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A Quantitative Method to Measure and Speciate Amines in Ambient Aerosol Samples

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Abstract: Ambient reactive nitrogen is a mix of nitrogen-containing organic and inorganic compounds. These various compounds are found in both aerosol- and gas-phases with oxidized and reduced forms of nitrogen. Aerosol-phase reduced nitrogen is predominately thought to include ammonium and amines. In ambient samples, the ammonium concentration is routinely determined, but the contribution of amines is not. We developed a method to discretely measure amines from ambient aerosol samples. It employs ion chromatography using a Thermo Scientific IonPac Dionex CS-19 column with conductivity detection and a three-step separation using a methanesulfonic acid eluent. This method allows for the quantification of 18 different amines, including the series of methylamines and the different isomers of butylamine. Almost all amines quantifiable by this technique were measured regularly when applying this method to ambient filter samples collected in Rocky Mountain National Park (RMNP) and Greeley, CO. The sum of the amines was ~0.02 μg m^{-3} at both sites. This increased to 0.04 and 0.09 μg m^{-3} at RMNP and Greeley, respectively, at the same time they were impacted by smoke. Analysis of separate, fresh biomass burning source samples, however, suggests that smoke is likely a minor emission source of amines in most environments.

Keywords: amines; ion chromatography; ambient aerosols; $PM_{2.5}$; reduced nitrogen

1. Introduction

Ambient reactive nitrogen is a mix of nitrogen-containing organic and inorganic compounds. These various compounds are found in both aerosol- and gas-phases that include oxidized and reduced forms of nitrogen. The aerosol-phase reduced nitrogen includes ammonium and amines. Ammonium is routinely measured in ambient aerosol, generally using ion chromatography, both in near real-time and from integrated filter measurements. Amines are not often quantified [1–3].

In general, amines in the atmosphere are not well understood. In 2011, Ge et al. [4] provided a review of ambient amines. This paper discussed the sources and fluxes of various amine compounds and provided information on gas-particle partitioning of atmospheric amines. From this summary, we concluded:

1. In ambient air, the most common amines are sets of methylamines and ethylamines.

2. The four principal emission sources are likely industrial combustion, biomass burning, animal husbandry, and the ocean. Many amines have been observed in the emissions from more than one of these sources.
3. Most amines are highly water-soluble. Wet deposition is likely the main route for removal to the surface. This limits their lifetimes and ability to be transported long distances. Amines have been detected in rainwater and fog water [5–7].
4. There are, consequently, specific regions where ambient amines could be important, especially environments that are downwind of and impacted by agricultural sources.

Chamber studies have shown that particle-phase aminium nitrate and sulfate salts can form when gas-phase amines undergo acid-base reactions or photooxidation [8,9]. In addition, a number of field studies have shown that organic nitrogen can be a significant fraction of organic aerosol [10–15]. However, the importance of amines to this particulate organic nitrogen is still uncertain.

Aerosol-phase amines are predominately measured in ambient air using expensive instrumentation or labor-intensive analytical methods. Single-particle mass spectrometry, thermal desorption-chemical ionization mass spectrometry, and compact time-of-flight aerosol mass spectrometry have detected aerosol-phase amines during a number of field studies [15–20]. However, along with requiring a trained operator to make these measurements, data processing is highly labor intensive. Derivatization of samples followed by analysis with high-performance liquid chromatography (HPLC) or gas chromatography (GC) have allowed for quantifying the concentrations of ambient amines in multiple locations [21–23]. However, such an approach is tedious and uses a large quantity of organic solvents. Although ion chromatography (IC) has shown promise, most methods previously used either only detected a few amines and/or were challenged by/did not address the overlap of common inorganic cations with the amines [18,24–26]. Place et al. [27] presented the most comprehensive IC method to date, quantifying 11 alkylamines, yet still this method had problems with suppressor and column degradation over time.

The research to date suggests that amines are present in ambient air and may be a significant contributor to reduced nitrogen deposition. However, our understanding of ambient amines is hindered by the lack of cost-effective direct measurements suitable for use in routine monitoring programs. Similar to the goals of better understanding organic nitrogen presented in a recent white paper from the National Atmospheric Deposition Program Total Deposition Science Committee [28], this suggests that it would be valuable to have an easier, more direct method to comprehensively and quantitatively measure and speciate aerosol-phase amines in ambient air. As noted in the white paper, there are needs for routine measurements to help understand spatial and temporal trends at the regional and continental scale, as well as speciated measurements to help understand their relative contribution to total nitrogen, source identification, and atmospheric process characterization.

In this work, we developed an ion chromatography method to discretely measure numerous amines in ambient aerosol samples. First, we outline the analytical method. Then we provide and discuss the applications of this method on routine ambient filter samples collected in Rocky Mountain National Park and Greeley, CO, along with biomass burning source samples.

2. Experimental Methods

2.1. Ion Chromatography Method for Measuring Amines

Aerosol-phase amines are likely present in ambient air. For example, Figure 1 shows a comparison of ion chromatograms representing analysis of an ambient filter sample collected in the Central Valley of California versus a cation calibration standard. As can be seen, there is clearly a noticeable extra peak appearing between the ammonium and potassium peaks in the ambient sample. This analysis was conducted on a typical cation chromatography column, the Thermo Scientific Dionex IonPac CS12-A column (Thermo Fisher Scientific, Waltham, MA, U.S.). What this means is that in the traditional cation separation methods employed to measure ammonium, there could be overlap with amines

(Figure 2), especially if the ammonium peak broadens at high concentrations. If this is true, then the ammonium would likely be overestimated and a portion of reduced nitrogen could be missed as amines go undetected.

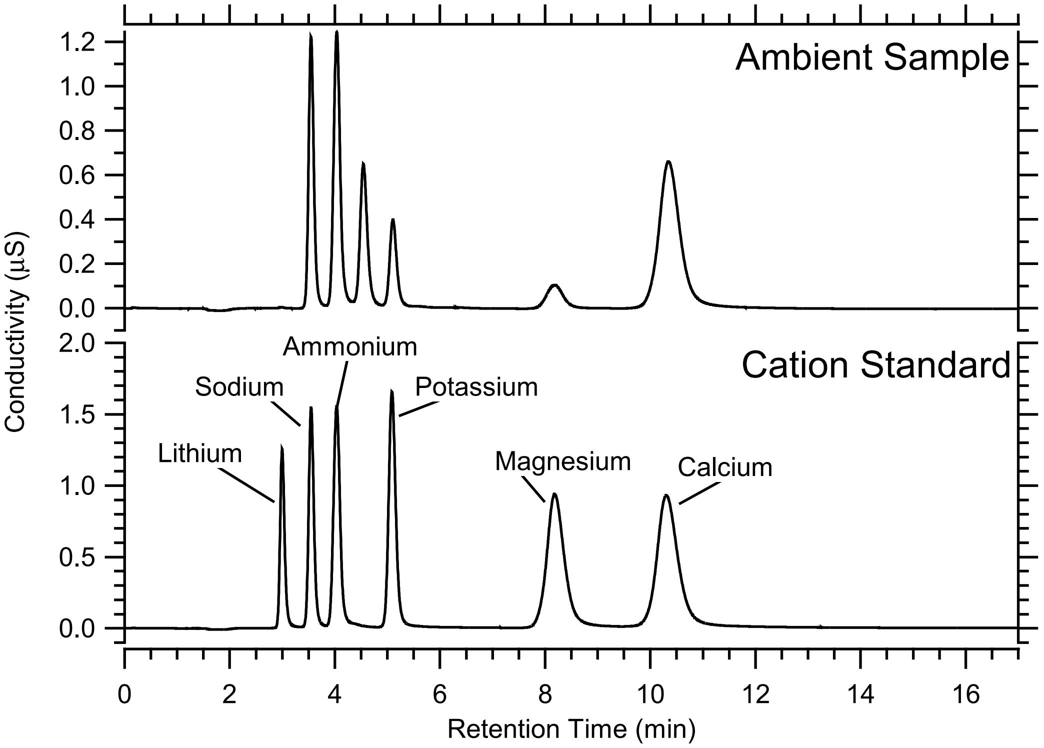

Figure 1. Chromatogram comparison of an ambient filter sample collected at the permanent monitoring station at Del Paso Manor in Sacramento County, CA on 7 November 2016 (top) and cation calibration standard (bottom). The separation was performed on a Thermo Scientific Dionex IonPac CS-12A (3 × 150 mm) column using an isocratic method with an eluent of 20 mM methanesulfonic acid at a flowrate of 0.5 mL min^{-1}. The extra peak in the ambient sample at 4.5 min is likely due to amines.

Given that amines were likely being observed using the Thermo Scientific Dionex IonPac CS-12A column (Figure 1), initially we tried manipulating that separation method to be able to separate and quantify multiple amines. This included extending the run time, changing the eluent concentration, and switching to a gradient elution method. However, we could not find optimum conditions that prevented multiple amines from overlapping or an overlap of ammonium and potassium with various amines. Three other Thermo Scientific Dionex columns—IonPac CS-17, CS-18, and CS-19—are available that are better suited to measuring amines. Therefore, all three of these columns were evaluated. For the CS-17 column, we never achieved complete separation of multiple amines from the inorganic cations commonly found in atmospheric aerosols. We were able to develop a gradient method that separated the amines and inorganic cations for the CS-18 column, but this column was only available in the 2 mm diameter format. This limited how low of a detection limit could be achieved for the amines as for typical ambient samples overloading of the column with inorganic cations would be likely, which would affect peak shape and separation. The CS-19 column, however, was ideal for measuring ambient amines, as the separation of the amines and inorganic cations could be optimized and it was available in the larger 4 mm diameter format, offering greater separation capacity. Therefore, only the details of the gradient separation method for the CS-19 column will be further discussed. This method would be adaptable for use on any type of gradient ion chromatograph. There would likely be some differences noticed in sensitivity as not all types of ion chromatographs have cation suppressors available.

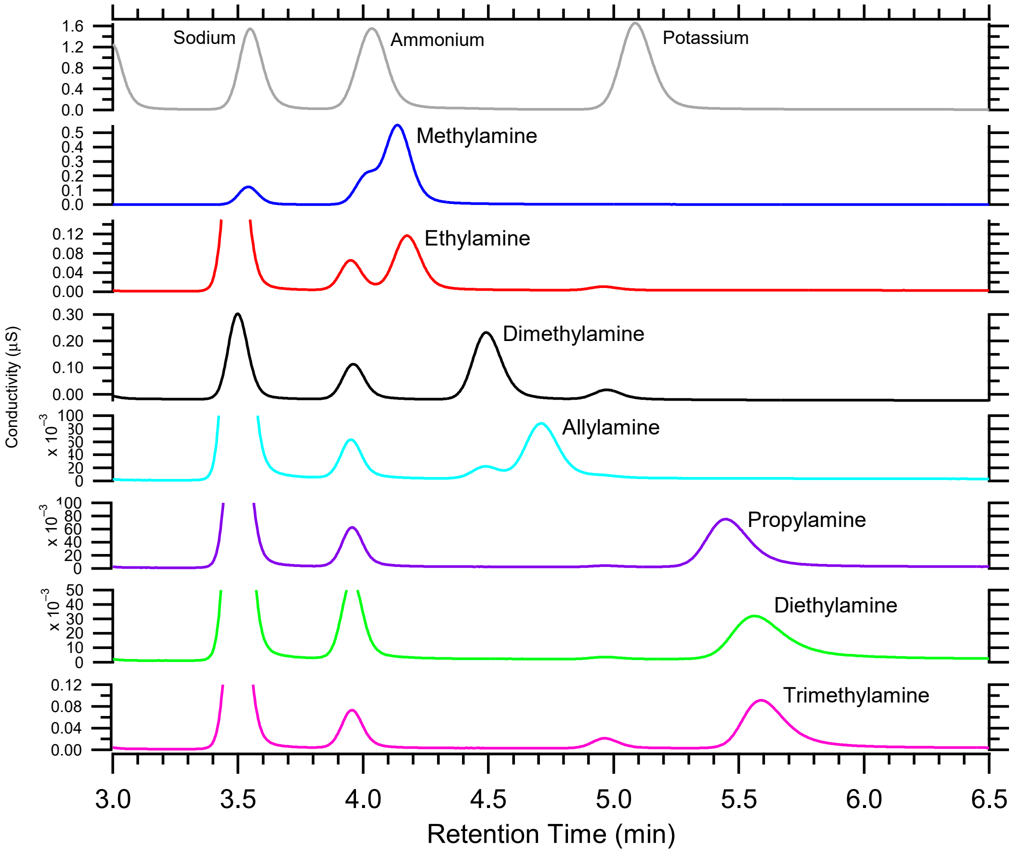

Figure 2. Chromatogram comparison of a cation and seven different amine calibration standards. The separation was performed on a Thermo Scientific Dionex IonPac CS-12A (3 × 150 mm) column using an isocratic method with an eluent of 20 mM methanesulfonic acid at a flowrate of 0.5 mL min^{-1}. Note only data from 3 to 6.5 min is being shown to illustrate the challenges with using this column to simultaneously measure the +1 inorganic cations and amines. It is observed that methylamine and ethylamine, as well as propylamine, diethylamine, and trimethylamine, overlap. In addition, there is overlap of ammonium with methylamine and ethylamine. Depending on the size of the ammonium peak, this could extend to dimethylamine and allylamine. Therefore, the ammonium concentration would be overestimated as these amines are being included in the integration of the ammonium peak. The same could be true for potassium, depending on the size of its peak, with propylamine, diethylamine, and trimethylamine.

The amine measurement was made using a Dionex DX-500 series ion chromatograph (Thermo Fisher Scientific, Waltham, MA, USA) with a Dionex GP-50 gradient pump (Thermo Fisher Scientific, Waltham, MA, USA) and Dionex ED-50 electrochemical detector (Thermo Fisher Scientific, Waltham, MA, USA) operating in conductivity mode. The column was heated continuously to 45 °C using a Dionex LC-25 column oven. A 4 mm Thermo Scientific Dionex CDRS 600 suppressor (Thermo Fisher Scientific, Waltham, MA, USA) was used to reduce background conductivity from the eluent and enhance signal-to-noise ratios for target analyte peaks. A Thermo Scientific Dionex IonPac CTC-1 trap column (Thermo Fisher Scientific, Waltham, MA, USA) (9 × 24 mm) for a 4 mm column was placed just downstream of the gradient pump. The eluents were DI Water (deionized water) and 10 mM methanesulfonic acid (MSA). Separation was completed on Thermo Scientific IonPac CS-19 guard (4 × 50 mm) and analytical (4 × 250 mm) columns in series. Each run had an eluent flowrate of 1.0 mL min^{-1} and lasted approximately 125 min. The separation had three steps. For the first 68 min, an isocratic elution with 0.3 mM MSA was performed to separate the +1 charged inorganic cations. Next, a linear gradient from 0.3 to 6 mM MSA was run for 17.9 min to separate the majority of the amines.

Then, an isocratic elution at 6 mM MSA was performed for 28.7 min to separate divalent inorganic cations. Finally, a 10.3 min re-equilibration step was performed to return the starting conditions.

The method was capable of separating a mix of common amines found in ambient air (Table 1); it was not capable of separating ethylamine from potassium. This was true even with adjusting the temperature of the column oven lower or higher. This was also true when attempting to lower the eluent concentration of the first isocratic step or instead performing gradient elution for the first step. Additionally, it was observed that utilizing gradient elution for the first separation step did not significantly decrease the retention time for any of the inorganic cations.

Table 1. List of the amines along with their retention times that can be identified using the Thermo Scientific Dionex IonPac CS-19 (4 × 250 mm) column following the method described in the main text.

Amine	Retention Time (min)
Ethanolamine	47.2
Methylamine	50.2
Diethanolamine	54.0
Ethylamine	58.2
Dimethylamine	63.0
Allylamine	67.6
Propylamine	74.3
Tert-butylamine	74.6
Trimethylamine	75.8
Diethylamine	76.2
Sec-Butylamine	77.8
Iso-Butylamine	79.0
Butylamine	81.0
Triethylamine	84.4
Dipropylamine	85.9
Amylamine	89.1
1,4-Diaminobutane	112.3
1,5-Diaminopentane	118.1

Two key factors proved critical for application of this method. The first was being able to adjust the suppressor current across the run since a low concentration of 0.3 mM MSA was used for the first step of the separation with much higher eluent concentrations later in the analysis. This adjustment not only helped the stability of the baseline but the life of the suppressor and the detection of the divalent inorganic cations. A suppressor deteriorated faster than usual when an excessive current was applied for long periods (i.e., during the first isocratic step), causing the divalent inorganic cations to lose their sharp peak shape. To address this challenge, we set the suppressor current to 1 mA for the first 71 min of the run, switched it to 18 mA until 118 min into the run, and then returned to 1 mA for the remainder. The second key factor was to use a large sample loop injection to maximize detection of the amines, as ambient amines are generally found in much lower concentrations than inorganic cations. We found a 1 mL sample loop to be optimal. The use of a 4 mm diameter separation column was, therefore, important to prevent sample overloading of column active sites.

An example calibration chromatogram using the amine method described above is shown in Figure 3a. Good separation of the inorganic cations and amines was achieved. Overall, this method was able to quantify 18 different amines. This includes the whole series of methylamines and the isomers of butylamine. Calibrations were linear over the wide concentration range tested from 0–250 µg L^{-1}. Example calibration curves for the series of methylamines are shown in Figure 4. Table S1 in the Supplementary Materials provides the equations for the calibration curves for the other amines. The method was sensitive with a limit of detection (LOD) for the various amines of 4 µg L^{-1}. Assuming collection of a filter samples for 24 h at a flowrate of 10 LPM, this was approximately 1 ng m^{-3}.

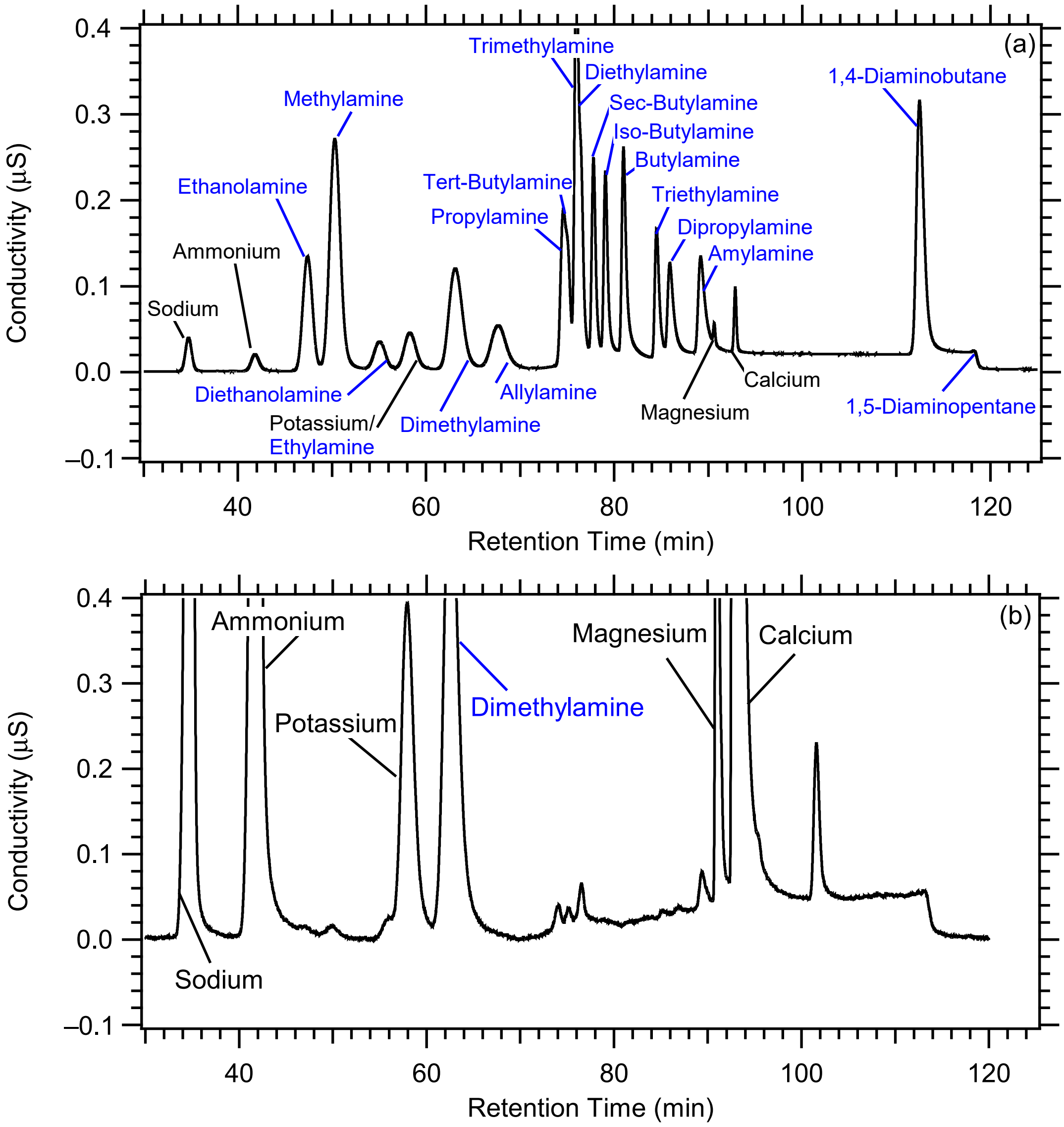

Figure 3. Chromatogram of (**a**) an amine calibration standard and (**b**) the same ambient filter sample collected in Sacramento County, CA shown in Figure 1. The separation was performed on a Thermo Scientific IonPac CS-19 (4 × 250 mm) column using the separation method described in the main text. Note the x-axis starts at 30 min since only lithium elutes before this retention time at 25 min. The peak observed at 102 min in plot b is unknown as currently no standard has been found to confirm its identity.

The same ambient filter sample extract analyzed on the IonPac CS-12A column (Figure 1) was run on the IonPac CS-19 column (Figure 3b). A very different chromatogram was obtained. When compared with the standard, we observed that the extra peaks in the ambient sample appeared to correspond to amines. The most abundant amine in the sample was dimethylamine. It was also quite clear that with the exception of dimethylamine, the amine peaks were much smaller than the inorganic cation peaks, but still clearly separable and quantifiable. This is illustrated in Figure 5, where the ambient $PM_{2.5}$ filter sample (see Figures 1 and 3) was compared to a blank filter sample. As shown, most amine peaks were only observed in the ambient filter sample. These results suggest that we have a sensitive and robust method for detecting amines.

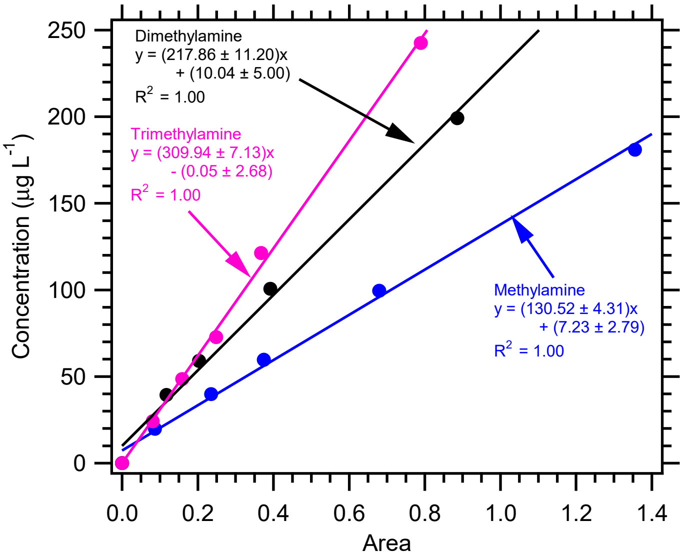

Figure 4. Typical calibration curves for methylamine, dimethylamine, and trimethylamine employing the Thermo Scientific Dionex IonPac CS-19 (4 × 250 mm) column using the separation method described in the main text. Uncertainties with the least square regression are one standard deviation.

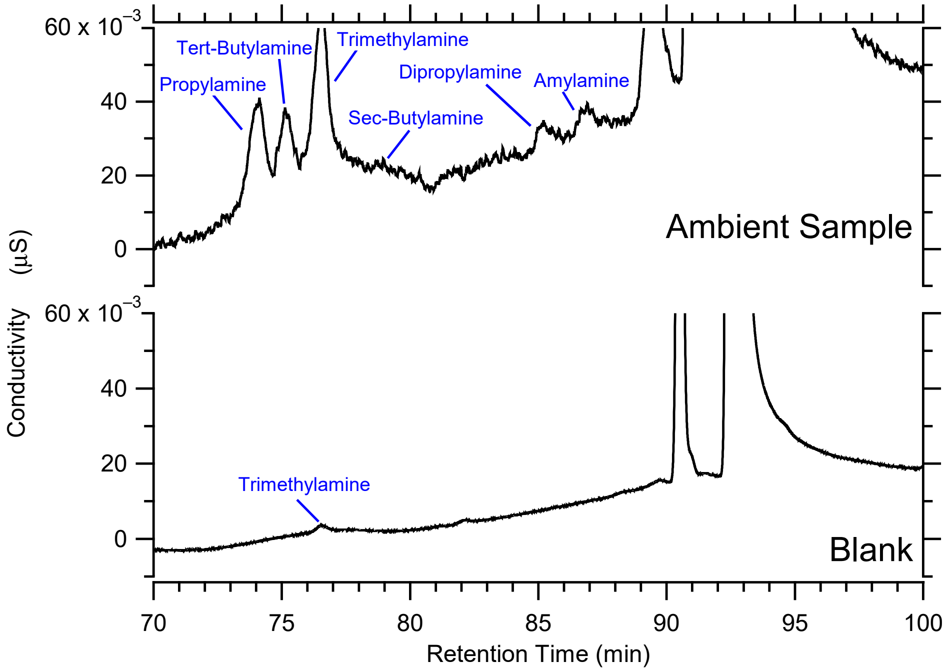

Figure 5. Chromatogram comparison of the same ambient filter sample shown in Figure 1 (top) and a blank (bottom) filter sample. The separation was performed on a Thermo Scientific Dionex IonPac CS-19 (4 × 250 mm) column using the separation method described in the main text. Note only data from 70 to 100 min, which includes the gradient and second isocratic step of the separation, are being shown to illustrate the low detection limit for the amines.

2.2. Aerosol Samples

URG annual denuder/filter pack samplers were operated at a site in Rocky Mountain National Park (RMNP) and in Greeley, CO. The RMNP site was located at the IMPROVE (Interagency Monitoring of Protected Visual Environments) site 15 km south of Estes Park, CO, near the base of Long's Peak. The Greeley site was located at the Weld County Tower sampling site on 35th St. This site is operated by the Colorado Department of Public Health and Environment and is close to agricultural sources including a large number of feed lot operations. Samples were collected at both sites from mid-July through mid-October in 2017.

For the URG sampler, ambient air was pulled through a $PM_{2.5}$ Teflon-coated cyclone, followed by sodium carbonate and phosphorous acid coated denuders used to collect inorganic gas, such as nitric acid and ammonia [29]. The air then passed through a 47 mm nylon filter to collect the particulate matter. Finally, the air passed through a second phosphorous acid denuder to collect any particulate ammonium that volatilized off the filter [1]. Volatilized nitric acid was efficiently retained by the nylon filter [30]. The URG system ran daily with a flowrate of 10 LPM in RMNP and weekly with a flowrate of 3 LPM in Greeley. The volume of air sampled at both sites was monitored and measured in real-time using a dry-gas meter. Blank samples were collected by installing a set of denuders and filter in the URG sampler for 24 h without the pump running.

Additionally, 14 controlled laboratory burns involving fuels known to burn in the Southwestern U.S. were conducted at Los Alamos National Laboratory using a small ventilated combustion chamber under a fume hood. Smoke from the combustion chamber was drawn through a PM_1 cyclone, mixed in a 34 L cylindrical stainless steel chamber, and then distributed to various instruments [31]. In the work presented in this paper, only data from the chemical analysis of the off-line filter samples are discussed. A 47 mm quartz filter sample was collected across each burn using a flowrate of 15.5 LPM controlled by a critical orifice. Before sampling the quartz filters were wrapped in aluminum foil and pre-baked at 550 °C for 12 h. After baking, the aluminum foil wrapped filters were stored in plastic bags in a sealed box until loaded into the filter holder. After sampling, the filters were stored frozen in individual petri dishes.

Each nylon filter was extracted in 6 mL DI Water in a polystyrene test tube and sonicated without heat for 40 min. Each quartz filter was extracted in 15 mL DI Water in a Nalgene Amber HDPE (high-density polyethylene) bottle, sonicated with heat [32] for 1.25 h, and then filtered using a 0.2 µm PTFE (polytetrafluoroethylene) syringe filter to remove any quartz filter fibers. A DI Water blank was performed with each set of extractions. The steps followed are standard operating procedure for filter extractions. No additional tests were performed in this work to examine the extraction recovery of the various amines.

All filter extracts were analyzed for amines using the method described above. They were also analyzed for anions using a Thermo Scientific Dionex IonPac AS-11HC column employing a sodium hydroxide gradient [33]. This method had a LOD for the various anions of ~1 ng m^{-3} and 10% uncertainty. Only the RMNP and biomass burning filter samples were analyzed for carbohydrates using high-performance anion-exchange chromatography with pulsed amperometric detection, as described by Sullivan et al. [34–36]. The LOD for the various carbohydrates was less than ~0.1 ng m^{-3}, with an uncertainty of 10%. Additionally, the biomass burning filters were analyzed for total nitrogen using a Shimadzu TOC V_{CSH+} + TMN-1, a total organic carbon analyzer with a total nitrogen module. The analyzer performed a high-temperature oxidation on a catalyst bed, which converted all reactive nitrogen in the sample to NO (nitrogen oxide) at 720 °C, and then detected this NO by chemiluminescence. By using a manual injection, a 2 mL aliquot of the filter extract was employed for this analysis, which provided a LOD of 1.2 µg N m^{-3} with an uncertainty of 10%. A file with the concentration data for each of the three sets of filter samples can be found in the Supplementary Materials.

3. Results and Discussion

Using the method described above, the amines were measured routinely from the 24 h filter samples collected in RMNP. As shown in Figure 6a, the largest contributors to the measured amine concentrations were ethanolamine, methylamine, diethanolamine, and dimethylamine. The amines tracked with ammonium. There also appeared to be a consistent background of about 0.02 µg m^{-3}. We can compare these results from RMNP to the weekly filter samples collected in Greeley, CO (Figure 6b). There was some correlation in the amines observed at both sites. On a few occasions, there was an even higher contribution in Greeley, often two times higher, of the same four dominant amines observed in RMNP. This could possibly be due to changes in the agricultural sources and activities in Greeley. The highest concentration of amines was observed in Greeley, during the sampling period starting on 30 August 2017. The highest RMNP amines concentrations were also observed for the sampling period following 30 August 2017. As mentioned above, the filter samples from RMNP were analyzed for carbohydrates. This included levoglucosan, a known biomass burning tracer, as it is an anhydrous sugar produced from the combustion of cellulose [37]. The increase in RMNP amine concentrations tracked a noticeable increase in levoglucosan from approximately 0.01 μg m^{-3} to 0.32 μg m^{-3}, which happened at this same time during the first week of September. The sum of the amines at RMNP doubled to about 0.04 μg m^{-3} during this same time, largely due to increases in concentrations of the four dominant amines.

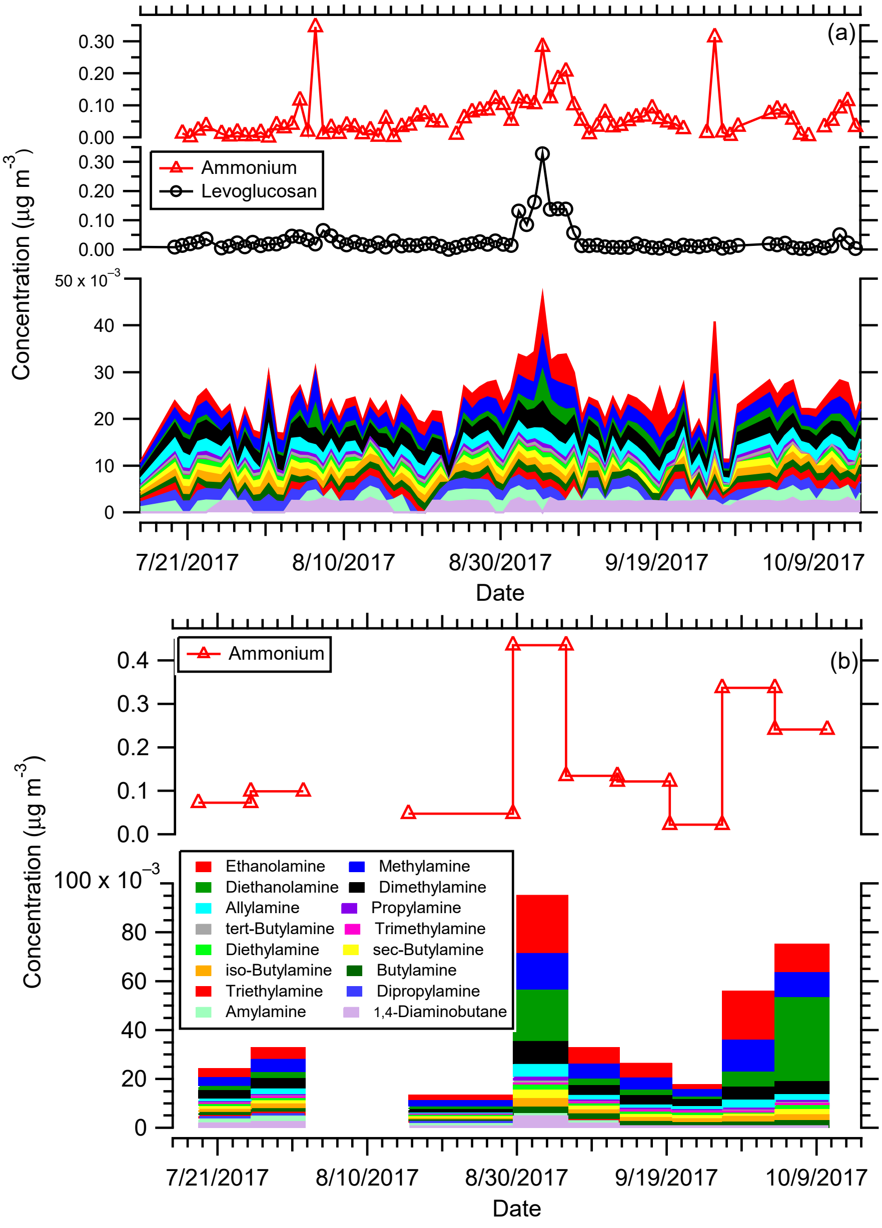

Figure 6. (**a**) Times series of levoglucosan, ammonium, and amines measured from daily filter samples collected at RMNP and (**b**) ammonium, and amines measured from weekly filter samples collected at Greeley, CO from 15 July to 15 October 2017.

A set of biomass burning source filter samples from the controlled laboratory burns mentioned above was run using the amine method. Figure 7a shows contributions of the various amines in the biomass burning source samples as a function of fuel type. There appears to be variability in the distribution of amines among fuel types (leaves, branches, grasses, and needles). It is interesting to note that the most abundant amines in the biomass burning source samples were typically dimethylamine and/or trimethylamine, whereas in ambient samples ethanolamine, methylamine, diethanolamine, and dimethylamine dominated. Although most of these amines have been previously observed from biomass burning (and other sources), it appears differences in their contributions were observed between fresh and aged/transport smoke, as well as likely laboratory burns versus wildfire smoke, both of which require further investigation. The smoke marker levoglucosan followed the same pattern as the amines with the exception of the burn involving Kochia leaves. Levoglucosan itself correlated with ethanolamine, diethanolamine, tert-butylamine, triethylamine, and amylamine (R^2 ranging from 0.51 to 0.76). Most of these amines were previously measured in the atmosphere but from sources other than biomass burning [4], suggesting more work is needed to understand the speciation of amines across various sources. The biomass burning sample total nitrogen measurements allowed an estimate of the various nitrogen-containing species to be determined. Although the amines tracked the ammonium concentrations, the amines often had a larger contribution than ammonium to the total nitrogen. Ammonium contributed, on average, 8% (range 2–14%) to total nitrogen. The sum of amines was 11% (range 3–37%) and nitrate was 6% (range 1–16%). Other presumably organic species dominated the total nitrogen budget (Figure 7b). This suggests that although biomass burning was likely a source of amines, it might be relatively minor in regions heavily impacted by other sources, such as agricultural activities.

All of the work presented here has focused on aerosol-phase amines. However, measuring gas-phase amines in ambient air is just as important. Gas-phase amines can undergo oxidation with hydroxyl radicals, nitrogen oxides, and ozone, as well as acid-base chemistry to form aerosol [4,8]. In addition, gas-phase amines are more effective than ammonia at enhancing nucleation. Of the monoamines, dimethylamine and trimethylamine stabilize sulfuric acid clusters most effectively [38]. Diamines can produce 10 times more particles than dimethylamine, suggesting that they are even more potent nucleating agents than monoamines [39].

The ion chromatography method presented here was also applied to the denuder samples collected as part of the URG denuder/filter pack samples collected in RMNP and Greeley. Denuder samples are the most common off-line gas-phase measurement used in ambient sampling. However, due to the combination of the low methanesulfonic acid concentration used in the first separation step, the low pH of the denuder extract from the phosphorous acid coating solution, and the column packing material, all peaks in the first separation step appeared as overlapping broad round-top peaks. Adjusting the injected sample volume did not have any effect on this. An attempt to use a pretreatment cartridge (Thermo Scientific Dionex OnGuard IIA) to adjust the pH of the sample led to the creation of amines from the pretreatment cartridge's packing material. Likely a new separation method using a different column would need to be developed for analysis of denuder samples for gas-phase amines or an assessment of the volatilization of particle-phase amines from a nylon filter.

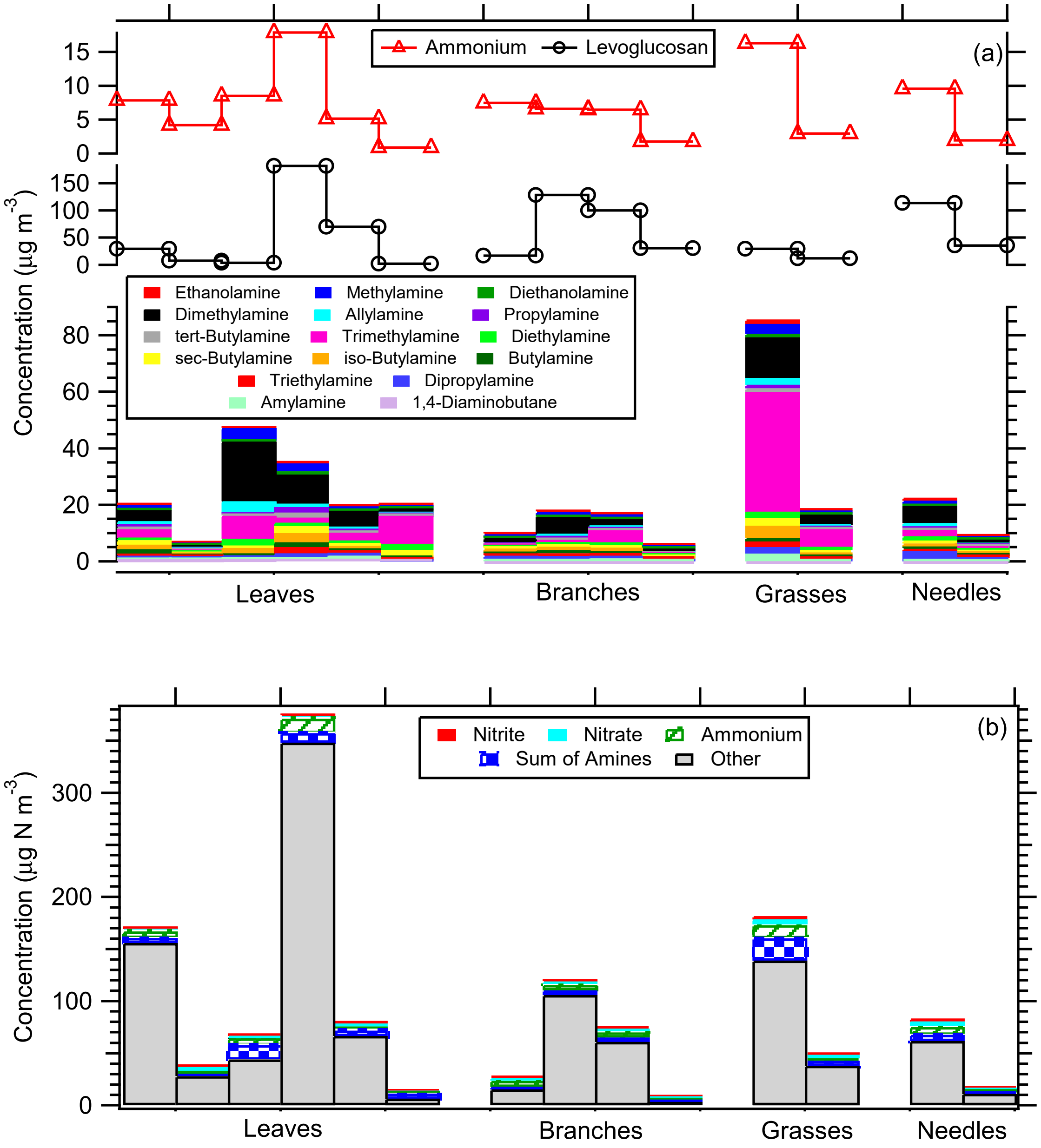

Figure 7. (**a**) Contribution of ammonium, levoglucosan, and the various particle-phase amines, and (**b**) nitrogen containing species to the total nitrogen from filter samples collected during controlled laboratory burns segregated by fuel type. In order, fuels for leaves: Siberian Elm, Russian Olive, Kochia, Cottonwood A, Cottonwood B, Four-Winged Salt Bush; branches: Russian Olive, Cottonwood A, Cottonwood B, Ponderosa Pine; grasses: Salt Grass, Sacaton Grass; needles: Pinon Pine, Ponderosa Pine.

4. Summary and Conclusions

In this study, we developed a robust and sensitive method to quantitatively measure common inorganic cations and 18 amines in ambient aerosol samples. This method employed a Thermo Scientific Dionex IonPac CS-19 column using a methanesulfonic acid eluent. The complete run time was 125 min and included three steps to allow separation of +1 cations, amines, and divalent cations. Two important factors for using this method included adjusting the suppressor current to slow the aging of the suppressor performance and using a large sample volume injection to increase measurement sensitivity. This led to linear calibrations over a wide concentration range and a LOD for various amines of less than 1 ng m^{-3} for a 24 h air sample collected at 10 LPM.

This method was applied to routine ambient aerosol samples collected in RMNP and Greeley, CO, as well as biomass burning source samples collected from controlled laboratory burns of fuels known to burn in theSouthwestern U.S. The four dominant amines were ethanolamine, methylamine, diethanolamine, and dimethylamine in both RMNP and Greeley. A constant amine background of 0.02 µg m^{-3} was observed in RMNP. Amine concentrations in Greeley were often near 0.02 µg m^{-3}, but weeks with average concentrations as high as 0.09 µg m^{-3} occurred. Greeley is closer to intensive agricultural activities including animal feeding operations than in RMNP. Analysis of the biomass burning source samples suggested that biomass burning is a source of amines. All amines measured by this method were identified with dimethylamine and trimethylamine dominating. Yet the sum of measured amines accounted for, on average, 11% of the total nitrogen in these samples. Overall, the analysis of the various filter samples using this IonPac CS-19 column method did suggest that amines are commonly present in ambient air, even in remote locations. If they are not accounted for, there is the potential to overestimate concentrations of sodium, ammonium, and potassium using traditional cation chromatography methods. In the example filter sample collected in the Central Valley, presented in Figures 1 and 3b, comparison of the peak areas obtained from these two chromatograms suggested that each of these three species would have been overestimated by ~10%.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4433/11/8/808/s1. Table S1 provides the calibration curve equations for the amines not plotted in Figure 4. There are also three data files with concentrations measured for various species determined from the collected filter samples: (1) in Rocky Mountain National Park, (2) in Greeley, CO, and (3) during controlled laboratory burns for fuels known to burn in the Southwestern U.S. In the data files, a -8888 means concentration is below detection limit and a -9999 means concentration data is missing.

Author Contributions: Conceptualization, A.P.S. and K.B.B.; methodology, A.P.S.; validation, A.P.S; formal analysis, A.P.S.; investigation, A.P.S.; data curation, A.P.S.; writing—original draft preparation, A.P.S.; writing—review and editing, A.P.S., K.B.B., C.M.C., M.K.D., B.A.S., and J.L.C.J.; visualization, A.P.S.; Funding acquisition, J.L.C.J. All authors have read and agreed to the published version of the manuscript.

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