



Project Summary

Atmospheric Measurements of Trace Pollutants: Long Path Fourier Transform Infrared Spectroscopy

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A four-year study to measure atmospheric concentrations of trace pollutants by kilometer pathlength Fourier transform infrared (FT-IR) absorption spectroscopy was conducted at two sites in the California South Coast Air Basin (CSCAB) from 1976 to 1979. During 1976 and 1977 the FT-IR facility was operated in Riverside, California, and provided valuable benchmark data. These included the first reported direct spectroscopic detection of trace levels of nitric acid and formaldehyde in the polluted troposphere, and confirmation of the suspected prevalence of high (NH_3) concentrations (>100 ppb in some instances) in the Riverside area which originate primarily from upwind agricultural sources.

During the last two years of the study (1978 and 1979), the FT-IR facility was operated in Claremont, California, a mid-basin site chosen to characterize episodes closer to the Pasadena-Azusa area which presently experiences the highest smog levels in the CSCAB. The 1978 study focused on extended monitoring periods and succeeded in recording a "classic" stagnant air episode with pollutant carryover and progressively increasing oxidant levels during the week of October 9-13, 1978. The FT-IR measurements included a 38-hour contin-

uous monitoring period for the more severe episodes of October 12 and 13, 1978. The most intense episode of that week (October 13) was characterized by peak pollutant levels of 454 ppb O_3 , 37 ppb PAN, 49 ppb HNO_3 , 19 ppb HCOOH , and 71 ppb HCHO .

Research in 1979 consisted of collaborative studies to validate newly developed analytical and sampling techniques for measuring HNO_3 , NH_3 , and HCHO . In these studies the km pathlength FT-IR spectroscopic technique served as the reference method. Among the studies conducted was a major EPA-sponsored field program to compare current analytical methods for gaseous HNO_3 and particulate nitrate.

Ambient air data which we have obtained for trace pollutant concentrations over a four-year period, together with the results of the collaborative studies to validate new methods of analysis of "non-criteria" pollutants, will provide a critically needed data base for stringently testing the chemical kinetic submodels of the current generation of widely used urban airshed models.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key

findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

During the past decade, the major efforts of federal, state and local agencies in the acquisition of an air monitoring data base have largely focused on the regulated or "criteria" pollutants, i.e., ozone (O_3), nitrogen dioxide (NO_2), total hydrocarbons, sulfur dioxide (SO_2) and total suspended particulates (TSP). At the same time, laboratory and smog chamber studies, as well as more comprehensive computer kinetic models of photochemical air pollution have increasingly stressed the importance of a number of trace atmospheric species and their roles in photochemical air pollution. These important species include formaldehyde (HCHO), formic acid (HCOOH), nitric acid (HNO_3), nitrous acid (HONO), and hydrogen peroxide (H_2O_2), as well as ammonia (NH_3). Until

recently, comparatively little progress had been made in characterizing the concentration ranges and the temporal and geographical distributions of these significant, but presently unregulated, air pollutants. This lack of data concerning the ambient concentrations of the so-called "non-criteria" pollutants was striking in view of their potential importance to atmospheric chemists and modelers, to control officials, and to others who are concerned with impacts on agriculture and human health.

In response to this need, in 1976 we initiated measurements of such species under an Environmental Protection Agency (EPA) sponsored program employing a kilometer pathlength FT-IR spectrometer originally designed and assembled by Dr. P.L. Hanst of the EPA-Research Triangle Park (RTP) Laboratories. This system provided an *in-situ* part per billion (ppb) detection capability for many oxygenated and nitrogenous pollutants for which reliable, alternative analytical methods were unavailable.

Instrumentation and Methods

The eight-mirror multiple reflection optics employed in this study consisted of four rectangular, in-focus (nesting) mirrors, separated by 22.5 m from four out-of-focus (collecting) mirrors. All mirrors were optically polished and gold-coated for maximum reflectivity in the infrared.

The cell consisted of a sectional rectangular aluminum frame (total dimensions: 0.81 x 0.84 x 23 m) with a lining of 50-micron thick FEP Teflon film. Figure 1 depicts the multiple-reflection cell coupled to the Fourier transform spectrometer system, which was housed in a 3.7 x 3.7 m air-conditioned building. Interfaced with the long path optics was a Digilab Model 296 Michelson IR interferometer (resolution $\geq 0.5 \text{ cm}^{-1}$) and an associated data system. A magnified image of the source element was focused at the entrance aperture of the cell and the beam exiting from the cell was sent to either of two

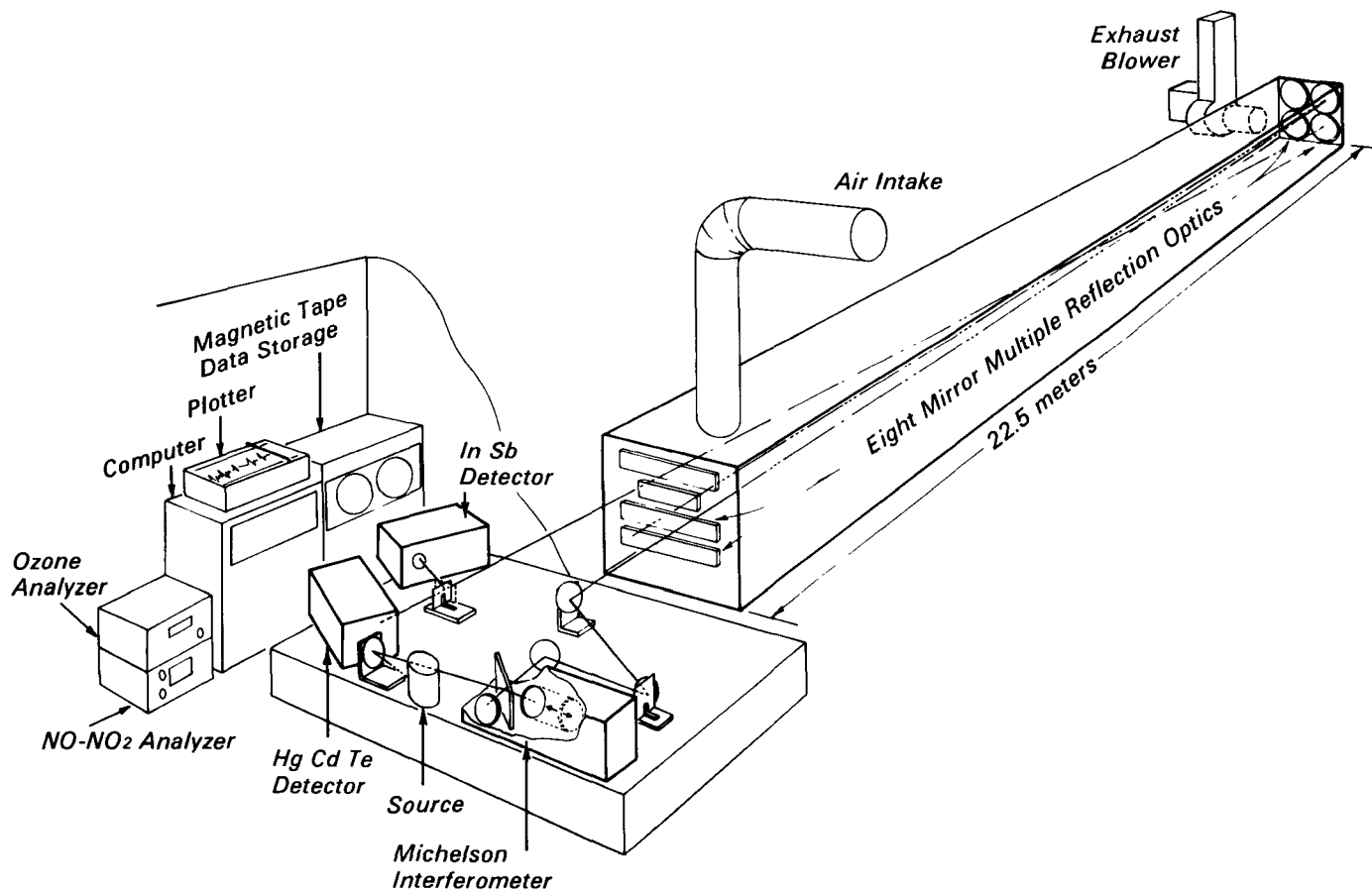


Figure 1. Kilometer pathlength Fourier transform infrared spectrometer.

liquid-N₂ cooled detectors: a photovoltaic InSb detector for the 2000 to 4000 cm⁻¹ range or a photoconductive HgCdTe detector for the 600 to 2000 cm⁻¹ region.

The sampling procedure consisted of drawing air into the cell at a rate of 330 liters sec⁻¹ for a minimum of four minutes before the start of an interferometer scan. This corresponded to a displacement of the previous air sample by a minimum of five volumes of fresh sample. Total pathlengths of 900 and 1080 meters and a resolution of 0.5 cm⁻¹ (16384 digitized points per interferogram) were routinely employed. Thirty or 40 interferograms were usually co-added to enhance the signal-to-noise ratio in the interferogram, and thus in the computer spectrum.

Results

Data from monitoring activities during 1976 and 1977 at Riverside, a site approximately 60 miles east and 8-12 hours downwind of the primary emission sources in the CSCAB, have been presented in literature and are only briefly discussed in the report. Results included the first direct spectroscopic detection of nitric acid and formaldehyde in the atmosphere, and confirmation of the previously suspected prevalence of relatively high levels of NH₃ in Riverside. Detailed data from 5-8 hour monitoring periods for a total of 3 episode days in October 1976 and 10 episode days in July-October 1977 are reported, along with supplemental air quality data for NO, NO₂, CO and nonmethane hydrocarbons.

In the summer of 1978, the FT-IR facility was moved from the UC-Riverside campus to Claremont, California, and was installed on the roof of the Jacobs Science Center of Harvey Mudd College. Although moderate pollution episodes were recorded for various days during the summer months, this report focuses on the week of October 9-13, 1978 during which extended periods of air monitoring were carried out, including data collection for a continuous 38-hour period for the more severe smog episodes on October 12 and 13. This week-long stagnant air episode was characterized by a monotonic rise in the daily peak O₃ readings from 0.16 ppm on Monday, October 9, to 0.45 ppm on Friday, October 13 and the measured concentrations of O₃, PAN, HNO₃, HCOOH and HCHO are reported as a function of time for each day of this

episode. The maximum concentrations observed each day are shown in Table 1.

Morning HCHO concentrations in Claremont were observed to be in the range of 20-40 ppb. A slight decrease in these concentrations occurred around the noon hours and prior to the peak O₃ readings. Well-defined HCHO peaks corresponding to O₃ maxima were observed during the more severe episodes of Thursday and Friday, October 12 and 13, with HCHO reaching a peak concentration of 71 ppb at about 1600 hr on the 13th. The observations in Claremont suggest that the high levels of HCHO reported in earlier studies in the 1950's and 1960's may indeed be approached under conditions of intense photochemical air pollution. Formaldehyde was also found to persist (at concentrations of ~20 ppb) during the night, an important observation in modeling the role of formaldehyde as an early morning catalyst for smog formation.

Formic acid levels were generally low, typically less than 10 ppb even during moderate episodes. This agrees with the majority of our measurements in 1977 at Riverside. The highest concentration of HCOOH observed at Claremont was 19 ppb.

Although we had accumulated substantial nitric acid data during the 1977 study in Riverside, these profiles consisted only of upper limits during many periods (i.e., concentrations were below the detection limit) and thus a detailed characterization of HNO₃ concentrations as a function of photochemical activity was not possible. In the Claremont study the rise in HNO₃ concentration was strongly coincident with the increase in oxidant levels (e.g., O₃ and PAN). The highest HNO₃ concentration measured was 49 ppb which coincided with the O₃ concentration of 454 ppb recorded on October 13.

The average NH₃ concentration measured in Claremont during the week of October 9-13 was ~8 ppb. An examination of our data obtained during the

months of July and August, 1978, also indicated that the NH₃ level in Claremont is generally less than 10 ppb. Thus, the NH₃ concentrations measured by FT-IR spectroscopy in Claremont were approximately five times lower than those found in Riverside during our 1976 and 1977 studies.

The recognition of artifactual errors in the widely accepted method for measuring nitrates in the atmosphere by sample collection on fiberglass filters provided impetus for researchers to develop new, more sensitive and selective techniques for the measurement of both gaseous and particulate nitrates. In 1978 the EPA developed a plan to conduct a field experiment that would bring together appropriate research groups to compare these measurement methods for nitrate and HNO₃. It was recognized at that time that the kilometer pathlength FT-IR spectroscopy could serve as a standard for nitric acid determination since this method involves an *in-situ*, nondestructive technique, and identification is made unambiguously by recognition of characteristic spectral features.

During the period August 27-September 3, 1979, a field study was conducted at the site of our long-path FT-IR facility in Claremont, California. While detailed results of the FT-IR monitoring are provided in this report, a full interpretation of the nitric acid intercomparison data, along with its implications for the data simultaneously gathered for particulate nitrate is the subject of a separate EPA-Battelle report.

Attempts made to detect other atmospheric species resulted in the following upper limits to their ambient concentrations for the periods and locations involved in this study: nitrous acid (HONO), 10 ppb; hydrogen peroxide (H₂O₂), 40 ppb; peroxyxynitric acid (HO₂NO₂), 8 ppb; peroxyalkyl nitrates (RO₂NO₂), 6 ppb; hydrochloric acid (HCL), 8 ppb; acrolein (CH₂=CHCHO), 15 ppb; ketene (CH₂=C=O), 6 ppb.

Table 1. Daily Maximum Concentrations (ppb) Observed in Claremont, CA by Kilometer Pathlength FT-IR Spectroscopy

Date	O ₃	PAN	NH ₃	HNO ₃	HCOOH	HCHO
October 9	163	6	11	18	5	23
10	227	14	23	28	5	30
11	280	13	13	30	7	31
12	360	22	13	29	17	52
13	454	37	25	49	19	71

Conclusions

This program has demonstrated the utility of long pathlength FT-IR spectroscopy for quantitatively measuring parts-per-billion levels of a number of nitrogenous and oxygenated compounds in ambient air.

Our results verified that HNO_3 , and not PAN, is the major nitrogen-containing product of photochemical smog and showed that HNO_3 levels correlate negatively with prevailing NH_3 concentrations. The data obtained in Riverside included numerous measurements of simultaneous NH_3 and HNO_3 concentrations; and these results support the hypothesis that particulate NH_4NO_3 is in equilibrium with its gas-phase precursors NH_3 and HNO_3 . In areas such as Claremont where average NH_3 levels are low (<10 ppb), the HNO_3 concentration during the peak of a smog episode may be expected to amount to approximately 10% of the O_3 concentration or more.

Our data established that ambient concentrations of HCOOH are low and will rarely be above 20 ppb even during severe smog episodes. This is approximately 4-10 times lower than earlier values reported from wet chemical and long pathlength FT-IR measurements. On the other hand, our results are consistent with early measurements by wet chemical techniques showing that high concentrations (~100 ppb) of HCHO may prevail during an intense siege of photochemical air pollution associated with high vehicular activity.

The value of long pathlength FT-IR spectroscopy as an analytical tool for air pollution studies should not be limited to the characterization of species found

in photochemical smog. Given the increasing awareness of the potential hazards posed by atmospheric releases of toxic materials and their degradation products, the kilometer pathlength FT-IR technique should continue to serve as a highly developed method for atmospheric monitoring.

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B. W. Gay, Jr., is the EPA Project Officer (see below).

The complete report, entitled "Atmospheric Measurements of Trace Pollutants: Long Path Fourier Transform Infrared Spectroscopy," (Order No. PB 81-179 848; Cost: \$11.00, subject to change) will be available only from:

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