Quantitation of eleven alkyl amines in atmospheric samples: Separating structural isomers by ion chromatography

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Abstract: Amines are important drivers in particle formation and growth, which has implications for Earth's climate. In this work, we developed an ion chromatographic (IC) method using sample cation-exchange preconcentration for separating and quantifying the nine most abundant atmospheric alkyl amines (monomethylamine ($MMAH^+$), dimethylamine ($DMAH^+$), trimethylamine ($TMAH^+$), monoethylamine ($MEAH^+$), diethylamine ($DEAH^+$), triethylamine ($TEAH^+$), monopropylamine ($MPAH^+$), isomonopropylamine ($iMPAH^+$), and monobutylamine ($MBAH^+$)) and two alkyl diamines 1, 4-diaminobutane ($DABH^+$) and 1, 5-diaminopentane ($DAPH^+$). Further, the developed method separates the suite of amines from five common atmospheric inorganic cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}). All 16 cations are greater than 95% baseline resolved and elute in a runtime of 35 minutes. This paper describes the first successful separation of $DEAH^+$ and $TMAH^+$ by IC and achieves separation between three structural isomer pairs, providing specificity not possible by mass spectrometry. The method detection limits for the alkyl amines are in the picogram per injection range and the method precision (± 1 σ) analyzed over 3 months was within 16 % for all the cations. The performance of the IC method for atmospheric application was tested with biomass-burning (BB) particle extracts collected from two forest fire plumes in Canada. In extracts of size-resolved BB samples from an aged plume we detected and quantified $MMAH^+$, $DMAH^+$, $TMAH^+$, $MEAH^+$, $DEAH^+$ and $TEAH^+$ in the presence of Na^+, NH_4^+, and K^+ at amines to inorganic cations molar ratios ranging from 1:2 to 1:1000. Quantities of $DEAH^+$ and $DMAH^+$ of 0.2 – 200 ng m^{-3} and 3 – 1200 ng m^{-3}, respectively, were present in the extracts and an unprecedented amines to ammonium molar ratio greater than one was observed in particles with diameters spanning 56 – 180 nm. Extracts of respirable fine mode particles ($PM_{2.5}$) from a summer forest fire in British Columbia in 2015 were found to contain $iMPAH^+$, $TMAH^+$, $DEAH^+$ and $TEAH^+$ at molar ratios of 1:300 with the dominant cations. The amines to ammonium ratio in a time-series of samples never exceeded 0.15 during the sampling of the plume. These results and an amines standard addition demonstrate the robustness and sensitivity of the developed method when applied to the complex matrix of biomass burning particle samples. The detection of multiple alkyl amines in the analyzed BB samples indicates that this speciation and quantitation approach can be used to constrain BB emission inventories and the biogeochemical cycling of these reduced nitrogen species.

1 Introduction

Particles in the atmosphere can modulate climate through their direct and indirect effect on the radiative balance of Earth's atmosphere (Boucher et al., 2013; Lohmann and Feichter, 2005). This potential warming or cooling effect of particles represents the greatest uncertainty in Earth's radiative forcing (Myhre et al., 2013). Additionally, particles with a diameter of 2.5 μm or less ($PM_{2.5}$) have been classified as carcinogens (IARC, 2016), and are estimated to be responsible for 3 million deaths annually worldwide (Stephen et al., 2012). Thus understanding the quantities, and the chemical and physical nature of the species involved in the formation and growth of new particles is of paramount importance.

Recent work has shown that organic compounds may contribute considerably to particle nucleation (Ehn et al., 2014; Ortega et al., 2016; Tröstl et al., 2016; Willis et al., 2016). In particular, the need to measure and quantify gaseous atmospheric alkyl amines has gained interest because of their exceptional ability to partake in atmospheric particle formation. Multiple laboratory investigations have shown the nucleation potential of methyl- and ethyl-substituted amines through gaseous acid-base chemistry reactions (Almeida et al., 2013; Angelino et al., 2001; Berndt et al., 2010; Berndt et al., 2014; Bzdek et al., 2010; Bzdek et al., 2011; Erupe et al., 2011; Jen et al., 2016a; Jen et al., 2016b; Lloyd et al., 2009; Murphy et al., 2007; Qiu et al., 2011; Silva et al., 2008; Smith et al., 2010; Wang et al., 2010a; Wang et al., 2010b; Yu et al., 2012; Zhao et al., 2011; Zollner et al., 2012). Theoretical calculations and studies have also found that amines have a high disposition to form atmospheric nanoparticles (Barsanti et al., 2009; Kurtén et al., 2008; Loukonen et al., 2014; Loukonen et al., 2010; Nadykto et al., 2015; Ortega et al., 2012). From these works, alkyl amines have been shown to form clusters via neutralization reactions at rates up to three orders of magnitude greater than ammonia (Almeida et al., 2013; Berndt et al., 2010; Bzdek et al., 2011; Kurtén et al., 2008; Loukonen et al., 2010; Nadykto et al., 2015), and readily exchange with ammonia in already formed ammonium-bisulfate molecular clusters (Bzdek et al., 2010; Lloyd et al., 2009; Qiu et al., 2011). These studies suggest that alkyl amines can compete with ammonia to form particles even though they have been quantified at mixing ratios that are three or more orders of magnitude less in the atmosphere (Chang et al., 2003; Ge et al., 2011; Schade and Crutzen, 1995). Atmospheric measurements made during new particle formation events have further confirmed that alkyl amines participate in particle formation at ambient concentrations and that these species may be present in most atmospheric particles (Creamean et al., 2011; Dall'Osto et al., 2012; Hodshire et al., 2016; Kulmala et al., 2013; Kürten et al., 2016; Ruiz-Jimenez et al., 2012; Smith et al., 2010; Tao et al., 2016).

Alkyl amine emissions to the atmosphere arise from both natural and anthropogenic sources (Ge et al., 2011). Short-chain alkyl amines such as the methylated and ethylated amines are predominantly reported in emission inventories. Measurements show that atmospheric alkyl amines are prevalent in ambient air across the globe, especially in the particle phase (Ge et al., 2011). For example, methyl and ethyl amines were measured by an aerosol time-of-flight mass spectrometer (AToFMS) at both rural and urban sites all across Europe (Healy et al., 2015). In particular, these amines have been measured in substantial quantities near animal husbandry operations (Kuhn et al., 2011; Lunn and Van de Vyver, 1977; Rabaud et al., 2003; Schade and Crutzen, 1995; Sorooshian et al., 2008), fisheries (Seo et al., 2011), and sewage-waste treatment facilities (Leach et al., 1999). Other anthropogenic sources include tobacco smoke (Schmeltz and Hoffmann, 1977), automobiles (Cadle and Mulawa, 1980) and cooking (Rogge et al., 1991; Schauer et al., 1999). The ocean is estimated to be the largest natural source

of alkyl amines, where they are released as volatile degradation products (Ge et al., 2011; Gibb et al., 1999a; Gibb et al., 1999b). Aliphatic amines have also been detected in smoldering stage biomass burning plumes. These have been estimated to represent a quarter of global methylated amine emissions (Lobert et al., 1990; Schade and Crutzen, 1995).

Real-time in-situ speciation and quantitation of atmospheric amines in the particle and gas phase can be difficult because alkyl amines are commonly found at or below parts per trillion by volume (pptv) mixing ratios in the atmosphere (Ge et al., 2011). Furthermore, the atmospheric matrix can be complex and ubiquitous atmospheric species can cause matrix effects for various analytical methods targeting these reduced nitrogen species. Being able to chromatographically resolve alkyl amines from the dominant base, ammonium, represents a major challenge when sampling the gas phase (Chang et al., 2003; Ge et al., 2011; Schade and Crutzen, 1995). Quantifying amines in particle samples, for example by ion chromatography, presents a greater challenge due to possible interferences from sodium, potassium, ammonium, magnesium and calcium whose concentrations are dependent on the particle source characteristics and the measurement location (Ault et al., 2013; Kovac et al., 2013; Sobanska et al., 2012; Sun et al., 2006). Particles frequently contain complex organic mixtures, such as high molecular weight organic compounds, which can cause further matrix effects during separation or direct analysis (Di Lorenzo and Young, 2016; Saleh et al., 2014).

Achieving full speciation of alkyl amines is important because the nucleation potential of amines has been shown to increase with basicity (Berndt et al., 2014; Kurtén et al., 2008; Yu et al., 2012). For example, although monopropylamine (MPA) and trimethylamine (TMA) are structural isomers of one another, MPA is likely to be a more potent nucleator due to its stronger basicity. The suite of alkyl amines that have been commonly detected in the atmosphere contains multiple structural isomers (e.g. monoethylamine (MEA) and dimethylamine (DMA)), making it difficult to speciate the amines using mass spectrometry (MS) without prior separation. Multiple field investigations sampling atmospheric particles using MS analysis have reported the detection of amine ion peaks but have been unable to assign them to a specific amine (Aiken et al., 2009; Denkenberger et al., 2007; Silva et al., 2008; Yao et al., 2016). Derivatization of alkyl amines coupled with HPLC or GC separation has been reported to aid in separation and quantitation of amine species (Akyüz, 2007; Huang et al., 2009; Fournier et al., 2008; Key et al., 2011; Possanzini and Di Palo, 1990). However, these approaches are time consuming, require optimization of reaction conditions, and employ phase separations, which use large quantities of consumables, reagents, and solvents. Capillary electrophoresis has also been employed for aqueous amine separation, however in either case derivatization was required (Dabek-Zlotorzynska and Maruszak, 1998) or the separation of atmospherically relevant cations was not addressed (Fekete et al., 2006). The use of ion chromatography to directly separate and quantify atmospheric alkyl amines has been demonstrated (Chang et al., 2003; Dawson et al., 2014; Erupe et al., 2010; Huang et al., 2014; Li et al., 2009; Murphy et al., 2007; VandenBoer et al., 2012; Verriele et al., 2012), yet the established IC methods struggle with coeluting cations (Huang et al., 2014; Murphy et al., 2007; VandenBoer et al., Verriele et al., 2012) or they do not address a full suite of atmospherically relevant alkyl amines and inorganic cations (Chang et al., 2003; Dawson et al., 2014; Erupe et al., 2010; Li et al., 2009).

In this work we demonstrate the separation and quantitation of the nine most abundant atmospheric alkyl amines, two alkyl diamines, and six inorganic cations through the use of ion chromatography. We show i) the separation method approach to maximizing peak resolution in the context of real-time atmospheric sampling and analysis; ii)

the effects of column temperature on amine coelution; iii) the method precisions, accuracies, sensitivities and limits of detection (LODs) for all alkyl amine and inorganic cations; and iv) application of the method to the complex matrix of atmospheric biomass burning particle extracts to demonstrate method sensitivity and robustness.

2 Methods

2.1 Chemicals and materials

Inorganic cation stock solutions were prepared from a primary mixed cation standard concentrate (Dionex six-cation II, Lot #150326, Thermo Scientific, Waltham, MA, USA) consisting of Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} chloride salts. Alkyl amines (MMA (monomethylamine, 40% w/w), DMA (dimethylamine, 40% w/w), TMA (trimethylamine, 25 % w/w), MEA (monoethylamine, 70 % w/w), DEA (diethylamine, >99% w/w), TEA (triethylamine, >99% w/w), MPA (monopropylamine, ≥ 99% w/w), iMPA (isomonopropylamine, ≥ 99% w/w) MBA (monobutylamine, 99.5% w/w), MEtA (monoethanolamine, ≥ 98% w/w), DAB (1,4-diaminobutane, >98.5% w/w) and DAP (1,5-diaminopentane, 95% w/w)) were purchased from Sigma-Aldrich (Oakville, ON, Canada). Calibration standards were prepared by serial dilution in 18.2 MΩ ultrapure deionized water (Barnstead Nanopure Infinity, Thermo Scientific, Waltham, MA, USA). Since these alkyl amine species will largely be protonated in solution we will denote each of these species in their cationic form (i.e. NR_3H^+) henceforth when referring to the condensed phase.

2.2 Ion Chromatography

A ThermoScientific ICS-2100 Ion Chromatography System (Thermo Scientific, Mississauga, ON, Canada) utilizing Reagent-Free Ion Chromatography (RFIC™) components was used to develop the separation of the selected amines and inorganic cations. A ThermoScientific methanesulfonic acid (MSA) eluent generator cartridge (EGC III, P/N: 074535) was used in conjunction with an ultrapure deionized water reservoir to supply the eluent mobile phase with H_3O^+ ions as the competing exchanger. A continuously regenerated trap column (CR-CTC II, P/N: 066262) was attached in series to the eluent cartridge to remove cation contaminants from the eluent, thereby improving instrument detection limits. Samples were preconcentrated on a cation exchange column (TCC-ULP1; 5 x 23 mm, P/N: 063783) using a ThermoScientific AS-DV autosampler to deliver the desired volume. Concentrated analytes were separated using ThermoScientific CG19 (4 x 50 mm, P/N: 076027) and CS19 (4 x 250 mm, P/N: 076026) guard and analytical cation-exchange columns. The column effluent was passed through a suppressor operating in recycle mode (CERS 500, 4 mm) prior to detection of the analytes using a DS6 heated conductivity cell thermostated at 30 °C. The eluent conductance was recorded at 5 Hz and the chromatographic peaks were analyzed using the Chromeleon™ 7 software package. A ThermoScientific CG15 (4 x 50 mm, P/N: 052200) guard column was added in-line later to attempt further improvement in analyte separation.

2.3 CS19 separation optimization

The gradient program used for the separation of methylamines, ethylamines, other alkyl amines and six inorganic cations on the CS19 cation-exchange column was optimized by combining analyte separation parameters from multiple isocratic elution runs at varying MSA concentrations (1 - 16 mM) and mobile phase flow rates (0.75 - 1.25 ml min^{-1}) at a column temperature of 30 °C. Maximum peak resolution was optimized using an eluent gradient program and the column temperature was increased to resolve co-eluting peaks (see Sect. 3.1.1).

Optimal separation of a suite of 15 cations was achieved using a mobile phase flow rate of 1.25 ml min^{-1} and a column temperature of 55 °C. The eluent gradient program is as follows: an initial MSA concentration of 1 mM held for 20 minutes, a step increase to 4 mM followed immediately by an exponential ramp to 10 mM over 10 minutes (Chromeleon curve factor = 7). The final concentration of 10 mM was held for an additional 5 minutes, yielding a total run time of 35 minutes. The IC was returned to initial conditions and re-equilibrated for 10 minutes as the next 1 ml sample aliquot was prepared for injection by the AS-DV. The suppressor current, optimized for this flow rate and the maximum eluent concentration in accordance with the calculation provided by the manufacturer, was set at 37 mA. The typical backpressure in the system at these conditions was 2100 psi. The Chromeleon method file for the method described above is detailed in Fig. S1.

2.4 Quality Assurance and Quality Control

Standards were prepared using Class A Corning polymethylpentene 50 (± 0.06) ml volumetric flasks that were rinsed 4 times with ethanol and 8 times with ultrapure water prior to use. Standards were stored in 60 ml brown Nalgene polypropylene bottles that were pre-cleaned in a 10 % HCl bath, followed by 8 sequential rinses with distilled and ultrapure water, respectively. The mixed amine standards and mixed inorganic cation standards were prepared separately and each cation standard set was composed of five calibration standards, two check standards and an ultrapure deionized water blank. Ranges and related parameters are denoted by mass injected, as the preconcentration column negates the effect of volume. All amine calibration standards had a mass calibration range of 5-500 ng. The mass range for each inorganic cation calibration is as follows: Li^+ (0.82-16 ng), Na^+ (7.8-160 ng), NH_4^+ (8.4-170 ng), K^+ (26-520 ng), Mg^{2+} (6.4-130 ng), and Ca^{2+} (18-360 ng). All calibration curves contained trace inorganic cation impurities from the ultrapure deionized water source or holding vessels that fell below the lowest calibration standard, and were corrected accordingly to allow for inter-day method performance comparison. Trace quantities of amines were not observed. An example of a calibration blank chromatogram is presented in Fig. S2.

Method precision for each methyl and ethyl amine cation was determined using standard calibration curves (n = 9) injected across five different days spanning three months. The precision for the propyl and butyl amines was determined using two standard calibration curves analyzed over one month. Method precision for Li^+, Na^+, NH_4^+ and K^+ was assessed using calibrations (n = 6) from three separate days spanning two months. Precision for each cation was calculated using the standard deviation (σ) in the slope of the linear calibration curves. Check standards positioned between the two highest and the two lowest calibration standards for each cation were used to determine method accuracy across the calibration range. The low check standard was 15 times greater than the lowest standard and the high check standard was 150 times higher than the lowest standard. Accuracy was determined by

the percent relative error between the known and calculated concentrations of the check standards. The limits of detection (LOD) for the singly-charged inorganic cations (n = 4) and methyl and ethyl amines (n = 5) were determined using calibration standard and calibration blank chromatograms from three or more separate days. The LODs for the propyl and butyl amines were determined using calibration standard and blank chromatograms from two separate days. The LODs are reported as concentrations resulting in a signal peak height to background noise ratio of three. The background noise was determined using the standard deviation of the conductance signal that fell within the retention time window for each analyte in their respective calibration blank chromatograms.

To assess the method robustness in the presence of a complex matrix the gradient method standard addition was performed on a subsample of a size-resolved BB particle extract (320 – 560 nm) (see Sect 2.5). Standard addition was performed by adding known quantities of methyl and ethyl amine solution to a 0.5 ml sample of the extract followed by dilution to 5 ml. The amount of the methyl and ethyl amines added to the internal calibration matched that of the external calibration. The slope and retention times for the methyl and ethyl amines from the internal calibration were calculated and compared to those performed externally to quantify matrix effects. Discussion of the analytical performance of the CS19 gradient program is presented in Sect. 3.1.2.

2.5 Size-resolved BB sample analysis

A size-resolved particle sample from a BB plume was collected using a nanoMOUDI II (nano micro-orifice uniform-deposit impactor, model 122-R, MSP Corp., Shoreview, MN, USA) in St. John's, Newfoundland on July 6, 2013. Satellite images of the plume smoke, HYSPLIT back trajectories, as well as, measured $PM_{2.5}$ concentrations reported by Environment and Climate Change Canada indicate that these plumes originated from boreal forest fires in northern Quebec and Labrador on July 4, 2013 and travelled via Labrador and the Gulf of St. Lawrence to the sampling site (Di Lorenzo and Young, 2016). The nanoMOUDI samples were collected on 13 aluminum substrate stages into size-resolved bins of atmospheric particles with a diameter range spanning 0.010 –18 µm. Air was sampled continuously for 25.5 hours at a flow rate of 30 L min^{-1}. A sub-sample of each aluminum substrate (10 % of the total substrate area) was extracted into a glass vial with 5 mL ultrapure deionized water by sonication (VWR Scientific Products/Aquasonic 150HT, Ultrasonic Water Bath) for 40 minutes. The extracts were filtered using a 0.2 µm polytetrafluoroethylene (PTFE) filter and stored in polypropylene vials at 4 °C prior to analysis by IC within 24 hours. Cation analytes within these samples all fell within their respective calibration ranges and did not require any further dilution. An aluminum substrate field blank was also transported and exposed to the ambient atmosphere briefly at the collection site before being stored in a sealed container for the duration of the sample collection, transported back with the samples, and extracted simultaneously following the same procedure. All calculated quantities were corrected with measurements of the field blank with the additional error from this correction propagated into our final reported values. The field blank chromatogram for the size-resolved BB samples is presented in Fig. S2.

2.6 BC fire sample analysis

The full method for the collection and extraction of BB particle samples collected during July wildfires in British Columbia is detailed in Di Lorenzo et al. (2016). Briefly, $PM_{2.5}$ samples were collected at two sites approximately

100 kilometers east of the biomass-burning location. The first site was located in Burnaby/Kensington Park (BKP) and the second was in North Vancouver/Second Narrows (NVSN). The particle samples were collected using real-time beta attenuation particle monitors (5030 SHARP Monitor at the BKP site, 5030i SHARP monitor at the NVSN site, Thermo Fisher Scientific, Waltham, MA, USA) at a 16.67 L min^{-1} flow rate in 8-hour intervals. Particles were collected on glass microfiber filter tape and stored at -20 °C until extracted. Approximately 37 % of each filter spot area was placed into a polypropylene vial with 10 ml of deionized water, and sonicated for 40 minutes. The extracts were filtered with PTFE syringe filters (3 mm diameter, 0.2 µm pore size, VWR International, Radnor, Pennsylvania, USA) and diluted by a factor of five with ultrapure deionized water so that all analytes were in the calibration range before being injected on the IC. During the extraction, an unexposed area of the glass microfiber filter tape was sampled and extracted for use as a field blank. All calculated quantities and errors were blank-corrected using the field blank.

3 Results and Discussion

3.1 Analytical method performance of CS19 cation exchange column

3.1.1 Separation approach and optimization of parameters

Our approach to separation involved injecting the highest mixed inorganic cation and mixed amine standards for the expected working range (0.1 – 2.5 µg ml^{-1}) at static flow rates (0.75 ml min^{-1}, 1 ml min^{-1}, and 1.25 ml min^{-1}) while systematically increasing the isocratic eluent concentration (4 mM - 16 mM). The quality of each isocratic method was assessed by calculating the peak-to-peak resolution (R_s) using the retention time (t_R) and peak width at base (w) determined from the highest standard for each pair of cations following Eq. (1):

$$R_S = \frac{2(t_{R2}-t_{R1})}{w_2+w_1}, \quad (1)$$

Using the upper limit of the expected working range for all analytes provides a lower limit on peak-to-peak resolution between these species. The peak-to-peak resolutions of the isocratic methods run using a 0.75 ml min^{-1} and 1.25 ml min^{-1} flow rate for the selected inorganic and alkyl amine cations are presented in Fig. S3 and S4. Peak-to-peak resolution between all peaks increased as the mobile phase ionic strength was lowered when the flow rate was held constant. This is in agreement with Eq. (2), the fundamental resolution equation, which describes peak-to-peak resolution in terms of an efficiency factor (N), retention factor (k), and a selectivity factor (α).

$$R = \left(\frac{\sqrt{N}}{4}\right)\left(\frac{k}{k+1}\right)\left(\frac{\alpha-1}{\alpha}\right), \quad (2)$$

With low mobile phase ionic strength, the retention factor of the analytes is expected to increase, leading to greater resolution, consistent with our observations. In contrast, the effect of flow rate on peak resolution is non-intuitive and must be obtained empirically. Lower flow rates increase the retention factor, which in turn increases resolution. However, an increase in mobile phase flow rate has a competing effect on the efficiency factor in Eq. (2). The efficiency term is governed by the theoretical plate height (H) as described by the Van Deemter equation (Eq. (3)), which highlights the competing effect of flow rate (µ) on peak resolution:

$$H = \mathrm{A} + \frac{B}{\mu} + C\mu\,, \qquad (3)$$

Figures S3 and S4 show no loss in peak resolution when using a higher flow rate (1.25 ml min^{-1} vs 0.75 ml min^{-1}). To confirm that there was no loss in efficiency at higher flows, Van Deemter plots were created, using $MMAH^+$ and $TEAH^+$ as representative early and late-eluting species, by plotting theoretical plate height versus flow rate (Fig. S5). To do this, the theoretical plate heights described in Eq. (3) were calculated using Eq. (4), which relates H to column length (L), t_R and w. The A, B and C terms of Eq. (3) were then determined by solving a system of equations using the calculated H values for $MMAH^+$ and $TEAH^+$ at three isocratic flow rates as they are located at opposite ends of the elution range of the six most abundant atmospheric alkyl amines (Fig. 1).

$$\frac{L}{H} = 16\left(\frac{t_R}{w}\right)^2, \qquad (4)$$

The Van-Deemter plots for $MMAH^+$ and $TEAH^+$ show no sacrifice in resolution when operating at higher flow rates and low eluent concentrations. The resolution between Mg^{2+} and Ca^{2+} as well as between $TMAH^+$ and $TEAH^+$ improved at the higher flow rate for all isocratic eluent concentrations. This was due to a decrease in peak width from diffusion band broadening. Furthermore, there was little to no sacrifice in resolution for all other cation peak pairs when operating at a higher flow rate. Of particular note, utilizing a 4 mM MSA isocratic separation at a 1.25 ml min^{-1} flow rate instead of a 0.75 ml min^{-1} flow resulted in a runtime that was 20 minutes shorter, which improves the applicability of IC for near-real-time analysis of hourly to bi-hourly atmospheric sample collection timescales. A shorter run time also improves the method throughput capacity for offline analyses and reduces total eluent consumption. For these reasons, the faster flow rate was selected in designing and optimizing a gradient program. Further isocratic methods using lower MSA concentrations (1 mM and 2 mM) were run at a 1.25 ml min^{-1} flow rate to quantify values of peak-to-peak resolution for the inorganic cations and alkyl amines before approaching a gradient method (Fig. S3 and S4). An increase in resolution greater than one was observed for all analyte pairs aside from $DEAH^+$/$TMAH^+$ when using a 1 mM MSA eluent concentration.

All gradient methods that were tested started with a 1 mM hold, followed by a step-wise increase and/or ramp to higher eluent concentrations at a column temperature of 30 °C. By combining the best isocratic separations for various pairs of cation analytes sequentially, iterative modifications were used to improve resolution based on Eq. (1-3) with the best separation method selected from amongst the iterations. Higher column temperature has been used to improve the quality of a separation method (Hatsis and Lucy, 2001; van Pinxteren et al., 2015; Rey and Pohl, 1996; Rey and Pohl, 2003). Therefore, column temperature was systematically increased to investigate if further improvement in peak-to-peak resolution was possible. Temperature effects on separation efficiency in ion chromatography are thermodynamically complex (Hatsis and Lucy, 2001; Kulis, K., 2004; Rey and Pohl, 1996), but typically result in increased peak resolution because of improvements in mobile phase diffusivity, which increases the efficiency term from Eq. (2). Higher temperatures can replicate the separation effects observed when adding an organic mobile phase modifier (Hatsis and Lucy, 2001; Rey and Pohl, 1996). Figures 1a and b show gradient separations at 30 °C and 55 °C respectively. At 30 °C, K^+ and $DMAH^+$ overlap considerably (R_S = 0.45) and $DEAH^+$ and $TMAH^+$ coelute. By increasing the column temperature to 55 °C, the extent of peak overlap between K^+ and neighboring alkyl amine cations is noticeably reduced (R_S > 1) and $DEAH^+$ and $TMAH^+$ are increasingly well resolved (R_S = 1.48). The effect of temperature on the separation of the alkyl amines is

demonstrated in Fig. 2, where the separation of $DEAH^+$ with $TMAH^+$ is achieved above 50 °C. The temperature increase also results in lower resolution between $DMAH^+$ and $MEAH^+$ from $R_S = 1.57$ to $R_S = 1.08$. In our method, a column temperature of 55 °C produced peak-to-peak resolutions greater than a value of one between all six alkyl amine cations and inorganic cations in the final gradient method, giving a 95 % separation between our target analytes and expected atmospheric interferences in the condensed phase. The peak-to-peak resolutions are summarized in Table 1. These represent a lower-limit in peak resolution since they were calculated using peak parameters at the upper limit of the working range, which was determined based on maximum mixing ratios or mass loadings expected for the analysis of atmospheric samples containing these analytes.

The separation method produced in this work is able to overcome previously reported IC coelution difficulties between $DEAH^+$ and $TMAH^+$ and between $MEAH^+$ and $DMAH^+$ (VandenBoer et al., 2012; Verriele et al., 2011). Both DMA and TMA have been identified as dominant amines in emission studies, so it is important to achieve accurate and specific quantitation of both species in gas and particulate atmospheric samples (Facchini et al., 2008; Kuwata et al., 1983; Müller et al., 2009; Van Neste and Duce, 1987). Multiple field campaigns have detected large quantities of gas-phase and particle-phase MEA and DEA in ambient air as well (Facchini et al., 2008; Müller et al., 2009; Sorooshian et al., 2009; Yang et al., 2005; Yang et al., 2004). In some cases clean up steps have been used to alleviate IC interferences from common atmospheric cation species in the quantitation of amines despite the fact that an 85% evaporation loss of the amines, in addition to the extra sample handling, was reported when using a solid phase extraction clean up (Huang et al., 2014). The CS19 IC method reported here is able to separate the most common atmospheric inorganic cations in addition to eleven common atmospheric amines (see additional separation of five additional alkyl amines in Sect 3.1.3). It can be easily applied to water-soluble atmospheric gas and particulate samples since they can be directly analyzed - without coelution or a clean-up step - with separation times of similar duration to many previously reported methods, including those employing an online IC method (Huang et al., 2014; Murphy et al., 2007; VandenBoer et al., 2012; Verriele et al., 2011).

3.1.2 Instrumental performance and comparison for the methyl amines, ethyl amines and inorganic cations

The performance statistics of the CS19 gradient method for each cation are summarized in Table 1. The method shows high reproducibility, with method precisions better than 10 % for most analytes. Although the instrumental response varied from month-to-month for each analyte, this variability was random and the calibration curve slopes for each analyte showed no systematic decrease over time. The larger variability in the $TMAH^+$ and $TEAH^+$ calibration curves ($\pm$ 16 % and $\pm$ 11 % respectively) is likely driven by their lower Henry's Law constants (K_H) in water (Christie and Crisp, 1967), resulting in volatilization losses from standards. Concurrently, this variability could be driven by partitioning losses along the flow path, particularly when the tri-subsituted amines reach the suppressor, which was not temperature-controlled. In future investigations it may be worthwhile to acidify the standards to ensure the amines are maintained in their charged form in the aqueous phase. Alternatively, to combat losses to neutral forms, use of a Salt Converter suppressor accessory (ThermoScientific, SC-CSRS 300, P/N: 067530), which keeps weak electrolytes in a separated sample fully protonated prior to their conductance measurement, may also aid in increasing long-term $TMAH^+$ and $TEAH^+$ precision.

The limits of detection (LODs) for each analyte are reported in Table 1 as both a range and as the average LOD (± 1σ). The LODs are reported in this manner to reflect the high day-to-day variability in the calculated LODs. This variability may be driven by i) the purity of the deionized water used for eluent generation; ii) instrumental baseline noise and trace contamination on the day of analysis; and iii) quality of labware cleaning prior to preparation of calibration blanks. Outliers in the LOD dataset were found to result from trace contamination of analytical labware, sampling vials, or from systematic errors made in the preparation of standards or injection of samples on the IC (e.g. leaking autosampler caps, failing retention of concentrator column). The Grubb's test was performed using a 95% confidence interval to statistically identify outliers from LOD data sets. Calculated detection limits were determined to lie in the picogram per injection range for all analytes. The LODs for the inorganic cations were 10 to 100 times lower than those of the alkyl amines, with the exception of Mg^{2+} and Ca^{2+}. Trace contamination of calcium in our ultrapure deionized water led to higher LODs for the divalent cations. Our method shows high accuracy in the upper range of the calibrations for the methyl and ethyl amines, with accuracies ranging from 90 – 100 %. The accuracy was much lower for each methyl and ethyl amine cation at the low end of the calibration range where amine concentrations were approximately 1.5 times the limit of quantitation (LOQ). Quantitation near the method LOQ was more sensitive to small integration changes, which affected the calculated peak area, even when performing integrations manually, and this resulted in greater method error. This is a drawback inherent to IC since wide analyte peaks are a result of persistently large stationary phase particle sizes, causing band broadening via longer flow paths and increased diffusion during separation (i.e. the A and B terms in Eq. (3)). The low alkyl amine accuracies may also be driven by their air-water partitioning properties, which could result in losses during sample handling and during sample injection. The low and high range accuracies for all inorganic cations, with the exception of ammonium, were high (80 – 120%) because concentrations were not near the limit of quantitation for these analytes. The low check standard accuracy for ammonium likely arises due to similar issues as those discussed above for the tri-substituted amines.

To further test the efficacy of the separation method, a standard addition calibration was performed in the presence of the complex BB matrix. The calibration slopes and retention times for each analyte from the standard addition and external calibration performed on the same day are listed in Table S1. The slopes for the two calibrations varied between 0 and 8 %, which is within the method calibration precisions presented in Table 1. Thus, the BB sample extracts did not exhibit matrix effects as the slopes were found to be within the expected instrument variability as determined by external calibration standard analysis. However, increasing retention times of approximately 0.3 – 0.5 minutes were observed for all cation analytes when performing the standard addition. This is an effect inherent in IC when samples with higher total quantities of cations are preconcentrated, resulting in a sample plug filling a greater volume of the stationary phase capacity. The initial weak mobile phase of the gradient method will therefore take a greater amount of time to elute all of the analyte cations from the preconcentration and analytical columns. This same increase in retention times is present in the external calibration with increasingly concentrated standards (Table 1).

Previous IC instrumental precisions reported for use in quantifying the six atmospheric methyl and ethyl amines range from 0.4 to 17.2 %, which are comparable to our method (Table S2; Chang et al., 2003; Dawson et al., 2014; Erupe et al., 2010; Huang et al., 2014; Li et al., 2009; VandenBoer et al., 2012; Verriele et al., 2012;). Our separation method shows greater average variability than others due to our numerous assessments (n = 9) over

multiple months, a more comprehensive analysis compared to previous reports. The sensitivity of this instrument is also similar to that of all other reported IC methods as the instrumental detection limits are in the picogram range. Only VandenBoer et al. (2012) and Chang et al. (2003) report lower detection limits and these are likely a result of a lower background signal from running the IC instruments online. Our method does not achieve instrumental limits of detection as low as those achieved using derivatization methods coupled with GC-MS or HPLC analysis (Akyüz, 2007; Fournier et al., 2008; Possanzini and Di Palo, 1990). However, multi-step derivatization methods are prone to losses that must be quantified with internal standards. These losses can lead to higher overall method detection limits, which is not the case for direct analysis of water-soluble samples. Derivatization methods are also difficult to employ for near-real-time analyses of the atmosphere, making the approach less analytically attractive. Further, the IC separation method presented here is able to address additional matrix effects that may result from other atmospheric species through the use of a sample pre-concentration column. Only positively charged species are retained in this pre-concentration step and injected through the IC system for analysis, negating matrix effects from non-charged and anion species, as demonstrated by the standard addition to the BB sample extract.

Employing a method that is capable of quantifying amines at very low mixing ratios is valuable since recent work has shown that parts per quadrillion by volume (ppqv) concentrations of gaseous amines can lead to particle formation and growth (Almeida et al., 2013). If our method were applied to online atmospheric ambient sampling of gases or particles the method could be used to detect amines at ppqv mixing ratios. For example, a detectable signal for 100 ppqv mixing ratios could be attained by sampling through a bubbler, filter, or denuder at a low flow rate of 3 L min^{-1} for 1 – 10 hours, depending on the amine. It may be possible to shorten the sample collection duration to an hourly timescale to detect ppqv mixing ratios of atmospheric amines if the method is interfaced with a high sensitivity MS detector. Verriele et al. (2014) observed a 5 – 30 fold improvement in method detection limits when interfacing their IC method with a MS detector.

3.1.3 Expanded amine catalogue for other common atmospheric species

The separation method developed was further investigated to elucidate its utility in quantifying monopropylamine (MPA), isomonopropylamine (iMPA) and monobutylamine (MBA), three additional amines that have been frequently detected in ambient air (Ge et al., 2011). In particular, this test was performed to assess their potential coelution with the fully separated methyl and ethyl amines. Without modification of the gradient method, we observed separation of these three additional amines from the original twelve cations with $R_s \geq 0.85$ (Fig. 3a). $MPAH^+$ and $iMPAH^+$ eluted between $DMAH^+$ and $TMAH^+$ and $MBAH^+$ eluted later, but before $TEAH^+$. The resolution is sufficient between all analyte peaks to allow quantitative analysis of the nine alkyl amine cations and six inorganic cations. The separation statistics for these additional amines are also presented in Table 1. Since the additional amines were injected after column degradation had occurred and retention times had noticeably shifted (see Fig. 3a vs. Fig. 1b and Sect 3.1.5 for further discussion), retention time and peak width were estimated using changes in separation parameters from the original method development for the methyl and ethyl amines. Peak widths for the propyl and butyl amines were assumed to have increased by approximately 50 %, consistent for the same increases observed for the methyl and ethyl amines as a result of the column degradation. Retention times for $MPAH^+$, $iMPAH^+$, and $MBAH^+$ were back-calculated to reflect the initial column conditions using these

corrected peak widths and the resolution values determined from the chromatogram presented in Fig. 3. The method precisions for $iMPAH^+$, $MPAH^+$ and $MBAH^+$ determined from two standard calibration injections ranged from 1 - 12 %. The reported average LODs for both propyl amines are the lowest of the alkyl amines, while $MBAH^+$ has the highest method LOD because it elutes in a region with a high background due to the step change in eluent composition not being completely suppressed. The method accuracies for the three additional amines assessed by both the high and low check standards were within 80 % for all analytes. However, the large standard deviations in the accuracies for all low check standards highlights the challenge of method reproducibility for these analytes near the limit of quantitation. This CS19 IC method can resolve three sets of alkyl amine structural isomers, therefore not only allowing full speciation of the suite of common atmospheric amines, but also overcoming a limitation of direct mass spectrometry analysis of the atmospheric matrix.

Since diamines have recently been shown to be potent sources of new particle formation and have been detected in field campaigns across the U.S.A. (Jen et al., 2016b), as well as near livestock, food processing factories and sewage facilities (Ge et al., 2011), quantitation of 1, 4-diaminobutane ($DABH^+$) and 1, 5-diaminopentane ($DAPH^+$) was tested using the CS19 gradient method. The two diamines eluted after all 15 analytes, with $DABH^+$ and Ca^{2+} having a peak-to-peak resolution of 3.16 and $DAPH^+$ and $DABH^+$ having a peak-to-peak resolution of 0.98. A single calibration curve was run to provide an estimate of the sensitivity and LOD for $DABH^+$ and $DAPH^+$ and the retention times for these two additional diamines were also back-calculated to reflect initial column conditions (Table 1). If the 10 mM MSA hold of the optimized method is extended by 5 minutes to give a total run time of 40 minutes, then $DABH^+$ and $DAPH^+$ can also be quantified. Ethanolamine (EAH^+), a compound employed in industry and CO_2 capture (Ge et al., 2011), was also analyzed by this IC method and found to have poor resolution with NH_4^+ and $MMAH^+$ ($R_S \leq 0.65$, Table 1). However, the peak is still identifiable in samples containing these analytes.

3.1.4 Method development with the addition of an inline CG15 guard column

As mentioned previously, IC methods in the literature have been unable to separate potassium from the methyl and ethyl amines (Huang et al., 2014; VandenBoer et al., 2012), and in our current method potassium has slight overlap with $MMAH^+$ ($R_S = 1.09$). We attempted to reduce peak overlap between potassium and the alkyl amines by adding a crown ether-functionalized CG15 guard column in-line after the CG19/CS19 columns. The addition of the CG15 column, which has increased selectivity for K^+, resulted in an increased retention time for potassium of 13 minutes. The best separation achieved using the additional guard column is shown in Fig. 3b, where K^+ still elutes within the alkyl amine retention region. The gradient method used to achieve the separation used a flow rate of 1 ml min^{-1}, a column temperature of 55 °C, and held a 1 mM MSA concentration for the first 30 minutes. The eluent concentration was step increased to 4 mM followed immediately by an exponential ramp to 10 mM over 20 minutes (Chromeleon curve factor = 7). The final concentration of 10 mM is held for an additional 15 minutes, yielding a total run time of 65 minutes. Even when holding the initial MSA concentration at 1 mM for 50 minutes, the separation was unable to fully resolve the alkyl amine peaks. An increase in retentivity for K^+ and NH_4^+ as well as many of the alkyl amines, indicated that the crown ether functionality was not selective for K^+ in this suite of analytes. With the addition of an organic modifier to the mobile phase or the ability to decrease column temperature, this increase in selectivity from the CG15 column might be harnessed to produce better separation.

However, due to the limitations of the ICS-2100 system using RFIC we were unable to investigate these parameters. Furthermore, although a passable separation may be achieved when using a run time greater than 60 minutes, this would not be as applicable to online analyses as the CG/CS19 method developed without the addition of the CG15 column. A stationary phase similar to that of the CG/CS19 columns, but with some of this crown ether selectivity could potentially yield better results than those presented here, particularly for the analysis of atmospheric samples containing large quantities of K^+ and amines.

3.1.5 Analytical column stability

Over the course of five months, peak retention times noticeably decreased and peak broadening of approximately 50 % occurred for all analytes. After more than 1000 sample and standard injections retention times had decreased by 1.9 ± 0.1 minutes depending on the cation. Peak-to-peak resolution, however, remained largely unchanged throughout the column degradation during standard and sample analysis, even with observed peak broadening. This is consistent with what has been previously reported in the literature when hundreds to thousands of injections have been run through an IC column (VandenBoer et al., 2011). This may also be a result of column degradation from operating the CS19 column at a temperature higher than that recommended by the manufacturers.

During the course of method development severe peak broadening and subsequent peak-to-peak resolution loss of magnesium and calcium was also observed. After the analysis of hundreds of samples the unresolved co-eluting divalent cations had a peak width greater than 10 minutes wide. The magnesium and calcium peak areas eventually became unresolved, with their combined peak area precision in the highest standard within 6 % (± 1σ) after 12 months of analysis. It was determined that this broadening effect observed for the Mg^{2+} and Ca^{2+} peaks was due to a malfunctioning suppressor. After replacing the suppressor, a peak-to-peak resolution greater than one was restored for these analytes. Furthermore, the cumulative analyte peak broadening that had occurred throughout method development and sample analysis for all the monovalent cations was also mitigated by installing the new suppressor. Retention times however were still shifted by 1.9 ± 0.1 minutes, indicating that analytical column degradation had still occurred.

3.2 Biomass-burning particle analysis and discussion

3.2.1 Size-resolved alkyl amines in particles from an aged biomass-burning plume

Biomass-burning particles often contain a complex mixture of water-soluble ions, organics, elemental carbon and other insoluble components, making them nonpareil for testing the robustness of an atmospheric measurement technique. Ions such as NH_4^+ and K^+ are consistently detected in biomass burning plumes, regardless of sampling location as they are well characterized as being co-emitted species (Capes et al., 2008; Hudson et al., 2004; Pósfai et al., 2003). Particles released during forest fires have also been shown to contain highly oxidized large molecular weight organics (Di Lorenzo and Young, 2016; Saleh et al., 2014). We tested the robustness of our method on water-extracted aged biomass-burning particle samples collected by a cascade impactor in St. John's, Canada. Gas-sorption and reaction artifacts are minimized due to the gaseous flow-path being directed around the nanoMOUDI impaction plates, therefore samples analyzed are representative of the particles in the atmosphere. An overlaid chromatogram of two different size-resolved particle samples (100 - 180 nm and 320 – 560 nm) shows

the presence of $MMAH^+$, $DMAH^+$ and $DEAH^+$ in the aged biomass burning samples with complete separation from K^+, NH_4^+ and Na^+ (Fig. 4). The maximum mass loadings for $MMAH^+$, $DMAH^+$ and $DEAH^+$ were found in particles with diameters (D_p) 320 – 560 nm and were 11 $\pm$ 3 ng m^{-3}, 208 $\pm$ 4 ng m^{-3}, 1300 $\pm$ 200 ng m^{-3}, respectively (Table S3). $TMAH^+$, $MEAH^+$ and $TEAH^+$ peaks were also detected in the BB size-resolved particle extracts. $TMAH^+$ and $TEAH^+$ reached mass loadings of 5 $\pm$ 3 ng m^{-2} and 4 $\pm$ 2 ng m^{-3}, respectively, while $MEAH^+$ never exceeded a concentration of 1 ng m^{-3} in any size-resolved particle fraction (Table S3). The relative loadings of NH_4^+, K^+ or Na^+ to individual amines in these samples ranged from 2:1 to 1000:1, demonstrating the robustness of this method to quantify amines. Lobert et al (1990) reported detecting C_1 – C_5 aliphatic amines from controlled biomass-burning experiments, which is consistent with our findings. BB-derived amines were also identified during the 2007 San Diego forest fires (Zauscher et al., 2013) with primary amines observed at approximately 6% by mass of organic content from an aged biomass burning particle sample in British Columbia (Takahama et al., 2011). However, few studies have addressed the speciation and quantitation of alkyl amines emitted from biomass-burning events. Schade and Crutzen (1995) estimated the emission rates for MMA, DMA, TMA and MEA from biomass burning sources based on controlled burn experiments, but do not include a BB emission rate for DEA or TEA. These emission inventories are yet to include emission rates from atmospheric BB measurements (Lobert et al., 1990; Schade and Crutzen, 1995).

In Figure 5a we show the molar ratio of the sum of the methyl and ethyl amines to ammonia which is considered to be the main atmospheric base, as a function of the size-resolved particles collected. The summed amine moles exceeded ammonium in the particle diameter range from 100 to 560 nm, and the ratio ranged from 0.5 to 1.9 in the fine mode ($PM_{1.0}$), with an average ratio of 0.92 in $PM_{1.0}$ calculated using nanoMOUDI bins up to this nominal cutoff. Quantities of NH_4^+ were below the detection limit in samples above 1 µm, yielding no values for the ratio. The large error bars in the ratios are driven by the low molar quantities of ammonium in the samples as well as a higher than normal variability in three extraction blanks (ultrapure deionized water in polypropylene tubes) injected on the day of analysis. For these reasons this method blank error was assigned to the size-resolved samples in place of the NH_4^+ error driven by the method precision and accuracy detailed in Table 1. To our knowledge, this is the first time that an amines to ammonium ratio greater than one has been reported in the $PM_{1.0}$ resolved fraction of atmospheric particles. An amines to ammonium ratio of 0.37 in fine mode aerosol ($PM_{1.8}$) was reported by VandenBoer et al. (2011), but most reported ratios have been below 0.1 (Ge et al., 2011). The high ratios we observed can be attributed to large quantities of $DEAH^+$ and $DMAH^+$. $MMAH^+$ was found to be in molar quantities 100 times less than that of ammonium while $TMAH^+$, $MEAH^+$ and $TEAH^+$ were found to be in molar quantities 1000 to 10000 times less than ammonium. Detecting such large molar ratio quantities of $DEAH^+$ and $DMAH^+$ to NH_4^+ in any particle sample is also unprecedented. Mono-substituted amines are the most frequently detected alkyl amines in atmospheric particles and at molar ratios to ammonium of 1:100 or lower (Ge et al., 2011; Gorzelska et al., 1990; Mader, 2004, Müller et al., 2009; Yang et al., 2005; Yang et al., 2004; Zhang et al., 2003). In most instances where di-substituted or tri-substituted amines have been identified in the particle phase, they are present at molar quantities equal to or less than the mono-substituted amines (Healy et al., 2015; Suzuki et al., 2001). Thus, such high quantities of $DMAH^+$ and $DEAH^+$ in these samples were unexpected and highly unusual compared to prior reports. In this case, the observation may be due to the fuel source of the fire or the interaction of the plume with a potent source of atmospheric amines. Previous work has identified di-substituted amines in large quantities

from feedlot plumes (Sorooshian et al., 2008) and in marine particles (Facchini et al., 2008; Gibb et al., 1999a; Müller et al., 2009; Sorooshian et al., 2009; Van Pinxteren et al., 2015; Youn et al, 2015). In fact, DMA and DEA have been reported as the second- and third-most abundant organic species in marine fine aerosol behind methanesulfonic acid during periods of high biological activity in the North Atlantic (Facchini et al., 2008). Other researchers have also suggested a moderate to high correlation between high biological activity and di-substituted amine particle mass loadings (Müller et al., 2009; Sorooshian et al., 2009). Laboratory investigations have shown that methylamines can be produced by marine phytoplankton degradation of quarternary amines to maintain an osmotic gradient as well as during periods of known zooplankton grazing (Gibb et al., 1999b). Based on the HYSPLIT back-trajectories calculated for these samples (Di Lorenzo, 2016), it is possible that the BB plume particles interacted with gaseous DMA and DEA emitted from inland agricultural sources along the St. Lawrence River, coastal phytoplankton blooms, or with enhanced amine emissions in the coastal zone, which has been observed in the marine boundary layer of California (Youn et al., 2015). The high concentrations of DMA and DEA produced by marine biological activity could then partition into the biomass burning particles and react to neutralize inorganic acids (e.g. sulfuric acid), form salts or amides with organic acids, or react with carbonyl moieties in the highly oxidized organic material produced via BB to form imines (Qiu and Zhang, 2013). If this explanation holds true then there may be preferential uptake of these amines over ammonia into the plume, as there is no evidence yet that suggests a larger agricultural or marine source of amines relative to ammonia to the atmosphere. In particular, a marine amines hypothesis, while consistent with observations in the literature, is beyond the scope of this work in terms of assigning a definitive DMA and DEA source.

3.2.2 Time series of amines in fresh biomass burning plume particles from British Columbia

Our method was also applied to a time series of $PM_{2.5}$ samples collected at two different locations (BKP and NVSN) during a forest fire in the Lower Fraser Valley in British Columbia in the summer of 2015. These $PM_{2.5}$ samples were collected every 8 hours while the plume was traversing each site and during collection the $PM_{2.5}$ concentration was in excess of 200 μg m^{-3}. The relative ages for the smoke plumes sampled at both sites were calculated to be 20 hours old, or less, and back trajectories indicated that the plume did not travel over the open ocean before being sampled (Di Lorenzo et al., 2016). In these test samples, the method was again able to detect the presence of four different amines ($iMPAH^+$, $TMAH^+$, $DEAH^+$, and $TEAH^+$) with loadings of Na^+, NH_4^+ and K^+ at ratios in excess of 100:1 (Figure S6). Furthermore, the method was not only able to determine the presence of isomonopropylamine, but also differentiate it from monopropylamine and trimethylamine, its two structural isomers. $iMPAH^+$, $TMAH^+$, $DEAH^+$, and $TEAH^+$ had maximum mass loadings in these fresher biomass-burning samples of 60 $\pm$ 40 ng m^{-3}, 9 $\pm$ 7 ng m^{-3}, 1.6 $\pm$ 0.8 ng m^{-3}, and 0.2 $\pm$ 0.1 ng m^{-3} respectively (Table S4). $iMPAH^+$ was the amine detected in the largest molar quantities at both sampling sites in British Columbia. The detection of $iMPAH^+$ has not previously been reported in biomass-burning emission inventories, and based on our measurements may be important to quantify in future controlled burn experiments. Our results differ from the study conducted by Takahama et al (2011) on the 2009 forest fires in British Columbia that reports the detection of primary amine groups, which further suggest that amine emissions from biomass burning and/or their incorporation into biomass burning particles are not well understood. Although our observed suite of amines includes $iMPAH^+$, there was no indication of other primary amines from the analyses of the BB particles. The calculated quantities for these samples may be biased high or low because the beta attenuation monitor used to

sample the BB particles can be prone to gas-phase blow-on or blow-off artifacts via sorption or reactive mechanisms, as per traditional filter sampling strategies. Although the extracted field blank was corrected for any positive sorption biases on the filter tape (e.g. Müller et al., 2009), it was unable to account for any reactive uptake of gas-phase amines during the sampling period. Therefore, the filter tape BB samples presented here represent a time-integrated particulate composition assuming thermodynamic equilibrium between the gas and particulate phases for the duration of collection for each sample.

A time-series of the amines to ammonium molar ratio as the smoke plume intrudes into both the BKP and NVSN sites is presented in Fig. 5b. There were either no amines present or they were present in concentrations below our detection limits in the ambient particles collected on the front edge of the plume intrusions. When the maximum $PM_{2.5}$ mass loading of the plume reached the sampling site at t = 0, we saw an absolute maxima in total amine concentration as well as a relative maxima in the particulate amine to ammonia molar ratio (Fig. 5b). The particulate amine concentrations and the amines to ammonia ratio then tapered off as the plume diluted and passed through the site. The measured amines to ammonia ratio in these samples is consistent with previously reported literature values (Ge et al., 2011). The measured amine species and quantities, as in the aged plume, could be indicative of the biomass-burning source fuel, fire type, or amine levels in air masses intercepted that were subsequently incorporated by partitioning and reacting into the condensed phase. Since the smoke plumes were less than a day old and the plume did not travel over the open ocean, it is less likely that offshore marine amine emissions interacted with the plume. However, the BKP and NVSN sampling sites are positioned in a coastal urban center and anthropogenic amine emissions from industry or animal husbandry operations nearby, as well as coastal amine emissions, may still have been incorporated into the plume before it was sampled.

4. Conclusions

We developed an ion chromatographic method that can separate and quantify nine dominant atmospheric alkyl amines and two alkyl diamines from common inorganic atmospheric cations. Ion chromatography methods reported in the literature cannot fully resolve alkyl amine peaks, nor separate interferences from potassium, magnesium and calcium. In this work, we report the ability to overcome these prevalent issues for atmospheric sampling with a rapidity that can also be applied to near real-time analyses of aqueous atmospheric extracts by IC. Additionally, the method is able to separate and quantify three pairs of structural isomers, a limitation for direct particle and gas sampling mass spectrometry instrumentation in quantifying atmospheric alkyl amines. The method detection limits are comparable to other published IC methods in the literature, however the described method is not as sensitive as instrumentation used in conjunction with derivatization methods coupled with GC-MS or LC-MS, which can suffer from sample processing losses.

The IC method is robust. Two sets of BB particle samples collected at two different locations in Canada were injected onto the IC column and the method detected and quantified amines in the presence of a complex matrix where inorganic analytes, such as K^+, reached ratios of 1000:1 relative to the alkyl amines. A standard addition demonstrated that the BB matrix does not have any influence on the ability of the IC method to quantify these analytes. This is a major improvement over all prior reports of the application of IC to the detection of amines in aqueous extracts of atmospheric particulate matter. Our results suggest that increasing focus on speciation and

quantitation of various alkyl amines from direct BB emissions and their propensity to undergo reactive uptake with biomass burning particles are needed to constrain global budgets of atmospheric sources and fate of alkyl amines.

Overall, the developed IC method shows promise for i) adoption into standard analysis of water soluble atmospheric extracts; ii) incorporation into online instrumentation already using ion chromatography for near real-time analysis of water soluble atmospheric samples; and iii) interfacing with high-resolution mass spectrometry for even higher analytical sensitivity, particularly where supporting measurements for ppqv-levels of amines may be stimulating new particle formation in the atmosphere.

Author contribution.

TCV designed the experiments and BKP, ATQ, and RAD carried them out. BKP 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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Figures

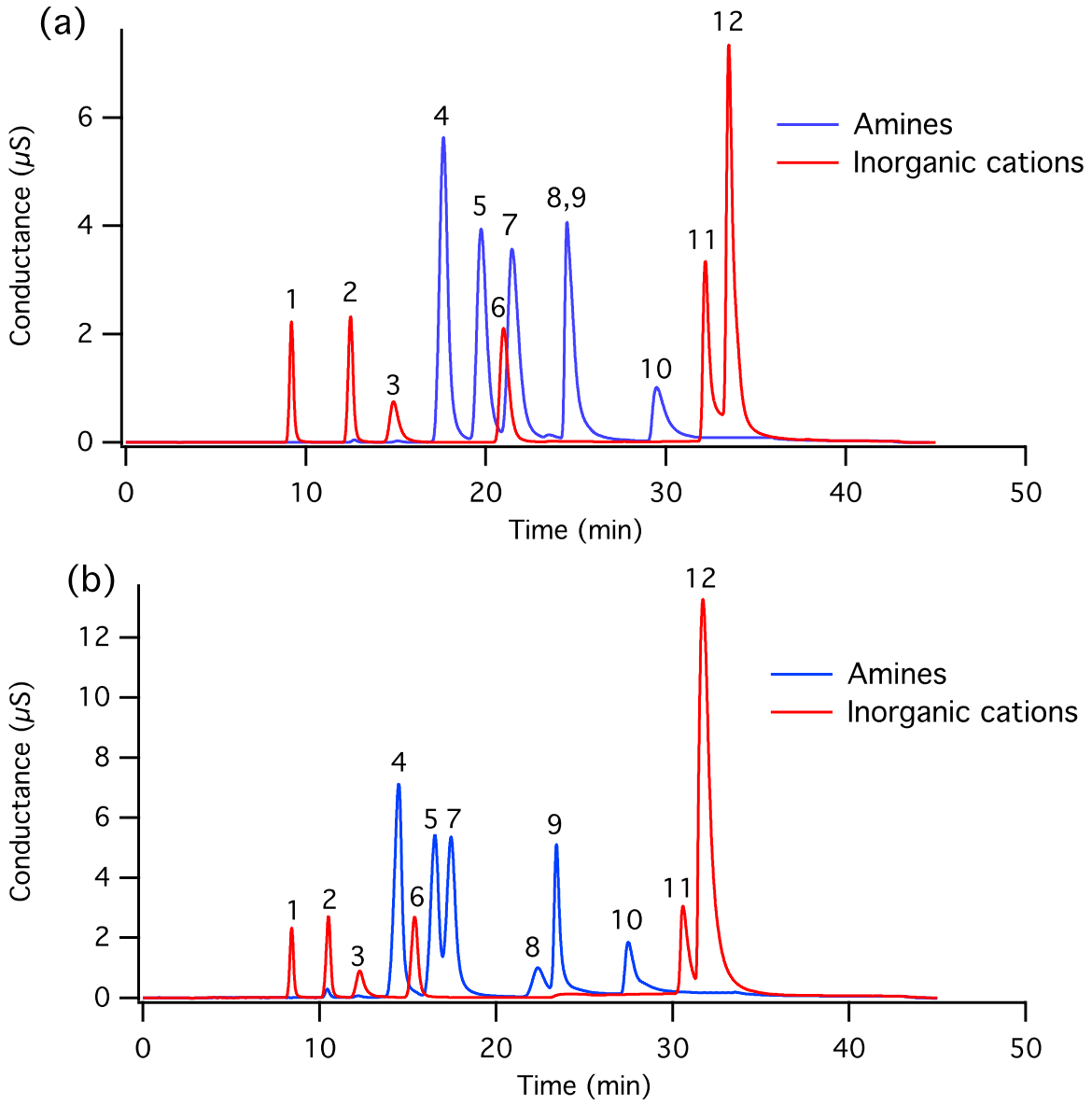

Figure 1. Separation of amine and inorganic cation standards with the highest resolution gradient program at (a) 30°C and (b) 55°C. The order of elution and mass of cation injected in (a) is as follows: Li^+ (1, 16 ng), Na^+ (2, 158 ng), NH_4^+ (3, 169 ng), $MMAH^+$ (4, 500 ng), $MEAH^+$ (5, 500 ng), K^+ (6, 524 ng), $DMAH^+$ (7, 500 ng), $TMAH^+$ (8, 500 ng), $DEAH^+$ (9, 500 ng), $TEAH^+$ (10, 500 ng), Mg^{2+} (11, 128 ng), and Ca^{2+} (12, 361 ng). Cation peaks represent the same mass injected and are labeled according to the same numeric identities in (b).

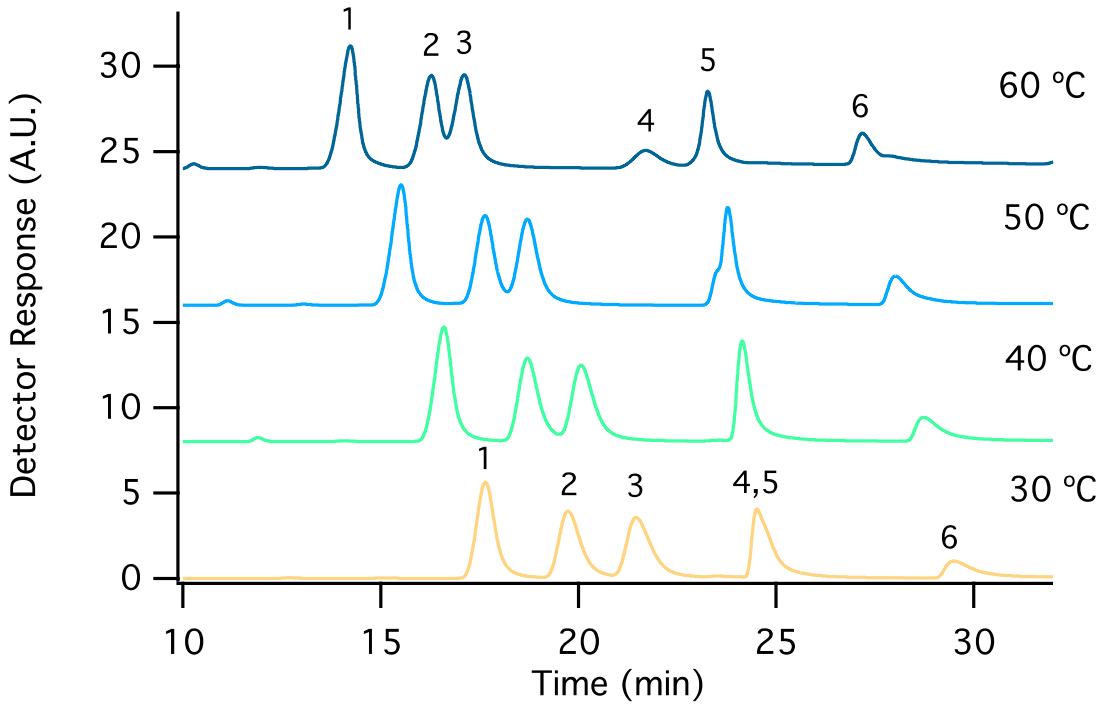

Figure 2. Separation of 1 µg ml^{-1} mixed amines standard with the final method gradient elution program at 30 °C, 40 °C, 50 °C and 60 °C. The peak elution order was $MMAH^+$ (1), $MEAH^+$ (2), $DMAH^+$ (3), $TMAH^+$ (4), $DEAH^+$ (5), and $TEAH^+$ (6). The separation of diethylamine (DEA) from trimethylamine (TEA) was achieved at column temperatures greater than 50 °C.

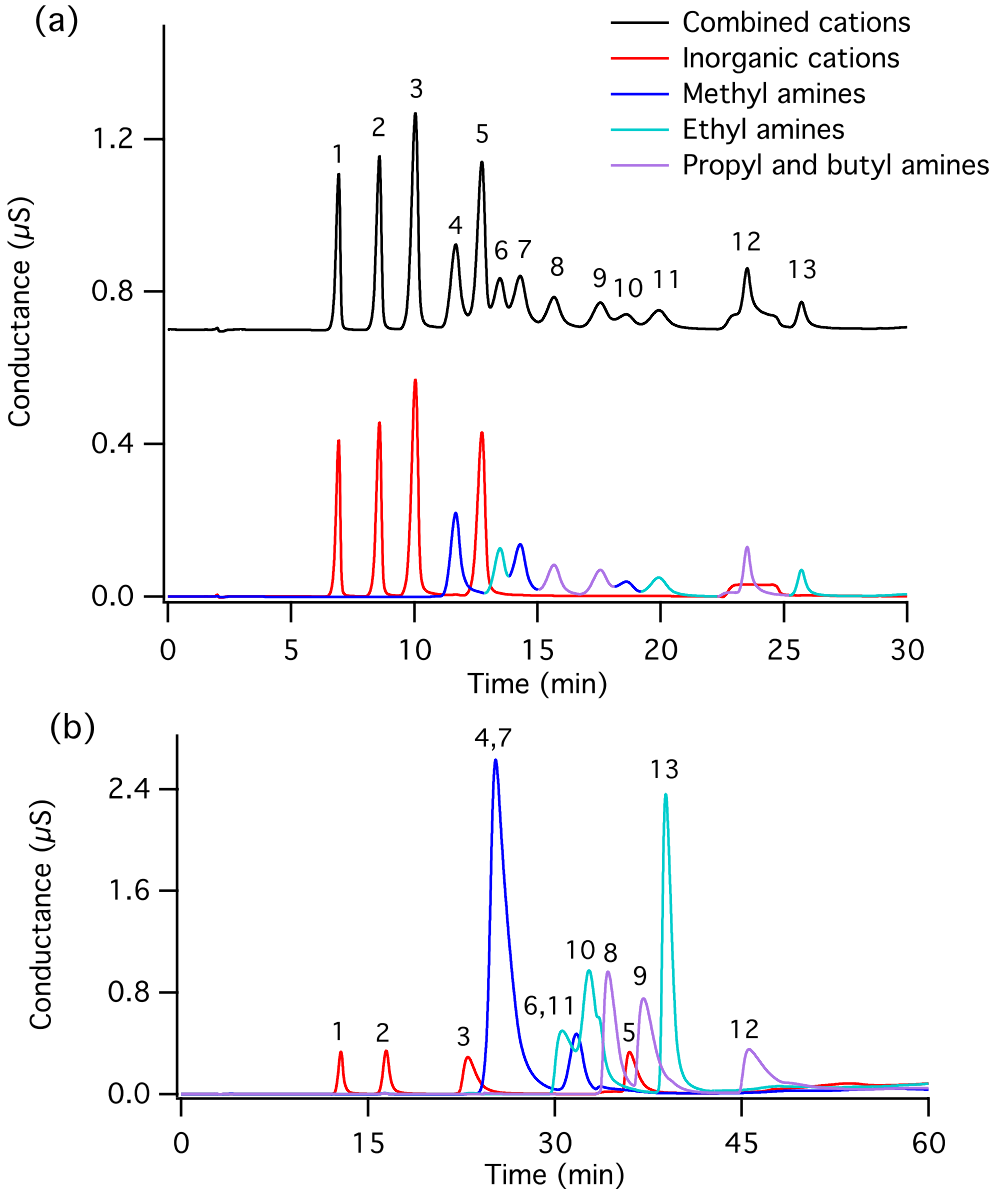

Figure 3. (a) Separation of amine and inorganic cation standards with the addition of $MPAH^+$, $iMPAH^+$ and $MBAH^+$ using the final gradient program. The order of elution and mass of cation injected in (a) is as follows: Li^+ (1, 1.6 ng), Na^+ (2, 16 ng), NH_4^+ (3, 17 ng), $MMAH^+$ (4, 50 ng), K^+ (5, 52 ng), $MEAH^+$ (6, 50 ng), $DMAH^+$ (7, 50 ng), $iMPAH^+$ (8, 50 ng), $MPAH^+$ (9, 50 ng), $TMAH^+$ (10, 50 ng), $DEAH^+$ (11, 50 ng), $MBAH^+$ (12, 50 ng), and $TEAH^+$ (13, 50 ng). (b) Separation of amine and inorganic cation standards with the addition of $MPAH^+$, $iMPAH^+$ and $MBAH^+$ and the addition of the CG15 column using a modified gradient program. Cation peaks are labeled accordingly to the same identities in (b) and the mass of analyte injected is as follows: Li^+ (1.6 ng), Na^+ (16 ng), NH_4^+ (17 ng), $MMAH^+$ (500 ng), K^+ (52 ng), $MEAH^+$ (500 ng), $DMAH^+$ (500 ng), $iMPAH^+$ (500 ng), $MPAH^+$ (500 ng), $TMAH^+$ (500 ng), $DEAH^+$ (500 ng), $MBAH^+$ (500 ng), and $TEAH^+$ (500 ng).

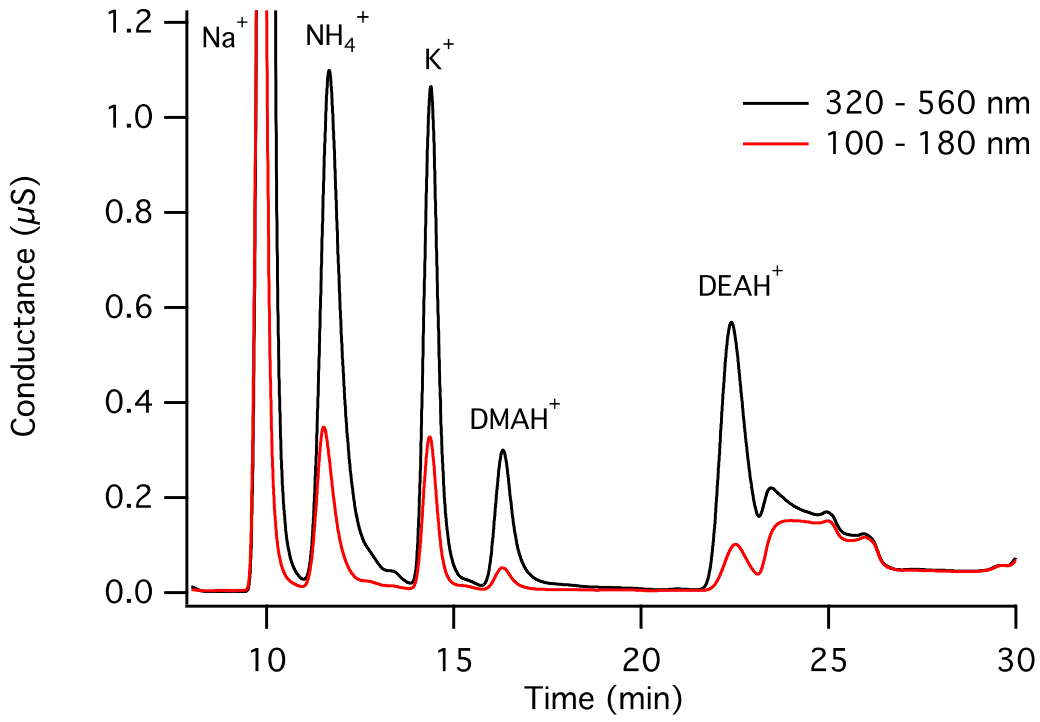

Figure 4. Overlaid chromatograms of MOUDI size-fractionated particle samples collected in St John's on July 6, 2013 during the intrusion of a biomass-burning plume that originated from Northern Labrador and Quebec. The robustness of the separation method for $MMAH^+$, $DMAH^+$ and $DEAH^+$ from the common inorganic cations is demonstrated for the 320-560 nm (Black) and 100-180 nm (Red) size bins.

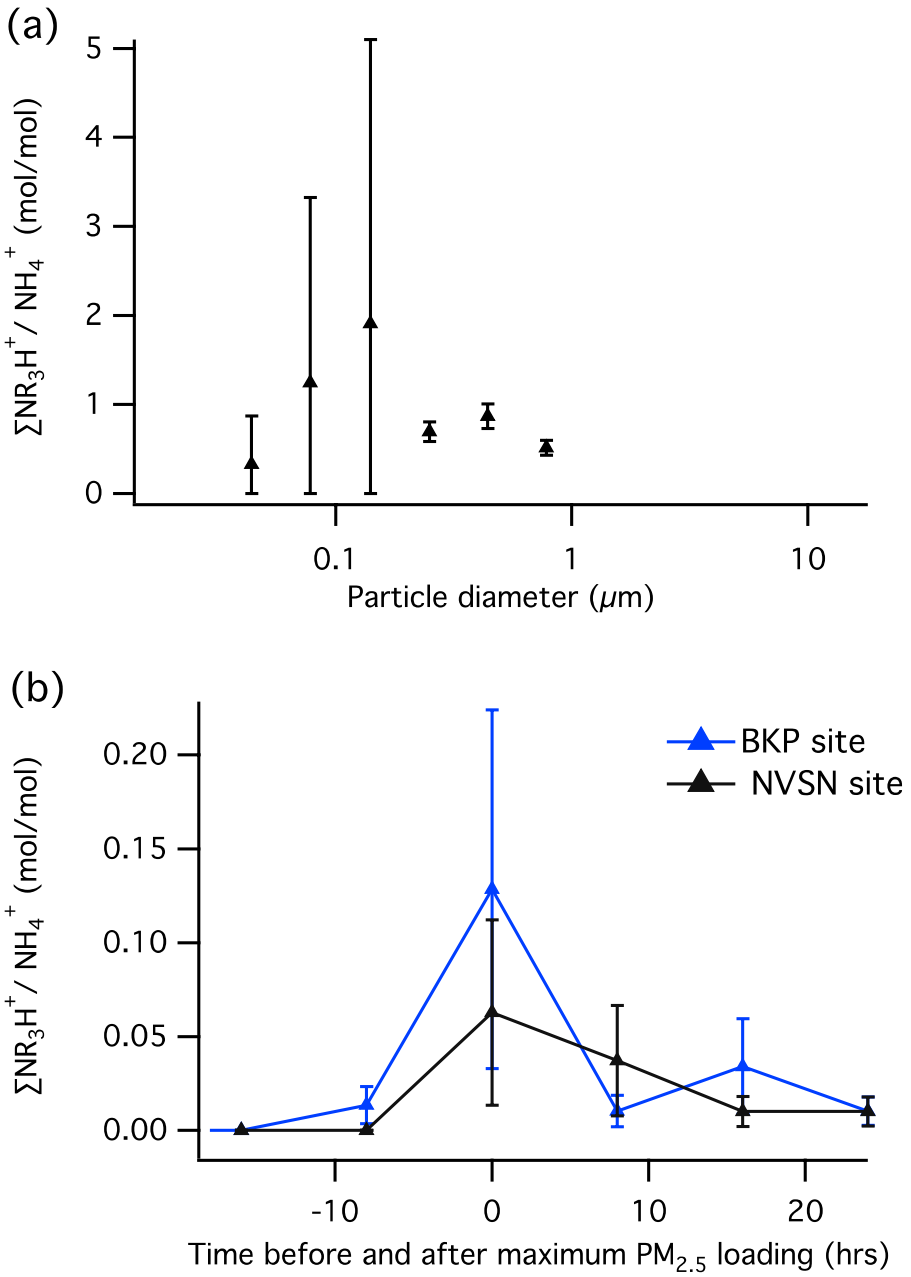

Figure 5. (a) Amines to ammonium ratio in the size-resolved aged biomass-burning sample originating from Quebec and Labrador in the summer of 2013. (b) Amines to ammonium ratio for the Burnaby/Kensington Park (BKP) site and North Vancouver/Second Narrows (NVSN) site in British Columbia during the summer 2015 wildfires. The error bars in the graph represent propagated error in the amine and ammonium quantities resulting from variability in the field blanks and check standards during the analysis of the samples.

Table 1. Separation characteristics and statistics for the CS19 gradient method. The retention time (t_r) ranges for the methyl amines, ethyl amines and inorganic cations were determined using retention time windows from a full calibration. The peak width and resolution were determined using the highest calibration standards amines (500 ng) and inorganic (160 – 520 ng) cations. The t_r range and peak width were back-calculated for $iMPAH^+$, $MPAH^+$, $MBAH^+$, $DABH^+$ and $DAPH^+$ based on the other alkyl amines responses to column degradation. Sensitivity, precision, average LOD, and LOD range were analyzed using multiple calibration standards and blanks (see Section 2.4). Upper and lower range accuracies were assessed using high and low check standards for the alkyl amines (n = 6) and inorganic cations (n = 4). The low check standards were 15 times more concentrated than the lowest calibration standard and the high check standards were 150 times more concentrated.

Cation	t_r (min)	Peak width (min)	Resolution	Sensitivity ($\mu S*min*mol^{-1}$)	Precision % ($\pm$ 1σ)	Upper range accuracy (%)	Lower range accuracy (%)	Average LOD (pg) ($\pm$ 1σ)	LOD range (pg)
Li^+	8.2 – 8.4	0.72	2.68	11.5E08	2	96 $\pm$ 5	82 $\pm$ 4	0.6 $\pm$ 0.2	0.3 - 0.8
Na^+	10.1 -10.3	0.73	1.87	5.04E08	2	95 $\pm$ 4	90 $\pm$ 6	8 $\pm$ 4	4 - 14
NH_4^+	11.8 – 12.1	1.18	0.65/1.85*	2.45E08	4	103 $\pm$ 4	50 $\pm$ 50	22 $\pm$ 17	7 - 47
$MEtAH^+$	12.7 – 13.0	0.99	0.56	2.2E08	---	---	---	3600 (n = 1)	---
$MMAH^+$	13.5 – 13. 8	0.86	1.09	1.42E08	5	98 $\pm$ 6	40 $\pm$ 30	300 $\pm$ 300	30 - 650
K^+	14.7 – 14.8	0.87	1.22	4.14E08	5	99 $\pm$ 2	94 $\pm$ 7	14 $\pm$ 11	4 - 28
$MEAH^+$	15.5 – 15.8	0.79	1.08	0.90E08	7	97 $\pm$ 5	40 $\pm$ 10	500 $\pm$ 200	200 - 700
$DMAH^+$	16.4 – 16.7	0.85	1.64	1.48E08	5	100 $\pm$ 10	30 $\pm$ 30	200 $\pm$ 300	40 - 650
$iMPAH^+$	18.2 – 18.5	0.79	2.24	0.84E08	4	90 $\pm$ 10	80 $\pm$ 80	70 $\pm$ 40	40 - 90
$MPAH^+$	20.1 – 20.4	0.88	1.55	0.62E08	12	88 $\pm$ 4	90 $\pm$ 90	50 $\pm$ 40	20 - 80
$TMAH^+$	21.2 -21.6	1.11	1.48	0.34E08	16	90 $\pm$ 10	30 $\pm$ 20	600 $\pm$ 300	300 - 1200
$DEAH^+$	22.6 – 22.7	1.18	2.51	0.76E08	8	97 $\pm$ 8	50 $\pm$ 30	400 $\pm$ 300	100 - 800
$MBAH^+$	25.3 – 25.6	0.43	3.12	0.62E08	1	80 $\pm$ 20	100 $\pm$ 80	910 $\pm$ 30	890 - 930
$TEAH^+$	27.3 – 27.7	0.95	3.40	0.85E08	12	96 $\pm$ 4	49 $\pm$ 6	800 $\pm$ 400	500 - 1400
Mg^{2+}	30.4 – 30.8	0.79	1.22	12.2E08	1	80 $\pm$ 20	100 $\pm$ 30	2000 $\pm$ 3000	200 - 4000
Ca^{2+}	31.6 – 32.9	1.05	3.16	14.3E08	2	90 $\pm$ 20	120 $\pm$ 20	3700 $\pm$ 200	3500 – 3800
$DABH^+$	36.6 – 36.9	1.48	0.98	4.5E08	---	---	---	1000 (n = 1)	---
$DAPH^+$	38.0 – 38.4	1.60	N/A	4.9E08	---	---	---	180 (n = 1)	---

* = resolution calculated for NH_4^+ and $MMAH^+$

1 --- = insufficient replicates

1