# Particulate Nitrate Measurement Using Nylon Filters

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## ABSTRACT

Nylon filters are a popular medium to collect atmospheric fine particles in different aerosol monitoring networks, including those operated by the U.S. Environmental Protection Agency and the Interagency Monitoring of Protected Visual Environments (IMPROVE) program. Extraction of the filters by deionized water or by a basic aqueous solution (typically a mixture of sodium carbonate and sodium bicarbonate) is often performed to permit measurement of the inorganic ion content of the collected particles. Whereas previous studies have demonstrated the importance of using a basic solution to efficiently extract gaseous nitric acid collected using nylon filters, there has been a recent movement to the use of deionized water for extraction of particles collected on nylon filters to eliminate interference from sodium ion ($Na^+$) during ion chromatographic analysis of inorganic aerosol cations. Results are reported here from a study designed to investigate the efficiency of deionized water extraction of aerosol nitrate ($NO_3^-$) and sulfate from nylon filters. Data were obtained through the conduct of five field experiments at selected IMPROVE sites. Results indicate that the nylon filters provide superior retention of collected fine particle $NO_3^-$, relative to Teflon filters, and that deionized water extraction (with ultrasonication) of collected $NO_3^-$ and sulfate is as efficient, for the situations studied, as extraction using a basic solution of 1.7 mM sodium bicarbonate and 1.8 mM sodium carbonate.

## IMPLICATIONS

Particulate nitrate ($NO_3^-$) is an important constituent of atmospheric aerosol particles at many locations. This study examines measurement artifacts associated with sampling fine particle $NO_3^-$ at several nonurban locations. Chief findings include: (1) nylon filters retain fine particle $NO_3^-$ much better than Teflon filters, with retention efficiencies close to 100%, and (2) extraction of nylon filters by sonication in deionized water provides efficient recovery of collected particulate $NO_3^-$.

## INTRODUCTION

Nitrate ($NO_3^-$) is often an important contributor to the inorganic fraction of atmospheric aerosol particles.[1–3] Ammonium nitrate ($NH_4NO_3$), generally the predominant form of $NO_3^-$ in submicron aerosol particles, is formed by reaction of gaseous nitric acid ($HNO_3$) and ammonia ($NH_3$) as shown in eq 1.[4]

$$NH_3(g) + HNO_3(g) \leftrightarrow NH_4NO_3(p) \qquad (1)$$
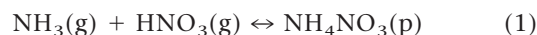
This reaction is reversible, with the equilibrium constant varying strongly with temperature and humidity.[5–8] Dissociation of $NH_4NO_3$ increases with increasing temperature and decreases with increasing relative humidity (RH) above the deliquescence point.[9] $NO_3^-$ can also be found in aerosol particles in other forms, including sodium nitrate ($NaNO_3$) and calcium nitrate [$Ca(NO_3)_2$], reflecting, for example, reactions of $HNO_3$ or its precursors with sea salt or suspended soil particles.[10] Most routine aerosol monitoring networks, however, assume that $NO_3^-$ measured is in the form of $NH_4NO_3$.

Because of the semivolatile nature of $NH_4NO_3$, its measurement in atmospheric aerosol is subject to significant sampling artifacts, which have been the subject of several prior investigations.[11–21] Positive $NO_3^-$ measurement artifacts, for example, can be caused by collection of gaseous $HNO_3$ and/or other nitrogen oxides with subsequent reaction on filter media. The use of diffusion denuders upstream of particle sampling filters can effectively remove $HNO_3$ (and perhaps other species depending on denuder coating), thereby minimizing this artifact.[3,22–24] If the denuder can be extracted and the extract analyzed, this approach offers the additional advantage of being able to quantify gas phase $HNO_3$

concentrations, aiding understanding of the gas-particle equilibrium described above.

Negative $NO_3^-$ sampling artifacts are also common.[12,13,25–33] Loss of $NH_4NO_3$ as a result of changing ambient conditions (e.g., T, RH, and/or gas phase concentrations of $NH_3$ or $HNO_3$) during a sampling interval can lead in some cases to significant biases in measured $NO_3^-$ concentrations. Such losses can be reduced by shortening sample periods, reducing filter face velocities, and limiting filter pressure drops,[34] but they remain problematic. A back-up filter (e.g., nylon or sodium chloride-impregnated glass fiber or cellulose) or denuder for trapping volatilized $HNO_3$ can also be used to quantify this loss artifact but requires additional sampling media and incurs additional labor and analytical costs.[35–42]

An alternative approach taken by the Interagency Monitoring of Protected Visual Environments (IMPROVE) network is to pass ambient air through a diffusion denuder, for $HNO_3$ removal, followed by particle sampling on a nylon filter.[1] Nylon filters have long been used for efficient collection of gaseous $HNO_3$.[32] The intent in using them for aerosol $NO_3^-$ collection is to collect particulate $NO_3^-$ (as well as other species) and to retain any $HNO_3$ volatilized from collected $NH_4NO_3$ particles. In theory, then, this approach permits accurate measurement of particulate $NO_3^-$ with the use of only a single filter.

Whereas several previous studies have compared various filter pack and denuder sampling methods,[17,21,26,32,37,43–47] use of nylon filters for particulate nitrate sampling has received relatively little attention.[31] Despite the lack of study, nylon filters have been widely used as the particle collection medium in the IMPROVE network[48] and the U.S. Environmental Protection Agency (EPA) $PM_{2.5}$ speciation network.[49]

Nylon membrane filters are made of thin layers of porous nylon.[50] They are a common choice as a back-up filter for high-efficiency $HNO_3(g)$ collection.[26,32,51–53] $HNO_3(g)$ interacts strongly with the nylon filter medium. Previous research found that a basic solution is needed to fully recover $HNO_3(g)$ collected on nylon filters.[12,13,31,54–57] Nylon filters used for $HNO_3$ collection are often extracted with an aqueous solution of 1.8 mM sodium carbonate ($Na_2CO_3$) and 1.7 mM sodium bicarbonate ($NaHCO_3$) to provide efficient recovery.[56] This solution composition is chosen to match the composition of eluent used for analysis of nitrate by a common ion chromatography (IC) technique. Extraction of nitric acid collected on nylon filters with deionized water has been shown to result in incomplete recovery.[58]

The IMPROVE network started using nylon filters to collect particles in 1987, and the soluble particulate species initially were recovered from the filter medium by a basic solution extraction.[59–61] In June 1997, IMPROVE began extracting nylon filters from selected sites, including Great Smoky Mountains National Park, Shenandoah National Park, and Dolly Sods/Otter Creek Wilderness, with deionized water.[62] Between January 1999 and October 2000 nylon filters from all of the IMPROVE sites were extracted with deionized water. After a brief period when extractions of nylon filters from most IMPROVE sites (all but the three sites mentioned above) were switched back to basic solution (between October 2000 and April 2001), nylon filters from all of the sites were again extracted with deionized water.[62]

The reason for using deionized water extraction is to permit analysis of particle cation concentrations by IC. Use of the sodium carbonate/sodium bicarbonate extraction solution introduces a large quantity of sodium ion ($Na^+$) to the aerosol extract, which prevents analysis of particle $Na^+$ concentrations and also strongly interferes with measurement of aerosol ammonium ion ($NH_4^+$), because the $Na^+$ and $NH_4^+$ peaks elute close to each other in typical IC separations.

The use of deionized water to extract nylon filters used for aerosol particle collection has become a common practice in particulate matter network operations, including those operated by the EPA[49] and IMPROVE.[63] Recently, concern has arisen about whether the water extraction adequately recovers collected particulate $NO_3^-$. In particular, there is concern that $HNO_3$ volatilized from $NH_4NO_3$ particles and recaptured by nylon filters may be so strongly bound that its efficient recovery necessitates use of a basic solution, as previously observed for direct nylon filter collection of $HNO_3$.[57,64] To examine this issue, a series of field experiments was designed at several IMPROVE monitoring locations where $NO_3^-$ is known to be an important contributor to aerosol concentrations. This article reports results of these studies with regard to recovery of particulate $NO_3^-$ from nylon filters by deionized water extraction with sonication and compares $NO_3^-$ retention efficiencies between denuded Teflon and nylon filters.

Because $NO_3^-$ is an important constituent of fine particles at many locations, its accurate measurement is important to understand particle sources and effects on visibility. Results of the field experiments described here are intended to help identify potential $NO_3^-$ measurement biases in current IMPROVE network protocols. More generally, these field experiments provide new insight into particulate $NO_3^-$ measurement using denuded nylon and Teflon filters, especially at nonurban locations.

## EXPERIMENTAL WORK
### Apparatus
*Annular Denuder/Filter-Pack Systems.* The annular denuder/filter-pack system (URG-3000C) used in this series of

field experiments was purchased from University Research Glassware, Inc. Ambient air is drawn through a cyclone (2.5-$\mu$m size cut, URG-2000-30EN) by a computerized sampling pump (URG-3000-02BAM). The airflow is controlled by a mass flow controller at a rate of ~10 lpm (volumetric equivalent) and monitored by a dry gas flow meter (URG-3000-02C). The sample air is passed along two 242-mm annular denuders in series with etched glass walls coated with chemicals that adsorb the gaseous species of interest. In this experiment, the first denuder is designed to collect gaseous $HNO_3$ (and other acidic gases) and the second to remove gaseous $NH_3$. The remaining airstream then passes through a two-stage Teflon-coated filter pack (URG-2000-22FB), which can be assembled with two nylon filters (Nylasorb, 1-$\mu$m pore size, 37-mm I.C.E. 450 membrane from Pall Corp.) in series or a Teflon (Teflo, 2-$\mu$m pore size, 37 mm from Pall Corp.) and a nylon filter. Nylasorb filters were used for these experiments because of high blank levels for some cation species in the nylon filters currently in use by IMPROVE, an important consideration for other study objectives, and the intent of IMPROVE to begin use of Pall Nylasorb filters for particle collection in the near future.

*Denuder Cleaning, Coating, and Drying Procedures.* Denuders are soaked and cleaned thoroughly with deionized water before coating. The first denuder utilizes a coating solution containing 10 g of $Na_2CO_3$ and 10 g of glycerol dissolved in 500 ml of deionized water and 500 ml of methanol. This denuder is intended to collect $HNO_3$ but also will collect HCl, $HNO_2$, and sulfur dioxide ($SO_2$). The second denuder, for $NH_3$ removal, is coated with a solution containing 10 g of phosphorous acid ($H_3PO_3$) dissolved in 100 ml of deionized water and 900 ml of methanol. The coating solutions were prepared right before the field campaigns or as needed during the field experiments.

After coating, the annular denuders were attached to a manifold (URG-2000-30 Hr) and dried using compressed $N_2$ or compressed air scrubbed to remove interfering contaminants by passage through a URG #30 drying train (URG-2000-30I) containing an ammonia scrubber (Perma Pure Inc.) filled with phosphoric acid-based scrubbing media and inert ceramic burl saddles in a polysulfone housing (initially $H_3PO_3$ on a quartz filter and glass wool were used; removes $NH_3$), silica gel (removes moisture), potassium permanganate on aluminum (removes NO), and activated carbon (removes ozone, $NO_2$, $SO_2$, $HNO_3$, hydrocarbons, etc.). A HEPA capsule filter (#12144, Pall Corp.) is installed at the entrance to the scrubber columns and the denuder drying manifold. An inlet vacuum guard filter (Vacu-Guard, Whatman) is used at the outlet to prevent particles from entering the drying manifold. Denuder

blanks were evaluated for both drying systems and found to be very low.

Each denuder is extracted using 10 ml of deionized water (rotating water across the collection surfaces for 5–6 min) immediately after sampling. Ten microliters of 30% hydrogen peroxide are added to a 5-ml portion of the $HNO_3$ denuder extract to ensure complete conversion of $SO_2$ to sulfate anion ($SO_4^{2-}$), which is determined by IC later. The extracts are refrigerated until later analysis in our laboratory at Colorado State University.

*Filter Handling and Extraction.* Blanks from both nylon and Teflon filters were tested for contaminants before use. Although contamination was not a problem, the filter batches showing the lowest background levels were selected for use. Filters were loaded into the filter packs in an ammonia-free glove box (an enclosed Plexiglas box with a $H_3PO_3$–$NH_3$ scrubbing system initially, then a Perma Pure ammonia scrubber system). After sampling, filters were unloaded again in this glove box and stored frozen in clean sample tubes until later extraction and analysis in our laboratory. As additional protection against potential artifact $NH_3$ neutralization, the filter tubes were stored in sealed plastic bags containing quartz filter sheets soaked with 1% $H_3PO_3$.

Nylon filters were extracted either with 5 ml of deionized water or with 5 ml of anion IC eluent (1.7 mM $NaHCO_3$/1.8 mM $Na_2CO_3$). During extraction the filters were sonicated for 30–45 min in an ultrasonic bath (Branson, 5210). Because Teflon filters are hydrophobic, 50 $\mu$l of ethanol was added to wet the filter surface[65] before deionized water extraction, also in the ultrasonic bath.

Nylasorb filters were also used to collect gaseous $HNO_3$ to conduct additional tests on extraction procedures. Nylon filters collected for this purpose were equally divided into four quarters. One quarter was extracted by deionized water with sonication, the second by deionized water without sonication, and the third and fourth quarters both by basic IC eluent with sonication.

*Sampling Train Modules.* Three different annular denuder/filter-pack train configurations were used in the five field deployments. A schematic diagram showing the components in each train is included as Figure 1.

The first configuration consists of a $PM_{2.5}$ cyclone, a carbonated-coated annular denuder for $HNO_3$ and sulfur dioxide collection, a $H_3PO_3$-coated annular denuder for ammonia collection, a nylon filter for particulate matter collection, a second nylon filter for collection of any $HNO_3$ released because of $NH_4NO_3$(p) evaporation from the first nylon filter, and a second $H_3PO_3$-coated annular denuder for collection of any ammonia released because of $NH_4NO_3$(p) evaporation from the front nylon filter. All
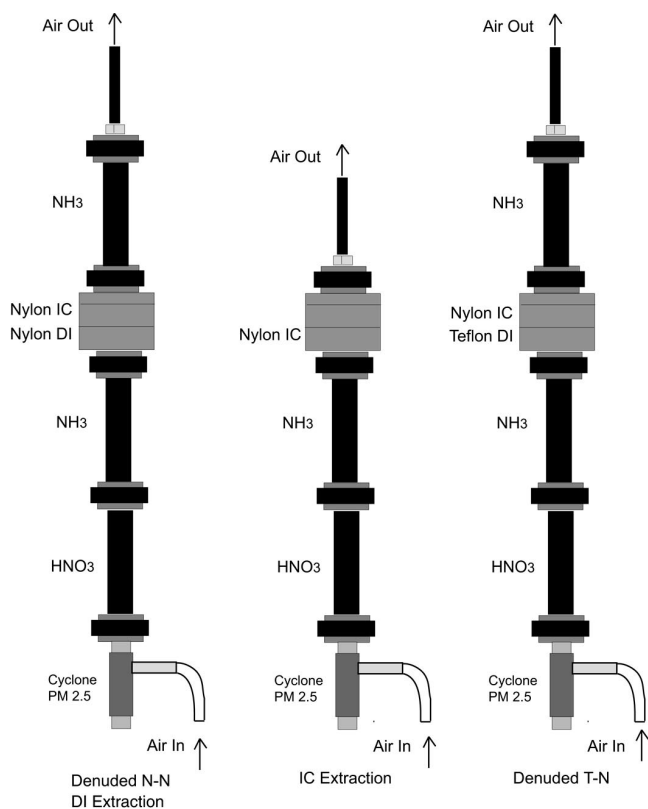
**Figure 1.** A schematic diagram of the annular denuder/filter pack configurations. Module 1 is on the left, module 2 in the center, and module 3 on the right.

of the components of this sampling train were extracted and analyzed. The extracts from the two denuders before the filter pack provided gaseous $HNO_3$, sulfur dioxide, and $NH_3$ concentrations. The first nylon filter was extracted with deionized water for both anion and cation analyses. The second nylon filter was extracted with the basic carbonate/bicarbonate solution (IC eluent) described above. This extraction procedure is indicated as "ion chromatography" in the figure.

The second sampling module is similar to the first but uses only one nylon filter in the filter pack with no back-up $NH_3$ denuder. The nylon filter was extracted using the $Na_2CO_3/NaHCO_3$ solution to compare with nylon filters extracted using deionized water. The denuders from this sampling train were extracted but not analyzed unless needed to verify suspicious values from the module 1 denuder results.

Sample module 3 consists of a pair of denuders to remove gaseous $HNO_3$, $SO_2$, and $NH_3$ upstream; a filter pack loaded with a Teflon filter for particle collection and a nylon filter for collection of volatilized $HNO_3$; and a downstream denuder to capture any ammonia volatilized from collected particles. This module, designed to compare losses of $NH_3$ and $HNO_3$ from particles collected on Teflon and nylon filters, was operated every third or fourth day during the field experiments.

*Denuder Train Blanks and Replicates.* A 24-hr blank denuder/filter pack module was collected several times during each field campaign to help determine measurement detection limits. Both Teflon–nylon (T-N) and nylon–nylon (N-N) filter packs were used to obtain blank samples. Replicate samples were collected every third or fourth day, by configuring module 3 to duplicate the module 1 setup, to estimate measurement precision.

*Sample Analysis.* Dionex IC systems were used to analyze denuder and filter extracts. Samples were programmed for continuous analysis using autosamplers (Spectra System AS 3500). The cation IC included an IP 20 isocratic pump, CD 20 conductivity detector, CG12A guard column, CS12A separation column, and a CSRS-ULTRA suppressor (all components from Dionex Corp.). The anion IC included a GP 40 gradient pump, CD 20 conductivity detector, AG4A-SC guard column, AS4A-SC separation column, and an ASRS-ULTRA suppressor. The cation eluent was 20 mM of methanesulfonic acid provided at a flow rate of 1 ml/min; the anion eluent was 1.8 mM $Na_2CO_3/$ 1.7 mM $NaHCO_3$ provided at a flow rate of 2 ml/min. Calibration was carried out daily using a series of anion and cation standards prepared from a stock solution made using analytical grade salts. Analytical accuracy was evaluated through regular analysis of independent, National Institute for Standards and Technology-traceable anion and cation standards purchased from Dionex Corp. Analytical precision was determined by replicate sample and standard analyses. Deionized water used in the field and laboratory was freshly prepared and possessed a resistivity in excess of 18 M ohm-cm.

## Field Study Sites

Four IMPROVE network sites, Bondville, IL, San Gorgonio Wilderness Area, CA, Hance Camp Grand Canyon, AZ, and Brigantine National Seashore, NJ, were selected for study based on historical observations of important seasonal $NO_3^-$ contributions to fine particle mass. Information about these sites and the study periods is summarized in Table 1. A field campaign of approximately one-month duration, scheduled during periods when high $NO_3^-$ concentrations were expected, was conducted at each site. Measurements were made in February 2003 in Bondville, a rural Midwestern site located in central Illinois. Measurements were made in April 2003 at San Gorgonio, an elevated, forested site in the mountains downwind of the Los Angeles air basin. Additional summer campaigns were conducted at San Gorgonio, which experiences the highest $NO_3^-$ concentrations measured in the IMPROVE network,[1] to examine potential artifact differences associated with changing ambient temperatures. Results from the first summer San Gorgonio campaign in July 2003 are not

**Table 1.** General site information.

| Site name | State | Longitude (dd) | Latitude (dd) | Elevation (m) | Study period |
|---|---|---|---|---|---|
| Bondville | IL | −88.3719 | 40.0514 | 211 | 02/01/03 to 02/27/03 |
| San Gorgonio Wilderness | CA | −116.9013 | 34.1924 | 1705 | 04/04/03 to 04/26/03 |
| Hance Camp, Grand Canyon | AZ | −111.9841 | 35.9731 | 2267 | 05/01/03 to 05/30/03 |
| San Gorgonio Wilderness | CA | −116.9013 | 34.1924 | 1705 | 07/01/03 to 07/30/03 |
| | | | | | 06/30/04 to 07/10/04 |
| Brigantine National Seashore | NJ | −74.4492 | 39.465 | 5 | 11/04/03 to 11/30/03 |

included here because of suspected laboratory quality control problems. A second 10-day summer campaign was conducted in July 2004 at San Gorgonio, results from which are presented below. The Grand Canyon study was conducted in May 2003. Measurements at Brigantine National Seashore were conducted in November 2003. Twenty-four-hour samples were collected daily at each location, running from 8:00 a.m. to 8:00 a.m. local standard time.

## RESULTS AND DISCUSSION

Samples were collected in each study according to the planned schedule. On a few days samples could not be collected for a full 24-hr period because of severe winter weather and/or power outages. Denuder and filter blank concentrations were low, resulting in excellent measurement detection limits. Min detection limits (95% confidence limit) for key measured species are summarized in Table 2. These values represent the pooled results from all five of the campaigns.[66] The method detection limits of gaseous $HNO_3$, $NH_3$, and $SO_2$ are 0.059 $\mu g/m^3$, 0.084 $\mu g/m^3$, and 0.037 $\mu g/m^3$. The min detection limits of $NO_3^-$, $SO_4^{2-}$, $NH_4^+$ are 0.069 $\mu g/m^3$, 0.047 $\mu g/m^3$, and 0.031 $\mu g/m^3$ for nylon filters, with similar values obtained

for Teflon filters. These results are similar to values obtained in our past research projects using similar measurement approaches.[67,68] Measurement precision, determined from comparison of replicate denuder and filter samples at all of the sites[66] was also satisfactory and consistent with our past experience. Table 3 summarizes the results. Relative standard deviations (RSD) for determination of gaseous $HNO_3$, $SO_2$, and $NH_3$ were 6.2%, 3%, and 11.2%, respectively. RSDs for particulate $NO_3^-$, $SO_4^{2-}$, and $NH_4^+$ were 6.3%, 7%, and 5.2%, respectively, with somewhat higher RSDs for trace species $Cl^-$, $Na^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$ (13.8%, 11.2%, 26.8%, 16.2%, and 14.5%, respectively).

## $NO_3^-$ and $SO_4^{2-}$ Recovery by Deionized Water Extraction

Extraction efficiencies for recovery of particulate $NO_3^-$ and $SO_4^{2-}$ from nylon filters are illustrated in Figures 2a and 2b. These plots compare the amount of each species recovered using deionized water extraction with the amount recovered using the basic extract solution (assumed to be 100% efficient). The samples were sonicated during extraction in both cases. Recoveries of $NO_3^-$ and $SO_4^{2-}$ by deionized water appear to match recoveries

**Table 2.** Min detection limits of major gaseous and particulate species.

| Species | Nylon filter ($\mu g/m^3$) | Teflon filter ($\mu g/m^3$) | Denuder ($\mu g/m^3$) |
|---|---|---|---|
| $Cl^-$ | 0.018 | 0.011 | — |
| $NO_3^-$ | 0.069 | 0.041 | — |
| $SO_4^{2-}$ | 0.047 | 0.099 | — |
| $Na^+$ | 0.008 | 0.019 | — |
| $NH_4^+$ | 0.031 | 0.050 | — |
| $K^+$ | 0.015 | 0.020 | — |
| $Mg^{2+}$ | 0.022 | 0.056 | — |
| $Ca^{2+}$ | 0.039 | 0.079 | — |
| $HNO_3(g)$ | — | — | 0.059 |
| $SO_2(g)$ | — | — | 0.037 |
| $NH_3(g)$ | — | — | 0.084 |

**Table 3.** Means and relative standard deviations (RSD) of major measured species

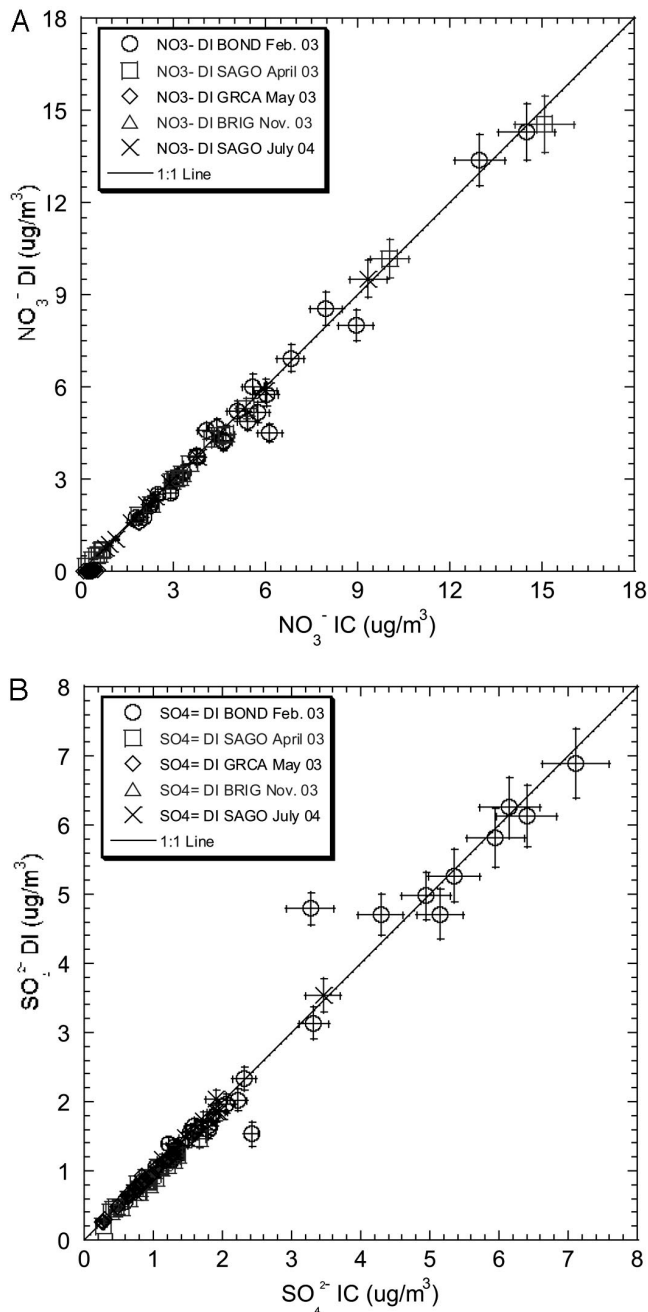| Species | $\bar{x}$, $\mu g/m^3$ | $N_s$ | RSD, % |
|---|---|---|---|
| $Cl^-$ | 0.125 | 25 | 13.8 |
| $NO_3^-$ | 2.15 | 31 | 6.3 |
| $SO_4^{2-}$ | 2.02 | 32 | 7.0 |
| $Na^+$ | 0.074 | 30 | 11.2 |
| $NH_4^+$ | 1.12 | 27 | 5.2 |
| $K^+$ | 0.037 | 33 | 26.8 |
| $Mg^{2+}$ | 0.028 | 33 | 16.2 |
| $Ca^{2+}$ | 0.136 | 33 | 14.5 |
| $HNO_3(g)$ | 0.59 | 22 | 6.2 |
| $SO_2(g)$ | 4.20 | 28 | 3.0 |
| $NH_3(g)$ | 0.47 | 21 | 11.2 |

**Figure 2.** (a) Nitrate ion recovery comparison between deionized water and basic IC eluent extractions. Error bars represent ± σ determined from replicate sample collection and analysis. (b) Sulfate ion recovery comparison between deionized water and basic IC eluent. Error bars represent ± σ determined from replicate sample collection and analysis.

associated with basic solution extraction in nearly all of the samples, representing a wide range of concentrations.

The observed values of the recovery ratio (water:basic IC eluent extraction concentrations; $R = [X]_{DI}:[X]_{IC}$ for $NO_3^-$ and $SO_4^{2-}$ are summarized in Table 4. Recovery ratios for $NO_3^-$ in the campaigns average (standard deviation shown in parentheses) 96% (8%), 98% (3%), 99% (3%), 99% (2%), and 106% (7%) in the Bondville, San

Gorgonio (April 2003), Grand Canyon, San Gorgonio (July 2004), and Brigantine campaigns, respectively. Based on the observed precision of $PM_{2.5}$ $NO_3^-$ measurement (RSD = 6.1%) we can determine that values of the recovery ratio for $NO_3^-$ <85.6% are significantly (95% confidence level) different from 100%.[66] Table 4 lists the fraction of values where a significant difference is seen, corresponding to 7.4%, 0%, 0%, 0%, and 0% of the sample days in the five campaigns. These results suggest that water extraction of collected $PM_{2.5}$ $NO_3^-$ exhibited an efficiency indistinguishable from the basic solution extraction on nearly all days in all of the campaigns, even those when significant $NH_3$ volatilization in 24-hr filter samples was observed to occur (based on analysis of back-up $NH_3$ denuders).

Additional laboratory tests were also conducted to investigate the necessity of sonicating samples during extraction. Our results show that deionized water extraction in the absence of sonication may leave some $HNO_3$ collected on nylon filters behind; observations ranged from 2% to 22% assuming that basic eluent extraction is complete. In contrast, samples extracted with deionized water accompanied by sonication show essentially complete $HNO_3$ recovery compared with the basic IC eluent extraction. Consequently, our results suggest that the current IMPROVE program nylon filter extraction protocol using deionized water and sonication to recover $NO_3^-$ is an acceptable practice.

Observations of $SO_4^{2-}$ recovery by water extraction from nylon filters are also summarized in Table 4. In this case, recovery ratios <87.8% were determined to be significantly different (95% confidence level) from 100%. The percentages of values exceeding this criterion were 3.7%, 27.3%, 0%, 0%, and 0% at Bondville, San Gorgonio (April 2003), Grand Canyon, San Gorgonio (July 2004), and Brigantine, respectively. All of the April 2003 samples were reanalyzed for sulfate to verify the observation of lower water extraction efficiency during that study, without significant change. The average 98% recovery of $NO_3^-$ during this period suggests that the lower sulfate extraction efficiency is not the result of a sample or extract volume error. The slight reduction in water extraction efficiency of sulfate at San Gorgonio in April was not expected. Possible explanations for this finding include strong binding of some particulate sulfate or $SO_2$ (which was perhaps not completely removed by the carbonate coated denuder) to the nylon filter. Nylon filters are known to exhibit some efficiency for $SO_2$ collection, although the efficiency seems to vary strongly between filter batches/types.[41,69–71] It is also possible that some less soluble (e.g., mineral) form of sulfate may have been present at the site in April.

**Table 4.** Extraction efficiency comparison between deionized water and the basic IC eluent.

| Recovery Ratio | $R = (NO_3^-)_{DI}:(NO_3^-)_{IC}$ | | | $R = (SO_4^{2-})_{DI}:(SO_4^{2-})_{IC}$ | | |
| --- | --- | --- | --- | --- | --- | --- |
| | Mean | Std. Dev. | % Days R Significantly < 1.0 | Mean | Std. Dev. | % Days R Significantly < 1.0 |
| Bondville, February 03 | 0.96 | 0.08 | 7.4 | 0.99 | 0.13 | 3.7 |
| San Gorgonio, April 03 | 0.98 | 0.03 | 0 | 0.93 | 0.08 | 27.3 |
| Grand Canyon, May 03 | 0.99 | 0.03 | 0 | 0.98 | 0.03 | 0 |
| San Gorgonio, July 04 | 0.99 | 0.02 | 0 | 1.00 | 0.03 | 0 |
| Brigantine, November 03 | 1.06 | 0.07 | 0 | 1.11 | 0.04 | 0 |

**$NO_3^-$ Loss by Teflon and Nylon Filters**

Losses of volatilized $NO_3^-$ between Teflon and nylon filters are compared from results obtained using sample modules 1 and 3. Recall that the airstream sampled by both filter types was denuded of $HNO_3$ and $NH_3$, and a back-up nylon filter was used to capture any loss of $NO_3^-$ ($BNO_3^-$) in the form of $HNO_3(g)$. We define total inorganic $NO_3^-$ as the sum of the $NO_3^-$ concentration obtained from the
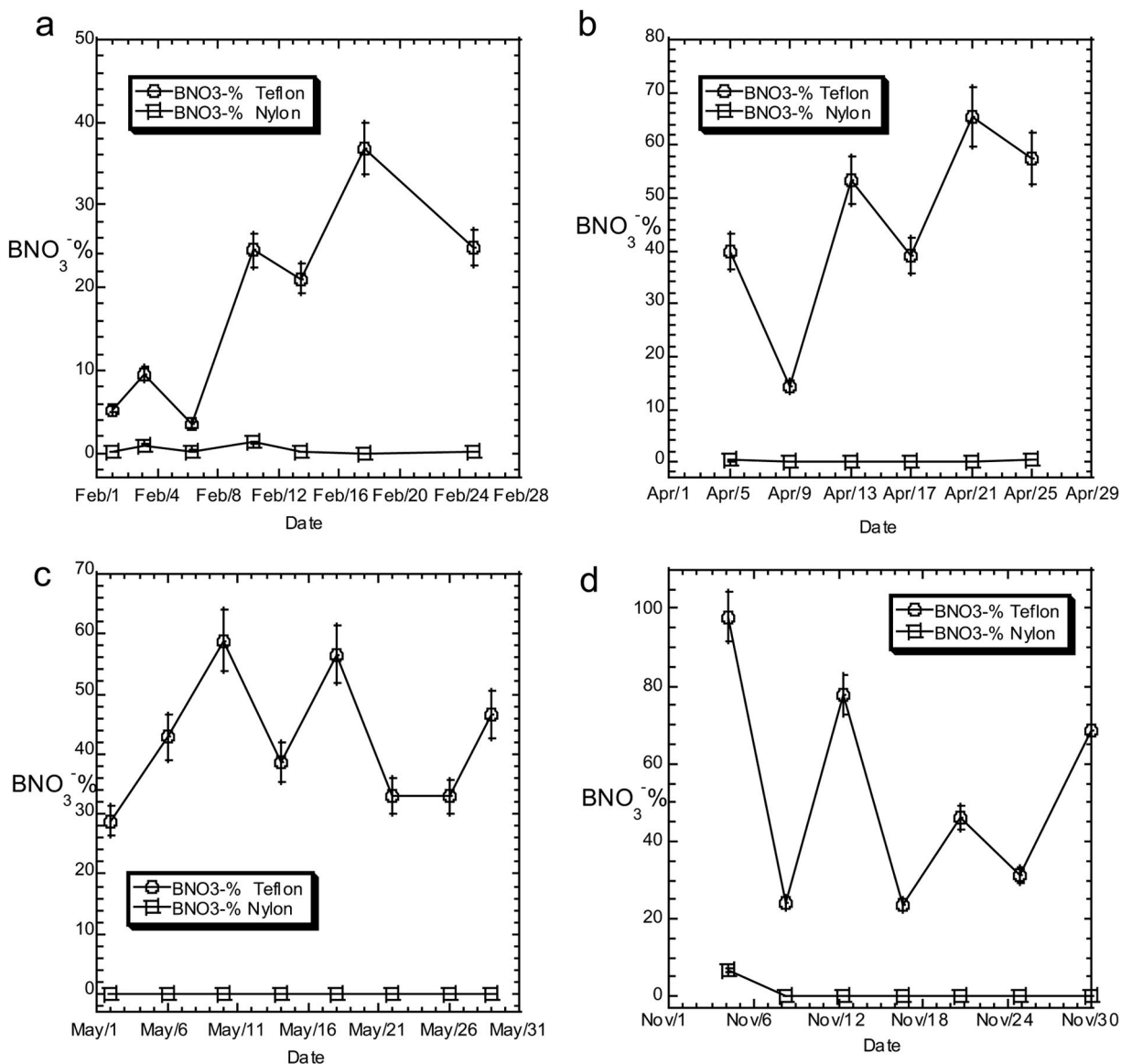


**Figure 3.** Comparison of $NO_3^-$ loss by denuded Teflon and nylon filters: (a) Bondville, (b) San Gorgonio April, (c) Grand Canyon, and (d) Brigantine. Error bars represent $\pm \sigma$ based on replicate sample collection and analysis.

first filter (either Teflon or nylon) and the $NO_3^-$ concentration measured with the back-up nylon filter. We can then define the percentage of $PM_{2.5}$ $NO_3^-$ lost in each system as:

$$BNO_3^- \% = \frac{BNO_3^-}{NO_3^- \ (prefilter) + BNO_3^-} \cdot 100\% \quad (2)$$

A comparison of $NO_3^-$ loss from Teflon and nylon filters in the field experiments is depicted in Figure 3, with a separate panel included for each campaign. The error bars shown are propagated uncertainties ($\pm\sigma$). Overall, nylon filters demonstrate far better retention of particulate $NO_3^-$ than Teflon filters during all four of the experiments. This result was expected and supports the choice of a nylon filter by IMPROVE and the EPA for single filter measurement of fine particulate $NO_3^-$. Average $NO_3^-$ losses from denuded N–N filter pack in Bondville, San Gorgonio April, Grand Canyon, and Brigantine are only 0.4%, 0.1%, 0%, and 2.2%, respectively. Low $NO_3^-$ loss amounts from nylon filters were also observed at San Gorgonio in July 2003 (0.7% on average), but these are subject to greater uncertainty because of the quality control problems for this campaign mentioned above. $NO_3^-$ loss measurements were not made in the July 2004 campaign because of resource constraints.

Average $NO_3^-$ losses from denuded Teflon filters in Bondville, San Gorgonio April, Grand Canyon, and Brigantine are 18%, 45%, 42%, 52%, respectively. Even higher losses were observed at San Gorgonio during the hot weather of July 2003, but these are not included because of greater uncertainty in measurements during this campaign. The observed losses result in 24-hr samples that began each day at 8 a.m. One might expect even larger losses on 24-hr samples begun at midnight, because of presumably greater accumulation of particulate $NO_3^-$ on the filter in advance of the peak temperature (and min RH) hours in the afternoon. The large $NO_3^-$ losses from denuded Teflon filters also raise a concern about potential negative biases in IMPROVE $PM_{2.5}$ mass concentrations, which are obtained currently using (undenuded) Teflon filters.[1,21,59–61,72]

Our findings are consistent with previous findings, for urban southern California, by Hering and Cass,[73] that the average $NO_3^-$ obtained from Teflon filter particle sampling is lower than that by denuded nylon filters. The results here extend these findings to a variety of nonurban sites and seasons. Ashbaugh and Eldred[21] recently studied $NO_3^-$ loss from Teflon filters in California and several IMPROVE sites and concluded that mass loss on Teflon filters caused by $NH_4NO_3$ volatilization can be a substantial fraction of the particulate mass.

Particulate $NO_3^-$ loss is caused by changes in the equilibrium between $NH_4NO_3(p)$ and gaseous $HNO_3$ and $NH_3$ according to eq 1.[5,15] The value of the equilibrium constant is a strong function of T and RH. $NH_4NO_3$ formation is generally favored at night, when temperatures decrease and RH increases. $NH_4NO_3$ tends to volatilize in the afternoon when T rises and RH drops. Volatilization of collected $NH_4NO_3$ particles, therefore, might be expected to show some degree of correlation with the magnitude of daily T and RH changes. One might also expect the degree of $NH_4NO_3$ volatilization off a denuded filter to correlate with the fractions of N($-$III) or N(V) in the gas phase in the sampled, ambient air. Denuding an equilibrated airstream of $HNO_3$ (or $NH_3$) will create a larger driving force for $NH_4NO_3$ evaporation when the equilibrium phase partitioning strongly favors the gas phase.

We investigated the effect of changing temperature on $NO_3^-$ loss for the denuded Teflon filters operated in each field campaign. Figure 4 shows the fraction of volatilized $NO_3^-$ ($BNO_3^-\%$) versus $\Delta$ T ($\Delta$ T = $T_{max} - T_{min}$). $T_{max}$ and $T_{min}$ are taken from 1-hr data. The data suggest a tendency for $NO_3^-$ volatilization to increase with increasing $\Delta$ T at some locations; however, the relationship is certainly not very strong, even in the best cases. The highest $\Delta$ T values, for example, were observed at Grand Canyon, which has $NO_3^-$ loss values in the middle of the observed range. It is not surprising that $\Delta$ T fails to completely explain the observed changes in $NO_3^-$ loss, because many other factors will also contribute to the degree of loss. $\Delta$ RH can also affect $NH_4NO_3$ gas/particle partitioning.[74–76] The $\Delta$ RH ($\Delta$ RH = $RH_{max} - RH_{min}$, 1-hr resolution) relation to $NO_3^-$ loss from the denuded Teflon
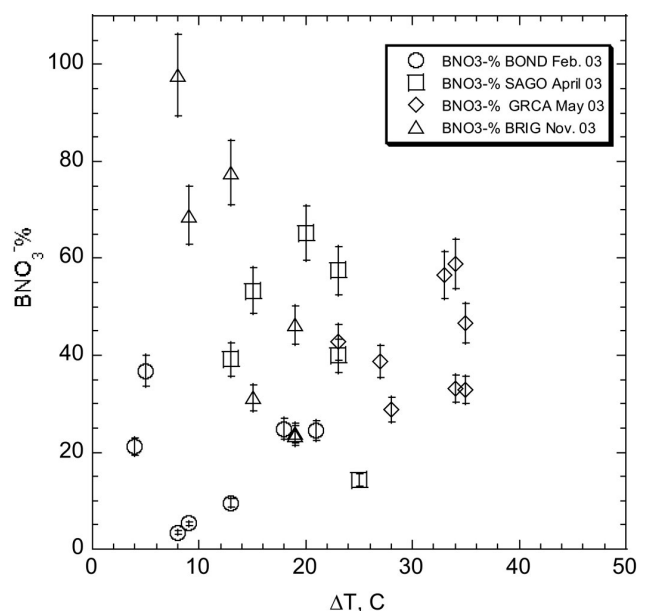


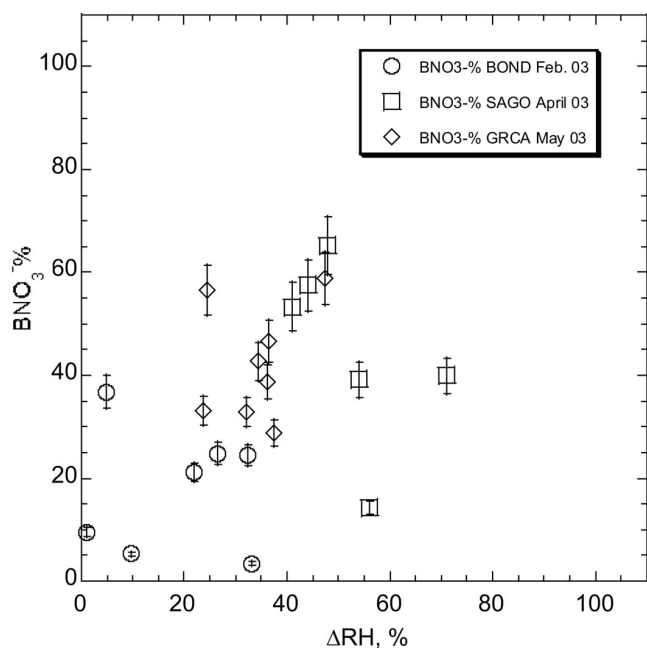**Figure 4.** Denuded Teflon filter $NO_3^-$ loss versus daily temperature difference. Errors are propagated representing $\pm$ $\sigma$.

**Figure 5.** Denuded Teflon filter $NO_3^-$ loss versus daily relative humidity difference. Errors are propagated representing $\pm \sigma$.



**Figure 6.** Denuded Teflon filter $NO_3^-$ loss versus $HNO_3(g):N(V)$. Errors are propagated representing $\pm \sigma$. The lines are linear regression fits. Fitting parameters including $R^2$, slope, and intercept are 0.47, 89, −48 (Bondville); 0.92, 334, 0 (San Gorgonio April); 0.57, 98, 0 (Grand Canyon); and 0.24, 67, 23 (Brigantine).

filters is illustrated in Figure 5. We see some correlation between $\Delta$ RH and $NO_3^-$ loss, but again it is rather weak. We attempted to explain the combined effect of $\Delta$ T and $\Delta$ RH on $NO_3^-$ loss through a multiple linear regression, but the fraction of variance explained remains rather small.

The ratio of $HNO_3$ (g) to total nitrogen in the V oxidation state $[N(V) = HNO_3 (g) + \text{Total } NO_3^- (p)]$ indicates the ambient partitioning of $NO_3^-$ between the gas and particle phases. In our case these data are only available as a 24-hr average. Previous investigators[17] have suggested that volatilization of $NH_4NO_3$ collected on a denuded filter will tend to be higher in cases where the ambient $NO_3^-$ partitioning favors the gas phase, because the removal of the gas phase constituent in this case creates a strong driving force to evaporate the particulate $NH_4NO_3$ to reestablish the ambient, presumably equilibrium, condition. The relation of volatilized $NO_3^-$ with the ambient fraction of N(V) in the gas phase is depicted in Figure 6. As the ratio of $HNO_3$ to the total N(V) increases, higher $NO_3^-$ loss is observed in each field experiment. Although the correlation is not simply linear, it shows a trend that agrees with Zhang and McMurry's conclusion[18] on particulate $NO_3^-$ sampling efficiency by Teflon filters that significant evaporative losses for a condensed species are expected when the species' gas phase concentration exceeds its particulate concentration. We also examined the dependence of the fraction of volatilized $NO_3^-$ on the fraction of N(−III) present in the gas phase as $NH_3$, but the correlation here was weak.
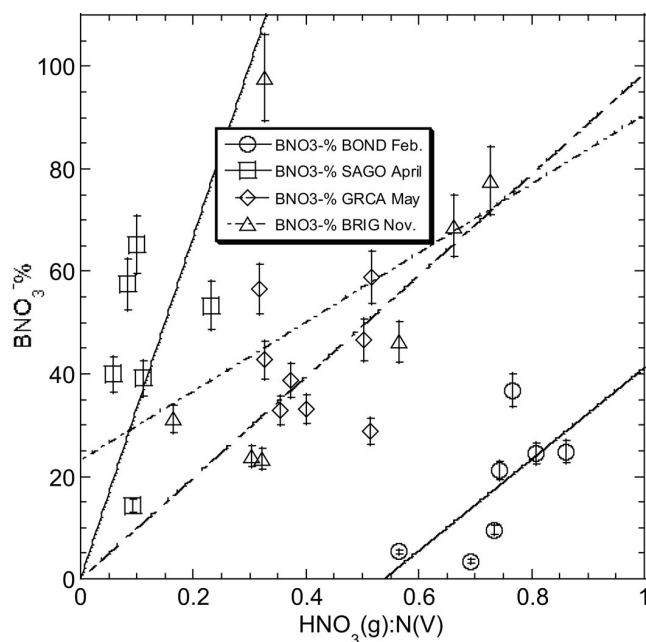
The $NO_3^-$ loss fraction is also expected to depend on other factors, including the time history of $NO_3^-$ particle collection on the filter (versus diurnal profiles of T and RH and changes in ambient concentrations of gaseous $HNO_3$ and $NH_3$),[34] aerosol acidity, and the chemical form of the collected $NO_3^-$. Data from a MOUDI impactor operated at Grand Canyon, for example, show that most $NO_3^-$ during our study there was present as coarse mode sodium or calcium nitrate and that the "fine" particle $NO_3^-$ sampled as $PM_{2.5}$ actually represents the lower tail of this coarse mode. Because these forms of $NO_3^-$ are not readily subject to losses by volatilization, one should not expect $NO_3^-$ loss patterns at this site to follow those observed at sites where $NH_4NO_3$ is the dominant $NO_3^-$ species.

**CONCLUSIONS**

Five field experiments were conducted at selected IMPROVE aerosol monitoring sites to examine issues related to sampling of aerosol $NO_3^-$. Different annular denuder/filter pack configurations were utilized to evaluate measurement precision, the efficiency of $NO_3^-$ extraction from nylon filters by deionized water, and losses of particulate $NO_3^-$ from denuded nylon and Teflon filters.

Deionized water was observed to be as efficient as a basic carbonate/bicarbonate solution in extracting particulate $NO_3^-$ sampled on nylon filters in all five of the campaigns. Laboratory study of the filter extraction procedure indicated that sonication is probably needed to ensure complete recovery of $NO_3^-$ collected on the filter.

PM$_{2.5}$ NO$_3^-$ loss from denuded nylon and Teflon filters was examined in each field campaign as well. NO$_3^-$ losses from denuded nylon filters were extremely small (<1%) at all of the sites, confirming the utility of nylon filters for providing a single-filter sampling solution for measurement of fine particle anion concentrations. As expected, significant NO$_3^-$ losses occurred from the denuded Teflon filters, with average losses of 18% at Bondville, 45% at San Gorgonio April, 42% at Grand Canyon, and 52% at Brigantine. Some correlation was observed between the fraction of NO$_3^-$ lost and the daily variation in temperature and RH, as well as the fraction of ambient N(V) in the gas phase.

This work represents an important evaluation of the efficiency of deionized water extraction of particulate NO$_3^-$ collected on nylon filters at a variety of nonurban locations and seasons where NO$_3^-$ comprises a significant fraction of fine particle mass. It also adds to the existing body of literature on the magnitude of NO$_3^-$ volatilization from denuded Teflon filters while confirming the efficiency of nylon filters in preventing NO$_3^-$ loss through recapture of volatilized HNO$_3$.

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