

Study of Inlet Materials for Sampling Atmospheric Nitric Acid

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The adsorption of nitric acid (HNO_3) from a flowing gas stream is studied for a variety of wall materials to determine their suitability for use in atmospheric sampling instruments. Parts per billion level mixtures of HNO_3 in synthetic air flow through tubes of different materials such that >80% of the molecules interact with the walls. A chemical ionization mass spectrometer with a fast time response and high sensitivity detects HNO_3 that is not adsorbed on the tube walls. Less than 5% of available HNO_3 is adsorbed on Teflon fluoropolymer tubing after 1 min of HNO_3 exposure, whereas >70% is lost on walls made of stainless steel, glass, fused silica, aluminum, nylon, silica-steel, and silane-coated glass. Glass tubes exposed to HNO_3 on the order of hours passivate with HNO_3 adsorption dropping to zero. The adsorption of HNO_3 on PFA Teflon tubing (PFA) is nearly temperature-independent from 10 to 80 °C, but below –10 °C nearly all HNO_3 that interacts with PFA is reversibly adsorbed. In ambient and synthetic air, humidity increases HNO_3 adsorption. The results suggest that Teflon at temperatures above 10 °C is an optimal choice for inlet surfaces used for in situ measurements of HNO_3 in the ambient atmosphere.

Introduction

Nitric acid (HNO_3) is important to the photochemistry of both the stratosphere and troposphere. HNO_3 is a reservoir for reactive nitrogen molecules NO and NO_2 in the upper troposphere and lower stratosphere and is therefore intimately connected with processes that control ozone (O_3) abundance in these regions. In the stratosphere, HNO_3 contributes to the formation of polar stratospheric clouds, on which heterogeneous reactions can release reactive chlorine that catalytically destroys O_3 (1, 2). In the troposphere, predictions of O_3 production and loss are improved with better knowledge of HNO_3 abundance (3). In the lower troposphere, HNO_3 is an important component of acid precipitation, and the associated wet removal of HNO_3 is often a sink of reactive nitrogen molecules.

HNO_3 readily adsorbs on many materials commonly used in measurement instruments, and this presents a challenge to the proper quantification of atmospheric HNO_3 concentrations. Sampling inlets that transport ambient air to a detector can change the concentration of HNO_3 in the air by wall adsorption and desorption processes and thus invalidate the measurement. Numerous studies that have investigated

HNO_3 sampling techniques (4–6) and intercompared measurement methods (7–10) are a testament to the difficulty of measuring this molecule. In the intercomparison studies, different HNO_3 measurement instruments often produced inconsistent results. A careful evaluation of HNO_3 adsorption on various materials under different conditions offers one possibility for reconciling poorly correlated measurements.

The recent development of a fast time response chemical ionization mass spectrometer (CIMS) for HNO_3 measurements (11, 12) has heightened interest in developing new inlets that transport ambient air to a detector without altering the HNO_3 concentration. Inlets with low HNO_3 adsorption are particularly important for airborne measurements (13), because a fast time response is required to obtain acceptable spatial resolution. However, aircraft inlets that minimize wall interaction (14) cannot always be integrated easily into other HNO_3 measurement instruments. Since wall interaction is significant in many sensitive HNO_3 sampling instruments, tests of inlet materials yield insights into the operating behavior of current instruments and design requirements for future instruments. Using a CIMS as a fast time response and high sensitivity HNO_3 detector, we examine the adsorption of HNO_3 on different materials under controlled conditions.

Experimental Section

Tubes made from TFE Teflon (TFE), PFA Teflon (PFA), FEP Teflon (FEP), polyvinylidene fluoride (PVDF), 6061 aluminum, glass, fused silica, nylon, 304 stainless steel, silica-coated steel, and silane-coated glass are tested for HNO_3 adsorption, since these materials are commonly used in HNO_3 sampling instruments. Restek Corporation (Bellefonte, PA) applied the silica coatings to the steel tubes, and silane coatings for glass tubes were obtained from United Chemical Technologies (Bristol, PA). All tubes are cleaned by flushing with water, ethanol, and then synthetic air. Tubes with either a 1 cm i.d. or 0.4–0.5 cm i.d. are cut to 30 cm lengths. Two different diameter tubes are used since the larger diameter tubes are more easily coated with silica or silane, while the smaller diameter tubes equilibrate to HNO_3 adsorption more rapidly.

The HNO_3 detector is a CIMS, which uses ion–molecule reactions to selectively detect trace quantities of neutral molecules. A ground-based CIMS (11) has recently measured atmospheric HNO_3 with a time response on the order of seconds and with sensitivities better than 1 Hz/ppbv (ppbv = parts per trillion by volume). SiF_5^- ions that selectively cluster to HNO_3 are mixed with sampled air in an ion–molecule reaction region. The product cluster ions pass through an aperture and then a quadrupole mass spectrometer to an electron multiplier. The signal from the $\text{HNO}_3 \cdot \text{SiF}_5^-$ cluster ions is proportional to the HNO_3 concentration in the sampled air. The HNO_3 source is a temperature and pressure controlled permeation tube (Kin-Tek, La Marque, TX) with a HNO_3 permeation rate measured independently by ion chromatography to be 16 ng/min. A continuous 20 sccm flow of synthetic air passes over the permeation cell and through PFA fittings and tubing that connect the HNO_3 source to the CIMS sample line that includes the material section under study. Consistent with the results presented below, the components of the CIMS sample line are PFA to minimize HNO_3 adsorption. The permeation source flow is mixed with 1 standard L per min (slpm) of dry synthetic air (<100 ppmv H_2O) to produce a 5.6 parts per billion by volume (ppbv) HNO_3 mixing ratio in the CIMS sample line. The 1 slpm flow, which is typical for

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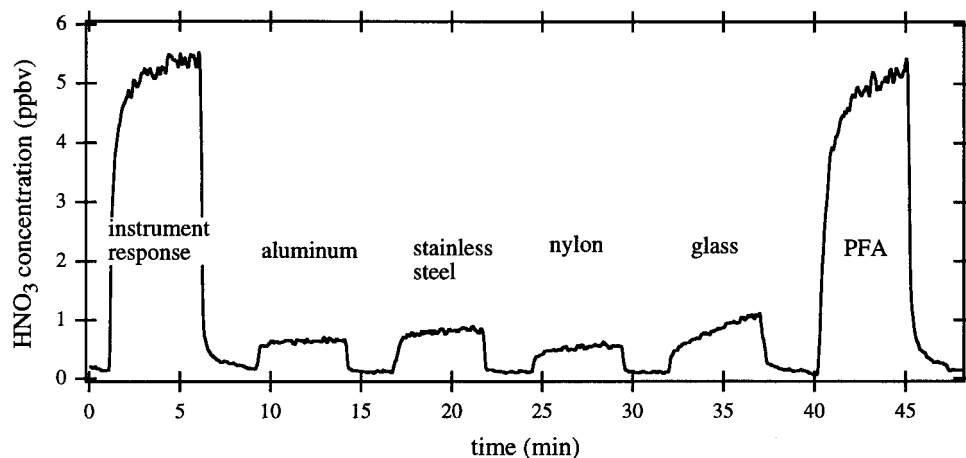


FIGURE 1. The signal from 5.6 ppbv HNO_3 in 1 slpm synthetic air that flows through 0.4–0.5 cm i.d. tubes of different materials, where $>80\%$ of the molecules interact with the tube walls. The rise in signal occurs when HNO_3 from a permeation source is introduced into the sample line at the inlet end of the sample tube, and the fall occurs when the HNO_3 source is disconnected.

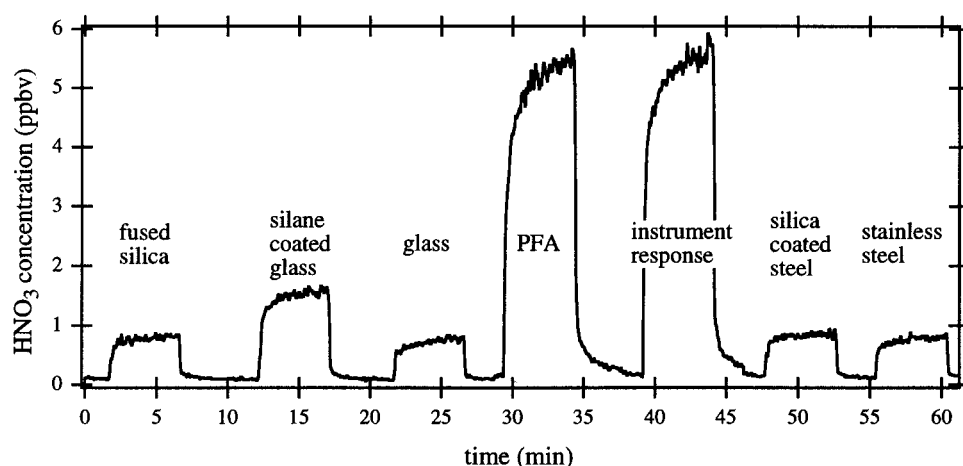


FIGURE 2. Same as Figure 1, except for the use of 1 cm i.d. tubes of the noted materials.

aircraft HNO_3 sampling instruments, ensures laminar flow in the sample tubes. The Reynolds number (Re) is ~ 300 for 1 cm i.d. tubes and ~ 600 for 0.5 cm i.d. tubes; turbulent flow occurs at $Re > 2200$. A tube length of 30 cm guarantees that a significant fraction of the HNO_3 interacts with the walls. For a 1 slpm laminar flow through a 30 cm long tube, calculations show that $>80\%$ of the molecules diffuse to the walls (15).

HNO_3 interaction with a wall material is measured by connecting the HNO_3 permeation source flow to the sample line at the inlet end of a tube and then disconnecting the permeation source flow after 5 min. The connection and disconnection is performed quickly with only a minor perturbation to the flow in the sample line and with all other components and connections unchanged. The instrument response to this HNO_3 exposure is the time-dependent HNO_3 signal when a short (3 cm) PFA section on which there is negligible adsorption is used in place of a 30 cm long tube in the sample line. The amount of HNO_3 removed by an inlet material is determined from the difference, after 5 min of HNO_3 exposure, between the signal obtained when the HNO_3 mixture flows through a 30 cm long tube of the material and when it flows through the short PFA section. The values at 5 min are determined by averaging the last 30 s of data before the HNO_3 source is removed.

HNO_3 adsorption is measured for tube temperatures between -30°C and 90°C . Temperature control is achieved by inserting 1 cm i.d. (1.27 cm o.d.) tubes into a copper sleeve that is wrapped in tubing filled with a circulating thermostated

fluid, so that the temperature of a tube can be continuously and rapidly varied. Since the sensitivity of the CIMS apparatus is a strong function of gas temperature in the ion–molecule reaction region, a 0.5 cm i.d., 0.7 m length of room-temperature PFA tube is added between the entrance to the CIMS apparatus and the tube to be tested. This thermal break, which decouples the gas temperature in the ion–molecule reaction region from that in the temperature-controlled tubes, is necessary only for these temperature-dependence studies. Temperature measurements confirm that the ion–molecule reaction region is effectively thermally decoupled from the sample tube.

Results and Discussion

Relative HNO_3 concentrations transmitted through 30 cm long 0.4–0.5 cm i.d. tubes made of aluminum, steel, nylon, glass, and PFA are shown in Figure 1. Figure 1 also shows the instrument response to HNO_3 exposure. TFE, FEP, and PVDF tubes have also been tested and show the same HNO_3 adsorption characteristics as PFA. After several seconds of exposure to HNO_3 in synthetic air, HNO_3 loss due to adsorption is $<5\%$ when the gas flows through a 30 cm long PFA tube at 22°C . Over 80% of the flow is calculated to interact with the walls, and HNO_3 loss on aluminum, steel and nylon tubes is measured to be $\sim 85\%$. This finding is consistent with Goldan et al. (5), who noted loss of HNO_3 on steel, and Huey et al. (11), who report that nylon wool removes HNO_3 from a gas flow with $>99\%$ efficiency.

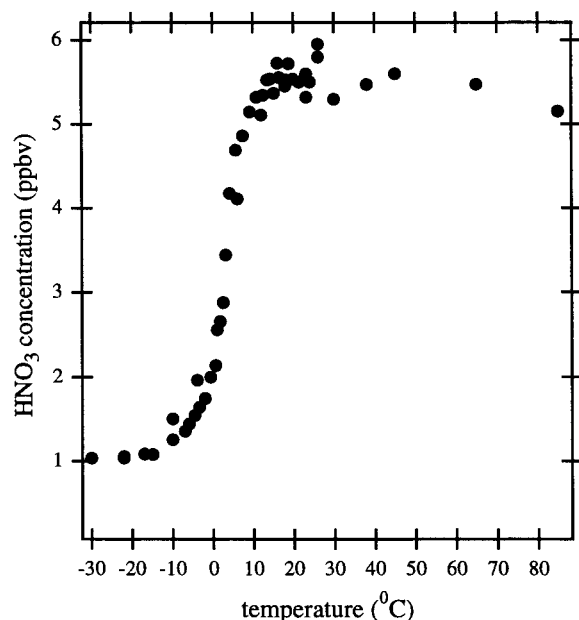


FIGURE 3. The temperature dependence of HNO₃ adsorption on PFA.

Figure 2 shows the relative HNO₃ concentrations transmitted through 1 cm i.d. tubes of fused silica, silane-coated glass, glass, PFA, silica-coated steel, and steel tubes at 22 °C. Again, PFA is shown to adsorb little HNO₃, while all other materials and coatings tested scavenge most HNO₃ that contacts the tube walls. Figure 2 shows that HNO₃ has essentially the same loss rate on tubes of many different materials, which indicates that the loss of HNO₃ on these tubes is controlled by diffusion to the wall and not the reaction probability (γ) of HNO₃ on the wall. For these experimental conditions, $\gamma > 10^{-5}$ leads to diffusion controlled wall loss. Results for 5 min exposures are shown here, and further tests demonstrated that HNO₃ transmission through aluminum, steel, and nylon tubes does not increase with over 1 h of HNO₃ exposure. Tests have also been performed on aluminum and steel tubes heated to 50 °C, and under all conditions studied the HNO₃ loss on these materials is irreversible.

Glass shows a different response to HNO₃ exposure than any of the metals or fluoropolymers tested. HNO₃ adsorption on glass decreases with time (Figure 1). After 1 h of continuous exposure to HNO₃ in synthetic air, 0.4 cm i.d. glass tubes passivate with HNO₃ absorption dropping to zero, while 1 cm i.d. glass tubes take longer to passivate as a consequence of their greater surface area. Glass tubes heated to 50 °C passivate ~20% more rapidly than those at 22 °C. This study demonstrates that glass will be passivated to HNO₃ adsorption if the surface is continuously exposed to HNO₃ for several hours. Thus, the use of glass to contain HNO₃ permeation tubes is warranted if concentrations are constant and exposure times are sufficient. Since only fluoropolymers among the many materials tested here adsorb a small fraction of HNO₃ from a dilute mixture with synthetic air, only the temperature dependence to HNO₃ adsorption on PFA is studied. Other fluoropolymers behave similarly to PFA at room temperature but are not studied further here. Figure 3 shows relative HNO₃ concentrations when 5.6 ppbv of HNO₃ in synthetic air flows through a temperature-controlled PFA tube. As temperature decreases, HNO₃ adsorption increases sharply near 10 °C, until nearly all HNO₃ that interacts with the walls is removed from the gas flow at -10 °C. The amplitude of the near constant signal below -10 °C is consistent with the calculation that 15% of the molecules do not interact with the walls.

Adsorbed HNO₃ is released from cold (<10 °C) PFA surfaces once the PFA is warmed. This reversibility of HNO₃ adsorption is quantified by examining the time-integrated HNO₃ concentration. When PFA tubes are exposed to HNO₃ for 5 min, time-integrated HNO₃ concentrations are the same for both warm and cold tubes if the cold tube is subsequently heated during the integration period. Hence, all HNO₃ that is adsorbed on cold PFA later desorbs if the PFA is warmed above 10 °C. This is in sharp contrast to steel tubing, for which HNO₃ desorption is not observed.

HNO₃ transmission through PFA tubes in humidified synthetic air or laboratory air at 22 °C can be dramatically different than the dry synthetic air results shown in Figures 1 and 2. In humidified synthetic air, adsorption increases with relative humidity (RH) in the tube. Following the exposure of a PFA tube to 5.6 ppbv HNO₃ in humidified synthetic air, adsorption drops below 10% in several seconds for RH <60%, while the same reduction in adsorption requires several minutes when the air is near 100% RH. No temperature dependence to the humidity response is observed for PFA between 22 and 50 °C.

HNO₃ adsorption on PFA in laboratory air varies considerably on a daily basis, presumably as a consequence of changes in ambient air composition. It is speculated that, in addition to water, ammonia or other molecules present in the ambient air react with HNO₃ on PFA surfaces to increase loss. Only some of this adsorption is reversible. Although PFA is far superior to all other materials tested for reducing HNO₃ adsorption, these results impose considerable constraints on the appropriateness of using PFA as a HNO₃ inlet. If wall interaction is significant, surface loss of HNO₃ to PFA may be minimal only in clean and dry air environments. For example, measurements that use nylon filters to collect HNO₃ (5) frequently use PFA prefilters to remove particulates from the sampled air. In ambient air, gas-phase HNO₃ may also be removed from the gas flow by these PFA filters.

Recommendations

The results presented here show that with >80% wall interaction, Teflon fluoropolymer tubes at 22 °C adsorb <5% of HNO₃ from a 5.6 ppbv mixture in synthetic air after 1 min of HNO₃ exposure, whereas tubes made of nylon and coated and uncoated metals and glasses remove >70% under similar conditions. Thus, Teflon can be broadly recommended over the other tested materials for use in atmospheric measurement instrumentation sample lines. However, the temperature dependence of HNO₃ adsorption indicates that PFA must be maintained above 10 °C to guarantee low adsorption. Since HNO₃ adsorption on a surface may increase in humid sampling environments or in the presence of other atmospheric constituents, further calibration of inlet properties may be required to achieve accurate HNO₃ measurements.

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Literature Cited

- (1) Fahey, D. W.; Murphy, D. M.; Kelly, K. K.; Ko, M. K. W.; Proffitt, M. H.; Eubank, C. S.; Ferry, G. V.; Loewenstein, M.; Chan, K. R. *J. Geophys. Res.* **1989**, *94*, 16665–16681.
- (2) Peter, Th. *Annu. Rev. Phys. Chem.* **1997**, *48*, 785–822.
- (3) Liu, S. C.; Trainer, M.; Carroll, M. A.; Hubler, G.; Montzka, D. D.; Norton, R. B.; Ridley, B. A.; Walega, J. G.; Atlas, E. L.; Heikes, B. G.; Huebert, B. J.; Warren, W. *J. Geophys. Res.* **1992**, *97*, 10463–10471.
- (4) Appel, B. R.; Povard, V.; Kothny, E. L. *Atmos. Environ.* **1988**, *22*, 2535–2540.

- (5) Goldan, P. D.; Kuster, W. G.; Albritton, D. L.; Fehsenfeld, F. C.; Connell, P. S.; Norton, R. B.; Huebert, B. J. *Atmos. Environ.* **1983**, *17*, 1355–1364.
- (6) Talbot, R. W.; Vijgen, A. S.; Harriss, R. C. *J. Geophys. Res.* **1990**, *95*, 7553–7561.
- (7) Hering, S. V.; Lawson, D. R.; Allegrini, I.; Febo, A.; Perrino, C.; Possanzini, J. E.; Sickles, J. E. II; Anlauf, K. G.; Wiebe, A.; Appel, B. R.; John, W.; Ondo, J.; Wall, S.; Braman, R. S.; Sutton, R.; Cass, G. R.; Solomon, P. A.; Eatough, D. J.; Eatough, N. L.; Ellis, E. C.; Grosjean, D.; Hicks, B. B.; Womack, J. D.; Horrocks, J.; Knapp, K. T.; Ellestad, T. G.; Paur, R. J.; Mitchell, W. J.; Pleasant, M.; Peake, E.; MacLean, A.; Pierson, W. R.; Brachaczek, W.; Schiff, H. I.; Mackay, G. I.; Spicer, C. W.; Steadman, D. H.; Winer, A. M.; Biermann, H. W.; Tuazon, E. C. *Atmos. Environ.* **1988**, *22*, 1519–1539.
- (8) Gregory, G. L.; Hoell, J. M. Jr.; Huebert, B. J.; Van Bramer, S. E.; LeBel, P. J.; Vay, S. A.; Marinaro, R. M.; Schiff, H. I.; Hastie, D. R.; Mackay, G. I.; Karecki, D. R. *J. Geophys. Res.* **1990**, *95*, 10089–10102.
- (9) Spicer, C. W.; Howes, J. E.; Bishop, T. A.; Arnold, L. H.; Stevens, R. K. *Atmos. Environ.* **1982**, *16*, 1487.
- (10) Fehsenfeld, F. C.; Huey, L. G.; Sueper, D. T.; Norton, R. B.; Williams, E. J.; Eisele, F. L.; Mauldin, R. L. III; Tanner, D. J. *J. Geophys. Res.* **1998**, *103*, 3343–3353.
- (11) Huey, L. G.; Dunlea, E. J.; Lovejoy, E. R.; Hanson, D. R.; Norton, R. B.; Fehsenfeld, F. C.; Howard, C. J. *J. Geophys. Res.* **1998**, *103*, 3355–3360.
- (12) Mauldin, R. L. III; Tanner, D. J.; Eisele, F. L. *J. Geophys. Res.* **1998**, *103*, 3361.
- (13) Talbot, R. W.; Dibb, J. E.; Lefer, B. L.; Scheuer, E. M.; Bradshaw, J. D.; Sandholm, S. T.; Smyth, S.; Blake, D. R.; Blake, J. J.; Sachse, G. W.; Collins, J. E.; Gregory, G. L. *J. Geophys. Res.* **1997**, *102*, 28303–28313.
- (14) Eisele, F. L.; Mauldin, R. L. III; Tanner, D. J.; Fox, J. R.; Mouch, T.; Scully, T. *J. Geophys. Res.* **1997**, *102*, 27993–28001.
- (15) Murphy, D. M.; Fahey, D. W. *Anal. Chem.* **1987**, *59*, 2753.

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