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Collection of Ammonia for High Time-Resolved Nitrogen Isotopic Characterization Utilizing an Acid-Coated Honeycomb Denuder

Wendell W. Walters*^{,†,‡} and Meredith G. Hastings^{†,‡}

[†]Department of Earth, Environmental, and Planetary Sciences, Brown University, 324 Brook Street, Providence, Rhode Island 02912, United States

[‡]Institute at Brown for Environment and Society, Brown University, 85 Waterman Street, Providence, Rhode Island 02912, United States

Supporting Information

ABSTRACT: Nitrogen stable isotope analysis ($\delta^{15}N$) of ammonia (NH₃) has shown potential to be a useful tool for characterizing emission sources and sink processes. However, to properly evaluate NH3 emission sources and sink processes under ambient conditions, it is necessary to collect and characterize the chemical speciation between NH₃ and particulate ammonium (p- NH_4^+ , together referred to as NH_x . Current NH_3 collection methods have not been verified for their ability to accurately characterize δ^{15} N-NH₃ and/or provide necessary chemical speciation (i.e., δ^{15} N-NH₃ and δ^{15} N-NH₄⁺). Here, we report on the suitability of an established collection device that can provide NH_x speciation, an acid-coated (2% citric acid (w/v) + 1%



glycerol (w/v) in 80:20 methanol to water solution) honeycomb denuder (HCD) with a downstream filter pack housed in the ChemComb Speciation Cartridge (CCSC), for characterizing δ^{15} N-NH₃ under a variety of laboratory-controlled conditions and field collections. The collection method was tested under varying NH₃ concentration, relative humidity, temperature, and collection time at a flow rate of 10 L per minute (LPM). The acid-coated HCD collection device and subsequent chemical processing for δ^{15} N-NH₃ analysis is found to have excellent accuracy and precision of $\pm 1.6\%$ (2 σ), with an operative capacity of ~400 μ g of collected NH₃ for concentrations \leq 207 ppb_v. This work presents the first laboratory verified method for δ^{15} N-NH₃ analysis and will be useful in future air quality studies.

mmonia (NH_3) is the primary alkaline molecule in the A atmosphere and plays a key role in numerous atmospheric processes that have important implications for human health and climate via new particle nucleation.^{1,2} Understanding NH₃ emission sources and sink processes, especially in urban areas, is a challenging task due to the coexistence of many locally produced sources including emissions from local traffic,³⁻⁶ fuel combustion, industrial processes, humans,⁷⁻¹¹ and transport of agricultural NH₃.¹²⁻¹⁴ Analysis of the stable isotope composition of trace gases is an established tool for quantifying emission sources,¹⁵ as various surface sources and sink processes often exhibit characteristic isotopic compositions ("fingerprints").¹⁶ This tool allows for an understanding of emission sources as well as means to track the chemical and physical processes responsible for removal of trace gases at a process level. Previous researchers have used this technique to evaluate contributions of various sources and sink processes of numerous relatively long-lived trace gases including methane (CH_4) ,^{17,18} carbon dioxide (CO_2) ,^{19,20} carbon monoxide (CO),^{21,22} and nitrous oxide (N_2O) .^{23,24} Applying this tool to relatively short-lived NH3 might also enable an evaluation of its emission sources and sink processes, providing distinct information amidst large spatial and temporal variabilities.

Previous measurements of the nitrogen (N) stable isotope composition of NH₃ (δ^{15} N-NH₃) (δ^{15} N(% $_{o}$) = [($^{15}R_{sample}$)/ $({}^{15}R_{\text{reference}}) - 1] \times 1000$, where ${}^{15}R$ is the ratio of ${}^{15}N/{}^{14}N$ and air N2 is the N isotopic reference.) emission sources have reported large NH₃ source δ^{15} N variability and suggest considerable overlap between various emission sources (Figure 1).²⁵⁻³¹ However, some of these observations also include NH₃ process driven δ^{15} N effects, such as NH₃ volatilization resulting in a gradual increase in δ^{15} N. Thus, there is a need to better diagnose δ^{15} N values associated with emissions sources, while also constraining chemical or physical process effects.

Numerous collection techniques have been used to collect NH_3 as NH_4^+ for off-line N isotopic analysis including wet scrubbers,^{25–27} passive diffusion samplers,^{31,33} an acidic absorbing solution contained within an evacuated gas sampling bulb,²⁸ and active sampling using acid impregnated filters^{29,30} (Figure 1). While these methods have been designed to accurately reflect NH₃ concentrations, they have not been laboratory-verified for their suitability for δ^{15} N-NH₃ analysis;

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Figure 1. Previously reported δ^{15} N-NH₃ values of NH₃ source emissions and NH₃ volatilization (e.g., fertilizer and animal waste).²⁵⁻³¹ Prior measurements have used a wide variety of NH₃ collection techniques (legend), and many sources and process driven effects (NH₃ volatilization) show large variations in δ^{15} N-NH₃. Coalfired power plants are indicated as CFPP.

therefore, the δ^{15} N accuracy and/or precision of these collection devices are uncertain. The potential for collection methods to impact δ^{15} N-NH₃ was highlighted in Skinner et al.,³² in which a comparison between several active and passive NH₃ collection devices including gas-scrubbing bubbler, moss bag, shuttle sampler, and diffusion tube revealed significantly different δ^{15} N-NH₃ values and variances even when sampling the same emission source (field fumigation site). This result, and the contrasting reported environmental values, questions the accuracy of previously reported δ^{15} N-NH₃ values.

An additional complication when sampling ambient air for δ^{15} N-NH₃ analysis is that NH₃ exists in thermodynamic equilibrium with nitric acid (HNO₃), hydrochloric acid (HCl), and their neutralized condensed phases including ammonium nitrate (NH₄NO₃) and ammonium chloride (NH₄Cl).^{34–39} NH₃ will also neutralize sulfuric acid (H₂SO₄), but due to the low vapor pressure of its product ammonium sulfate ((NH₄)₂SO₄), it resides nearly completely in the condensed phase.³⁹ The coexistence of NH₃ and NH₄⁺, together referred to as NH_x, makes it possible that N isotopic equilibrium between NH₃ and NH₄⁺ could occur,^{25,29} which will scramble the ¹⁴N and ¹⁵N isotopes between NH₃ and NH₄⁺ based on statistical mechanics:⁴⁰

$${}^{15}\text{NH}_3 + {}^{14}\text{NH}_4^+ \rightleftharpoons {}^{14}\text{NH}_3 + {}^{15}\text{NH}_4^+$$
 (R1)

The theoretical equilibrium constant (*K*) or isotopic fractionation factor (α) for R1 is 1.034 ± 0.002 at 298.1 K,⁴⁰ indicating that isotopic equilibrium will favor the partitioning of ¹⁵N into p-NH₄⁺, resulting in higher δ^{15} N values in p-NH₄⁺ than in NH₃ (eq 1).

$$K_{298.1K} = \alpha_{298.1K} = \frac{{}^{15}\text{NH}_4^{+}/{}^{14}\text{NH}_4^{+}}{{}^{15}\text{NH}_3/{}^{14}\text{NH}_3} = 1.034 \pm 0.002$$
(1)

Additionally, unidirectional neutralization reactions involving NH₃ and H₂SO₄ have been suggested to result in a kinetic isotope effect leading to the initial δ^{15} N of p-NH₄⁺ to be -28% relative to ambient NH₃ based on relative diffusion rates of 14 NH₃ and 15 NH₃.⁴¹ Therefore, speciated δ^{15} N measurements of NH_x could provide valuable information

about NH₃ gas to particle conversion and new particle formation, indicating whether p-NH₄⁺ is formed under either kinetic or equilibrium controlled processes. Due to the potential for $\delta^{15}N$ of ambient NH₃ to be altered during particle formation, it is critical that under ambient air sampling conditions the collection technique must allow for the speciation of NH_x to evaluate the impact of NH₃ neutralization reactions/thermodynamic equilibrium on δ^{15} N-NH₃. The denuder-filter combination is an established NH₃ sampling technique that will effectively speciate NH_v.⁴²⁻⁴⁸ In this system, NH₃ is first removed from the sampled air stream on an acid-coated glass denuder followed by collection of p-NH₄⁺ on a downstream filter pack. These methods have been in use for decades using several denuder geometries including a simple boroscillate tube,⁴² honeycomb denuder,^{43,44} and annular denuder^{45,49} geometries to measure NH_r concentrations.^{12,47,50–52}

Here we present a new application of the denuder-filter sampling technique for characterizing δ^{15} N-NH₃. We have extensively tested a commercially available honeycomb denuder coated with an acid solution and housed in a ChemComb Speciation Cartridge, which has been well-characterized for its ability to speciate gas and particulate matter components, ^{43,44} for its suitability for δ^{15} N-NH₃ analysis under a variety of simulated environmental conditions and field collections. This work is a crucial step in developing a record of reliable δ^{15} N-NH₃ measurements. Ultimately, a field deployable method suitable for δ^{15} N-NH₃ analysis and capable of achieving high time-resolved measurements will help make considerable progress on evaluating spatial and temporal variability in environmental NH₃ emission sources and sink processes.

EXPERIMENTAL SECTION

NH₃ Collection Using an Acid-Coated Honeycomb **Denuder.** NH₃ is collected on a honeycomb denuder (HCD) coated with a 2% citric acid (w/v) 1% glycerol (w/v) in an 80:20 methanol to ultrahigh purity water (18.2 M Ω , Milli-Q (MQ)) solution and housed in a ChemComb Speciation Cartridge (CCSC). We note that a range of acid coating solutions may be used to capture NH₃ including phosphoric acid and oxalic acid:⁴⁹ however, we have limited our tests to citric acid due to its low $[NH_4^+]$ blanks compared to other acids,⁴² making it more suitable for environmental research and the need for high-time-resolved measurements. The employed sampling system has been extensively described and characterized in previous works.^{43,44} Briefly, the CCSC contains a polytetrafluoroethylene (PTFE) coated inlet to limit NH₃ loss (previous work has found this inlet to have an NH₃ transmission efficiency greater than 97.3% utilizing this PTFE coating⁵³) and a PTFE coated stainless steel PM_{2.5} impactor that removes particulate matter larger than 2.5 μ m and facilitates an evenly distributed flow through the 212 hexagonal channels of the HCD at a flow rate of 10 L per minute (LPM). The indented circular reservoir of the impactor plate was evenly covered with PTFE grease (Chemours Krytox GPL 207) to prevent particle bounce and to limit NH_3 absorption. Within the CCSC, a borosilicate transition piece allows laminar flow to be achieved followed by two acid-coated HCDs in series that are separated by a PTFE spacer. The first "capture" HCD is used to remove NH3 from the sampled airstream, and the second HCD is used as control to check for possible NH₃ breakthrough in our control tests. After the

Analytical Chemistry



Figure 2. Schematic diagram of the experimental setup for the evaluation of NH_3 collection using an acid-coated honeycomb denuder housed in the ChemComb Speciation Cartridge. The sample lines were made of polyvinylidene fluoride, and the three-way union connectors were made from PTFE to limit the absorption of NH_3 .

HCD, there is an available filter pack within the CCSC to collect particulate matter on a filter, though this was not used during our control tests of NH_3 collection. An image of the sampling apparatus is provided in the Supporting Information (Figure S1).

NH₃ Collection Experiments. The laboratory NH₃ collection setup is depicted in Figure 2. Briefly, a 20.7 $(\pm 1\%)$ ppm_v flow of NH₃ in N₂ tank (Praxair) was controlled using a mass-flow controller. This tank was diluted to achieve variable [NH₃] using the laboratory N₂ compressed gas line that was further purified using Molecular Sieve 5 Å and silica gel. NH₃ was not detectable in the purified N₂ gas line. The N₂ compressed gas line was divided using a 3-way union fitting made from PTFE with one of the lines passing through a gaswashing bottle containing MQ water and then through a water trap, allowing for separate N₂ lines containing "wet" N₂ and "dry" N_2 . The flow rates of wet N_2 and dry N_2 were controlled using separate rotameters. Altering the relative flow rate of wet N₂ to dry N₂ allowed for testing various levels of relative humidity (RH). The flow of wet N_2 and dry N_2 were combined using a PTFE 3-way union fitting. The total N₂ flow was then combined with the flow from the NH₃ tank using another 3-way PTFE union fitting that was also connected to the inlet of the CCSC. The outlet of the CCSC was connected to a rotameter to ensure that "in-flow" was approximately equal to the "out-flow", and temperature (± 0.5 °C) and RH ($\pm 3\%$) were monitored in the excess out-flow (Elitech GSP-6). Due to the reactiveness or "stickiness" of NH₃ with surfaces, all tubing in our setup was composed of polyvinylidene fluoride (PVDF), which has been shown to be chemically inert to NH₃.

The sampling cartridge is designed for an optimal flow rate of 10 LPM,⁴³ so all experiments were conducted at this flow rate. Variable "target" NH₃ concentrations ([NH₃]) were tested including 31.3, 107, 207, and 2070 ppb_v; however, we note the possibility that the [NH₃] in the gas tank may not be as accurate as reported, and that NH₃ loss in the sampling line may lower the actual flowed [NH₃]. The targeted [NH₃] encompass a range somewhat typical of what is expected for a range of environmental sampling conditions, including near emission sources and ambient air. Ambient conditions will likely have $[NH_3]$ lower than 31.3 ppb_v (e.g., near single ppb_v levels),50 but this was the lowest concentration we could achieve given a mass flow controller minimum flow rate of 0.015 LPM. However, this should not limit our evaluation of the applicability of this collection technique because denuders are limited by high concentrations of the gases to be

denuded,⁴³ such that lower concentrations should be denuded as efficiently as the higher tested concentrations. NH₃ flow tests were also conducted over a variety of temperatures by placing the sampling cartridge and inlet in an ice bath and heating the sample line and cartridge using heat tape to test the NH₃ collection efficiency under a variety of environmentally relevant temperatures. After NH₃ collection, the HCD and single-channel denuder tube were extracted using 30 mL of MQ water. NH₄⁺ blanks in the extraction solution were always found to be less than 0.3 μ M-NH₄⁺ (n = 12), near our analytical detection limit (see below).

Due to NH₃ reactiveness with surfaces, we also evaluated the CCSC as a source of NH₃ loss (e.g., PTFE coated inlet and PTFE coated impactor plate) and a potential source for δ^{15} N-NH₃ fractionation. This was tested by collecting NH₃ using a perfluoroalkoxy (PFA) gas-scrubbing impinger containing 30 mL of a 2% citric acid solution connected in series with a second PFA impinger to check for breakthrough. These control tests were conducted at an $[NH_3]$ of 2070 ppb_v, a flow rate of 1 LPM, and for a collection time of 5 min. An impinger with an acidic scrubbing solution is an established efficient collector of NH₃ (e.g., U.S. EPA Method 17) but does not adequately provide the speciation of NH, that suits our needs for δ^{15} N-NH₃ determination in ambient air. After NH₃ collection, the solution contained within the gas scrubbing impinger were transferred to a 50 mL centrifuge tube and stored in a refrigerator until future concentration and isotope analysis.

 $[\dot{N}H_4^+]$ Concentration and $\delta^{15}N$ Isotopic Analysis. All collected NH4⁺ samples were analyzed for their concentration using colorimetric analysis based on the indophenol blue method⁵⁵ that was automated using a discrete UV-vis analyzer (Westco SmartChem 2.0). Reproducibility calculated from replicate measurements was $\pm 0.5 \ \mu M-NH_4^+$. The determination of δ^{15} N-NH₄⁺ follows previously described methods.⁵⁶ Briefly, samples are diluted to at least 10 μ M-NH₄⁺ using MQ water to a volume of 10 mL in 50 mL vials that are acidwashed, triple-rinsed with MQ water, and ashed at 500 °C for 4 h. The samples are then oxidized to nitrite (NO_2^{-}) using hypobromite (BrO⁻) in an alkaline solution, which was synthesized as previously described in Zhang et al.⁵⁶ Since accurate isotopic measurements are sensitive to the conversion of NH_4^+ to NO_2^- (i.e., incomplete conversion would lead to undesirable δ^{15} N fractionation),⁵⁶ reaction conditions including volume of the oxidation solution and reaction time were optimized for our sample matrix. $[NO_2^{-}]$ oxidation yields were

measured using a standard colorimetric absorption technique (e.g., U.S. EPA Method 353.2) automated using a discrete UV–vis analyzer (Westco SmartChem 2.0). Reproducibility based upon replicate measurements of samples and quality control standards was found to be $\pm 0.3 \ \mu$ M-NO₂⁻. Next, 0.4 mL of 0.4 M sodium arsenite (NaAsO₂) was added to the samples to remove remaining BrO⁻.

Once the NH_4^+ samples are converted to NO_2^- , they can be routinely analyzed for their N isotopic composition using previously established chemical methods that convert NO₂⁻ to N_2O .^{56,57} Briefly, 20 nmol of NO_2^- samples are transferred to 20 mL vials that were acid-washed, triple-rinsed with MQ water, and ashed at 500 °C for 4 h. Vials are crimp capped with PTFE/butyl septa and flushed with helium (He) for 10 min. NO_2^- is subsequently reduced to N_2O using 2 mL of 1 M sodium azide buffered in 30% acetic acid solution.⁵⁷ Subsequently, the solutions are neutralized using 6 M NaOH with a 0.1% phenolphthalein solution to indicate when the solutions reached pH > 8.2, which is done to limit the possibility of toxic hydrazoic acid (HN₃) from escaping into the laboratory. Samples are then analyzed for their $\delta^{15}N-N_2O$ composition using an automated N₂O extraction system coupled to a continuous flow Isotope Ratio Mass Spectrometer for m/z 44, 45, and 46 measurements.⁵⁸ In each sample batch, unknowns are calibrated with respect to two internationally recognized NH4+ isotopic reference materials, IAEA-N2 and USGS25, with δ^{15} N values of 20.3% and -30.3%, respectively,^{59,60} that are run between approximately every 10 unknowns. The isotopic standards undergo the exact same chemical processing as the unknowns and are used to correct for isotopic fractionation resulting from the chemical conversion of NH4⁺ to N2O. For each batch sample analysis, replicates of two NO2⁻ standards with known isotope values (RSIL-N7373 and RSIL-N10219 with $\delta^{15}N = -79.6\%$ and (1.8%), respectively)⁶¹ are run as a quality control to monitor the conversion of NO₂⁻ to N₂O and system stability. Corrections to determine δ^{15} N-NH₄⁺ are performed by accounting for isobaric influences, blank effects, and calibrating the unknowns to the internationally recognized δ^{15} N-NH₄⁺ standards.

RESULTS AND DISCUSSION

The evaluation of the performance of a collection method for the isotopic analysis of a reactive gas should involve a check of the following parameters (adapted from Perrino et al.⁴⁸).

(1) Matrix suitable for isotopic analysis. The matrix of the collection reagent must be suitable for the processing associated with converting the collected reaction product to an appropriate form for isotopic analysis.

(2) Collection efficiency. The collection method must be shown to be a quantitative sink for the target analyte to limit an isotopic bias.

(3) Selectivity of the collection method. The collection method should only retain the target analyte and no other compounds should yield the same reaction product. This is expected to be a trivial requirement for NH_3 since it is the primary inorganic alkaline gas.⁴⁹

(4) Known operative capacity. The operative capacity (defined as the amount of target analyte that can be collected while maintaining a collection efficiency >95%)⁶² must be known for the intended sample collection duration.

(5) Stability of reaction product. The collected reaction product should not be released or compromised once collected.

(6) Comparison to other collection devices. Generally, there are no internationally recognized isotopic standards for reactive gases. Therefore, the potential bias of the collection device, primarily inlet loss, needs to be evaluated. For example, by comparison with other collection devices in which this bias is expected to be low.

(7) Field applicability. Field applicability of the collection method should be demonstrated for the intended sample collection times with collection performed in replicates.

Matrix Effect on NH_4^+ Oxidation. The limiting step in δ^{15} N-NH₄⁺ analysis utilizing methods described in Zhang et al.⁵⁶ is the oxidation of NH₄⁺ to NO₂⁻. Thus, we evaluated the impact of our sample matrix, 2% citric acid + 1% glyercol coating solution extracted in 30 mL of MQ, on the conversion of NH₄⁺ to NO₂⁻ for a variety of reaction parameters including variable BrO⁻ amounts and reaction times. Solutions containing 10 mL of 10 μ M-NH₄⁺ were created using either the sample matrix or MQ water and were oxidized using either 1 or 2 mL of the alkaline BrO⁻ solution. Triplicates were performed for each unique matrix and BrO⁻ volume combination. Figure 3 displays the NO₂⁻ oxidation yields



Figure 3. Effect of reaction time, BrO⁻ volume addition, and sample matrix on the oxidation of NH_4^+ to NO_2^- and stability of the NO_2^- reaction product. Quantitative oxidation is achieved within 20 minutes for both 1 and 2 mL additions of BrO⁻, and the NO_2^- product is stable for at least 31.5 h.

that were measured as a function of time ranging from 0.2 to 31.5 h. Quantitative NH_4^+ to NO_2^- oxidation is found in our sample matrix for both 1 and 2 mL additions of the alkaline BrO⁻ solution, and complete oxidation is achieved in as early as 20 minutes (Figure 3). Additionally, quantitative conversion was found to be maintained for up to 31.5 h, indicating $[NO_2^{-}]$ stability in the oxidation solution (Figure 3). Therefore, it is our recommendation that 1 mL of the alkaline BrO⁻ solution is enough to ensure complete NH₄⁺ oxidation to NO₂⁻ for a 20-min reaction time in a 10-mL solution containing 10- μ M of NH₄⁺. Since incomplete NH₄⁺ to NO₂⁻ oxidation would result in an undesirable isotope effect, it is also our recommendation that oxidation yields should be checked for each sample. Once converted to NO_2^{-} , samples can be readily reduced to N₂O using azide in an acetic acid buffer as previously described. ^{56,57} We find δ^{15} N-NH₄⁺ for isotopic standards in the sample matrix to have a standard deviation of 0.6% and 0.7% (1 σ) for IAEAN2 (n = 29) and USGS25 (n =27), respectively, resulting in an overall pooled standard

deviation of 0.7%. Overall, these results demonstrate the sample matrix to be suitable for δ^{15} N-NH₄⁺ analysis.

NH₃ Collection Performance. The collection efficiency of the 2% citric acid + 1% glycerol coated HCD for NH₃ capture for varying sampling conditions is displayed in Figure 4.



Figure 4. Summary of NH₃ capture data utilizing a 2% citric acid + 1% glycerol coated honeycomb denuder (HCD) and a gas scrubbing impinger containing a 2% citric acid solution (GSI) including (a) NH₃ collection efficiency (%) as a function of amount of collected ammonia (μ g) from laboratory flow tests for a range of [NH₃] and (b) measured δ^{15} N-NH₃ as a function of collection efficiency for the laboratory flow tests. Collection efficiency of 95% (minimum target) is indicated as the solid black line. When NH₃ collection efficiency was found to be >95%, the measured δ^{15} N-NH₃ was found to be ($\bar{x} \pm 2\sigma$) - 2.5 ± 1.6% (n = 75) and -2.4 ± 2.0% (n = 5) for the HCD and GSI, respectively.

Collection efficiency (E; eq 2) and total recovery (Q; eq 3) were calculated according to

$$E = 100(1 - Q_2/Q_1) \tag{2}$$

$$Q_{\rm TOT} = Q_1 + Q_2 \tag{3}$$

where 1 and 2 refer to the capture and breakthrough denuder, respectively. Overall, NH₃ collection efficiency was found to be higher than the 95% threshold⁶² under most sampling conditions for a collection amount up to 388.8 μ g of NH₃, except for the flow tests at an extremely elevated [NH₃] of 2070 ppb_v (Figure 4). At this elevated [NH₃], collection efficiency was observed to quickly diminish after an NH₃ collection amount of 14.8 μ g. This result is consistent with Koutrakis et al.⁴³ that found the acid coated HCD to be best suited for an [NH₃] lower than 200 ppb_v. Our results indicate excellent NH₃ collection efficiency between 1.3 to 388.8 μ g-NH₃ for a collection time up to 24 hours (Table S1). Since we found collection efficiency to deteriorate for NH₃ collection amounts greater than 388.8 μ g of NH₃ (Figure 4), we suggest this amount as the operative capacity of the collection system.

The measured δ^{15} N-NH₃ for the NH₃ capture tests are also shown in Figure 4. When collection efficiency is found to be >95%, we find reproducible δ^{15} N-NH₃ values with a 2σ of $\pm 1.6\%$ (*n* = 75). Interestingly, the measured 2σ is very close reproducibility of our NH₄⁺ isotopic standards of 1.4% (2σ), suggesting that the limiting factor in our analysis is the off-line processing for δ^{15} N analysis rather than NH₃ collection. When collection efficiency is less than 95%, we observe an undesirable δ^{15} N-NH₃ isotope effect (Figure 4); thus, it is critical to stay within the operative capacity of the tested NH₃ collection device. Based on ANOVA single factor analysis, we find no statistical differences in δ^{15} N-NH₃ for any of the simulated conditions when collection efficiency is >95% (pvalue is 0.97), suggesting that the tested collection technique is suitable for a variety of environmental conditions (i.e., temperature and relative humidity) except for elevated $[NH_3]$ (e.g., >2000 ppb_v). We note that we do not know the absolute δ^{15} N-NH₃ value of our NH₃ tank, but comparison with other collection devices can indicate any potential sampling artifacts that might bias our δ^{15} N-NH₃ values such as NH₃ loss on the sampling cartridge inlet (see below).

Stability of Collected NH₄⁺. Previous work utilizing a 1% citric acid coating solution found significant NH₃ desorption as high as 41% after 12 h, which could severely limit its use for atmospheric sampling for extended periods of time⁴⁹. We tested for this possibility in our sampling system by loading approximately the same amount of NH₃ on several denuders and immediately extracted the NH₄⁺ reaction product as well as waited 24 and 72 h before extraction. This test was conducted in triplicates for each extraction time, and the extracted [NH₄⁺], δ^{15} N-NH₃, and calculated desorption loss are displayed in Table 1. Based on the average of the three

Table 1. Summary of the Results of NH_3 Desorption Following Capture on a 2% Citric Acid +1% Glyercol Coated HCD^{*a*}

elapsed time (h)	Q_{TOT} (μ g)	E(%)	δ^{15} N-NH $_3$ (%)	desorbed amount (%) ^b
0	11.2 ± 1.2	98.5 ± 0.1	-2.9 ± 0.5	
24	11.0 ± 0.8	97.8 ± 0.3	-2.7 ± 0.6	1.8
72	10.8 ± 0.7	98.0 ± 0.7	-2.3 ± 0.3	3.6

"Values are displayed as averages ($\pm 1\sigma$) for triplicates and indicate the amount of collected NH₃ (Q_{TOT}), collection efficiency (*E*), δ^{15} N-NH₃, and calculated percentage of desorbed NH₃. ^{*b*}Calculated as $100(1 - Q_{\text{TOT}(24\text{ortsb})}/Q_{\text{TOT}(00)})$.

replicates for each test condition, we estimate a desorption of 1.8% and 3.6% for 24-h and 72-h, respectively. However, we find no statistical differences between Q_{TOT} , E(%), or δ^{15} N-NH₃ between the immediately extracted samples and those that were extracted after 24 and 72 h. This suggests that NH₃ desorption in our sampling system and coating solution is minimal for a period up to 72 h. Both our flow tests and Koutrakis et al.⁴³ found an NH₃ collection efficiency of >99.5% for 24-h flow times, further suggesting that the 2% citric acid + 1% glycerol coating solution on a HCD should be sufficient for extending sampling periods (up to at least 24 h). While we can only speculate on differences in NH₃ desorption between our work and Perrino and Gherardi,⁴⁹ we can point out that we have tested a HCD coated with a 2% citric acid + 1% glycerol

solution while Perrino and Gherardi⁴⁹ performed their testing using an annular denuder coated with a 1% citric acid solution.

Comparison to Other NH₃ Collection Devices. Collection efficiencies and δ^{15} N-NH₃ for the gas-scrubbing impinger (GSI) are also displayed in Figure 4. Overall, collection efficiency was always found to be greater than 99.2% and δ^{15} N-NH₃ were found to be $-2.4 \pm 2\%$ ($\pm 2\sigma$), respectively, for 5 trials (Table S2). The measured δ^{15} N-NH₃ are found to be in statistical agreement with the measured δ^{15} N-NH₃ from the acid-coated HCD housed in a CCSC ($-2.7 \pm 1.6\%$) when collection efficiency was >95% (Figure 2). This comparison indicates that similar δ^{15} N-NH₃ values were achieved for the various NH₃ collection devices, suggesting that the CCSC housing is not a significant source of NH₃ loss and does not impart a δ^{15} N-NH₃ bias compared to other collection devices in which inlet loss is assumed to be negligible.

Field Applicability. Ambient urban air in Providence, RI, U.S.A. was sampled in replicates (side-by-side collections) for varying times including 1 (n = 3), 24 (n = 5), and 48 (n = 4)hours by flow-controlling an air sampling pump attached to the outlet of the CCSC to 10 LPM (Table S3). Collection efficiency was found to be >98% for each sampled time interval (Figure 4), further indicating minimal NH₃ desorption for sampling periods up to 48 h utilizing our collection approach. The collected NH₃ amount ranged from 1.7 to 66.9 μ g of NH₃, which is well-within the tested operative capacity (~400 μ g of NH₃) of the collection device (Figure 4). Average reproducibility, calculated as the average of absolute differences between the collected replicate samples for NH₃ and δ^{15} N-NH₃ is 0.010 \pm 0.008 μ mol/m³ and 0.9 \pm 0.7%, respectively. Additionally, the average percent error between replicate concentration measurements is found to be 16.9 \pm 9.3%. The observed average reproducibility in δ^{15} N-NH₃ is close to our recommended 2σ error for this method of $\pm 1.6\%$ based on our laboratory control tests. The interpretation of the measured δ^{15} N-NH₃ is beyond the scope of this work; however, these samples show that the tested method allows for high-time resolution (on order of an hour) and reliable δ^{15} N-NH₃ measurements for sampling periods up to 48 h. We note that the collection time resolution of this method is dependent upon achieving a minimum needed for isotopic analysis. For this study, 20 nmol samples were processed, therefore requiring a minimum of 0.34 μ g of NH₃ for field collections.

CONCLUSION

We have critically evaluated a 2% citric acid + 1% glycerol coated HCD for its suitability for δ^{15} N-NH₃ analysis that has included a careful consideration of reagent blanks, matrix effects, collection efficiency, selectivity, operative capacity, reaction product stability, and isotopic bias. Our results indicate the tested method to be appropriate for δ^{15} N-NH₃ determination with a precision of $\pm 1.6\%$ (2 σ ; n = 75), for an operative capacity (collection efficiency >95%) of ~400 μ g of collected NH₃. Our field tests indicate that the collection method is suitable for δ^{15} N-NH₃ characterization of ambient air with δ^{15} N-NH₃ resolution on the order of an hour. The high time resolution and excellent δ^{15} N-NH₃ precision of this method will be applied in future work to improve our understanding of NH₃ emission sources, sink processes, and diurnal patterns of NH₃. Additionally, the denuder-filter pack combo collection technique has the potential to be extended

for isotopic analysis of other gaseous compounds such as sulfur dioxide (SO₂), nitric acid (HNO₃), and nitrogen dioxide (NO₂) using an appropriate HCD coating for quantitative gas collection. Utilizing the acid-coated HCD for NH₃ collection, a carbonate-coated HCD for acidic gas collection (e.g., HNO₃ and SO₂), and an appropriate filter for PM_{2.5} collection could enable the simultaneous determination of δ^{15} N-NH₃ and δ^{15} N-NH₄⁺(p) and a new tool for investigating the atmospheric dynamics of NH_x.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.anal-chem.8b01007.

Sampling apparatus image (Figure S1); summary of honeycomb denuder control tests (Table S1); summary of gas scrubbing impinger control tests (Table S2); and summary of ambient air replicate samples (Table S3) (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: wendell walters@brown.edu.

ORCID 0

Wendell W. Walters: 0000-0001-6346-9840

Notes

The authors declare no competing financial interest.

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