**INTRODUCTION**

Nitric acid and ammonia are compounds 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 (TDLAS), 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 populations density rural village of Addison, New York • Surrounded by parklands, and forested areas

**Nitric Acid Measurement Method**

We use a model 425 chemiluminescence instrument to measure HNO3 by denuder difference in conjunction with NOy. The method involves using the switching technique of the commercial NOx/NOY/NO analyzer but instead of "NO" and "NOY" measurement modes, the modified instrument uses "NOY-NH3" and "NOY" measurement modes. The "NOY-NH3" mode involves passing the sample through a chemically coated stainless steel denuder and a heated molybdenum convertor before it enters the analyzer's reaction and detection chamber.

The denuder difference method relies on the selective removal of the targeted species (in this case HNO3) in one NOx - like measurement channel while another channel - identical except for the denuder - measures "true" NOx. The difference between these channels is then the "NOy". Based on information from the EPA Compendium of Methods10, 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 NO. An uncoked denuder was used for about a year from February of 2002 to September of 2003, but it was also unsatisfactory. Finally, in October of 2005, 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.

**Results – NH3, and HNO3 Observations**

**Flow Schematic of IMS Analyzer**

**Schematic of IMS Detection Cell**

**Results – Gas-Aerosol Equilibrium**

**PM Nitrate Formation**

- RH is important - simplest case is for RH < deliquescence RH, then

\[ \text{RH} \cdot \text{Kp} = \text{prod} \]

⇒

- RRH < 1

**Observation Statistics: March – May 2006**

**Calculated Nitrate Aerosol Production Tendencies**

- March 9 – STN measures 6.73 μg/m3 PM10 nitrate (24-hour average)
- Gasphase HNO3 + H2O if all HNO3 is converted to nitrate aerosol each hour, the average production rate is 3.24 μg/m3/h
- March 30 – STN measures 6.73 μg/m3 PM10 nitrate (24-hour average)
- RRH at the end of the day is roughly equal to ‘prod’, so tendency to produce aerosol falls dramatically at that point

**Summary of Findings**

- Continuous, almost routine measurement of HNO3 and NH3 is possible
- Denuder difference with chemiluminescence seems robust for HNO3 measurements
- AMS for NH3 is easy to use and sensitive - but still suffers from time response (memory effect) issues
- Both species are ubiquitous, but present at low concentrations in rural areas (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 concentration require additional modeling

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