

EXECUTIVE SUMMARY

to

**ABSOLUTE MEASUREMENTS OF NITRIC ACID BY  
KILOMETER PATHLENGTH FT-IR SPECTROSCOPY AND THEIR  
INTERCOMPARISON WITH OTHER MEASUREMENT METHODS**

Final Report

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## EXECUTIVE SUMMARY

A newly assembled kilometer pathlength FT-IR spectrometer was operated by the Statewide Air Pollution Research Center (SAPRC) to provide absolute measurements of gaseous  $\text{HNO}_3$  and  $\text{NH}_3$  during the intercomparison study of nitrogen species methods which was sponsored by the California Air Resources Board (ARB). This field study was held at Claremont, CA in September 11-19, 1985 with participation by investigators from 19 research laboratories based in the United States, Canada and Italy. The longpath FT-IR method was one of only two spectroscopic techniques that were employed for the measurement of gaseous  $\text{HNO}_3$ . The SAPRC additionally operated its longpath differential optical absorption spectrometer (DOAS) system alongside the FT-IR system to provide supplementary data on HONO,  $\text{NO}_2$ , and the  $\text{NO}_3$  radical.

The FT-IR instrumentation used in the present study consisted of a Sirius 100 spectrometer (Mattson Instruments, Inc.) equipped with a liquid  $\text{N}_2$ -cooled HgCdTe detector, fitted with external transfer optics, and interfaced to a 25-meter basepath, gold-coated, multiple-reflection optical system. Sampling was conducted by natural transport of air into the open optical path with spectral records being made of the air parcel at 2.4 meter above ground, the height of the system's optical axis. Routine monitoring consisted of 5 minute scan averaging at  $0.125 \text{ cm}^{-1}$  resolution and a total pathlength of 1150 meters with four to five spectra being recorded per hour. Detection sensitivities for  $\text{HNO}_3$  and  $\text{NH}_3$  were approximately 4 ppb and 1.5 ppb, respectively.

Most of the field study period was characterized by low levels of pollution so that  $\text{HNO}_3$  concentrations were totally below the FT-IR detection sensitivity for two days and only slightly above the detection limit for 2-4 hour durations during three other days. The most significant FT-IR data for comparison purposes for the remaining three days, when longer periods of detectable  $\text{HNO}_3$  levels prevailed, were those recorded during the moderately severe smog episode of September 14 when  $\text{O}_3$  levels peaked at  $>0.2$  ppm and  $\text{HNO}_3$  concentrations were above the FT-IR detection limit most of the daytime hours. A peak value of 26 ppb was recorded at 3:45 p.m. and high hourly average  $\text{HNO}_3$  concentrations of 21 and 19 ppb were measured during the hours 3-4 p.m. and 4-5 p.m., respectively. A

significant portion of the FT-IR data on some of the days was reported as upper limit values due to interferences to the spectra by intermittent (and untraceable) noise.

The higher FT-IR detection sensitivity for  $\text{NH}_3$  afforded a more precise set of data than those obtained for  $\text{HNO}_3$ . Concentrations of 2-4 ppb were common background  $\text{NH}_3$  levels in Claremont during the field study but very high instantaneous concentrations, such as the value of 84 ppb measured at 8:56 a.m. on September 16, occurred when winds from the south-southeast direction transported  $\text{NH}_3$  from the agricultural areas of Chino and Ontario. Such wind conditions clearly occurred during the morning hours of September 16 and 17 and early afternoon of September 12 when maximum hourly average  $\text{NH}_3$  concentrations of 33, 46 and 57 ppb, respectively, were measured.

The longpath DOAS measurements of HONO and  $\text{NO}_2$  for the 8-day duration of the field study are reported here as supplemental data, although support for the operation of this spectrometer system originated from our other ARB field study (Contract No. A4-081-32). Although the  $\text{NO}_3$  radical was one of the species intended for measurement by DOAS, its concentration was above the detection limit of 0.02 ppb only during a one-hour period around 8 p.m. each of the two days, September 13 and 14. The concentrations of  $\text{NO}_2$  were always above the 4 ppb detection sensitivity, the hourly average varying from a minimum of 9 ppb recorded during the early afternoon hours of September 15 to a maximum of 135 ppb measured during the period 9-10 p.m. on September 12. Significant levels of HONO were observed from the late evening (9 or 10 p.m.) to the early morning hours (up to 8 a.m.) with observed concentrations ranging from the 0.6 ppb detection limit to a maximum of 2.6 ppb around midnight of September 15/16.

Hourly average concentrations of  $\text{HNO}_3$ ,  $\text{NH}_3$ ,  $\text{NO}_2$  and HONO are presented here, along with calculated average concentrations for specified sampling periods. However, no extended interpretation of the FT-IR and DOAS data, in the context of the results from other measurement techniques, is made in this final report. Such discussions will be more appropriate at a later date when the totality of data is made available by the project coordinators to all the individual participants of the intercomparison study.