FIELD COMPARISON OF MEASUREMENT METHODS FOR NITRIC ACID

ARB Contract # A4-164-32

Executive Summary

Prepared by:

Susanne V. Hering
Department of Chemical Engineering
University of California
Los Angeles, CA 90024

Prepared for:

Douglas R. Lawson, Project Officer
Research Division
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

April 20, 1987

Executive Summary

Project Description and Objectives

The Nitrogen Species Methods Comparison Study was a field comparison of methods for measuring atmospheric concentrations of nitric acid and other nitrogenous species. Investigators from 20 different research groups participated in the study, which was held at Pomona College in Claremont, CA, located in the eastern portion of the Los Angeles Basin. Instruments were operated side-by-side for an eight day period, from September 11 to September 19, 1985.

The principal objective of the study was to evaluate routine measurement methods for nitric acid which could be used in the 1987 Southern California Air Quality Study. Continuous methods for nitric acid included Fourier transform infrared spectroscopy (FTIR) , tunable diode laser absorption spectroscopy (TDLAS), and the tungstic acid technique (TAT). Time integrated techniques included filter packs (FP), the denuder difference method (DDM), the annular denuder method (ADM), and the transition flow reactor (TFR).

Some of these nitric acid methods were compared in the earlier 1979 Claremont study, in which attention was directed toward artifacts arising from the facile conversion between particulate and gaseous nitrates. The present study also directs attention to differences between daytime and nighttime measurements, and to short-term *vs* long-term sampling.

Approach

The study consisted of four parts:

(1) Interlaboratory comparison of analysis of Teflon® and nylon quality assurance filters containing known amounts of nitrate and sulfate.

(2) Replicate measurements with instruments of the same design and from the same research group, located at different positions on the sampling platform.

(3) Side-by-side sampling with all instruments in the field over an 8-day period.

(4) Simultaneous measurements of meteorological data and of potential interferents such as peroxyacetyl nitrate and nitrous acid.

The analysis of quality assurance filters (No. 1) allows us to assess variability not attributable to the sampling method, while replicate units (No. 2) allow us to assess variability due to instrument siting. The side-by-side sampling (No. 3) includes variability due to measurement method, instrument siting and chemical analysis.

Results for Nitric Acid

Principal results with regard to the nitric acid measurement methods are, as follow:

(1) There are statistically significant, systematic differences in the nitric acid concentrations obtained by the different measurement techniques and sampler configurations employed in the Nitrogen Species Methods Comparison Study. For each sampling period in the study, reported nitric acid concentrations varied among samplers by as much as a factor of four. The standard deviation among all reported values for nitric acid increased linearly with the nitric acid loadings, corresponding to a consistent coefficient of variation of 40%. This variation is much larger than for analysis of the filters upon which known amounts of nitrate had been deposited (better than 11% accuracy for most groups), or for replicate samplers operated by the same group (12% to 27% variability).

(2) Overall, the highest reported concentrations are from the filter packs, lower concentrations are given by the annular denuders and tunable diode laser absorption spectrometers. Values from the denuder difference method and the transition flow reactors are close to the mean of the methods. When the nitric acid concentrations are high enough to be detected by the FTIR, the FTIR values are nearest those obtained by the denuder difference method; however, values from each method are within the reported uncertainty. The mean FTIR value for the high nitric acid sampling periods is within 3% of the mean of the other methods.

(3) The filter pack method gives higher results for both daytime and nighttime sampling. Differences are also seen among the filter packs operated by different groups. Filter pack sampler #GF3 is higher than the DDM by a factor of 1.25 whereas filter pack #CF1 is higher by 1.4.

(4) In some cases differences exist in the implementation of the measurement method by different groups, as well as differences between types of measurements. The three annular denuders do not give the same results. Nitric acid concentrations from #EA1 are greater than from #QA1, which are greater than from #IA1 (#EA1 > #QA1 > #IA1). For the two TAT systems, nitric acid concentrations from #AC1 are greater than from #TC1. The six denuder difference samplers, including the dichotomous samplers, report values which are not statistically different from each other. Similarly, values from the two transition flow reactors are not statistically different, nor do the values from the two TDLAS systems differ from one another.

(5) In the absence of a reference standard for the entire study, measurement methods are compared to the average of four denuder difference method samplers. For the annular denuders, the ratios to the DDM value for #EA1, #QA1 and #IA1 are 1.0, 0.8 and 0.6 respectively. For the transition flow reactor the ratio of means to the DDM is 1.09. For the two dichotomous samplers operated as denuder difference samplers, the ratio of means to the DDM is 0.93 .

(6) For three of the samplers, there were large differences in the relative performance between daytime and nighttime sampling. The TDLAS instruments gave low daytime and high nighttime readings in comparison to the other measurements. This is most marked on the last three days of the study. Ratios of means to the DDM are 0.77 daytime and 1.65 nightime. The TAT system #TC1 is low during the day and high at night. The opposite diurnal response is seen with filter pack #JF1 which is high during the day and low at night. The FP, ADM, DDM and TFR averages do not exhibit significant diurnal variations with respect to the mean of methods.

Recommendations

Due to the lack of an absolute reference standard for the entire study, we cannot make a definitive statement as to the most accurate nitric acid measurement method. Furthermore, the choice of measurement method depends upon the length of time per sampling period, and the expected ambient nitric acid concentrations. With these qualifications, our recommendations with regard to monitoring methods for nitric acid are, as follow:

(1) In studies where large nitric acid concentrations are to be measured over short (4-hour) time periods, the denuder difference method appears to be the most accurate and reliable monitoring technique. It is not precise when nitric acid concentrations are low, below about 25 neq/m^3 (0.6 ppb), depending on analytical sensitivity and the HNO_3 to fine particle nitrate concentration ratio.

(2) In studies where total inorganic nitrate concentrations are to be monitored, the filter packs are a good choice. They give an upper bound on nitric acid and an accurate measure of the sum of particle nitrate and nitric acid. The filter packs gave the most precise and reproducible results, as judged by replicate samplers operated by the same group.

(3) The transition flow reactor and the dichotomous sampler (operated as a denuder difference sampler) gives results similar to the denuder difference method, and should be considered as a possible monitoring method.

(4) The tungstic acid technique and the annular denuder methods require additional development before they can be employed as a routine monitoring method.