EXECUTIVE SUMMARY

TO

STUDIES OF DRY ACID DEPOSITION IN THE SOUTH COAST AIR BASIN: INTERMETHOD COMPARISON OF PROCEDURES FOR NITRIC ACID AND AMMONIA

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FINAL REPORT

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Introduction

Nitric acid and ammonia are difficult species to measure in the atmosphere. This difficulty results from their relatively low concentrations, tendency to adsorb on surfaces and, with nitric acid, the presence of other nitrogen oxides at much higher concentrations. Nevertheless, the importance of nitric acid in acidification of surfaces by wet and dry deposition makes accurate measurement of this acid of unusual importance. Because ammonia neutralizes atmospheric acidic species, including nitric acid, the accurate measurement of this species is also vital to efforts to model atmospheric acidification, especially in relation to spatial variations in atmospheric acidity.

Objectives

A field study was performed in parallel with about seventeen other research groups to compare methods for nitric acid ammonia and related species. The overall objective was to assess the degree of agreement between methods and, by comparison to techniques which purport to measure nitric acid unambiguously, to infer the accuracy of less direct methods.

Procedures

The methods we employed were (1) a semi-real time technique for nitric acid (HNO_3) and ammonia (NH_3) utilizing tungstic acid coated denuder tubes (TAT), (2) the denuder difference method (DDM) for HNO_3, fine particle NO_3^- and total fine inorganic NO_3^-,

(3) a filter pack method for gaseous NH_3 and particulate NH_4^+, and (4) a denuder collection procedure for NH_3 using oxalic acid-coated tubes. These were operated at Claremont, CA during the period September 11 through September 19, 1985.

Results

The DDM yielded HNO_3 results averaging about 30% higher than those by a spectroscopic method, the tunable diode laser (TDL) method. However, partial loss of HNO_3 was probable in the inlet lines of the TDL method. Compared to the DDM, the TAT results exhibited a pronounced day-night effect; during daylight periods, the TAT and DDM HNO_3 results displayed relatively good agreement. This contrasts with earlier results at Riverside in which the TAT was higher by 50%. During nighttime hours, when HNO_3 levels were very low, the TAT HNO_3 was about 6 times that by the DDM. The cause may relate to collection of NO_x species other than HNO_3. Since NO_2 is not significantly retained on tungstic acid tubes, the results are consistent with at least partial retention of other nitrogen oxides whose concentrations are expected to increase during nighttime hours.

Ammonia results with the TAT were variable in relation to the filter pack (FP) method. The FP/TAT NH_3 ratio of results ranged from 0.6 to 3, increasing with temperature. The TAT showed much greater temperature sensitivity than the FP for NH_3 sampling. The ammonia results with the TAT are considered uncertain by a factor of two. The FP method NH_3 results averaged 50% too high compared to those by the denuder tube method.

Principal Conclusions

1. The denuder difference method (DDM) for nitric acid is accurate within about 20%.

2. The tungstic acid technique (TAT) nitric acid values during daytime periods, at sites with high HNO_3, can range from good agreement to 50% higher relative to results with the DDM.

3. Ammonia concentrations measured with TAT are subject to error of a factor of two.

4. The filter pack (FP) method yields results which are consistently too high. The degree of error is expected to vary. For the present study the FP method averaged about 50% too high.

Implications for Regulatory Programs

1. At this time, TAT is best considered a research tool, inappropriate for monitoring nitric acid in direct support of efforts to control NO_x emissions to reduce nitric acid formation.

2. The DDM provides reliable nitric acid concentration measurements and, while requiring laboratory analyses and, therefore, relatively slow and expensive, can be used in support of regulatory or other programs concerned with control of atmospheric nitric acid formation.