chromatograms, and $[^{34}SO_4]_{liquid}$ is the known liquid-phase concentration of the ³⁴SO₄ internal standard. Peak areas are reported in units of μg s m⁻³, and liquid concentrations are reported in ppb. Details of the quantification of the A³⁴S internal standard are provided in SI Section S2.

3. Results and Discussion

3.1 Analysis of Inorganic and Organic Standards Using IC-AMS

A commercial 7-anion standard solution containing NaF (0.2 ppm), NaCl (1 ppm), NaNO₂ (1 ppm), NaBr (1ppm), NaNO₃ (1 ppm), K₃PO₄ (2 ppm) and Na₂SO₄ (1 ppm) was analyzed to characterize the IC-AMS system's response to inorganic species, with the chromatograms shown in Figure 1a and 1b. Chloride, bromide, nitrate and sulfate showed well defined chromatographic peaks in the AMS, with peak width similar to those measured by the conductivity detector,



indicating minimal band broadening after going through the aerosolization interface between IC and AMS. Additionally, the ratio of major ion fragments for each species matches what is expected for the pure species (Figure S2). In contrast, no AMS signal was detected for fluoride, nitrite, or phosphate, indicating that these compounds are either volatilized during nebulization or are not vaporized or ionized under AMS conditions.

A cation standard containing LiCl (0.1 ppm), NaCl (0.4 ppm), NH₄Cl (0.4 ppm), KCl (0.4 ppm), CaCl₂ (0.8 ppm), and MgCl₂ (2 ppm) was also analyzed. As expected, Ca and Mg were not detected by the AMS due to their refractory nature. Additionally, Li was also not detected as the AMS was set to only detect ions with $m/z \geq 12$ amu. Both Na and K were detected but showed significant peak tailing, suggesting slow volatilization of the material on the thermal vaporizer or adhesion to the ionizer (Drewnick et al., 2015). Quantification of these species through AMS detection is further complicated by uncertainties in their RIEs, as surface ionization may occur on the tungsten vaporizer (Drewnick et al., 2015). Nevertheless, AMS measurements are still useful as they could provide unambiguous detection of other compounds that co-elute with these inorganic cations. Ammonium showed a peak at a retention time (r.t.) of 11 minutes, consistent with the retention time of NH₄⁺ measured by the conductivity detector, and displayed fragmentation consistent with ammonium (Figure S3) suggesting that the separation of ammonium and amine containing compounds is possible using this method.

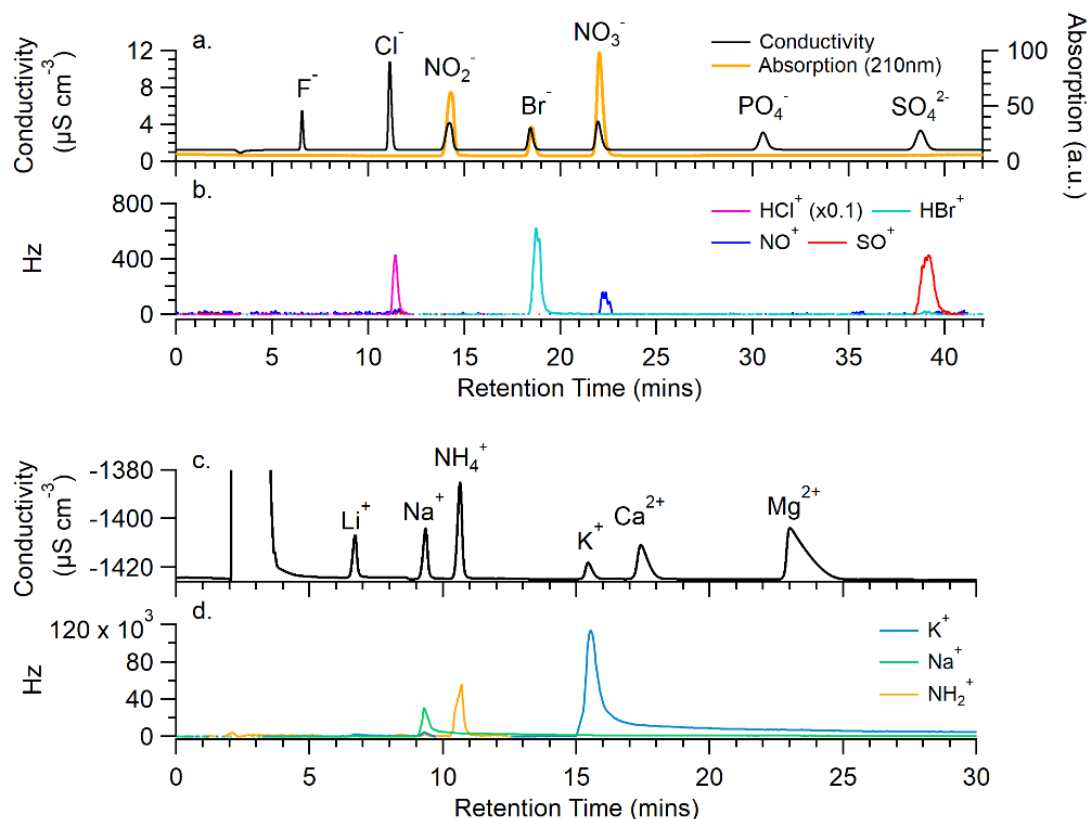




Figure 2: Chromatograms of inorganic anion and cation standard mixtures measured using the IC-AMS system. (a) Conductivity chromatogram and 210 nm absorbance signal for the anion mixture. (b) Corresponding AMS ion chromatograms for selected characteristic fragment ions. (c) Conductivity chromatogram for the cation mixture. (d) Corresponding AMS ion chromatograms for selected cation-related ions.

To evaluate species recovery and potential losses within the IC system and during nebulization, solutions with known concentrations of ammonium sulfate, ammonium nitrate, and sucrose were analyzed (Figure 3). Sucrose was chosen as a model organic compound due to its low volatility and known response within the AMS (Canagaratna et al., 2015; Kiland et al., 2019). All three compounds show strong linear relationships ($r^2 \geq 0.98$) between AMS-derived concentrations and the known concentration in the solution. Sulfate and sucrose, both of which are essentially non-volatile compounds, show slopes near unity, indicating minimal loss of material prior to reaching the AMS. In contrast, the calculated nitrate concentration was approximately 41% lower than expected, likely due to volatilization of this species during the nebulization and drying processes. This result implies that although the measurement of semi-volatile material may be biased low, this could be corrected by applying a constant correction factor. Future work will focus on precise temperature control of the micro-nebulization system to better quantify and correct for evaporative loss of semi-volatile components.

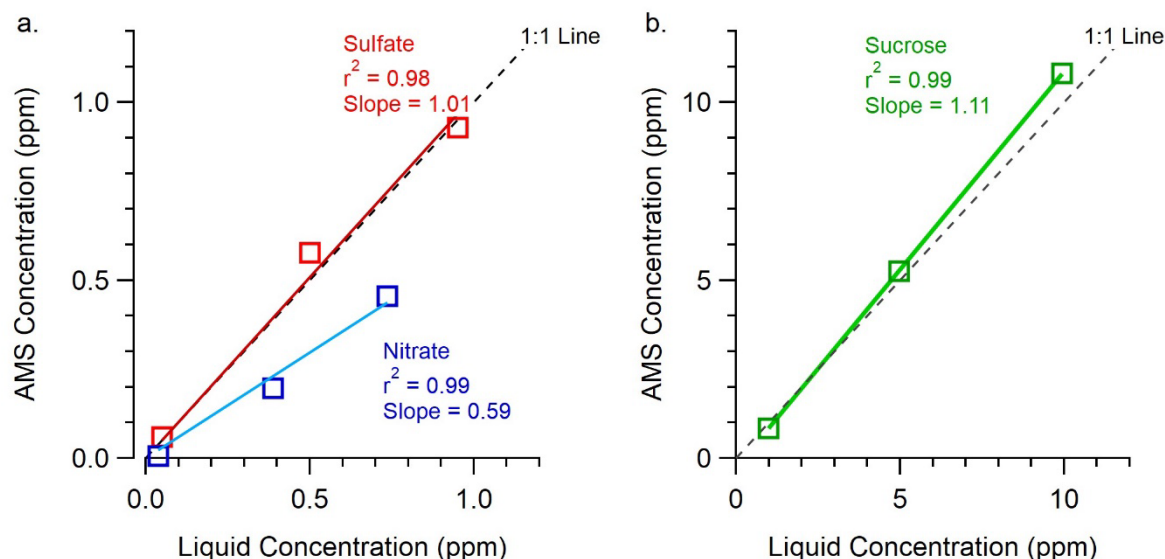


Figure 3: Comparison of AMS-derived liquid concentrations with prepared liquid concentrations for standard solutions. (a) Sulfate from ammonium sulfate and nitrate for ammonium nitrate, and (b) sucrose. Solid lines show linear regressions, and dashed lines indicate 1:1 agreement. Regression slopes and r^2 values are shown for each analyte.

Three atmospherically relevant organic compounds with spanning a range of polarities and functional groups were also analyzed, and the chromatograms of selected major AMS fragment ions are shown in Figure 4. Levoglucosan ($C_6H_{10}O_5$)



is a widely used tracer for biomass burning aerosol (Alfarra et al., 2007; Schauer et al., 2001), while glycolic acid ($C_2H_4O_3$) and oxalic acid ($C_2H_2O_4$) are products of secondary atmospheric processing, particularly through aqueous-phase reactions (McNeill, 2015; Sorooshian et al., 2006; Warneck, 2005). These compounds differ in chemical functionality: levoglucosan is highly oxygenated ($O/C = 0.83$) but lacks carboxylic acid functional groups, while glycolic acid and oxalic acid are representative of mono- and di-carboxylic acids, respectively. The AMS fragment ions shown in Figure 4 were chosen as they are expected to be major fragments through comparison with NIST standard spectra (Figure S4) (Linstrom, 2023)..

Levoglucosan eluted at 3.2 minutes, concurrent with the IC “water-dip”, indicating minimal retention on the anion-exchange column and consistent with its neutral character under the separation conditions (Figure 4a). In contrast, glycolic acid and oxalic acid eluted at 5.9 and 25 minutes, respectively, reflecting stronger interactions with the stationary phase due to their carboxylic acid functionality and greater anionic character under the eluent conditions (Figure 4b, c). The glycolic acid chromatogram shows clear increases in CHO^+ and CH_3O^+ concurrent with the conductivity peak. However, the AMS signal is relatively low, likely due to partial losses during nebulization associated with the semi-volatile nature of this compound. The CHO^+ signal is also relatively noisy because of overlap with the $^{15}N^{14}N^+$ ion. Oxalic acid shows distinct increases in CO_2^+ , CHO_2^+ and $CH_2O_2^+$ that are coincident with the conductivity peak, demonstrating that the AMS detects characteristic fragment ions for the separated organic acid.

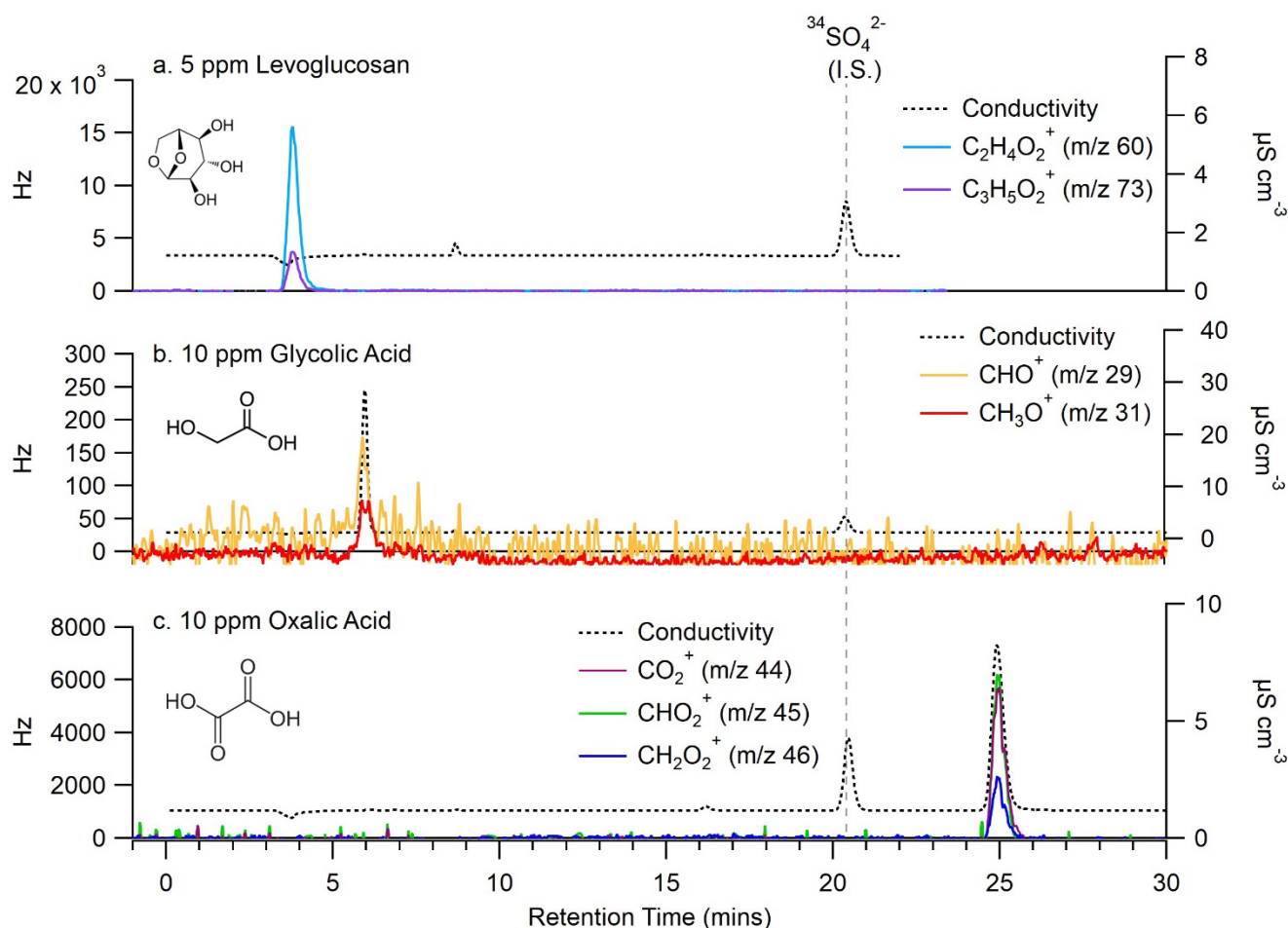


Figure 4: IC-AMS chromatograms for single-component organic standards dissolved in Milli-Q water: (a) 5 ppm Levoglucosan, (b) 10 ppm Glycolic acid, and (c) 10 ppm Oxalic acid. Colored traces show selected AMS fragment ion chromatograms characteristic of each compound, while black dashed traces show the corresponding IC conductivity signal. The gray dashed vertical line indicates the retention time of the $^{34}\text{SO}_4^{2-}$ internal standard (I.S.). Conductivity is shown on the right axis, and AMS ion signals are reported as ion count rates in Hz.

3.2 IC-AMS Analysis of Wildfire-Influenced Ambient PM

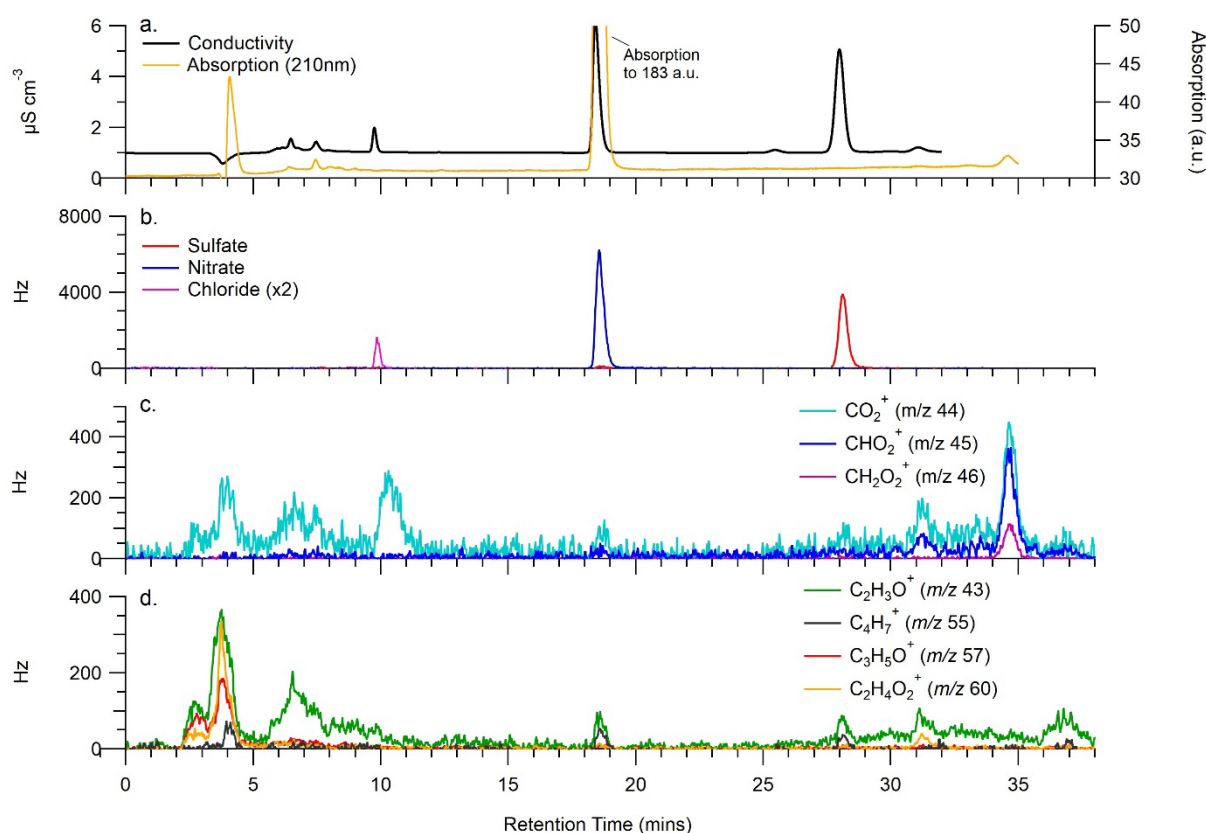
Figure 5 shows the chromatograms from an extract of a filter sample collected at the Mt. Bachelor Observatory during the Biomass Burning Observation Project (BBOP) in summer 2013. Concurrent online HR-AMS measurements indicate that this sample was dominated by aged wildfire emissions with an elevated oxygen-to-carbon (O/C) ratio (Zhou et al., 2017). The largest conductivity peaks correspond to inorganic nitrate, sulfate, and to a lesser extent, chloride (Figure 5a, b).



Using equation 1, the concentrations of chloride, nitrate and sulfate in the sample extract determined by IC-AMS were compared to those measured using the IC conductivity detection. The chloride concentrations agreed well between the two methods, with values of 76 ppb from IC-conductivity and 77 ppb from IC-AMS. In contrast, concentrations of sulfate and nitrate measured by IC-conductivity were substantially lower than determined by IC-AMS. Sulfate was measured at 543 ppb by IC-conductivity compared with 667 ppb by IC-AMS, while nitrate concentrations were 355 ppb and 1126 ppb, respectively. After accounting for evaporative losses in the IC-AMS system, the IC-AMS nitrate concentration increased further to 1588 ppb. It is possible that this discrepancy can be partially explained by co-elution of organonitrates, which have been found to be abundant in aged biomass burning emissions and have been observed at MBO (Farley et al., 2025)

However, there are also other increases in conductivity throughout the IC run (i.e. at 6.4, 7.5, and 31.1 minutes) suggesting the presence of other ionic species, likely including organic ions. Distinct absorbance peaks were also observed at 4.0 and 34.4 minutes, indicating the presence of UV-absorbing organic matter. Although the present study measured absorbance at 210 nm to leverage higher absorption cross sections in the UV range, these signals suggest the presence of chromophores; extending optical detection to longer, atmospherically relevant wavelengths would enable more direct characterization of brown carbon (BrC).

Chromatograms of selected AMS organic fragments further demonstrate the utility of LC-AMS for separating chemically distinct compounds that produce overlapping fragment ions in bulk AMS spectra (Figure 6c-d). A substantial fraction of the organic signal elutes between 2 and 5 minutes, indicating weak retention on the IC column. This early-eluting material consists of a complex mixture of non-oxygenated and mono-oxygenated fragments, including $C_2H_4O_2^+$, which is associated with anhydrous sugars such as levoglucosan, and $C_4H_7^+$, a reduced hydrocarbon fragment, consistent with biomass burning influence. Following this initial mixture, a broad feature enriched in $C_2H_3O^+$ and CO_2^+ is observed between 5 and 9 minutes, indicating the elution of more oxidized compounds such as carbonyls, esters, and carboxylic acids. Although CO_2^+ is observed in multiple regions of the chromatogram, CHO_2^+ is strongly enhanced only at 31 and 34.4 minutes. In addition, $CH_2O_2^+$, a prominent fragment in the AMS spectrum of oxalic acid, also peaks at 34.4 min (Farley et al., 2023). Together with the coincident UV absorbance signal, these spectral patterns support the assignment of the 34.4 min peak to oxalic acid, which has been identified in BB emissions previously (Gao et al., 2003; Pratt et al., 2011).



245 Figure 5: IC-AMS chromatograms of an ambient filter extract collected during BBOP and impacted by aged wildfire smoke. (a) IC conductivity and 210 nm absorbance chromatograms. (b) AMS ion chromatograms for major inorganic species. (c-d) Selected AMS organic fragment ion chromatograms, highlighting chemically distinct features resolved by the chromatographic separation. AMS signals are reported as ion count rates in Hz, while conductivity and absorbance are shown in $\mu\text{S cm}^{-3}$ and arbitrary units, respectively.

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Conclusions and Outlook

We have developed a novel analytical method that couples liquid chromatography with aerosol mass spectrometry (LC-AMS). The method improves the chemical characterization of aqueous environmental samples, including aerosol extracts, cloud and fog waters, and precipitation samples. The LC separates dissolved constituents based on their chromatographic retention behavior, which reflects physiochemical properties such as charge and polarity, while the AMS provides quantitative detection and reproducible mass spectral fingerprints. The integrated LC-AMS approach therefore provides significantly greater chemical information than either technique alone.

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Although extensive fragmentation during vaporization and 70 eV electron impact ionization in the AMS limits direct identification of parent compounds, the resulting fragmentation patterns are highly reproducible, allowing for robust comparisons with laboratory standards, reference spectra, and archived AMS field data. In addition, the AMS ionization efficiencies are relatively uniform and are routinely calibrated, which support semi-quantitative analysis of diverse organic compounds or compound classes with reduced reliance on authentic standards. This capability is particularly valuable for complex environmental samples, where many constituents are unknown or not commercially available.

In this study, ion chromatography was used to target water-soluble ionic and polar species. However, the LC-AMS approach can be extended to other chromatographic modes. For example, reversed-phase LC could expand chemical coverage to less polar compounds, while hydrophilic interaction liquid chromatography is well suited for the separation of highly polar or hydrophilic species. In addition, extending absorbance measurements to atmospherically relevant wavelengths would enable better characterization of BrC chromophores and facilitate the identification of AMS-based markers for BrC.

One limitation of the current LC-AMS method is the potential loss of semi-volatile species, such as ammonium nitrate and small organic acids, during aerosol generation and drying. When compound identity and volatility are known, such losses can be quantified and corrected through calibration. However, for unknown constituents in complex mixtures, the LC-AMS-derived concentrations may underestimate true concentrations.

Overall, LC-AMS provides a flexible analytical platform that complements both bulk aerosol mass spectrometry and highly speciated LC-MS methods based on soft ionization, such as electrospray ionization. Its enhanced chemical resolution improves the characterization of aerosol sources, atmospheric processing, and climate- and health-relevant properties of complex aerosol mixtures.

Code, data, or code and data availability

All data sets including HR-AMS mass spectral data and IC chromatograms are available upon request from Qi Zhang, dkwzhang@ucdavis.edu.

Supplement link

The document provides additional information on IC-AMS data processing, quantification, and method validation.

Author contributions

QZ and RNF designed the experiments. RNF and CRN carried them out. RNF performed data analysis. RNF and QZ prepared the manuscript with contributions from all co-authors.



Competing interests

The authors declare that they have no conflict of interest.

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References

295

Alfarra, M. R., Prevot, A., Szidat, S., Sandradewi, J., Weimer, S., Lanz, V. A., Schreiber, D., Mohr, M., and Baltensperger, U.: Identification of the Mass Spectral Signature of Organic Aerosols from Wood Burning Emissions, *Environ Sci Technol*, 41, 5770-5777, <https://doi.org/10.1021/es062289b>, 2007.

300

Allan, J. D., Jimenez, J. L., Williams, P. I., Alfarra, M. R., Bower, K. N., Jayne, J. T., Coe, H., and Worsnop, D. R.: Quantitative sampling using an Aerodyne aerosol mass spectrometer 1. Techniques of data interpretation and error analysis, *Journal of Geophysical Research: Atmospheres*, 108, 10.1029/2002jd002358, 2003.

Avery, A. M., Williams, L. R., Fortner, E. C., Robinson, W. A., and Onasch, T. B.: Particle detection using the dual-vaporizer configuration of the soot particle Aerosol Mass Spectrometer (SP-AMS), *Aerosol Science and Technology*, 55, 254-267, 10.1080/02786826.2020.1844132, 2020.

305

Bates, J. T., Fang, T., Verma, V., Zeng, L., Weber, R. J., Tolbert, P. E., Abrams, J. Y., Sarnat, S. E., Klein, M., Mulholland, J. A., and Russell, A. G.: Review of Acellular Assays of Ambient Particulate Matter Oxidative Potential: Methods and Relationships with Composition, Sources, and Health Effects, *Environ Sci Technol*, 53, 4003-4019, 10.1021/acs.est.8b03430, 2019.

310

Brent, L. C., Reiner, J. L., Dickerson, R. R., and Sander, L. C.: Method for characterization of low molecular weight organic acids in atmospheric aerosols using ion chromatography mass spectrometry, *Anal Chem*, 86, 7328-7336, 10.1021/ac403937e, 2014.

315

Bros, P., Darfeuil, S., Jacob, V., Elazzouzi, R., Tusha, D., Rousseau, T., Weng, J., Winiger, P., El Haddad, I., Hueglin, C., Uzu, G., and Jaffrezou, J.-L.: Quantification of 21 sugars in tropospheric particulate matter by ultra-high-performance liquid chromatography tandem mass spectrometry, *Atmospheric Measurement Techniques*, 18, 6315-6327, 10.5194/amt-18-6315-2025, 2025.

Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E., Davidovits, P., and Worsnop, D. R.: Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer, *Mass Spectrom Rev*, 26, 185-222, 10.1002/mas.20115, 2007.



- 320 Charbouillot, T., Gorini, S., Voyard, G., Parazols, M., Brigante, M., Deguillaume, L., Delort, A.-M., and Mailhot, G.: Mechanism of carboxylic acid photooxidation in atmospheric aqueous phase: Formation, fate and reactivity, *Atmospheric Environment*, 56, 1-8, 10.1016/j.atmosenv.2012.03.079, 2012.
- Collier, S., Zhou, S., Onasch, T. B., Jaffe, D. A., Kleinman, L., Sedlacek, A. J., 3rd, Briggs, N. L., Hee, J., Fortner, E., Shilling, J. E., Worsnop, D., Yokelson, R. J., Parworth, C., Ge, X., Xu, J., Butterfield, Z., Chand, D., Dubey, M. K., Pekour, M. S.,
325 Springston, S., and Zhang, Q.: Regional Influence of Aerosol Emissions from Wildfires Driven by Combustion Efficiency: Insights from the BBOP Campaign, *Environ Sci Technol*, 50, 8613-8622, 10.1021/acs.est.6b01617, 2016.
- Cui, T., Zeng, Z., Dos Santos, E. O., Zhang, Z., Chen, Y., Zhang, Y., Rose, C. A., Budisulistiorini, S. H., Collins, L. B., Bodnar, W. M., de Souza, R. A. F., Martin, S. T., Machado, C. M. D., Turpin, B. J., Gold, A., Ault, A. P., and Surratt, J. D.:
330 Development of a hydrophilic interaction liquid chromatography (HILIC) method for the chemical characterization of water-soluble isoprene epoxydiol (IEPOX)-derived secondary organic aerosol, *Environ Sci Process Impacts*, 20, 1524-1536, 10.1039/c8em00308d, 2018.
- Drewnick, F., Diesch, J. M., Faber, P., and Borrmann, S.: Aerosol mass spectrometry: particle–vaporizer interactions and their consequences for the measurements, *Atmospheric Measurement Techniques*, 8, 3811-3830, 10.5194/amt-8-3811-2015, 2015.
- Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, *Atmospheric Chemistry and Physics*, 11, 11069-11102, 10.5194/acp-11-11069-2011, 2011.
335
- Farley, R., Zhou, S., Collier, S., Jiang, W., Onasch, T. B., Shilling, J. E., Kleinman, L., Sedlacek Iii, A. J., and Zhang, Q.: Chemical Evolution of Biomass Burning Aerosols across Wildfire Plumes in the Western U.S.: From Near-Source to Regional Scales, *ACS EST Air*, 2, 677-691, 10.1021/acsestair.5c00002, 2025.
- 340 Farley, R. N., Collier, S., Cappa, C. D., Williams, L. R., Onasch, T. B., Russell, L. M., Kim, H., and Zhang, Q.: Source apportionment of soot particles and aqueous-phase processing of black carbon coatings in an urban environment, *Atmospheric Chemistry and Physics*, 23, 15039-15056, 10.5194/acp-23-15039-2023, 2023.
- Gao, S., Hegg, D. A., Hobbs, P. V., Kirchstetter, T. W., Magi, B. I., and Sadilek, M.: Water-soluble organic components in aerosols associated with savanna fires in southern Africa: Identification, evolution, and distribution, *Journal of Geophysical Research: Atmospheres*, 108, 10.1029/2002jd002324, 2003.
345
- Ge, X., Shaw, S. L., and Zhang, Q.: Toward understanding amines and their degradation products from postcombustion CO₂ capture processes with aerosol mass spectrometry, *Environ Sci Technol*, 48, 5066-5075, 10.1021/es4056966, 2014.
- Ge, X., Wexler, A. S., and Clegg, S. L.: Atmospheric amines – Part I. A review, *Atmospheric Environment*, 45, 524-546, <https://doi.org/10.1016/j.atmosenv.2010.10.012>, 2011.
- 350 Goldstein, A. H. and Galbally, I.: Known and Unexplored Organic Constituents in the Earth’s Atmosphere, *Environmental Science & Technology*, 41, 1514–1521, 2007.
- Hettiyadura, A. P. S., Stone, E. A., Kundu, S., Baker, Z., Geddes, E., Richards, K., and Humphry, T.: Determination of atmospheric organosulfates using HILIC chromatography with MS detection, *Atmospheric Measurement Techniques*, 8, 2347-2358, 10.5194/amt-8-2347-2015, 2015.
- 355 Huang, R. J., Li, W. B., Wang, Y. R., Wang, Q. Y., Jia, W. T., Ho, K. F., Cao, J. J., Wang, G. H., Chen, X., Ei Haddad, I., Zhuang, Z. X., Wang, X. R., Prévôt, A. S. H., O’Dowd, C. D., and Hoffmann, T.: Determination of alkylamines in atmospheric aerosol particles: a comparison of gas chromatography–mass spectrometry and ion chromatography approaches, *Atmospheric Measurement Techniques*, 7, 2027-2035, 10.5194/amt-7-2027-2014, 2014.
- Jimenez, J. L., Canagaratna, M. R., Drewnick, F., Allan, J. D., Alfarra, M. R., Middlebrook, A. M., Slowik, J. G., Zhang, Q.,
360 Coe, H., Jayne, J. T., and Worsnop, D. R.: Comment on “The effects of molecular weight and thermal decomposition on the sensitivity of a thermal desorption aerosol mass spectrometer”, *Aerosol Science and Technology*, 50, i-xv, 10.1080/02786826.2016.1205728, 2016.



- Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang, X., Smith, K. A., Morris, J. W., and Davidovits, P.: Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer, *Journal of Geophysical Research: Atmospheres*, 108, 10.1029/2001jd001213, 2003.
- Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., E, Dunlea, J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of Organic Aerosols in the Atmosphere, *Science*, 326, 1525-1529, 10.1126/science.1180353, 2009.
- Kwiedzinski, C., Weller, C., van Pinxteren, D., Brüggemann, M., Mertes, S., Stratmann, F., and Herrmann, H.: Determination of highly polar compounds in atmospheric aerosol particles at ultra-trace levels using ion chromatography Orbitrap mass spectrometry, *Journal of Separation Science*, 44, 2343-2357, <https://doi.org/10.1002/jssc.202001048>, 2021.
- Laskin, A., Laskin, J., and Nizkorodov, S. A.: Chemistry of atmospheric brown carbon, *Chem Rev*, 115, 4335-4382, 10.1021/cr5006167, 2015.
- Linstrom, P. J. M., W. G.: NIST/EPA/NIH Mass Spectral Library, 2023.
- Mazzoleni, L. R., Ehrmann, B. M., Shen, X., Marshall, A. G., and Collett, J. L., Jr.: Water-Soluble Atmospheric Organic Matter in Fog: Exact Masses and Chemical Formula Identification by Ultrahigh-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, *Environmental Science & Technology*, 44, 3690-3697, 10.1021/es903409k, 2010.
- McNeill, V. F.: Aqueous organic chemistry in the atmosphere: sources and chemical processing of organic aerosols, *Environ Sci Technol*, 49, 1237-1244, 10.1021/es5043707, 2015.
- Nault, B. A., Croteau, P., Jayne, J., Williams, A., Williams, L., Worsnop, D., Katz, E. F., DeCarlo, P. F., and Canagaratna, M.: Laboratory evaluation of organic aerosol relative ionization efficiencies in the aerodyne aerosol mass spectrometer and aerosol chemical speciation monitor, *Aerosol Science and Technology*, 57, 981-997, 10.1080/02786826.2023.2223249, 2023.
- Niedek, C. R., Mei, F., Zawadowicz, M. A., Zhu, Z., Schmid, B., and Zhang, Q.: Quantitative chemical assay of nanogram-level particulate matter using aerosol mass spectrometry: characterization of particles collected from uncrewed atmospheric measurement platforms, *Atmospheric Measurement Techniques*, 16, 955-968, 10.5194/amt-16-955-2023, 2023.
- Onasch, T. B., Trimborn, A., Fortner, E. C., Jayne, J. T., Kok, G. L., Williams, L. R., Davidovits, P., and Worsnop, D. R.: Soot Particle Aerosol Mass Spectrometer: Development, Validation, and Initial Application, *Aerosol Science and Technology*, 46, 804-817, 10.1080/02786826.2012.663948, 2012.
- Park, M., Joo, H. S., Lee, K., Jang, M., Kim, S. D., Kim, I., Borlaza, L. J. S., Lim, H., Shin, H., Chung, K. H., Choi, Y. H., Park, S. G., Bae, M. S., Lee, J., Song, H., and Park, K.: Differential toxicities of fine particulate matters from various sources, *Sci Rep*, 8, 17007, 10.1038/s41598-018-35398-0, 2018.
- Parworth, C. L., Young, D. E., Kim, H., Zhang, X., Cappa, C. D., Collier, S., and Zhang, Q.: Wintertime water-soluble aerosol composition and particle water content in Fresno, California, *Journal of Geophysical Research: Atmospheres*, 122, 3155-3170, 10.1002/2016jd026173, 2017.
- Pratt, K. A., Murphy, S. M., Subramanian, R., DeMott, P. J., Kok, G. L., Campos, T., Rogers, D. C., Prenni, A. J., Heymsfield, A. J., Seinfeld, J. H., and Prather, K. A.: Flight-based chemical characterization of biomass burning aerosols within two prescribed burn smoke plumes, *Atmospheric Chemistry and Physics*, 11, 12549-12565, 10.5194/acp-11-12549-2011, 2011.
- Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of Emissions from Air Pollution Sources. 3. C1-C29 Organic Compounds from Fireplace Combustion of Wood, *Environmental Science & Technology*, 35, 1716-1728, <https://doi.org/10.1021/es001331e>, 2001.



- 410 Sorooshian, A., Varutbangkul, V., Brechtel, F. J., Ervens, B., Feingold, G., Bahreini, R., Murphy, S. M., Holloway, J. S., Atlas, E. L., Buzorius, G., Jonsson, H., Flagan, R. C., and Seinfeld, J. H.: Oxalic acid in clear and cloudy atmospheres: Analysis of data from International Consortium for Atmospheric Research on Transport and Transformation 2004, *Journal of Geophysical Research: Atmospheres*, 111, 10.1029/2005jd006880, 2006.
- Warneck, P.: Multi-Phase Chemistry of C2 and C3 Organic Compounds in the Marine Atmosphere, *Journal of Atmospheric Chemistry*, 51, 119-159, 10.1007/s10874-005-5984-7, 2005.
- 415 Yatarelli, R. L. N., Mohr, C., Stark, H., Day, D. A., Thompson, S. L., Lopez-Hilfiker, F. D., Campuzano-Jost, P., Palm, B. B., Vogel, A. L., Hoffmann, T., Heikkinen, L., Äijälä, M., Ng, N. L., Kimmel, J. R., Canagaratna, M. R., Ehn, M., Junninen, H., Cubison, M. J., Petäjä, T., Kulmala, M., Jayne, J. T., Worsnop, D. R., and Jimenez, J. L.: Estimating the contribution of organic acids to northern hemispheric continental organic aerosol, *Geophysical Research Letters*, 42, 6084-6090, 10.1002/2015gl064650, 2015.
- 420 Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimojo, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, *Geophysical Research Letters*, 34, 10.1029/2007gl029979, 2007.
- 425 Zhou, S., Collier, S., Jaffe, D. A., Briggs, N. L., Hee, J., Sedlacek Iii, A. J., Kleinman, L., Onasch, T. B., and Zhang, Q.: Regional influence of wildfires on aerosol chemistry in the western US and insights into atmospheric aging of biomass burning organic aerosol, *Atmospheric Chemistry and Physics*, 17, 2477-2493, 10.5194/acp-17-2477-2017, 2017.