

EXECUTIVE SUMMARY

DETERMINATION OF ACIDITY IN AMBIENT AIR

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INTRODUCTION

Nitric acid in the atmosphere is believed to contribute substantially to the acidification of rainwater and dry-deposited atmospheric material in California. Accordingly, accurate and rapid methods for the measurement of this acid can be important in assessing potential adverse health and welfare effects, mechanisms of formation, and in developing possible control strategies for minimizing airborne concentrations of this acid.

Of the gaseous acids thought to be present in ambient air in relatively high (e.g. parts-per-billion) level, hydrochloric acid has probably received the least attention. Nevertheless, it offers many of the same potential adverse effects as does nitric acid. Prior to this study, no measurements of hydrochloric acid in California ambient air had been reported.

The alkaline gas, ammonia, plays a key role in limiting the concentration of gaseous acids such as nitric and hydrochloric acids, and the extent of conversion of these acids to light-scattering particles. Measurements of the concentrations of these acids must be made in parallel with ammonia determinations in order to infer the maximum concentrations of airborne acids before neutralization and to understand the spacial and temporal variations in acid concentration.

Objectives

A laboratory and field study was performed to construct and evaluate an automated, semi-continuous monitor for ambient air concentrations of nitric acid (HNO_3) and ammonia (NH_3) utilizing tungstic acid coated denuder tubes. In addition, atmospheric concentrations of hydrochloric acid (HCl) were determined. Manual techniques for atmospheric NH_3 measurement were also compared.

Procedures

A laboratory study assessed the influence of design parameters to achieve a workable automated sampler for HNO_3 and NH_3 . Interference in HNO_3 measurements was determined with nitrogen dioxide, nitrous acid, and particulate ammonium nitrate. Alternative methods for NH_3 as well as a method for HCl collection and analysis were assessed.

Atmospheric sampling was done on the campus of the University of California (Riverside) during the period 9/7 - 9/21/84, with samplers mounted on the roof of a mobile laboratory. In addition to the automated tungstic acid technique (TAT), HNO_3 was measured by the denuder difference method (DDM), considered the reference procedure for HNO_3 . The DDM employs filter collection and subsequent laboratory analysis. Ammonia and HCl were measured with impregnated filter methods. In addition, NH_3 was measured by a denuder tube collection procedure.

Results

Nitrous acid was the only material studied which exhibited significant interference in nitric acid response with the automated TAT. The efficiency of the tungstic acid coated tubes for nitric acid and ammonia ranged from 91 to 98%. Oxalic acid coated denuder tubes provided NH_3 measurements equivalent, within 20%, to those with oxalic acid-impregnated filters. Hydrochloric acid sampling with Teflon prefilters and triethanolamine-potassium hydroxide coated cellulose after-filters provided an efficiency of at least 92%.

Pollution levels during atmospheric sampling in Riverside ranged from extraordinarily light to moderate photochemical smog ($\text{O}_3 > 0.30$ ppm). Nitric acid levels with the automated TAT showed 1 hour average values up to $45 \mu\text{g}/\text{m}^3$ (17.5 ppb). These values showed moderate correlation with O_3 ($r = 0.78$) and high correlation ($r = 0.94$) with HNO_3 by the DDM. However, the HNO_3 values averaged about 50% higher than those by the reference procedure. The difference in atmospheric results between the automated TAT and DDM is believed to reflect the retention on tungstic oxide coated tubes of unidentified (possibly organic) nitrogen oxides. Similar discrepancies between the TAT and other HNO_3 methods have been reported.

Ammonia measurements with impregnated filters showed high correlation ($r = 0.98$) with oxalic acid-coated denuder tube collected samples but the former averaged 12% higher. This is consistent with partial volatilization of ammonium salts from the Teflon prefilter. Ammonia measurements with the automated TAT were not quantitative

because of difficulties in calibration. At relatively high concentrations, TAT response to NH_3 atmosphere appeared to be linear, however. Further modification of the TAT is needed to permit reliable NH_3 determinations.

Hydrochloric acid values, estimated by observed levels of gaseous chloride, ranged up to $3 \mu\text{g}/\text{m}^3$ with a pronounced diurnal variation, maxima occurring during the period 0800-1200 or 1200-1600 hr. Particulate chloride levels were similar in magnitude to those for HCl and showed no correlation with HCl.

Principal Conclusions

1. An automated HNO_3 monitor can be reproducibly calibrated and used to obtain semi-real time ambient air measurements which are highly correlated with atmospheric HNO_3 .
2. Unidentified, atmospheric nitrogen oxides are also retained on tungstic acid coated denuder tubes which, in the present study, caused a 50% positive interference. Without modification to improve its selectivity, the automated TAT offers limited reliability as a reference method for nitric acid.
3. Nitrogen dioxide and particulate ammonium nitrate do not appear to interfere in the TAT method. However nitrous acid (HONO) shows a substantial positive interference. It is unlikely that HONO caused a substantial fraction of the observed interference, however.

4. Ammonia is more difficult to sample correctly with the automated TAT. Further work is needed to obtain a reliable automated NH_3 monitor.
5. Atmospheric hydrochloric acid levels in Riverside are low ($\leq 3 \mu\text{g}/\text{m}^3$) with pronounced daytime maxima.
6. Triethanolamine-KOH impregnated cellulose filters cannot be recommended for HCl collection if ion chromatographic analysis is intended.
7. Phase II of this investigation should include further improvements in the automated TAT to permit NH_3 measurements, further interferent studies with the TAT, atmospheric trials at sites with both low and high levels of HCl, NH_3 and HNO_3 , and assessment of the contribution of gaseous acids to atmospheric particulate acidity.

Implications for Regulatory Programs

1. A continuous method for accurately monitoring atmospheric nitric acid is very desirable for potential regulatory actions regarding nitrogen oxide emissions.
2. The automated tungstic acid technique provides at least a reliable upper limit to nitric acid concentrations.

3. Concentrations of hydrochloric acid measured in this program are low relative to those for nitric acid. However, judgements on the need for regulatory action regarding hydrochloric acid should only be made when more extensive measurements are available, especially at sites near the western edge of the South Coast Air Basin.