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Laboratory
Research Triangle Park NC 27711

Research and Development

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Project Summary

Long Path Laser Ozone Monitor Evaluation

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The purpose of the study reported here was to evaluate a long pather laser air pollution monitor developed for the U.S. Environmental Protection Agency (EPA) by the General Electric (GE) Company. The monitor was known as ILAMS (Infrared Laser Atmospheric Monitoring System) and designed explicitly for measuring the ambient ozone concentration.

The evaluation program was conducted in both the laboratory and under field conditions. In addition to the evaluation several system modifications were carried out; such as, the addition of a beam steering system, the addition of a He-Ne laser alignment system, and various improvements in laser alignment techniques.

The field study portion of the evaluation was carried out as a part of the North-East Regional Oxidant Study (NEROS) and was conducted during the month of August 1979. The problem areas identified during the field test were the corner cube reflectors and the irregularity in the laser beam cross-section. The retro-reflectors returned six separate lobes all of which were displaced from the optical center line to form a wave front approximating a toroid. The irregularity in the beam cross-section was previously identified by G.E. However, it was assumed that the irregularities were a function of frequency and closely spaced frequencies would correlate. This assumption does not appear to be valid.

The experiments conducted, the modifications made, and the problems identified are completely described in the report.

This report was submitted in fulfillment of Grant R80665001 by the University of Michigan under sponsorship of the U.S. Environmental Protection Agency. This report covers a period from Dec. 1, 1978 to Sept. 30, 1980 and work was completed as of May 1, 1981.

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

The grant effort at the University of Michigan initially consisted of a program to evaluate and redesign the ILAMS to eliminate problems encountered in the acceptance tests of Oct. 1978. The grant was later expanded to include the use of the ILAMS to obtain vertical ozone profiles as part of an EPA summer field study, the North East Regional Oxidant Study, designed to examine the fate and transport of various air pollutants.

The NEROS application required a long path system capable of measuring over a kilometer distance with a retro-reflector to return radiation to the source location, the type of measurement situation envisioned for the ILAMS. The decision to commit the ILAMS in the NEROS was made after the zero drift problem was identified and eliminated. Additional field performance tests were planned prior to NEROS use and supplemental funds for the field study were provided. The preparations for the NEROS, the NEROS testing and the eventual transfer of equipment to the EPA at Research Triangle Park, N.C. concluded the grant activities.

Results

The ILAMS consists of four main units: a CO_2 laser, a mini-computer, a teletype, and interface electronics.

The laser will be described by referring to Figure 1. The lasing cavity follows a zigzag path starting from M_1 to M_2 to M_3 to M_4 to the diffraction grating to M_4 to M_5 to M_6. The lasing lines are selected by a mask which has four separate apertures placed in front of the chopper. The chopper blade has four fixed slots at different radii such that the apertures are opened in succession as the chopper rotates. Hence, each line lases for a time period equal to ⅛ of the chopper rotation period about 2.5 milli-seconds.

The laser output beam follows a path from M_7 to M_8 and through L_1 and L_2 to the beam splitter. Part of the output energy passes through the beam splitter to M_9 where it is focused on the reference detector. The remainder of the output beam is reflected off the beam splitter to M_{11}, M_{12} and the telescope output mirror M_{13}. The beam traverses the measurement path and is returned by a retro-reflector to the telescope and back through the beam splitter to the signal detector.

The chopper position signal and the signals developed by the two detectors are fed to the interface electronics for input to the mini-computer. The first computer operation is to form a ratio between the return signal and the reference signal. An automatic gain control then adjusts the signal such that the largest of the four ratios is equal to ½. The logarithms of the four ratios are calculated and multiplied by -1000. This information is printed on the teletype with each data printout. The computer program also multiplies each logarithm by a pre-selected weighting factor and calculates the appropriate differences which are also printed by the terminal. The difference of the weighted logarithms of the ratios should be proportional to the ozone concentration.

The computer software permits the operator to set a number of parameters such as: the weighting functions, data printout rate, number of data points to be averaged, system time constant, and scaling constants. The basic requirement is that the system measures the difference in absorption between two lines with known absorption coefficients over a known optical path. The difference in absorption is a measure of the ozone concentration.

Pronounced zero drifting of the ILAMS was reduced an order of magnitude by removing the zinc selenide windows on the reference and signal detectors. The system was tested in a short pathlength configuration for a period of 8 hours with a maximum equivalent noise variation of 5 ppb.

The optical effect which was the source of the system zero drift or noise is very well known. In fact, it is common in infrared systems for two reasons: one, the index of refraction of the optical materials is usually quite high which leads to high reflections and two, the window polishing techniques are similar to those used for ultra-violet components, which give surface flatness of high precision ($\lambda/10$).

Normally, etalons must be very carefully made in order to achieve the required precision. However, if a window normally intended for use in the visible is used in the infrared, the required precision may inadvertently be obtained. The window as an etalon is shown in Figure 2.

This sketch assumes that the window is perfectly flat which, of course, is not the case. However, it illustrates that a very small variation in the angle of incidence could produce a large modulation of the output signal. An equivalent noise level of 5 ppb (1 km path) represents an absorption difference for the two lines at 1056 cm^{-1} and 1054 cm^{-1} of 0.6%. This modulation could be simulated by a phase shift of 0.5° between the two wavelengths being compared. In the idealized case shown in the sketch of 0.5° phase shift translates to a change in the angle of incidence of something less than 0.001 degrees.

The problem can be completely avoided in any future designs by simply wedging the windows.

At about the same time that the zero drift problem of the ILAMS was solved plans were being formulated for the summer 1979 North East Regional Oxidant Study (NEROS). The overall purpose of NEROS was to develop models which could be used for predicting the long range transport of air pollutants. During the early planning stages, it was suggested that a long path laser designed to measure ozone might be used to determine both the height, formation time, and break-up time of the nocturnal inversion. This assumed that a 1000 foot tower could be located for mounting the required retro-reflectors. If the inversion information were available, one of the current theories regarding the transport of air pollutants could be tested.

The essence of the theory is that those pollutants generated in a metropolitan area during the daylight hours can be trapped under a subsidence inversion. However, shortly after dark, they are cut off from the ground by the formation of a nocturnal inversion. Then, during the night, the polluted air mass, caught between the two inversions, is transported many miles down wind by the geostrophic wind until the nocturnal inversion is broken up the next morning by surface heating. This could explain the observation of high pollutant levels in some remote rural areas.

To monitor the vertical ozone distribution a beam steering mechanism was required so that slant paths through the atmospheric from the ILAMS (located in a van) to retro-reflectors positioned at different locations on the tower could be defined. A system was designed and fabricated using a commerical package including a gear drive package and associated microprocessor purchased from Aerotech. This system was installed in the GM van that housed the ILAMS. It met the following design requirements: (1) azimuth adjustment: 360° ± 0.0015°; (2) elevation adjustment : 2 to 23° above horizon ± 0.0015°; (3) beam control of elevation by microprocessor, of azimuth by manual control; (4)

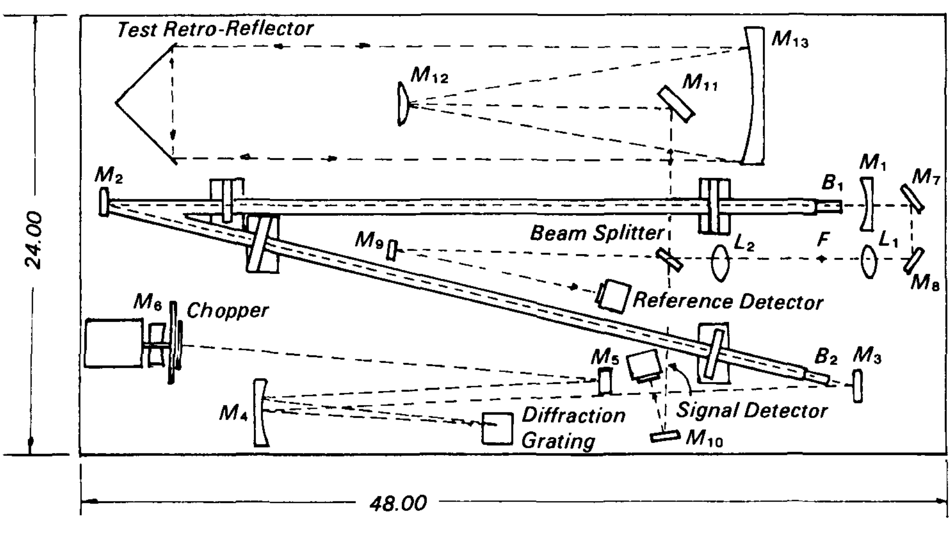

Figure 1. *ILAMS Optics—laboratory test.*

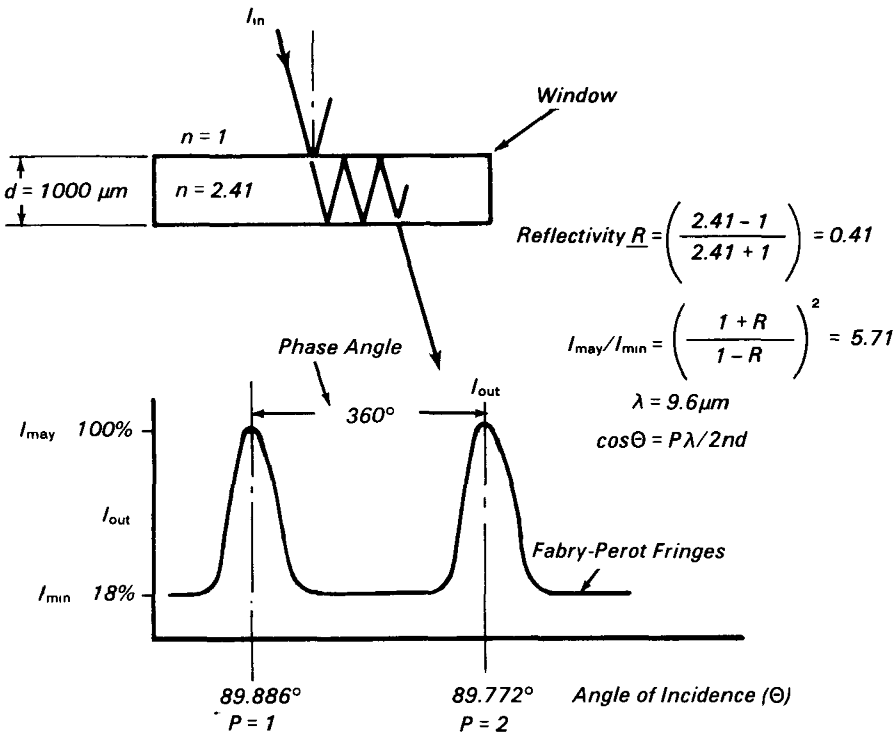

Figure 2. *Fabry-Perot Window Effect*

beam slew rate: 30 seconds or less between positions.

ILAMS calibration using the pairs of $C^{12}O^{16}{}_2$ laser lines P_{12}-P_{24}, P_{12}-P_{10}, and P_{26}-P_{24} in this 9 micron band was performed by using a multipass optical cell in which known ozone concentrations could be established. The minimum resolvable ozone concentration change using the P_{12}-P_{24} lines and a 179.9 meter folded path was 2.8 ppb. A set of typical values including extrapolated values for an optical path length of 850 meters is shown in Table 1.

Table 1. *Minimum Resolvable Ozone Concentration Line Pair vs. Range*

Line Pair	*179.9 meters*	*850 meters*
P_{12}-P_{24}	2.8 ppb	0.59 ppb
P_{12}-P_{10}	4.4 ppb	0.93 ppb
P_{26}-P_{24}	6.3 ppb	1.34 ppb

In preparation for field tests in the NEROS, the ILAMS was set up with an ambient air path. Experiments were performed to measure the variation in apparent ozone concentration (due to energy partitioning) with movement of the laser intensity pattern on the retro-reflectors. These variations were significant but reproducible so that off-set errors could be measured when no ozone was present, and the corrections applied in the field measurements. The designed positioning accuracy of 0.25 arc minutes essentially eliminated positioning errors.

The ILAMS was transported to Hallam, Pennsylvania, arriving on location July 30, 1979. The system was arranged as shown in Figure 3 using the WGAL-TV tower for positioning the retro-reflectors. With the system in place, experiments were begun to perform the long path monitoring. The main objective of providing useful information on the vertical distribution of ozone was not achieved due to several system problems: (1) breakage of the laser tube during transport; (2) inadequacy of the optical system to collect the return laser signal; (3) substitution of a low capacity vacuum pump for use with the laser. Evaluation of the optical system was carried out at the field site using a He-Ne laser. The return signal consisted of a six-sided lobe pattern the spreading of which depended on the particular retro-reflector being used. The result of this fact was that the return optics only collected a fraction of the return energy. This problem could be solved by using retro-reflectors with more accurate joining of the constituent intersecting plane sides or by using larger collection optics. The remaining two problems require minor corrective efforts.

The ILAMS was transferred to the U.S. E.P.A. for further evaluation.

Conclusions

The conclusions for the grant can be grouped into four categories: (1) redesign of the ILAMS; (2) controlled testing results; (3) NEROS results; (4) final system status.

Redesign

A crucial factor in the ILAMS operation is the maintenance of a stable relationship (ratio) of power returned from the remotely placed reflector, I_s, to the output from the CO_2 laser, I_r, under short pathlength conditions (no ozone or atmospheric burden). Using a short pathlength configuration, the drift in I_s/I_r for the wavelengths was reduced by an order of magnitude by

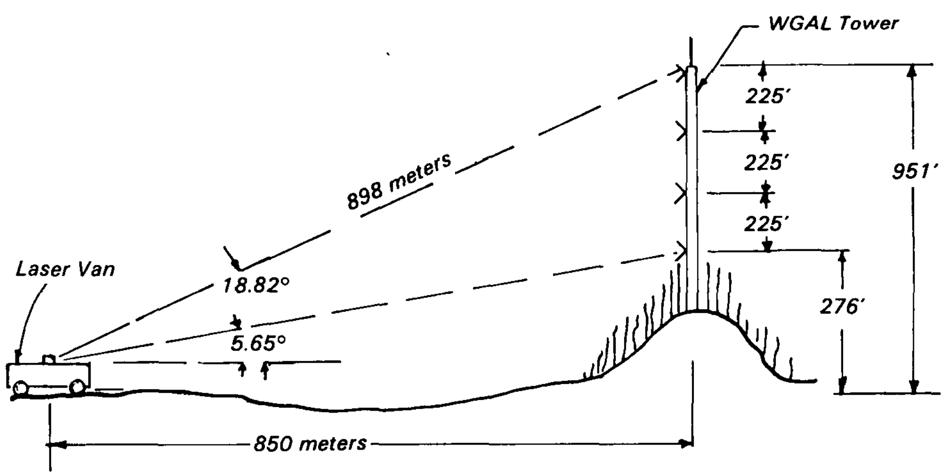

Figure 3. *Measured Optical Path Locations on WGAL Tower*

removing the windows covering the pyroelectric detectors and thereby eliminating temperature dependent Fabry-Perot interference effects.

Controlled Testing

The ILAMS was successfully modified to locate distant targets in a vertical plane by installing an Aerotech ARS 304 Elevation Drive. Additional modifications were incorporated which permitted a He-Ne laser to be used for all optical alignments, i.e., for aligning optical components in the system and for sighting in on the remotely placed retro-reflectors. Prior to testing in the NEROS the ILAMS was tested along a 210 m path at the University of Michigan. The path was defined by the CO_2 laser source mounted in a sheltered area and a retro-reflector placed on a tripod on the ground outside. Test conclusions were: the automatic steering would be capable of positioning the beam on targets located at 850m, the NEROS field distance, and the expected noise equivalent signal at the same distance would be 26.5 ppb of ozone with a 34 second integration time.

NEROS Results

In the process of placement of the ILAMS in the EPA van, the ILAMS CO_2 laser tube was cracked. This effectively prevented participation in the NEROS since the system could not be returned to operational status by efforts made in the field. However, some tests were made to examine the quality of signal return from retroreflectors placed, as originally intended, on a television antenna at various heights. A He-Ne alignment laser was used to give a visual display of the pattern of energy returned to the ILAMS. These patterns showed a significant variation among reflectors in the six lobe pattern of the return beam. Each of the six return lobes was displaced from the geometric centerline so that the return pattern in the best case had a torus shape and low energy near the center of the beam. In the worst case virtually no signal would have been returned inside the collecting aperture.

Final System Status

Due to the limited funds remaining after the NEROS, the ILAMS was returned to EPA for transfer to EPA's inhouse contractor Northrop Services, Inc. (NSI). The system was placed in operational status and a demonstration test was performed over a 350 m optical path. The beam steering performed satisfactorily, but the laser output power was low. The responsibility for correcting this problem was assumed by NSI.

Recommendations

There are two areas of effort which deserve additional attention in dealing with the ILAMS. One is the testing of the system in its present configuration with the possible replacement of the CO_2 laser tube which appears to be slightly bowed and is likely responsible for the present low power output from the system. The testing should be a dedicated attempt to run the system over a period of time with no pressure to perform in a field test. This is the only way to objectively judge the feasibility of the laser-based long path approach to atmospheric monitoring. The second area of effort is the updating of the system with state-of-the-art components which would improve the system performance, e.g., a waveguide laser of much smaller size and alternative signal processing procedures to correspond to simpler wavelength modulation techniques. This second area of effort should only be pursued if the advantages of a long path monitor are actually needed to pursue EPA's current objectives.

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The complete report, entitled "Long Path Laser Ozone Monitor Evaluation," (Order No. PB 83-196 006; Cost: $10.00, subject to change) will be available only from:
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Project Summary

Measurements of Formaldehyde and Hydrogen Peroxide in the California South Coast Air Basin

Greg Kok

The chemiluminescent reaction between formaldehyde (HCHO) and gallic acid has been adapted for the determination of HCHO in ambient systems. The system has a detection limit of 1 ppbv for gas-phase HCHO, based on a one-hour integrated sample. An unknown negative interference is present when ambient air is sampled under conditions of severe photochemical smog.

Measurements of HCHO and hydrogen peroxide (H_2O_2) have been made in rainwater collected in Claremont, California, during the winter storm seasons 1979-1981. HCHO levels show a regular pattern, with the initial rainfall containing 500-800 ppbm. These levels decrease rapidly as the storm progresses. H_2O_2 levels show wide variations during the course of a storm, ranging from a few ppbm to over 800 ppbm.

Measurements of gas-phase HCHO have been made at several locations in the California South Coast Air Basin. Under low to moderate levels of photochemical smog, primary sources appear to dominate HCHO levels and concentrations of 5-10 ppbv have been measured. Under conditions of more intense photochemical smog, HCHO levels of up to 40 ppbv have been measured. Strong diurnal patterns are noted when high levels of HCHO are present.

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

The objective of this program was to develop the chemiluminescent reaction between gallic acid and formaldehyde (HCHO) into an analytical technique for HCHO in ambient systems. In addition, rainwater and gas-phase measurements of HCHO and other species were made in the California South Coast Air Basin.

Measurements of HCHO in ambient systems are important to an understanding of atmospheric chemistry for the following reasons:

- HCHO can be easily photolyzed to form free radicals. If substantial quantities of HCHO are present in the early morning, photolysis of it will accelerate photochemical smog formation.
- HCHO is a strong eye irritant. Accurate measurements of HCHO can help to define sources of eye irritation.
- Sinks for HCHO are poorly defined. Measurements of HCHO in rainwater can help to provide information on this removal pathway.

Analytical Instrument Development

The chemiluminescent reaction between HCHO and gallic acid (3,4,5, trihydroxy-benzoic acid) has been developed into a technique for quantitating HCHO in aqueous solution. The technique is applied in order to determine HCHO in ambient air and rainwater.

For the determination of HCHO in the gas phase, HCHO is collected and concentrated in aqueous solution using a Saltzman bubbler. The aqueous solution is then analyzed directly for HCHO using the chemiluminescent technique. The detection limit is better than one part per billion by volume (1 ppbv), based on a one-hour integrated sample. An automated system for gas-phase HCHO has been developed that collects and analyzes samples on an hourly basis without operator intervention.

The chemiluminescent analytical technique has been tested with a wide variety of potentially interfering substances commonly found in ambient samples. No interferences were observed. Testing of this technique in parallel with other HCHO analytical techniques under low to moderate smog conditions in the California South Coast Air Basin indicated reasonable agreement between the chemiluminescent technique and other methods. Under severe smog conditions, as evidenced by ozone levels greater than 350 ppbv, parallel testing indicated that the chemiluminescent technique was influenced by a negative interference that reduced the signal output by approximately 50%. The identity of the interference is unknown.

Rainwater Measurements of Formaldehyde and Hydrogen Peroxide

Measurements of HCHO and hydrogen peroxide (H_2O_2) were made in Claremont, California during seven precipitation events in the winter months of 1980 and 1981. The precipitation was collected in fractions of typically 0.8 - 1.1 mm. The rate of rainfall was also recorded to observe changes in chemical concentration as a function of rainfall rate.

Levels of HCHO in the rainwater sampled generally show a regular trend, with the initial precipitation containing an HCHO level of 500-800 parts per billion by mass (ppbm). The level drops off rapidly as the precipitation continues; typically, after 6-8 mm of rainfall the HCHO reaches a relatively constant level of 50-100 ppbm. It does not appear that the concentration of HCHO in precipitation is influenced by the rainfall rate.

In contrast to HCHO levels, H_2O_2 levels varied considerably during the course of precipitation, with no discernable patterns. Measurements of H_2O_2 in rainwater gave concentrations ranging from a few ppbm to over 800 ppbm. During some precipitation events it appeared that an increase in the concentration of H_2O_2 was accompanied by increase in precipitation intensity. No explanation is readily apparent for the widely varying concentrations of H_2O_2 in rainwater.

Gas-Phase Measurements of HCHO and H_2O_2

Gas-phase measurements of HCHO and H_2O_2 have been made at several locations in the California South Coast Air Basin during the summer months of 1979 and 1980. Since gas-phase HCHO can be present from both primary and secondary sources, efforts were made to determine the contribution of each source to HCHO levels in the Basin. Measurements of HCHO made under conditions of low photochemical smog or at sites in the western part of the California South Coast Air Basin generally gave HCHO levels of 5-10 ppbv. These concentrations are presumably indicative of HCHO levels from primary sources. Measurements of HCHO made at Claremont, in the eastern part of the California South Coast Air Basin, yielded a range of HCHO levels from 5 ppbv for light smog conditions up to 40 ppbv for intense smog conditions (ozone >350 ppbv). An examination of the O_3 and HCHO data taken at Claremont over a three-year period 1978-80 indicates that a good correlation can be obtained between maximum ozone levels on a given day and maximum HCHO levels.

The validity of the gas-phase H_2O_2 data collected in parts of this study is in question due to a variable ozone reaction that can produce either a positive or negative interference in the analysis. Hydrogen peroxide measurements made in the absence of ozone, generally at night, show slowly varying levels of H_2O_2 between 2 and 5 ppbv. Since the only known source of gas-phase H_2O_2 is via photochemical reaction, it was not expected that night time levels of H_2O_2 would be that high. Measurements of gas-phase H_2O_2 made in the presence of photochemical smog are widely varying, ranging from 2 to 12 ppbv, with no apparent correlation with smog intensity.

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The complete report, entitled "Measurements of Formaldehyde and Hydrogen Peroxide in the California South Coast Air Basin," (Order No. PB 83-196 725; Cost: $14.50, subject to change) will be available only from:

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