

INTRODUCTION

Nitric acid and ammonia are trace gases that are not routinely monitored at atmospheric chemistry and air quality measurement sites, but are of great interest to scientists and policy makers as they try to understand the air quality problems of oxidant and particulate matter formation. The EPA NCORE program strategy lists both nitric acid and ammonia as target species for continuous measurement, but there are not yet recommended continuous methods for either species. Measurement methods for these species have been proposed, deployed and intercompared many times in the past twenty years. As shown by the intercomparisons, and by a handful of more recent studies, the methods that exhibit the greatest accuracy, precision, and stability tend to be research methods like Chemical Ionization Mass Spectrometry (CIMS), Tunable Diode Laser Absorption Spectrometry (TLAS), and Liquid Scrubbing followed by detection using HPLC, fluorimetry, or optical absorption.

The drawback inherent in these powerful techniques is their resource requirements, both in terms of initial outlay, and in terms of highly skilled labor. In this study we report on the deployment and operation of instrumentation for measuring nitric acid and ammonia that can be operated continuously and year round with relatively modest investments in equipment and labor. Data for a three month period in late winter and spring of 2006 is presented and discussed.

SITE DESCRIPTION

- Pinnacle State Park (PSP)**
- Low population density rural village of Addison, New York
 - Surrounded by parklands, and forested areas

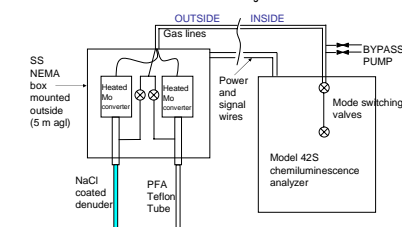


Nitric Acid Measurement Method

We use a model 42S chemiluminescence instrument to measure HNO₃ by denuder difference in conjunction with NO_x. The method involves using the switching technique of the commercial NO/NO₂/NO_x analyzer – but instead of “NO” and “NO_x” measurement modes, the modified instrument uses “NO_x-HNO₃” and “NO_x” measurement modes. The “NO_x-HNO₃” mode involves passing the sample through a chemically coated annular denuder and a heated molybdenum converter before it enters the analyzer’s reaction and detection chamber.

The denuder difference method relies on the selective removal of the target species (in this case HNO₃) in one NO_x-like measurement channel, while another channel – identical except for the denuder – measures “true” NO_x. The difference between these channels is then the HNO₃. Based on information from the EPA Compendium of Methods 10, sodium carbonate was initially selected as the active chemical for nitric acid removal in 2000. Sodium carbonate was effective in chemically removing HNO₃ in the gas stream, but in early to mid-2002 we discovered that the Na₂CO₃ denuder captured not only the HNO₃, but also roughly 15% of the NO₂. An uncoated denuder was used for about a year from October of 2002 to September of 2003, but was also unsatisfactory. Finally, in October of 2003, a denuder coating of 1% sodium chloride was tried. This appears to be the optimum chemical coating material for selective removal of HNO₃ and has been used ever since. Analog signals from the analyzer are averaged with a one minute base period and transferred automatically to a computer for storage.

Schematic of HNO₃ Method



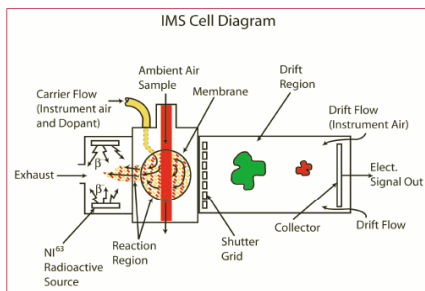
Ammonia Measurement Method

The ammonia analyzer is an AirSentry Ion Mobility Spectrometer (IMS) purchased from Particle Measuring Systems (Boulder, CO). The technique utilizes ionization of the NH₃ molecule followed by electrostatic extraction of the ions into a drift chamber and detection at a collector plate. The shutter field producing the extraction field is pulsed periodically to allow ions into the drift tube; and ion time-of-flight is used to identify the ammonia ion. Confirmation of the ion identification and of the quantification is obtained through the measured addition of a dopant molecule (in this case dimethyl methylphosphonate – (CH₃)₂PO₂).

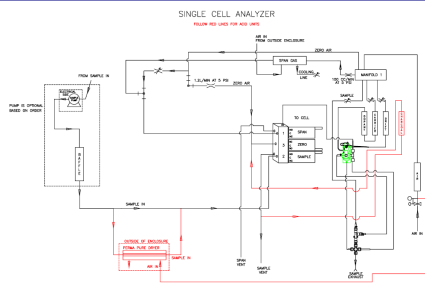
Ambient air is sampled at ≈2.5 l/min through a heated, silica-coated 4.8 mm I.D. (1/4” nominal O.D.) stainless steel inlet line. In addition, a supply of clean, dry air (dew point below -40°C, flow rate less than 5 l/min) at a delivery pressure of 20-120 psig must be supplied to the analyzer. This instrument air flows into the IMS analyzer cell on one side of a semi-permeable membrane, and the ambient air sample flows into the cell on the other side of the membrane. NH₃ in ambient air passes through the membrane and is picked up by purified instrument air which delivers it to the reaction region. Low level beta energy from a sealed nickel-63 radiation source ionizes the sample. The ions are drawn out of the reaction region and flow counter to the drift gas flow. During this counter flow period the ions separate in time based on their chemical and physical properties before being detected by a Faraday plate detector at the end of the drift tube. Detection selectivity is achieved through specificity of the semi-permeable membrane, and through the consistent time-of-flight of the ammonia ions as they traverse the stable drift flow. Zero response and calibration checks are performed from the front channel keypad. (Note that calibration checks require the optional add-on permeation source.)

The AirSentry uses eight individual time-of-flight spectra to produce each sample concentration, which equates to an averaging period of less than 0.2 seconds. Samples may be further averaged using a user selectable smoothing factor (we used a smoothing factor of 250 for the field measurements), which calculates a rolling average concentration value. These values are transferred as a serial string to a computer and recorded once a minute.

Schematic of IMS Detection Cell



Flow Schematic of IMS Analyzer

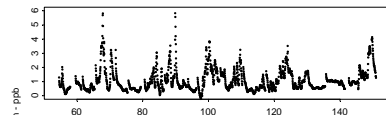


Research Measurements at PSP

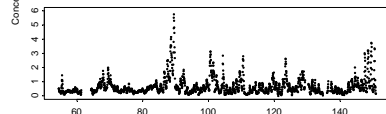
- Gases: O₃, NO, NO₂, NO_y, CO, SO₂ (non-polar C₂-C₁₀ hydrocarbons through 2005)
- Continuous PM: PM_{2.5} and PM₁₀ Mass, PM_{2.5} sulfate and carbon
- Integrated PM Filters: PM_{2.5} Mass (FRM), chemically separated PM_{2.5} from STN and IMPROVE networks
- Scattering: NGN-3a nephelometer
- Meteorology: T, RH, WS, WD, rain, radiation, pressure

Results – NH₃ and HNO₃ Observations

Ammonia at Pinnacle State Park, Addison, NY - 2006



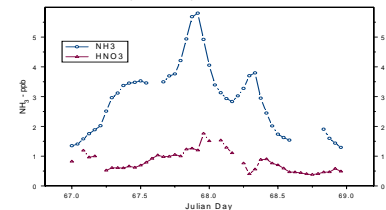
Nitric Acid at Pinnacle State Park, Addison, NY - 2006



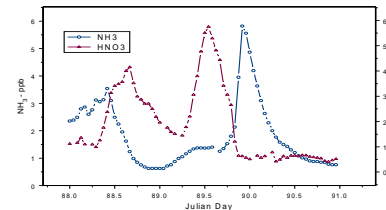
Observation Statistics: March – May 2006

	NH ₃	HNO ₃
Mean	1.06 ppb	0.66 ppb
Standard Dev.	0.77 ppb	0.62 ppb
Median	0.87 ppb	0.48 ppb
Maximum	5.82 ppb	5.75 ppb
Est. MDL	0.3 ppb	0.2 ppb
Completeness	90.1%	85.4%

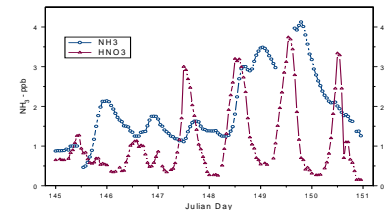
NH₃ and HNO₃ - March 9-10, 2006



NH₃ and HNO₃ - March 30 - April 1, 2006



NH₃ and HNO₃ - May 26-31, 2006



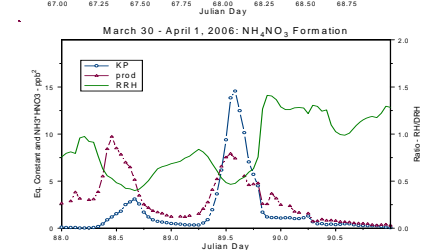
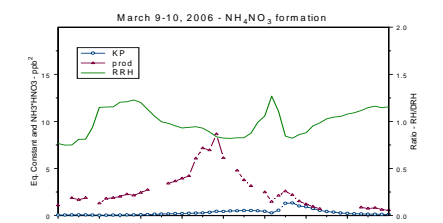
Response Time – Memory Effect Concerns

- Note that on the previous figure the HNO₃ drops below 1 ppb each night
- However, NH₃ does not drop very much between peak concentrations
- We believe this is due – at least in part – to changing uptake and release of NH₃ on the sample handling lines, switching valves, and IMS membrane – and not to changing ambient NH₃.
- An “unaffected” ammonia measurement method may be required to conclusively resolve this issue.

Results – Gas-Aerosol Equilibrium

PM Nitrate Formation

- RH is important- simplest case is for RH < deliquescence RH, then NH₄NO₃ is solid and the equilibrium relation is simply
 $K_p(T) = [NH_3][HNO_3]$ (units – ppb²)
- Hour averaged temperature is used to
 Calculate DRH (used below to decide if simple case applies)
 Calculate Kp(T)
- Use measurements to calculate “prod” = [NH₃][HNO₃]
- RRH = (measured RH)/DRH(T) – the ratio of ambient RH to the NH₄NO₃ deliquescence RH determines the “case”
 RRH < 1 ⇒ NH₄NO₃ solid – simplest case
 RRH > 1 ⇒ NH₄NO₃ liquefied and equilibrium shifts to aerosol phase by up a factor of 10
- If prod > K_p, equilibrium favors aerosol formation



Calculated Nitrate Aerosol Production Tendencies

- March 9 – STN measures 6.73 μg/m³ PM_{2.5} nitrate (24-hr average)
 Gaseous HNO₃ < NH₃; if all HNO₃ is converted to nitrate aerosol each hour, the average production rate is 3.24 μg/m³/hr
- March 30 - STN measures 6.73 μg/m³ PM_{2.5} nitrate (24-hr average)
 K_p at the end of the day is roughly equal to “prod”, so tendency to produce aerosol falls dramatically at that point
 Estimated average production rate is higher for this rate – 4.62 μg/m³/hr – so clearly the losses are greater as well
- More detailed modeling (including transport and losses) is required for quantitative treatment of this process

Summary of Findings

- Continuous, almost routine measurement of HNO₃ and NH₃ is possible
- Denuder difference with chemiluminescence seems robust for HNO₃ (NaCl denuder)
- IMS for NH₃ is easy to use and sensitive - but still suffers from time response (memory effect) issues
- Both species are ubiquitous, but present mainly at low concentration levels in the rural Northeast (at least away from sources)
- Ammonia and Nitric Acid are often elevated during the same day or two day period, but their peaks are anti-correlated
- Along with temperature and RH, one can easily determine the tendency to produce nitrate aerosol, but details of the rate of accumulation and expected mass concentrations require additional modeling

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