



1 Quantitation of nine alkyl amines in atmospheric samples: 2 Separating structural isomers by ion chromatography

3 Bryan K. Place^{1,2}, Aleya T. Quilty², Robert A. Di Lorenzo¹, Susan E. Ziegler² and Trevor C.
4 VandenBoer²

5 ¹Department of Chemistry, Memorial University, St. John's, NL, Canada

6 ²Department of Earth Sciences, Memorial University, St. John's, NL, Canada

7 Correspondence to: T. C. VandenBoer (tvandenboer@mun.ca)

8 **Abstract:** Amines are important drivers in particle formation and growth, which has implications for Earth's
9 climate. In this work, we developed an ion chromatographic (IC) method using sample cation-exchange
10 preconcentration for separating and quantifying the nine most abundant atmospheric alkyl amines
11 (monomethylamine (MMAH⁺), dimethylamine (DMAH⁺), trimethylamine (TMAH⁺), monoethylamine
12 (MEA⁺), diethylamine (DEAH⁺), triethylamine (TEAH⁺), monopropylamine (MPAH⁺), isomonopropylamine
13 (iMPAH⁺), and monobutylamine (MBAH⁺)). Further, the developed method separates the suite of amines from
14 five common atmospheric inorganic cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺). All 14 cations are greater than 95%
15 baseline resolved and elute in a runtime of 35 minutes. This paper describes the first successful separation of
16 DEAH⁺ and TMAH⁺ by IC and achieves separation between three structural isomer pairs, providing specificity
17 not possible by mass spectrometry. The method detection limits for the alkyl amines are in the picogram per
18 injection range and the method precision ($\pm 1 \sigma$) analyzed over 3 months was within 16 % for all the cations. The
19 performance of the IC method for atmospheric application was tested with biomass-burning (BB) particle
20 extracts collected from two forest fire plumes in Canada with large loadings of K⁺. In extracts of size-resolved
21 BB samples from an aged plume we detected and quantified MMAH⁺, DMAH⁺, TMAH⁺, MEAH⁺, DEAH⁺ and
22 TEAH⁺ in the presence of Na⁺, NH₄⁺, and K⁺ at amines to inorganic cations molar ratios ranging from 1:2 to
23 1:1000. Quantities of DEAH⁺ and DMAH⁺ of 0.2 – 200 ng m⁻³ and 3 – 1200 ng m⁻³, respectively, were present
24 in the extracts and an unprecedented amines to ammonium molar ratio greater than one was observed in particles
25 with diameters spanning 56 – 180 nm. Extracts of respirable fine mode particles (PM_{2.5}) from a summer forest
26 fire in British Columbia in 2015 were found to contain iMPAH⁺, TMAH⁺, DEAH⁺ and TEAH⁺ at molar ratios of
27 1:300 with the dominant cations. The amines to ammonium ratio in a time-series of samples never exceeded 0.15
28 during the sampling of the plume. These results demonstrate the robustness and sensitivity of the developed
29 method when applied to the complex matrix of biomass burning particle samples. The detection of multiple alkyl
30 amines in the analyzed BB samples indicates that this speciation and quantitation approach can be used to
31 constrain BB emission inventories and the biogeochemical cycling of these reduced nitrogen species.

32



1 1 Introduction

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

9 Recent work has shown that organic compounds may contribute considerably to particle nucleation (Ehn et al.,
10 2014; Ortega et al., 2016; Tröstl et al., 2016; Willis et al., 2016). In particular, the need to measure and quantify
11 gaseous atmospheric alkyl amines has gained interest because of their exceptional ability to partake in
12 atmospheric particle formation. Multiple laboratory investigations have shown the nucleation potential of
13 methyl- and ethyl-substituted amines through gaseous acid-base chemistry reactions (Almeida et al., 2013;
14 Angelino et al., 2001; Berndt et al., 2010; Berndt et al., 2014; Bzdek et al., 2010; Bzdek et al., 2011; Erupe et al.,
15 2011; Jen et al., 2016; Lloyd et al., 2009; Murphy et al., 2007; Qiu et al., 2011; Silva et al., 2008; Smith et al.,
16 2010; Wang et al., 2010a; Wang et al., 2010b; Yu et al., 2012; Zhao et al., 2011; Zollner et al., 2012).
17 Theoretical calculations and studies have also found that amines have a high disposition to form atmospheric
18 nanoparticles (Barsanti et al., 2009; Kurtén et al., 2008; Loukonen et al., 2014; Loukonen et al., 2010; Nadykto
19 et al., 2015; Ortega et al., 2012). From these works, alkyl amines have been shown to form clusters via
20 neutralization reactions at rates up to three orders of magnitude greater than ammonia (Almeida et al., 2013;
21 Berndt et al., 2010; Bzdek et al., 2011; Kurtén et al., 2008; Loukonen et al., 2010; Nadykto et al., 2015), and
22 readily exchange with ammonia in already formed ammonium-bisulfate molecular clusters (Bzdek et al., 2010;
23 Lloyd et al., 2009; Qiu et al., 2011). These studies suggest that alkyl amines can compete with ammonia to form
24 particles even though they have been quantified at mixing ratios that are three or more orders of magnitude less
25 in the atmosphere (Chang et al., 2003; Ge et al., 2011; Schade and Crutzen, 1995). Atmospheric measurements
26 made during new particle formation events have further confirmed that alkyl amines participate in particle
27 formation at ambient concentrations and that these species may be present in most atmospheric particles
28 (Creamean et al., 2011; Dall'Osto et al., 2012; Hodshire et al., 2016; Kulmala et al., 2013; Kürten et al., 2016;
29 Ruiz-Jimenez et al., 2012; Smith et al., 2010; Tao et al., 2016).

30 Alkyl amine emissions to the atmosphere arise from both natural and anthropogenic sources (Ge et al., 2011).
31 Short-chain alkyl amines such as the methylated and ethylated amines are predominantly reported in emission
32 inventories and measurements show that atmospheric alkyl amines are prevalent in ambient air across the globe,
33 especially in the particle phase (Ge et al., 2011). For example, methyl and ethyl amines were measured by an
34 aerosol time-of-flight mass spectrometer (ATOFMS) at both rural and urban sites all across Europe (Healy et al.,
35 2015). In particular, these amines have been measured in substantial quantities near animal husbandry operations
36 (Kuhn et al., 2011; Lunn and Van de Vyver, 1977; Rabaud et al., 2003; Schade and Crutzen, 1995; Sorooshian et
37 al., 2008), fisheries (Seo et al., 2011), and sewage-waste treatment facilities (Leach et al., 1999). Other
38 anthropogenic sources include tobacco smoke (Schmeltz and Hoffmann, 1977), automobiles (Cadle and Mulawa,
39 1980) and cooking (Rogge et al., 1991; Schauer et al., 1999). The ocean is estimated to be the largest natural



1 source of alkyl amines, where they are released as degradation products (Ge et al., 2011; Gibb et al., 1999a; Gibb
2 et al., 1999b). Aliphatic amines have also been detected in smoldering stage biomass burning plumes and are
3 estimated to represent a quarter of global methylated amine emissions (Lobert et al., 1990; Schade and Crutzen,
4 1995).

5 Real-time speciation and quantitation of atmospheric amines in the particle and gas phase can be difficult
6 because alkyl amines are commonly found at or below parts per trillion by volume (pptv) mixing ratios in the
7 atmosphere (Ge et al., 2011). Furthermore, the atmospheric matrix can be complex and ubiquitous atmospheric
8 species can cause matrix effects for various analytical methods. Being able to chromatographically resolve
9 ammonium from the alkyl amines represents a major challenge when sampling the gas phase, since quantities of
10 ammonia are often orders of magnitude greater than the alkyl amines (Chang et al., 2003; Ge et al., 2011; Schade
11 and Crutzen, 1995). Quantifying amines in particle samples, however, presents a greater challenge due to
12 possible ionic interferences from sodium, potassium, ammonium, magnesium and calcium concentrations
13 dependent on the particle source characteristics and the measurement location (Ault et al., 2013; Kovac et al.,
14 2013; Sobanska et al., 2012; Sun et al., 2006). Particles also frequently contain complex high molecular weight
15 organic compounds, which can cause further matrix effects during separation or direct analysis (Di Lorenzo and
16 Young, 2016; Saleh et al., 2014).

17 Achieving full speciation of alkyl amines is important because the nucleation potential of amines has been
18 shown to increase with basicity (Berndt et al., 2014; Kurtén et al., 2008; Yu et al., 2012). For example, although
19 monopropylamine (MPA) and trimethylamine (TMA) are structural isomers of one another, MPA is likely to be
20 a more potent nucleator due to its stronger basicity. The suite of alkyl amines that have been commonly detected
21 in the atmosphere contains multiple structural isomers (e.g. monoethylamine (MEA) and dimethylamine
22 (DMA)), making it difficult to speciate the amines using mass spectrometry (MS) without prior separation.
23 Multiple field investigations sampling atmospheric particles using MS analysis have reported the detection of
24 amine ion peaks but have been unable to assign them to a specific amine (Aiken et al., 2009; Denkenberger et
25 al., 2007; Silva et al., 2008; Yao et al., 2016). Derivatization of alkyl amines coupled with HPLC or GC
26 separation has been reported to aid in separation and quantitation of amine species (Akyüz, 2007; Huang et al.,
27 2009; Fournier et al., 2008; Key et al., 2011; Possanzini and Di Palo, 1990). However, these approaches are time
28 consuming, require optimization of reaction conditions, and employ phase separations, which use large
29 quantities of consumables, reagents, and solvents. Capillary electrophoresis has also been employed for aqueous
30 amine separation, however in either case derivatization was required (Dabek-Zlotorzynska and Maruszak, 1998)
31 or the separation of atmospherically relevant cations was not addressed (Fekete et al., 2006). The use of ion
32 chromatography to directly separate and quantify atmospheric alkyl amines has been demonstrated (Chang et al.,
33 2003; Dawson et al., 2014; Erupe et al., 2010; Huang et al., 2014; Li et al., 2009; Murphy et al., 2007;
34 VandenBoer et al., 2012; Verrielle et al., 2012), yet the established IC methods struggle with coeluting cations
35 (Huang et al., 2014; Murphy et al., 2007; VandenBoer et al., Verrielle et al., 2012) or they do not address a full
36 suite of atmospherically relevant alkyl amines and inorganic cations (Chang et al., 2003; Dawson et al., 2014;
37 Erupe et al., 2010; Li et al., 2009).

38 In this work we demonstrate the separation and quantitation of the nine most abundant atmospheric alkyl amines
39 and six inorganic cations through the use of ion chromatography. We show i) the separation method approach to



1 maximizing peak resolution in the context of real-time atmospheric sampling and analysis; ii) the effects of
2 column temperature on amine coelution; iii) the method precisions, accuracies, sensitivities and limits of
3 detection (LODs) for all alkyl amine and inorganic cations; and iv) application of the method to the complex
4 matrix of atmospheric biomass burning particle extracts to demonstrate method sensitivity and robustness.

5

6 **2 Methods**

7 **2.1 Chemicals and materials**

8 Inorganic cation stock solutions were prepared from a primary mixed cation standard concentrate (Dionex six-
9 cation II, Lot #150326, Thermo Scientific, Waltham, MA, USA) consisting of Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}
10 chloride salts. Alkyl amines (MMA (40% w/w), DMA (40% w/w), TMA (25 % w/w), MEA (70 % w/w), DEA
11 (>99% w/w), TEA (>99% w/w), MPA ($\geq 99\%$ w/w), iMPA ($\geq 99\%$ w/w) and MBA (99.5% w/w)) were
12 purchased from Sigma-Aldrich (Oakville, ON, Canada). Calibration standards were prepared by serial dilution in
13 18.2 M Ω ultrapure deionized water (Barnstead Nanopure Infinity, Thermo Scientific, Waltham, MA, USA).
14 Since these alkyl amine species will largely be protonated in solution we will denote each of these species in
15 their cationic form (i.e. NR_3H^+) henceforth when referring to the condensed phase.

16 **2.2 Ion Chromatography**

17 A ThermoScientific ICS-2100 Ion Chromatography System (Thermo Scientific, Mississauga, ON, Canada)
18 utilizing Reagent-Free Ion Chromatography (RFICTM) components was used to develop the separation of the
19 selected amines and inorganic cations. A ThermoScientific methanesulfonic acid (MSA) eluent generator
20 cartridge (EGC) III (P/N: 074535) was used in conjunction with an ultrapure deionized water reservoir to supply
21 the eluent mobile phase with H_3O^+ ions as the competing exchanger. A continuously regenerated trap column
22 (CR-CTC II, P/N: 066262) was attached to the eluent cartridge in series to remove cation contaminants from the
23 eluent prior to analysis, thereby reducing method detection limits. Samples were preconcentrated on a cation
24 exchange column (TCC-ULP1; 5 x 23 mm, P/N: 063783) using a ThermoScientific AS-DV autosampler to
25 deliver the desired volume. Concentrated analytes were separated using ThermoScientific CG19 (4 x 50 mm,
26 P/N: 076027) and CS19 (4 x 250 mm, P/N: 076026) guard and analytical cation-exchange columns. The column
27 effluent was passed through a suppressor operating in recycle mode (CSRS 300, 4 mm) prior to detection of the
28 analytes using a DS6 heated conductivity cell thermostated at 30 °C. The eluent conductance was recorded at 5
29 Hz and the chromatographic peaks were analyzed using the Chromeleon 7 software package. A
30 ThermoScientific CG15 (4 x 50 mm, P/N: 052200) guard column was added inline later to attempt further
31 improvement in analyte separation.

32 **2.3 CS19 separation optimization**

33 The gradient program used for the separation of methylamines, ethylamines, other alkyl amines and six inorganic
34 cations on the CS19 cation-exchange column was optimized by combining analyte separation parameters from
35 multiple isocratic elution runs at varying MSA concentrations (1 - 16 mM) and mobile phase flow rates (0.75 -



1 1.25 ml min⁻¹) at a column temperature of 30 °C. Maximum peak resolution was optimized using an eluent
2 gradient program and the column temperature was increased to resolve co-eluting peaks (see Sect. 3.1.1).

3 Optimal separation of a suite of 15 cations was achieved using a mobile phase flow rate of 1.25 ml min⁻¹ and a
4 column temperature of 55 °C. The eluent gradient program is as follows: an initial MSA concentration of 1 mM
5 held for 20 minutes, a step increase to 4 mM followed immediately by an exponential ramp to 10 mM over 10
6 minutes (Chromleon curve factor = 7). The final concentration of 10 mM was held for an additional 5 minutes,
7 yielding a total run time of 35 minutes. The IC was returned to initial conditions and re-equilibrated as the next
8 sample was prepared for injection by the AS-DV.

9 **2.4 Quality Assurance and Quality Control**

10 Standards were prepared using Class A Corning polymethylpentene 50 (± 0.06) ml volumetric flasks that were
11 rinsed 4 times with ethanol and 8 times with ultrapure water prior to use. Standards were stored in 60 ml brown
12 Nalgene polypropylene bottles that were pre-cleaned in a 10 % HCl bath, followed by 8 sequential rinses with
13 distilled and ultrapure water, respectively. The mixed amine standards and mixed inorganic cation standards
14 were prepared separately and each cation standard set was composed of five calibration standards and two check
15 standards. Ranges and related parameters are denoted by mass injected, as the preconcentration column negates
16 the effect of volume. All amine calibration standards had a mass calibration range of 5-500 ng. The mass range
17 for each inorganic cation calibration is as follows: Li⁺ (0.82-160 ng), Na⁺ (7.8-160 ng), NH₄⁺ (8.4-170 ng), K⁺
18 (26-520 ng), Mg²⁺ (6.4-130 ng), and Ca²⁺ (18-360 ng).

19 Method precision for each methyl and ethyl amine cation was determined using standard calibration curves (n =
20 9) injected across five different days spanning three months. The precision for the propyl and butyl amines was
21 determined using two standard calibration curves analyzed over one month. Method precision for Li⁺, Na⁺, NH₄⁺
22 and K⁺ was assessed using calibrations (n = 6) from three separate days spanning two months. Precision for each
23 cation was calculated using the standard deviation (σ) in the slope of the linear calibration curves. Check
24 standards positioned between the two highest and the two lowest calibration standards for each cation were used
25 to determine method accuracy across the calibration range. The low check standard was 15 times greater than the
26 lowest standard and the high check standard was 150 times higher than the lowest standard. Accuracy was
27 determined by the percent relative error between the known and calculated concentrations of the check
28 standards. The limits of detection (LOD) for the singly-charged inorganic cations (n = 4) and methyl and ethyl
29 amines (n = 5) were determined using calibration standard and calibration blank chromatograms from three or
30 more separate days. The LODs for the propyl and butyl amines were determined using calibration standard and
31 blank chromatograms from two separate days. The LODs are reported as concentrations resulting in a signal
32 peak height to background noise ratio of three. The background noise was determined using the standard
33 deviation of the conductance signal that fell within the retention time window for each analyte in their respective
34 calibration blank chromatograms. Discussion of the analytical performance of the CS19 gradient program is
35 presented in Sect. 3.1.2. and divalent cations in Sect. 3.1.5.



1 2.5 Size-resolved BB sample analysis

2 A size-resolved particle sample from a BB plume was collected using a NanoMOUDI II (Nano micro-orifice
3 uniform-deposit impactor, model 122-R, MSP Corp., Shoreview, MN, USA) in St. John's, Newfoundland on
4 July 6, 2013. Satellite images of the plume smoke, HYSPLIT back trajectories, as well as, measured PM_{2.5}
5 concentrations reported by Environment and Climate Change Canada (Di Lorenzo and Young, 2016) indicate
6 that these plumes originated from boreal forest fires in northern Quebec and Labrador on July 4, 2013 and
7 travelled via Labrador and the Gulf of St. Lawrence to the sampling site. The nanoMOUDI samples were
8 collected on 13 aluminum substrate stages in to size-resolved bins of atmospheric particles with a diameter range
9 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
10 of each aluminum substrate (10 % of the total substrate area) was extracted into a glass vial with 5 mL ultrapure
11 deionized water by sonication (VWR Scientific Products/Aquasonic 150HT, Ultrasonic Water Bath) for 40
12 minutes. The extracts were filtered using a 0.2 µm polytetrafluoroethylene (PTFE) filter and stored in
13 polypropylene vials at 4 °C prior to analysis by IC within 24 hours.

14 2.6 BC fire sample analysis

15 The full method for the collection and extraction of BB particle samples collected during July wildfires in British
16 Columbia is detailed in Di Lorenzo et al. (2016). Briefly, PM_{2.5} samples were collected at two sites
17 approximately 100 kilometers east of the biomass-burning location. The first site was located in
18 Burnaby/Kensington Park (BKP) and the second was in North Vancouver/Second Narrows (NVSN). The
19 particle samples were collected using real-time beta attenuation particle monitors (5030 SHARP Monitor at the
20 BKP site, 5030i SHARP monitor at the NVSN site, Thermo Fisher Scientific, Waltham, MA, USA) at a 16.67 L
21 min⁻¹ flow rate in 8-hour intervals. Particles were collected on glass microfiber filter tape and stored at -20 °C
22 until extracted. Approximately 37% of each filter spot area was placed into a polypropylene vial with 10 ml of
23 deionized water, and sonicated for 40 minutes. The extracts were filtered with PTFE syringe filters (3 mm
24 diameter, 0.2 µm pore size, VWR International, Radnor, Pennsylvania, USA) and diluted by a factor of five with
25 ultrapure deionized water before being injected on the IC.

26

27 3 Results and Discussion

28 3.1 Analytical method performance of CS19 cation exchange column

29 3.1.1 Separation approach and optimization of parameters

30 Our approach to separation involved injecting the highest mixed inorganic cation and mixed amine standards for
31 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)
32 while systematically increasing the isocratic eluent concentration (4 mM - 16 mM). The quality of each isocratic
33 method was assessed by calculating the peak-to-peak resolution (R_s) using the retention time (t_R) and peak width
34 at base (w) determined from the highest standard for each pair of cations following Eq. (1):



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

2 Using the upper limit of the expected working range for all analytes therefore provides a lower limit on peak-to-
 3 peak resolution between these species. The peak-to-peak resolutions of the isocratic methods run using a 0.75 ml
 4 min⁻¹ and 1.25 ml min⁻¹ flow rate for the selected inorganic and alkyl amine cations are presented in Fig. S1 and
 5 S2. Peak-to-peak resolution between all peaks increased as the mobile phase ionic strength was lowered when
 6 the flow rate was held constant. This is in agreement with Eq. (2), the fundamental resolution equation, which
 7 describes peak-to-peak resolution in terms of an efficiency factor (N), retention factor (k), and a selectivity factor
 8 (α).

$$9 \quad R = \left(\frac{\sqrt{N}}{4}\right) \left(\frac{k}{k+1}\right) \left(\frac{\alpha-1}{\alpha}\right), \quad (2)$$

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

$$16 \quad H = A + \frac{B}{\mu} + C\mu, \quad (3)$$

17 Figures S1 and S2 show no loss in peak resolution when using a higher flow rate (1.25 ml min⁻¹ vs 0.75 ml min⁻¹).
 18 To confirm that there was no loss in efficiency at higher flows, Van Deemter plots were created, using
 19 MMAH⁺ and TEAH⁺ as representative early and late-eluting species, by plotting theoretical plate height versus
 20 flow rate (Fig. S3). To do this, the theoretical plate heights described in Eq. (3) were calculated using Eq. (4),
 21 which relates H to column length (L), t_R and w. The A, B and C terms of Eq. (3) were then determined by
 22 solving a system of equations using the calculated H values for MMAH⁺ and TEAH⁺ at three isocratic flow
 23 rates.

$$24 \quad \frac{L}{H} = 16 \left(\frac{t_R}{w}\right)^2, \quad (4)$$

25 The Van-Deemter plots for MMAH⁺ and TEAH⁺ show no sacrifice in resolution when operating at higher flow
 26 rates and low eluent concentrations. The resolution between Mg²⁺ and Ca²⁺ as well as between TMAH⁺ and
 27 TEAH⁺ improved at the higher flow rate for all isocratic eluent concentrations. This was due to a decrease in
 28 peak width from diffusion band broadening. Furthermore, there was little to no sacrifice in resolution for all
 29 other cation peak pairs when operating at a higher flow rate. Of particular note, utilizing a 4 mM MSA isocratic
 30 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
 31 shorter, which improves the applicability of IC for near-real-time analysis of hourly to bi-hourly atmospheric
 32 sample collection timescales. A shorter run time also improves the method throughput capacity for offline
 33 analyses and reduces total eluent consumption. For these reasons, the faster flow rate was selected in designing
 34 and optimizing a gradient program. Further isocratic methods using lower MSA concentrations (1 mM and 2
 35 mM) were run at a 1.25 ml min⁻¹ flow rate to quantify values of peak-to-peak resolution for the inorganic cations



1 and alkyl amines before approaching a gradient method (Fig. S1 and S2). An increase in resolution greater than
2 one was observed for all analyte pairs aside from DEAH⁺/TMAH⁺ when using a 1 mM MSA eluent
3 concentration.

4 All gradient methods that were tested started with a 1 mM hold, followed by a step-wise increase and/or ramp to
5 higher eluent concentrations at a column temperature of 30 °C. By combining the best isocratic separations for
6 various pairs of cation analytes sequentially, iterative modifications were used to improve resolution based on
7 Eq. (1-3). The best separation method was selected from amongst the iterations and the column temperature was
8 then systematically increased to investigate if further improvement in peak-to-peak resolution was possible.
9 Temperature effects on separation efficiency in ion chromatography are thermodynamically complex (Hatsis and
10 Lucy, 2001; Kulis, K., 2004; Rey and Pohl, 1996), but typically result in increased peak resolution because of
11 improvements in mobile phase diffusivity, which increases the efficiency from Eq. (2). It has been demonstrated
12 that using higher temperatures can replicate the separation effects observed when adding an organic mobile
13 phase modifier (Hatsis and Lucy, 2001; Rey and Pohl, 1996). Figures 1a and 1b show gradient separations at 30
14 °C and 55 °C respectively. At 30 °C, K⁺ and DMAH⁺ overlap considerably ($R_S = 0.45$) and DEAH⁺ and TMAH⁺
15 coelute. By increasing the column temperature to 55 °C, the extent of peak overlap between K⁺ and neighboring
16 alkyl amine cations is noticeably reduced ($R_S > 1$) and DEAH⁺ and TMAH⁺ are increasingly well resolved ($R_S =$
17 1.48). The effect of temperature on the separation of the alkyl amines is demonstrated in Fig. 2, where the
18 separation of DEAH⁺ with TMAH⁺ is achieved above 50 °C. The temperature increase also results in lower
19 resolution between DMAH⁺ and MEAH⁺ from $R_S = 1.57$ to $R_S = 1.08$. A column temperature of 55 °C produced
20 peak-to-peak resolutions greater than a value of one between all alkyl amine cations in the final gradient method,
21 giving a 95 % separation between our target analytes and expected atmospheric interferences in the condensed
22 phase. The peak-to-peak resolutions are summarized in Table 1. These represent a lower-limit in peak resolution
23 since they were calculated using peak parameters at the upper limit of the working range, which was determined
24 based on typical mixing ratios or mass loadings expected for the analysis of atmospheric samples containing
25 these analytes.

26 The separation method produced in this work is able to overcome previously reported IC coelution difficulties
27 between DEAH⁺ and TMAH⁺ and between MEAH⁺ and DMAH⁺ (VandenBoer et al., 2012; Verrielle et al.,
28 2011). Both DMA and TMA have been identified as dominant amines in emission studies, so it is important to
29 achieve accurate and specific quantitation of both species in gas and particulate atmospheric samples (Facchini et
30 al., 2008; Kuwata et al., 1983; Müller et al., 2009; Van Neste and Duce, 1987). Multiple field campaigns have
31 detected large quantities of MEA and DEA in ambient air as well (Facchini et al., 2008; Müller et al., 2009;
32 Sorooshian et al., 2009; Yang et al., 2005; Yang et al., 2004). In some cases clean up steps have been used to
33 alleviate IC interferences from common atmospheric cation species in the quantitation of amines despite the fact
34 that an 85% evaporation loss of the amines, in addition to the extra sample handling, was reported when using a
35 solid phase extraction clean up (Huang et al., 2014). The CS19 IC method reported here is able to separate the
36 most common atmospheric inorganic cations in addition to the six most common atmospheric amines. It can be
37 easily applied to water-soluble atmospheric gas and particulate samples since they can be directly analyzed -
38 without coelution or a clean-up step - with separation times of similar duration to many previously reported



1 methods, including those employing an online IC method (Huang et al., 2014; Murphy et al., 2007; VandenBoer
2 et al., 2012; Verrielle et al., 2011).

3 3.1.2 Method performance and comparison

4 The performance statistics of the CS19 gradient method for each cation are summarized in Table 1. The method
5 shows high reproducibility, with method precisions better than 10 % for most analytes. The larger variability in
6 the TMAH⁺ and TEAH⁺ calibration curves (± 16 % and ± 11 % respectively) over time could likely be driven by
7 their lower Henry's Law constants (K_H) in water (Christie and Crisp, 1967), resulting in volatilization losses
8 from standards. Concurrently, this variability could be driven by partitioning losses along the flow path,
9 particularly when the tri-substituted amines reach the suppressor, which is not temperature-controlled. In future
10 investigations it may be worthwhile to acidify the standards to ensure the amines are maintained in their charged
11 form in the aqueous phase. Alternatively, to combat losses to neutral forms, use of a Salt Converter suppressor
12 accessory (ThermoScientific, SC-CSRS 300, P/N: 067530), which keeps weak electrolytes in a separated sample
13 fully protonated prior to their conductance measurement, may also aid in increasing long-term precision.

14 The limits of detection (LODs) for each analyte are reported in Table 1 as both a range and as the average LOD
15 ($\pm 1\sigma$). The LODs are reported in this manner to reflect the high day-to-day variability in the calculated LODs.
16 This variability may be driven by i) the purity of the deionized water used for eluent generation; ii) instrumental
17 baseline noise and trace contamination on the day of analysis; and iii) quality of labware cleaning prior to
18 preparation of calibration blanks. Outliers in the LOD dataset were found to result from trace contamination of
19 analytical labware, sampling vials, or from systematic errors made in the preparation of standards or injection of
20 samples on the IC (e.g. leaking autosampler caps, failing retention of concentrator column). The Grubb's test
21 was performed using a 95% confidence interval to statistically identify outliers from LOD data sets. Calculated
22 detection limits were determined to lie in the picogram per injection range for all analytes. The LODs for the
23 inorganic cations were 10 to 100 times lower than those of the alkyl amines. Our method shows high accuracy in
24 the upper range of the calibrations for the analytes, with accuracies ranging from 94 – 103 %. The accuracy was
25 much lower for each alkyl amine cation at the low end of the calibration range at concentrations approximately
26 1.5 times the LOQ. Quantitation near the method LOQ was more sensitive to small integration changes, which
27 affected the calculated peak area, even when performing integrations manually, and this resulted in greater
28 method error. This is a drawback inherent to IC since wide analyte peaks are a result of persistently large
29 stationary phase particle sizes, causing band broadening via longer flow paths and increased diffusion during
30 separation (i.e. the A and B terms in Eq. (3)). The low alkyl amine accuracies may also be driven by their air-
31 water partitioning properties, which could result in losses during sample handling and during sample injection.
32 The low-range accuracies for all inorganic cations, with the exception of ammonium, were still high (80 – 94%)
33 because concentrations were not near the limit of quantitation for these analytes. The low check standard
34 accuracy for ammonium is likely due to the similar issues discussed above for the amines.

35 Previous IC method precisions reported for use in quantifying the six atmospheric methyl and ethyl amines range
36 from 0.4 to 17.2 %, which are comparable to our method (Table 2; Chang et al., 2003; Dawson et al., 2014;
37 Erupe et al., 2010; Huang et al., 2014; Li et al., 2009; VandenBoer et al., 2012; Verrielle et al., 2012;). Our
38 method shows greater average variability than other methods due to our numerous assessments (n = 9) over



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

14 Employing a method that is capable of quantifying amines at these very low mixing ratios is valuable since
15 recent work has shown that ppqv concentrations of gaseous amines can lead to particle growth (Almeida et al.,
16 2013). If our method were applied to online atmospheric ambient sampling of gases or particles the method
17 could be used to detect amines at sub-pptv mixing ratios. For example, a detectable signal for 100 ppqv mixing
18 ratios could be attained by sampling through a bubbler, filter, or denuder at a low flow rate of 3 L min^{-1} for 1 –
19 10 hours, depending on the amine. Sampling may be possible to shorten to an hourly timescale to detect sub-pptv
20 mixing ratios of atmospheric amines if the method is interfaced with a high sensitivity MS detector. Verrielle et
21 al. (2014) observed a 5 – 30 fold improvement in method detection limits when interfacing their IC method with
22 a MS detector.

23 3.1.3 Expanded amine catalogue for other common atmospheric species

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



1 method precisions for iMPAH⁺, MPAH⁺ and MBAH⁺ determined from two standard calibration injections
2 ranged from 1.3 – 11.9 %. The reported average LODs for both propyl amines are the lowest of the alkyl amines,
3 while MBAH⁺ has the highest method LOD because it elutes in a region with a high background due to the step
4 change in eluent composition not being completely suppressed. The method accuracies for the three additional
5 amines assessed by both the high and low check standards were within 80 % for all analytes. However, the large
6 standard deviations in the accuracies for all low check standards highlights the challenge of method
7 reproducibility for these analytes near the limit of quantitation.

8 **3.1.4 Method development with the addition of an inline CG15 guard column**

9 As mentioned previously, IC methods in the literature have been unable to separate potassium from the methyl
10 and ethyl amines (Huang et al., 2014; VandenBoer et al., 2012) and in our current method potassium has slight
11 overlap with MMAH⁺ ($R_s = 1.09$). We attempted to reduce peak overlap between potassium and the alkyl
12 amines by adding a crown ether-functionalized CG15 guard column, which has increased selectivity for
13 potassium, after the CG19/CS19 columns. The addition of the CG15 column resulted in an increased retention
14 time for potassium of 13 minutes, as expected by using a stationary phase with higher selectivity. The best
15 separation achieved using the additional guard column is shown in Fig. 3b, where K⁺ still elutes within the alkyl
16 amine retention region. The gradient method used to achieve the separation used a flow rate of 1 ml min⁻¹, a
17 column temperature of 55 °C, and held a 1 mM MSA concentration for the first 30 minutes. The eluent
18 concentration was step increased to 4 mM followed immediately by an exponential ramp to 10 mM over 20
19 minutes (Chromleon curve factor = 7). The final concentration of 10 mM is held for an additional 15 minutes,
20 yielding a total run time of 65 minutes. Even when holding the initial MSA concentration at 1 mM for 50
21 minutes, the separation was unable to fully resolve the alkyl amine peaks. An increase in retentivity for K⁺ and
22 NH₄⁺ as well as many of the alkyl amines, indicated that the crown ether functionality was not selective for K⁺ in
23 this suite of analytes. With the addition of an organic modifier to the mobile phase or the ability to decrease
24 column temperature, this increase in selectivity from the CG15 column might be harnessed to produce a better
25 separation. However, due to the limitations of the ICS-2100 system using RFIC we were unable to investigate
26 these parameters. Furthermore, although a passable separation may be achieved when using a run time greater
27 than 60 minutes, this would not be as applicable to online analyses as the CG/CS19 method developed without
28 the addition of the CG15 column. A stationary phase similar to that of the CG/CS19 columns, but with some of
29 this crown ether selectivity could potentially yield better results than those presented here for the analysis of
30 atmospheric samples containing large quantities of K⁺ and amines, such as biomass burning particulate samples.

31 **3.1.5 Analytical column stability**

32 Over the course of five months, peak retention times noticeably decreased for all analytes. This is consistent with
33 what has been previously reported in the literature when hundreds to thousands of injections have been run
34 through an IC column (VandenBoer et al., 2012). However, this may also be a result of column degradation from
35 operating the CS19 column at a temperature higher than that recommended by the manufacturers. If this is the
36 case, in order to prolong column life it is recommended to run the gradient method at a temperature of 30 °C
37 when conducting offline analysis of samples. If there is an indication that DEAH⁺ or TMAH⁺ are present in the
38 analyzed sample, the column temperature can be increased to separate and quantify the two species. The column



1 temperature may also be increased to better resolve DMAH⁺ with K⁺ if high concentrations of either species are
2 present.

3 During the course of method development peak loss of magnesium and calcium was also observed. Cleanup and
4 eventual replacement of all IC components one by one was not able to resolve this issue. Since retention of
5 magnesium and calcium on this column or others (e.g. CS12A) never returned, method statistics were calculated
6 for the two cations using the limited calibrations and chromatograms prior to the occurrence of this system issue.
7 Accuracy for both cations was unable to be assessed before peak loss occurred. Though loss of magnesium and
8 calcium during the investigation was unfortunate and unexplained, it did not influence the separation of the
9 analytes of interest, and the method was still successfully applied to real samples after the loss had occurred.

10 3.2 Biomass-burning particle analysis and discussion

11 3.2.1 Size-resolved alkyl amines in particles from an aged biomass-burning plume

12 Biomass-burning particles often contain a complex mixture of water-soluble ions, organics, elemental carbon
13 and other insoluble components, making them nonpareil for testing the robustness of an atmospheric
14 measurement technique. Ions such as NH₄⁺ and K⁺ are consistently detected in biomass burning plumes,
15 regardless of sampling location as they are well characterized as being co-emitted species (Capes et al., 2008;
16 Hudson et al., 2004; Pósfai et al., 2003). Particles released during forest fires have also been shown to contain
17 highly oxidized large molecular weight organics (Di Lorenzo and Young, 2016; Saleh et al., 2014). We tested
18 the robustness of our method on water-extracted aged biomass-burning particle samples collected by a cascade
19 impactor in St. John's, Canada. An overlaid chromatogram of two different size-resolved particle samples (100 -
20 180 nm and 320 - 560 nm) shows the presence of MMAH⁺, DMAH⁺ and DEAH⁺ in the aged biomass burning
21 samples with complete separation from K⁺, NH₄⁺ and Na⁺ (Fig. 4). The maximum mass loadings for MMAH⁺,
22 DMAH⁺ and DEAH⁺ were found in particles with diameters (D_p) 320 - 560 nm and were 11 ± 3 ng m⁻³, 208 ± 4
23 ng m⁻³, 1300 ± 200 ng m⁻³, respectively (Table S1). TMAH⁺, MEAH⁺ and TEAH⁺ peaks were also detected in
24 the BB size-resolved particle extracts. TMAH⁺ and TEAH⁺ reached mass loadings of 5 ± 3 ng m⁻² and 4 ± 2 ng
25 m⁻³ respectively, while MEAH⁺ never exceeded a concentration of 1 ng m⁻³ in any size-resolved particle fraction
26 (Table S1). Lobert et al (1990) reported detecting C₁ - C₅ aliphatic amines from controlled biomass-burning
27 experiments, which is consistent with our findings. BB derived amines were also identified during the 2007 San
28 Diego forest fires (Zauscher et al., 2013) and primary amines were observed to make up approximately 6% by
29 mass of organic content from an aged biomass burning particle sample in British Columbia (Takahama et al.,
30 2011). However, few studies have addressed the speciation and quantitation of alkyl amines emitted from
31 biomass-burning events. Schade and Crutzen (1995) estimated the emission rates for MMA, DMA, TMA and
32 MEA from biomass burning sources based on controlled burn experiments, but do not include a BB emission
33 rate for DEA or TEA. These emission inventories are yet to include emission rates from atmospheric BB
34 measurements (Lobert et al., 1990; Schade and Crutzen, 1995).

35 In Figure 5a we show the molar ratio of the sum of the methyl and ethyl amines to ammonia (which is
36 considered to be the main atmospheric base), as a function of the size-resolved particles collected. The summed
37 amine moles exceeded ammonium from 100 to 560 nm, ranged from 0.5 to 1.9 in the fine mode (PM₁), with an



1 average ratio of 0.92 in PM_1 calculated using nanoMOUDI bins up to this nominal cutoff. Quantities of NH_4^+
2 were below the detection limit, above 1 μm , yielding no values for the ratio. The large error bars in the ratios are
3 driven by the low molar quantities of ammonium in the samples as well as a higher than normal variability in the
4 method blank error on the day of analysis. For these reasons this method blank error was assigned to the size-
5 resolved samples in place of the NH_4^+ error driven by the method precision and accuracy detailed in Table 1. To
6 our knowledge, this is the first time that an amines to ammonium ratio greater than one has been reported in any
7 size resolved fraction of atmospheric particles. An amines to ammonium ratio of approximately 0.05 was
8 reported by Gibb et al. (1999b) but all other reported ratios have been below 0.05 (Ge et al., 2011). These high
9 ratios we observed can be attributed to large quantities of $DEAH^+$ and $DMAH^+$. $MMAH^+$ was found to be in
10 molar quantities 100 times less than that of ammonium while $TMAH^+$, MEA^+ and $TEAH^+$ were found to be in
11 molar quantities 1000 to 10000 times less than ammonium. Detecting such large molar ratio quantities of
12 $DEAH^+$ and $DMAH^+$ to NH_4^+ in any particle sample is also unprecedented. Mono-substituted amines are the
13 most frequently detected alkyl amines in atmospheric particles and at molar ratios to ammonium of 1:100 or
14 lower (Ge et al., 2011; Gorzelska et al., 1990; Mader, 2004; Müller et al., 2009; Yang et al., 2005; Yang et al.,
15 2004; Zhang et al., 2003). In most instances where di-substituted or tri-substituted amines have been identified in
16 the particle phase, they are present at molar quantities equal to or less than mono-substituted amines (Healy et
17 al., 2015; Suzuki et al., 2001). Thus, such high quantities of $DMAH^+$ and $DEAH^+$ in these samples were
18 unexpected and highly unusual compared to prior reports. In this case, the observation may be due to the fuel
19 source of the fire or the interaction of the plume with a potent source of atmospheric amines. Previous work has
20 identified di-substituted amines in large quantities from feedlot plumes (Sorooshian et al., 2008) and in marine
21 particles (Facchini et al., 2008; Gibb et al., 1999a; Müller et al., 2009; Sorooshian et al., 2009; Youn et al, 2015).
22 In fact, DMA and DEA have been reported as the second- and third-most abundant organic species in marine
23 fine aerosol behind methanesulfonic acid during periods of high biological activity in the North Atlantic
24 (Facchini et al., 2008). Other researchers have also suggested a moderate to high correlation between high
25 biological activity and di-substituted amine particle mass loadings (Müller et al., 2009; Sorooshian et al., 2009).
26 Laboratory investigations have shown that methylamines can be produced by marine phytoplankton degradation
27 of quarternary amines to maintain an osmotic gradient as well as during periods of known zooplankton grazing
28 (Gibb et al., 1999b). Based on the HYSPLIT back-trajectories calculated for these samples (Di Lorenzo, 2016), it
29 is possible that the BB plume particles interacted with gaseous DMA and DEA emitted from offshore and
30 coastal phytoplankton blooms or with enhanced amine emissions in the coastal zone as observed in the marine
31 boundary layer of California (Youn et al., 2015). The high concentrations of DMA and DEA produced by marine
32 biological activity could then partition into the biomass burning particles and react to neutralize inorganic acids
33 (e.g. sulfuric acid), form salts or amides with organic acids, or react with carbonyl moieties in the highly
34 oxidized organic material produced via BB to form imines (Qiu and Zhang, 2013). This marine amines
35 hypothesis, while consistent with observations in the literature, is beyond the scope of this work in terms of
36 assigning the DMA and DEA source.

37 3.2.2 Time series of amines in fresh biomass burning plume particles from British Columbia

38 Our method was also applied to a time series of $PM_{2.5}$ samples collected at two different locations (BKP and
39 NVSN) during a forest fire in the Lower Fraser Valley in British Columbia in the summer of 2015. These $PM_{2.5}$



1 samples were collected every 8 hours while the plume was traversing each site and the PM_{2.5} concentration was
2 in excess of 200 µg m⁻³. The relative ages for the smoke plumes sampled at both sites were calculated to be 20
3 hours old or less and back trajectories indicated that the plume did not travel over the open ocean before being
4 sampled (Di Lorenzo et al., 2016). In these test samples, the method was again able to detect the presence of four
5 different amines (iMPAH⁺, TMAH⁺, DEAH⁺, and TEAH⁺) with loadings of Na⁺, NH₄⁺ and K⁺ at ratios in excess
6 of 100:1. Furthermore, the method was not only able to determine the presence of isomonopropylamine, but also
7 differentiate it from monopropylamine and trimethylamine, its two structural isomers. iMPAH⁺, TMAH⁺,
8 DEAH⁺, and TEAH⁺ had maximum mass loadings in these fresher biomass-burning samples of 60 ± 40 ng m⁻³, 9
9 ± 7 ng m⁻³, 1.6 ± 0.8 ng m⁻³, and 0.2 ± 0.1 ng m⁻³ respectively (Table S2). iMPAH⁺ was the amine detected in
10 the largest molar quantities at both sampling sites in British Columbia. The detection of iMPAH⁺ has not
11 previously been reported in biomass-burning emission inventories, and based on our measurements may be
12 important to quantify in future controlled burn experiments. Our results differ from the study conducted by
13 Takahama et al (2011) on the 2009 forest fires in British Columbia that reports the detection of primary amine
14 groups, which further suggest that amine emissions from biomass burning and/or their incorporation into
15 biomass burning particles are not well understood. Although our observed suite of amines includes iMPAH⁺,
16 there was no indication of other primary amines from the analyses of the BB particles.

17 A time-series of the amines to ammonium molar ratio as the smoke plume intrudes into both the BKP and NVSN
18 sites is presented in Fig. 5b. There were either no amines present or they were present in concentrations below
19 our detection limits in the ambient particles collected on the front edge of the plume intrusions. When the
20 maximum PM_{2.5} mass loading of the plume reached the sampling site at t = 0, we saw an absolute maxima
21 in total amine concentration as well as a relative maxima in the particulate amine to ammonia molar ratio (Fig. 5b).
22 The particulate amine concentrations and the amines to ammonia ratio then tapered off as the plume diluted and
23 passed through the site. The measured amines to ammonia ratio in these samples is consistent with previously
24 reported literature values (Ge et al., 2011). The measured amine species and quantities, as in the aged plume,
25 could be indicative of the biomass-burning source fuel, fire type, or amine levels in air masses intercepted that
26 were subsequently incorporated by partitioning and reacting into the condensed phase. Since the smoke plumes
27 were calculated to be 20 hours old or less and back trajectories indicated that the plume did not travel over the
28 open ocean, it is less likely that offshore marine amine emissions interacted with the plume. However, the BKP
29 and NVSN sampling sites are positioned in a coastal urban center and anthropogenic amine emissions from
30 industry or animal husbandry operations nearby, as well as coastal amine emissions, may still have been
31 incorporated into the plume before it was sampled.

32 4. Conclusions

33 We developed an ion chromatographic method that can separate and quantify nine dominant atmospheric alkyl
34 amines from common inorganic atmospheric cations. Ion chromatography methods reported in the literature
35 cannot fully resolve alkyl amine peaks, nor separate interferences from potassium, magnesium and calcium. In
36 this work, we report the ability to overcome these prevalent issues for atmospheric sampling with a rapidity that
37 can also be applied to near real-time analyses of aqueous atmospheric extracts by IC. Additionally, the method is
38 able to separate and quantify three pairs of structural isomers, a limitation for direct particle and gas sampling



1 mass spectrometry instrumentation in quantifying atmospheric alkyl amines. The method detection limits are
2 comparable to other published IC methods in the literature, however the described method is not as sensitive as
3 derivatization methods coupled with GC-MS or LC-MS.

4 The method is robust. Two sets of BB particle samples collected at two different locations in Canada were
5 injected onto the IC column and the method detected and quantified amines with the presence of a complex
6 matrix where inorganic analytes, such as K^+ , reached ratios of 1000:1 relative to the alkyl amines. This is a
7 major improvement over all prior reports of the application of IC to the detection of amines in aqueous extracts
8 of atmospheric particulate matter. Our results suggest that increasing focus on speciation and quantitation of
9 various alkyl amines from direct BB emissions and their propensity to undergo reactive uptake with biomass
10 burning particles are needed to constrain global budgets of atmospheric sources and fate of alkyl amines.

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

16

17 *Author contribution.*

18 TCV designed the experiments and BKP, ATQ, and RAD carried them out. BKP prepared the manuscript with
19 contributions from all co-authors.

20 *Competing interests.*

21 The authors declare that they have no conflict of interest

22 *Acknowledgements.*

23 The authors thank Geoff Doerksen at the Lower Fraser Valley Air Quality Monitoring Network in British
24 Columbia for supplying biomass burning samples. Thanks to Joseph Bautista for help collecting biomass
25 burning samples in St. John's, as well as Jamie Warren and Kathryn Dawe for their assistance in method
26 development. Finally, the authors would like to thank Dr. Cora Young for her helpful comments in the writing of
27 the manuscript. TCV was supported by a Government of Canada Banting Postdoctoral Fellowship and the ICS-
28 2100 was procured through the Canadian Foundation for Innovation. Funding for this work was provided by the
29 Government of Newfoundland and Labrador Department of Forestry and Agrifoods through a Centre for
30 Forestry Science and Innovation grant (Project No. 221269).

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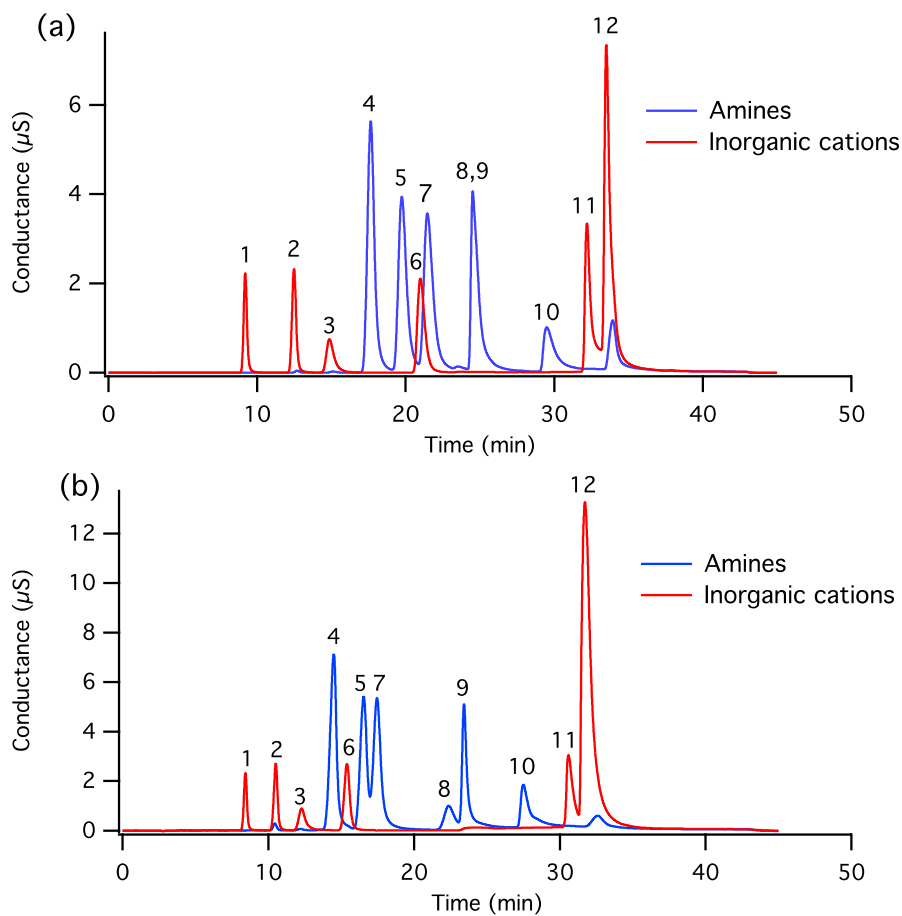
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1 **Figures**

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6 Figure 1. Separation of amine and inorganic cation standards with the highest resolution gradient program at (a)
7 30 °C and (b) 55 °C. The order of elution in (a) is as follows: Li⁺ (1), Na⁺ (2), NH₄⁺ (3), MMAH⁺ (4), MEAH⁺
8 (5), K⁺ (6), DMAH⁺ (7), TMAH⁺ (8), DEAH⁺ (9), TEAH⁺ (10), Mg²⁺ (11), and Ca²⁺ (12). Cation peaks are
9 labeled according to the same identities in (b).

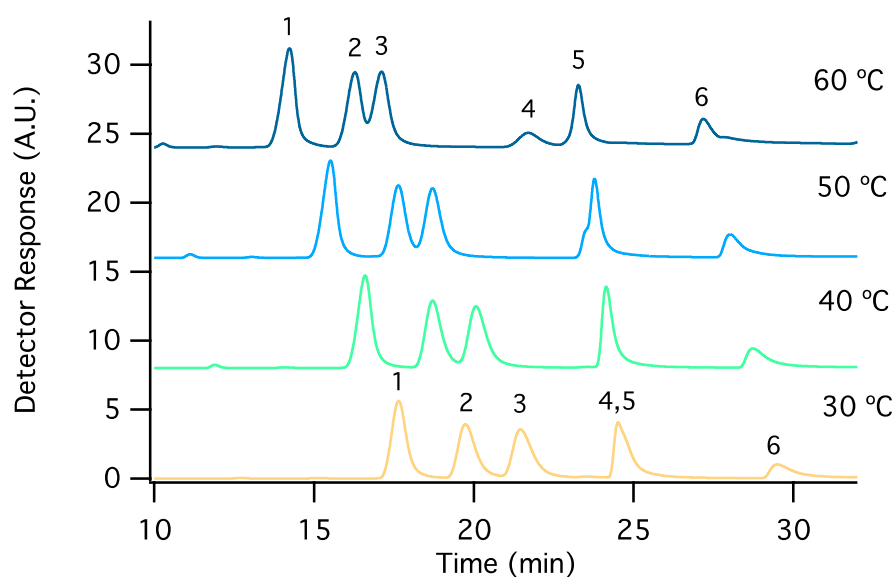
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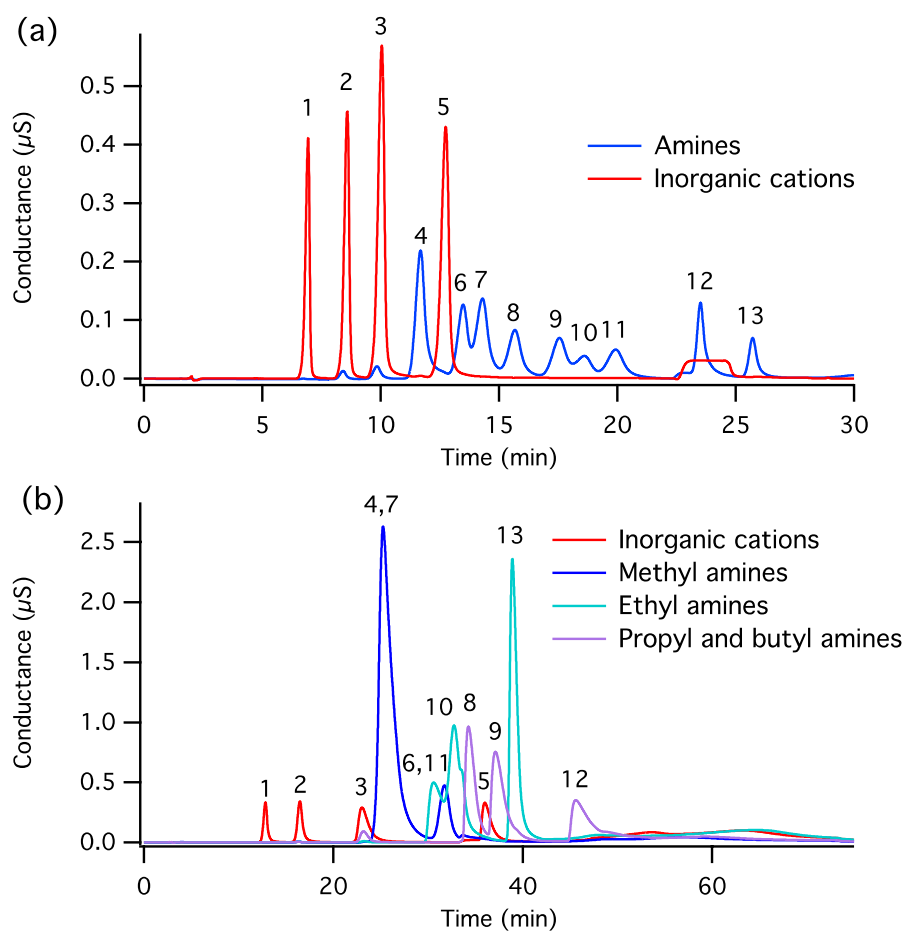
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4 Figure 2. Separation of $1 \mu\text{g ml}^{-1}$ mixed amines standard with the final method gradient elution program at 30
 5 °C, 40 °C, 50 °C and 60 °C. The peak elution order was MMAH⁺ (1), MEAH⁺ (2), DMAH⁺ (3), TMAH⁺ (4),
 6 DEAH⁺ (5), and TEAH⁺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

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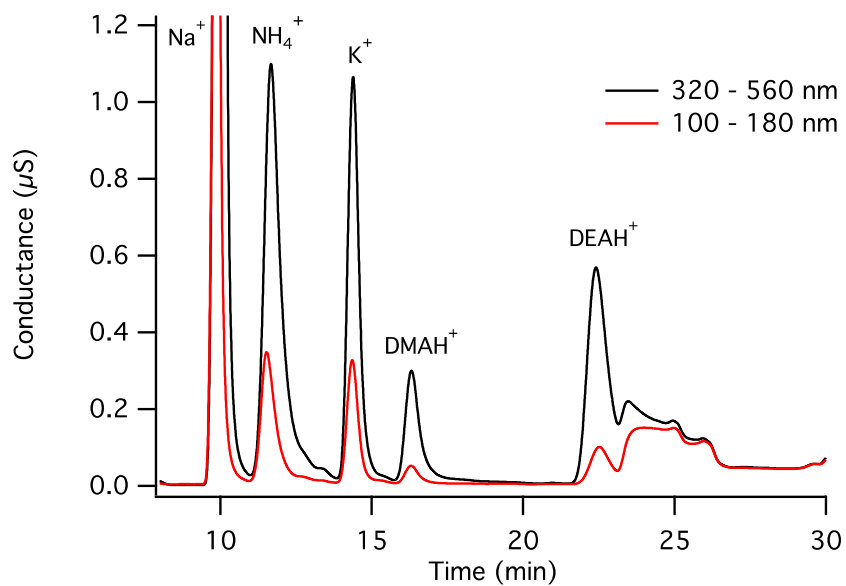
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4 Figure 3. (a) Separation of amine and inorganic cation standards with the addition of MPAH⁺, iMPAH⁺ and
5 MBAH⁺ using the final gradient program. The order of elution in (A) is as follows: Li⁺ (1), Na⁺ (2), NH₄⁺ (3),
6 MMAH⁺ (4), K⁺ (5), MEAH⁺ (6), DMAH⁺ (7), iMPAH⁺ (8), MPAH⁺ (9), TMAH⁺ (10), DEAH⁺ (11), MBAH⁺
7 (12), and TEAH⁺ (13). (b) Separation of amine and inorganic cation standards with the addition of MPA, iMPA
8 and MBA and the addition of the CG15 column using a modified gradient program. Cation peaks are labeled
9 according to the same identities in (b).

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2 Figure 4. Overlaid chromatograms of MOUDI size-fractionated particle samples collected in St John's on July 6,
3 2013 during the intrusion of a biomass-burning plume that originated from Northern Labrador and Quebec. The
4 robustness of the separation method for MMAH⁺, DMAH⁺ and DEAH⁺ from the common inorganic cations is
5 demonstrated for the 320-560 nm (Black) and 100-180 nm (Red) size bins.

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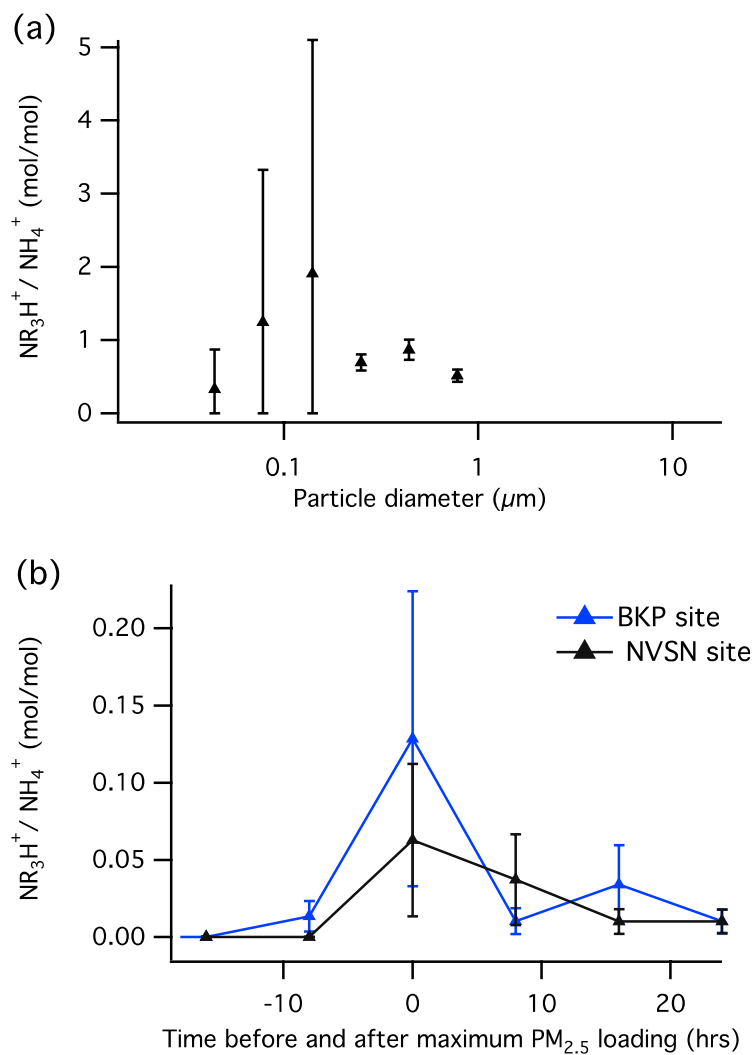
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4 Figure 5. (a) Amines to ammonium ratio in the size-resolved aged biomass-burning sample originating from
5 Quebec and Labrador in the summer of 2013. (b) Amines to ammonium ratio for the Burnaby/Kensington Park
6 (BKP) site and North Vancouver/Second Narrows (NVSN) site in British Columbia during the summer 2015
7 wildfires.



1 Tables

2 Table 1. Separation characteristics and statistics for the CS19 gradient method. Retention times (t_r), peak width and resolution were determined using the highest
 3 calibration standard for the alkyl amine (500 ng) and inorganic (160 – 520 ng) cations. Sensitivity, precision, average LOD, and LOD range were analyzed using multiple
 4 calibration standards and blanks (see Section 2.4). Upper and lower range accuracies were assessed using six high and low check standards ($n = 6$) for the alkyl amine
 5 cations and four high and low check standards ($n = 4$) for the inorganic cations. The low check standards were 15 times more concentrated than the lowest standard and
 6 the high check standards were 150 times more concentrated than the lowest standard.

Cation	t_r (min)	Peak width (min)	Resolution	Sensitivity ($\mu\text{S}^*\text{min}$ mol^{-1})	Precision (\pm 1σ) (%)	Upper range accuracy (%)	Lower range accuracy (%)	Average LOD (\pm 1σ) (pg)	LOD range (pg)
Li ⁺	8.56	0.72	2.68	11.5E08	2	96 \pm 5	82 \pm 4	0.6 \pm 0.2	0.3 - 0.8
Na ⁺	10.50	0.73	1.87	5.04E08	2	95 \pm 4	90 \pm 6	8 \pm 4	4 - 14
NH ₄ ⁺	12.28	1.18	1.85	2.45E08	4	103 \pm 4	50 \pm 50	22 \pm 17	7 - 47
MMAH ⁺	14.17	0.86	1.09	1.42E08	5	98 \pm 6	40 \pm 30	300 \pm 300	30 - 650
K ⁺	15.11	0.87	1.22	4.14E08	5	99 \pm 2	94 \pm 7	14 \pm 11	4 - 28
MEAH ⁺	16.12	0.79	1.08	0.90E08	7	97 \pm 5	40 \pm 10	500 \pm 200	200 - 700
DMAH ⁺	17.01	0.85	1.64	1.48E08	5	100 \pm 10	30 \pm 30	200 \pm 300	40 - 650
iMPAH ⁺	18.35	0.79	2.24	0.84E08	4	90 \pm 10	80 \pm 80	70 \pm 40	40 - 90
MPAH ⁺	20.22	0.88	1.55	0.62E08	12	88 \pm 4	90 \pm 90	50 \pm 40	20 - 80
TMAH ⁺	21.76	1.11	1.48	0.34E08	16	90 \pm 10	30 \pm 20	600 \pm 300	300 - 1200
DEAH ⁺	23.45	1.18	2.51	0.76E08	8	97 \pm 8	50 \pm 30	400 \pm 300	100 - 800
MBAH ⁺	25.47	0.43	3.12	0.62E08	1	80 \pm 20	100 \pm 80	910 \pm 30	890 - 930
TEAH ⁺	27.62	0.95	3.40	0.85E08	12	96 \pm 4	49 \pm 6	800 \pm 400	500 - 1400
Mg ²⁺	30.59	0.79	1.22	12.2E08	1	---	---	2000 \pm 3000	200 - 4000
Ca ²⁺	31.72	1.05	N/A	14.3E08	2	---	---	3700 \pm 200	3500 - 3800



1 Table 2. Analytical performance of other IC methods used for the determination of atmospheric methyl and ethyl
 2 amines by conductivity detection (CD) or mass spectrometry (MS).

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Analyte	Detection method	Pre-conc	Column	LOD (pg)	Precision (%)	Reference
MMAH ⁺	CD	Yes	CS10	31	2 – 2.7	Chang et al., 2003
	CD	Yes	CS12A	18	4.5	VandenBoer et al., 2012
	CD	No	CS14	2500	3.8	Verrielle et al., 2012
	MS	No	CS14	500	5.8	Verrielle et al., 2012
	CD	Yes	CS17	540	4.8	VandenBoer et al., 2012
	CD	Yes	CS19	30 - 650	5	This work
	CD	No	Metrosep C2	21500	0.4	Erupe et al., 2010
	CD	Yes	Metrosep C4	2100	12.2	Huang et al., 2014
	CD	No	Metrosep C4	160	7.3	Dawson et al., 2014
DMAH ⁺	CD	Yes	CS10	40	2 – 2.7	Chang et al., 2003
	CD	Yes	CS12A	25	1	VandenBoer et al., 2012
	CD	No	CS14	4000	10.5	Verrielle et al., 2012
	MS	No	CS14	150	11.4	Verrielle et al., 2012
	CD	Yes	CS17	870	14	VandenBoer et al., 2012
	CD	No	CS17	1500	1.2	Li et al., 2009
	CD	Yes	CS19	40 - 650	5	This work
	CD	No	Metrosep C2	23000	1.4	Erupe et al., 2010
	CD	Yes	Metrosep C4	3800	15.7	Huang et al., 2014
TMAH ⁺	CD	No	Metrosep C4	320	1.1	Dawson et al., 2014
	CD	Yes	CS10	26	2 – 2.7	Chang et al., 2003
	CD	Yes	CS12A	220	1	VandenBoer et al., 2012
	CD	No	CS14	2500	N/A	Verrielle et al., 2012
	MS	No	CS14	500	12.2	Verrielle et al., 2012
	CD	Yes	CS17	1580	3.3	VandenBoer et al., 2012
	CD	No	CS17	2000	3.5	Li et al., 2009
	CD	Yes	CS19	300 - 1200	16	This work
	CD	No	Metrosep C2	38000	1.1	Erupe et al., 2010
MEAH ⁺	CD	No	Metrosep C4	970	6.1	Dawson et al., 2014
	CD	Yes	CS10	37	2 – 2.7	Chang et al., 2003
	CD	Yes	CS12A	33	12	VandenBoer et al., 2012
	CD	No	CS14	1000	5.1	Verrielle et al., 2012
	MS	No	CS14	500	7.9	Verrielle et al., 2012
	CD	Yes	CS17	790	10	VandenBoer et al., 2012
	CD	Yes	CS19	200 - 700	7	This work



	CD	Yes	Metrosep C4	2200	4.3	Huang et al., 2014
DEAH ⁺	CD	Yes	CS12A	195	14	VandenBoer et al., 2012
	CD	No	CS14	N/A	N/A	Verriete et al., 2012
	MS	No	CS14	35	9	Verriete et al., 2012
	CD	Yes	CS17	1140	3.5	VandenBoer et al., 2012
	CD	Yes	CS19	100 - 800	8	This work
	CD	Yes	Metrosep C4	4100	4.6	Huang et al., 2014
TEAH ⁺	CD	Yes	CS12A	32000	2	VandenBoer et al., 2012
	CD	Yes	CS17	1870	5.9	VandenBoer et al., 2012
	CD	Yes	CS19	500 - 1400	12	This work
	CD	Yes	Metrosep C4	15900	5.1	Huang et al., 2014

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