Investigations of the Diffusion Deuder Tube for Measurements of Atmospheric Nitric Acid

Rolando Rael
New Mexico Highlands University
Las Vegas, New Mexico
INVESTIGATION OF THE DIFFUSION DENUDER TUBE METHOD
FOR THE MEASUREMENT OF ATMOSPHERIC NITRIC ACID

Rolando Rael
New Mexico Highlands University

August 8, 1983

Submitted to the Office of EEO/Employee Relations, Personnel Department of the National Center for Atmospheric Research.

*The National Center for Atmospheric Research is sponsored by the National Science Foundation.
Introduction

With a greater concern for the effects of pollution on the atmosphere, scientists have become highly involved in the development of sensitive instruments that will aid in the study of pollution and its potentially hazardous effects on society.

One of the main concerns today is the formation of acid rain from large amounts of pollutants emitted by industrial power plants and automobiles. As the need for more energy increases, the burning of fossil fuels increases, and with it increasing amounts of nitrogen oxides (NO\textsubscript{x}) and sulfur oxides (SO\textsubscript{x}) are being released into the atmosphere. These are converted into a variety of chemical compounds which lead to the formation of undesired things such as acid rain. Of the pollutants associated with acid rain formed from SO\textsubscript{x} and NO\textsubscript{x}, sulfuric acid and nitric acid are by far the most abundant. In the process of this paper, one will become familiar with the behavioral aspects of nitric acid (HNO\textsubscript{3}) and the aspects concerning the measurement of nitric acid in the gaseous state under atmospheric conditions simulated in the laboratory.

Although nitric acid may be formed by various processes in the atmosphere, the following is one of great importance:

\[ \text{NO}_2 + \text{OH} \xrightarrow{M} \text{HNO}_3 \]

Once nitric acid is formed in the atmosphere and because it is highly soluble in water, it is brought downward to the Earth's surface in various forms of precipitation such as snow and rain. With the increasing acidity of rainfall, acid rain has become of great concern to
scientists, due in part to the effects on aquatic and terrestrial ecosystems in the United States and parts of Canada. As the acidity of rainfall increases, the destruction of lakes and rivers becomes more evident. On the land surface, acid rain is eroding rock and metal and greatly acidifying productive fertile soil.

As the government continues to be blind to the hazards of acid rain, scientists must provide the government with abundant amounts of reliable and conclusive evidence that the hazards of acid rain exist and that there must be a stop to it before it has an irreversible effect. This is why at such institutions as the National Center for Atmospheric Research (NCAR), new and more efficient techniques are being developed for the measurement of ambient pollutants.

At NCAR, research is being undertaken to probe the use of a tungstic, acid-coated denuder tube for the measurement of atmospheric nitric acid. Prior measurements of nitric acid have been made by use of either nylon, glass or teflon filters. The following is a list of possible flaws in the usage of filters for measurements (Forrest et al., 1980; Shaw et al., 1981):

- Due to the long sampling periods (4 hr-24 hr) required, interference by particulates and gases at high humidities may produce artifacts.
- Nylon and teflon filters are subjected to positive interference if particulate NO₃⁻ volatizes from the teflon filter when placed prior to the nylon filter.
- Retainment of nitric acid on a prefilter resulting from reactions with, or adsorption by, the collection of particulate matter.
Due to an oversight, page 3 was excluded when the report was bound. Apologies are offered to Rolando Rael, the author of the paper, and to the readers.

- Reaction of collected particulate nitrates with co-collections of strong acids, to release gaseous nitric acid.

- Volatilization of ammonium nitrate from the filter to form gaseous ammonia and nitric acid.

The use of the diffusion denuder tube is not entirely a new concept. The basis of employing the denuder tubes is to detect and determine amounts of ammonia and nitric acid in ambient air by passing a laminar flow of ambient sample air through a hollow tube coated with an acid or base coating on the inner walls. Gases diffuse to the walls and are chemisorbed on the coating. Heating of the tube converts adsorbed gases to a form which may be detectable on a chemiluminescent \( \text{NO}_x \) machine. In the early stages of the use of denuder tubes, both the Environmental Protection Agency and the Brookhaven National Laboratories (Spicer \textit{et al.}, 1981) used them for the measurement of nitric acid. Older denuder tubes employed the use of a base coating or a magnesium oxide coating, but they developed interference from other atmospheric species and the use of prefilters were necessary to minimize these interferences (Shaw \textit{et al.}, 1981; Forrest \textit{et al.}, 1982).

More recently, Braman and Shelly (1981) developed an improved denuder tube using a tungstic acid inner coating. They have used it to measure gaseous ammonia and nitric acid. Nitric acid collected in the inner coating of the denuder tube which was heated to approximately 350°C, released \( \text{NO}_2 \) and was carried into a chemiluminescent \( \text{NO}_x \) machine by a helium carrier gas. The following processes were proposed by Braman and Shelly:
• \( \text{WO}_2(\text{OH})_2 + 2\text{HNO}_3 + \text{WO}_2(\text{NO}_3)_2 + 2\text{H}_2\text{O} \) (load period)

• \( \text{WO}_2(\text{NO}_3)_2 \xrightarrow{\Delta} 1/2\text{O}_2 + 2\text{NO}_2 + \text{WO}_3 \)

• \( \text{WO}_2(\text{NO}_3)_2 \xrightarrow{\Delta} 1/2\text{O}_2 + \text{NO} + \text{WO}_2(\text{OH})_2 \)

Braman and Shelly (1981) used the NO\textsubscript{x} analyzer in the NO\textsubscript{x} mode as they reported most of the adsorbed gas was released as NO\textsubscript{2}.

**Purpose of NCAR Research**

The purpose of the ongoing investigation at NCAR on the denuder tube is to link Braman's work to NCAR's work and examine the correlation between the two. The main purpose of the tests was to eventually be able to monitor gaseous nitric acid and have the capability to check for interference and artifacts that may be caused by such things as humidity, NO\textsubscript{2}, or a combination of both that might hinder measurements of nitric acid.

**Experimental Data and Techniques**

I. **Preparation of Tungstic Acid Denuder Tube.** The denuder tubes were constructed essentially as described by Braman and Shelly (1981). In the preparation of a denuder tube, a 45 cm hollow quartz tube was first washed with a hot sodium hydroxide solution and rinsed with distilled water and then with dilute hydrofloric acid to slightly etch the inner surface of the tube. The tube was then placed in a drying oven and left to dry. The tube was then installed in a vacuum system with a 50 cm piece of tungsten wire inserted through the center of the tube (the
wire must be kept tight or an improper coating will occur as a result of expansion of the wire when heated). The vacuum system is then pumped to a pressure of 0.5 torr and the tungsten wire was heated using a current of about 12 amps. The tube was left under this condition for 1/2-2 hrs; the period depended on how heavy a coating was desired. During these procedures, a blue tungsten oxide coating should be seen depositing on the inner walls of the tube. The tube was then removed from the vacuum system and the blue coating was then converted to a yellow tungsten oxide coating by the process of passing oxygen at atmospheric pressure through the blue coated tube which is heated at about 500°C in a small furnace. If no visible defects in the coating are detectable, the tube was considered ready for testing (Figure 1).

II. General Experimental Setup. A schematic diagram of the flow system used in these studies is conveyed in Figures II and III. The system may appear to be complicated. Prior studies of various setups had shown that nitric acid and water mixtures in air gave erratic results when the mixture flowed through teflon solenoid valves of various types, as long equilibration times were required when the gas mixture was changed. In the present system the nitric acid mixture is conveyed into the system through teflon tubing, but no valves are used up to the denuder tube itself. As well, only a nitrogen carrier gas entered the nitrogen oxide chemiluminescent instrument.

Air (U.S. Welding, breathing-grade air) from high pressure cylinders was introduced into the system through a molecular sieve trap for further purification and regulated by means of Tylon mass flow (SCCM) controllers. The air entering the main mixing manifold was controlled by two separate controllers. Of the total 600 SCCM of air running in the system, one
<table>
<thead>
<tr>
<th>% R.H.</th>
<th>Peak (γ) HNO₃</th>
<th>ppbv</th>
</tr>
</thead>
<tbody>
<tr>
<td>49&quot; Tube (1st Day)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>7.4</td>
<td>21.45</td>
</tr>
<tr>
<td>25</td>
<td>6.6</td>
<td>19.13</td>
</tr>
<tr>
<td>50</td>
<td>5.7</td>
<td>16.53</td>
</tr>
<tr>
<td>75</td>
<td>4.6</td>
<td>13.34</td>
</tr>
<tr>
<td>100</td>
<td>3.9</td>
<td>11.31</td>
</tr>
<tr>
<td>49&quot; Tube (2nd Day)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>6.6</td>
<td>21.45</td>
</tr>
<tr>
<td>10</td>
<td>6.4</td>
<td>20.80</td>
</tr>
<tr>
<td>30</td>
<td>6.3</td>
<td>20.48</td>
</tr>
<tr>
<td>60</td>
<td>5.7</td>
<td>18.53</td>
</tr>
<tr>
<td>90</td>
<td>4.6</td>
<td>14.95</td>
</tr>
<tr>
<td>9-1/2&quot; Tube (3rd Day)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>6.6</td>
<td>21.45</td>
</tr>
<tr>
<td>25</td>
<td>6.0</td>
<td>19.50</td>
</tr>
<tr>
<td>50</td>
<td>5.3</td>
<td>17.23</td>
</tr>
<tr>
<td>75</td>
<td>4.3</td>
<td>13.98</td>
</tr>
<tr>
<td>100</td>
<td>3.1</td>
<td>10.08</td>
</tr>
<tr>
<td>9-1/2&quot; Tube (4th Day)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>6.6</td>
<td>21.45</td>
</tr>
<tr>
<td>10</td>
<td>6.3</td>
<td>20.48</td>
</tr>
<tr>
<td>30</td>
<td>6.1</td>
<td>19.83</td>
</tr>
<tr>
<td>60</td>
<td>5.2</td>
<td>16.90</td>
</tr>
<tr>
<td>90</td>
<td>3.8</td>
<td>12.35</td>
</tr>
</tbody>
</table>
controller passed, say, 300 SCCM of air through a distilled water
bubbler or humidifier. The other 300 SCCM of air entered the system
directly as dry air. By changing the fraction of air exiting the two
controllers, it was possible to generate various humidities in the
600 SCCM air stream. Various gas species such as nitric acid could be
added to the system using a flow controller with a small quantity of air
passing through a glass trap in a water bath held at a constant temperature
which contained a permeation device. The permeation rates used in this
experiment were based on the manufacturer's calibrations.

The mixture of gases was loaded into the denuder tube at room
temperature for periods of usually 30 seconds varying every four minutes
in the following manner: A loading pump (P) drew one-half (300 SCCM[plus])
of 600 SCCM[plus] total) of the mixture from the mixing manifold into
the denuder tube through Valve 1 and a tylan flow controller (A). The
gaseous mixture is adsorbed onto the tungstic acid coating in the denuder
tube and then the tube is heated for one minute at an approximate tempera-
ture of 500°C. During the heat cycle, Valve 3 opens to allow N₂ to
enter the system to the denuder tube. The N₂ carrier gas loads the
gases from the denuder tube which have been converted to NO by the
heating of the tungstic acid coating into the NOₓ machine to be analyzed
(refer back to Figure III). The mixture that is carried into the NOₓ
machine is going in in the form of NO. The NO enters a reaction vessel
where the NO reacts with ozone (O₃) to form nitrogen dioxide (NO₂).
Some of the NO₂ is converted NO₂⁺ (⁺ refers to NO₂ in an excited state).
NO₂⁺ gives off a photon and is detected in the machine by a photo-
multiplier tube. The signal was displayed on a strip chart recorder
(Figure IV). The system is automatically run at four-minute cycles by means of automatic timers (Chronotrol). All valves, cooling and heating cycles, are programmed into the timer's memory and turned off and on without manual assistance.

III. Experiment #1. The Effects of Changes in Humidity on the Measurement of Nitric Acid Using the Diffusion Denuder Tube System. In tests of the denuder device a nitric acid (HNO₃) permeation device calibrated to release 38 n gm/min at 40°C was used. A carrier flow of air at 30 SCCM entered the system's glass trap in the water and passed over the permeating device and carried the mixture into the mixing manifold. With the total gas flow of 630 SCCM, a mixing ratio of 21.5 ppbv of nitric acid was present in the mixing manifold.

Relative humidities of 0, 10, 25, 30, 50, 60, 75, 90 and 100 percent were randomly chosen for these tests. The experiments were run over a period of 4 days with 45 to 50 minute runs at each humidity. Figure V shows a chart trace for humidities of 0, 25, 50, 75 and 100 percent. Prior to running the experiments, it was thought that different lengths of the mixing manifold might affect the outcome of the tests. It was thought that longer manifolds might increase possible surface loss of HNO₃ in the manifold prior to HNO₃ entering the denuder tube than with a short manifold. Consequently, tests were made with the use of a 1/4" by 49" long manifold and a 1/4" by 9-1/2" long manifold. The following observations were made:

(1) It was observed that as the humidity of the air streams was increased, the heat cycle signal peak on the recorder decreased. Virtually always, the largest decrease occurred when the humidity was changed from 0% to a humidity of 10 to 25% (Figure VI).
\( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \)  
GROUND STATE

\( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2^* \)  
EXCITED STATE

\( \text{NO}_2^* \rightarrow \text{NO}_2 + h\nu \)  
YIELD OF PHOTON

**FIG. IV**
(2) It was also often observed that at high relative humidities (greater than 60%), a much longer time was required for peak heights to equilibrate. The amount of time for equilibration at high humidities was 1 to 3 hours.

Results. Figure VIIA shows the effects of humidity upon the HNO₃ signal peak for the experiments. The results of the experiments are expressed in terms of apparent nitric acid that would be measured relative to the 0% humidity mixing ratio (Table I). It is clearly noticeable that a significant reduction in the HNO₃ signal occurred as the humidity was increased. For example, the loss averaged about 45% between 0% and the highest humidities tested (90-100%) whereas between 10% and 50% relative humidity, there was on the average a 15% loss (Figure VII).

The tests also indicated that the dependence of the HNO₃ signal on humidity changed little for the short 9-1/2" manifold or the long 49" manifold. It appears that the loss of HNO₃ signal did not occur in the mixing manifold. Thus, the loss is occurring either on the tube fitting into the denuder tube, the 2" section of bare quartz in the denuder tube, or on the coating itself.

IV. Experiment #2. The Addition of NO₂ to the Denuder System Along with HNO₃ at Various Humidities. There exists the possibility of surface reactions generating HNO₃ when NO₂ and water vapor are present in the sampling manifold. Laboratory simulations were carried out by adding NO₂ to the mixing manifold. According to Braman (1982), the tungstic acid coating on the denuder tube did not collect NO₂ during laboratory tests. For most experiments done during the ten-week period, NO₂ was added upstream prior to the release of HNO₃ onto the mixing manifold. The NO₂, like the HNO₃, was released from a permeation
device which was calibrated to release 110 ngm/min of NO₂ at 30°C. This corresponded to a mixing ratio of 83.7 ppbv. The NO₂ from the glass trap was added to the main stream and manifold in an air carrier of 10 SCCM through a three-way valve. Again the main flow was kept at 600 SCCM. Both 9-1/2" and 49" mixing manifolds were used in the experiments. First, the experiment was run with HNO₃ only at a designated relative humidity for about 45 minutes and then NO₂ was directed into the manifold for another 45 minutes. After tests were run at humidities of 0, 10, 25, 30, 50, 60, 75, 90 and 100 percent, the system was run without HNO₃ in the air stream. The tests were repeated with a lower permeation rate of approximately (27 ngm/min ± 20%). The following observations were noted:

(1) With the addition of NO₂ to the system, there was a small but noticeable increase in the known HNO₃ heat peak. Again the largest effects were usually observed when the system was run at 0% relative humidity (Figure VIII and IV).

(2) What was also evident and very interesting was that a peak roughly half the size of the known heat peak was observed while the denuder tube was swept out by the N₂ carrier gas prior to heating the denuder tube. This peak was labeled as a "sweep" peak and must be due to the release of NO since the NOₓ machine was run in the NO mode.

(3) All peak signals (HNO₃, HNO₃ + NO₂, and "sweep") decreased with an increase in humidity (Figure IX).

(4) With the system running with no HNO₃ being added, only NO₂, water and air, the "sweep" peak was still apparent as well as a small peak signal was given off when the tube was heated.
FIG. IX

HNO₃ + NO₂ AT % RH
(5) Observations made with the much smaller 27 ngm/min NO₂ permeation device showed a much smaller sweep peak.

(6) If the system without HNO₃ permeation into the system is used and the heater is disconnected, the "sweep" peak stayed level for about four cycles and then began to decrease in size. This suggested that the "sweep" peak was generated as a result of NO₂ to NO conversions by the denuder tube surface coating, but the surface remained an active converter only if the denuder tube was heated periodically. Thus, when the heater was turned off, the denuder surface was slowly deactivated for NO₂ to NO conversion (Figure XI).

Conclusions Regarding the NO₂ Tests.

(1) When large amounts of NO₂ (83.7 ppbv compared to 21.5 ppbv of HNO₃) are added to the system only a small increase (6-7%) in the nitric acid peak was observed. The increase was very nearly the same when the added NO₂ was only about 20.5 ppbv. The increase was also still observed if a nylon wool filter was placed in the exit tubing of the NO₂ permeation tube. Since HNO₃ is removed by nylon, this ensures that the extra signal was not due to generation of HNO₃ prior to the mixing manifold. A small heat peak signal was also observed when NO₂ only was added to the mixing manifold. At present, we are not sure whether the increase in the heat peak with NO₂ present is due to generation of HNO₃ in the manifold or on the denuder surface or whether the denuder does collect a small fraction of NO₂. However, for realistic mixing ratios of ambient NO₂, the interference by NO₂ and water in measurements of HNO₃ should be negligible. Further tests are required.
(2) In our system, NO₂ to NO conversion was observed on a freshly heated denuder surface. Although this does not affect the measurement of HNO₃, it does preclude the use of the NOₓ analyzer to monitor ambient NO or NO₂ during the load cycle of the experiment.

Conclusions

During the past ten weeks of testing for the effects of humidity and NO₂ on the use of the denuder tube for the measurement of nitric acid, some conclusive answers have been found and many questions raised as well. Further experiments are required and tests repeated at much smaller mixing ratios for nitric acid.

The first tests showed the effect on the denuder tube's capability to measure nitric acid at various humidities for our experimental setup. If the denuder tube is to be used out in the field, frequent calibrations made by adding known amounts of nitric acid to the ambient air stream must be made and the results suggest that the humidity be kept below about 50%.

From the tests involving HNO₃, water and NO₂, we conclude that the interference should be negligible for realistic ambient levels of NO₂.

In order to say that the denuder tube will allow accurate measurements of atmospheric HNO₃ free from interferences by other atmospheric species, further tests in the laboratory must be made. The addition of other species and combinations of other species such as O₃, PAN, N₂O₅, HONO and particulates to the lab system need to be tested.
Acknowledgements

I would like to thank all the people at NCAR for their help and support during my stay at NCAR. I would especially like to thank Mr. David Armstead and Ms. Martha Aguilar for the opportunity to work at NCAR. I would also like to thank Teresa LaCrue for her assistance throughout the summer. I would like to give special recognition to Dr. Brian Ridley and Mr. Art Wartburg for their patience and time spent teaching me what is involved in the study of science.
References