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## Claremont Atmospheric Free-Radical Study:

Measurements of Formaldehyde, Hydrogen Peroxide, Nitric Acid, Nitrous Acid, Peroxyacetyl Nitrate, Nitrogen Dioxide, Nitrogen Oxides, Ozone, Carbon Monoxide, Hydrocarbons (C<sub>1</sub>-C<sub>12</sub>), and Carbonyl Compounds (C<sub>1</sub>-Benzaldehyde)

**CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY**



**AIR RESOURCES BOARD  
Research Division**



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Final Report to the  
**STATE OF CALIFORNIA  
AIR RESOURCES BOARD**

in

completion of research under  
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92-327

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## ACKNOWLEDGMENTS

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We acknowledge Mr. John Pisano of Unisearch for the late hours he put in struggling with a balky canister filling system while attempting to obtain quality grab samples of VOC's. We also thank Dr. Kochi Fung and his colleagues at ATMAA for providing the VOC canisters and carbonyl cartridges and performing the analysis. The rapid turn-around of the canisters and their assistance in trouble-shooting the "sometimes" automated canister filling system was particularly appreciated.



## EXECUTIVE SUMMARY

During September 1994 the Los Angeles Atmospheric Free Radical Study (LAAFRS) was carried out in the greater Los Angeles area under the auspices of the State of California Air Resources Board. The overall goal of the study was to provide experimental data on HO and HO<sub>2</sub> radicals in urban air, along with other relevant atmospheric species, for use in testing photochemical models. Although the original intent was to make measurements at 3 sites, designated for upwind, downwind and source measurements, logistics only permitted measurements at the downwind site that was located in a gravel pit adjacent to the campus of Claremont College.

Unisearch under funding from ARB employed a variety of high quality instrumentation to provide real-time measurements of H<sub>2</sub>O<sub>2</sub>, HCHO, HNO<sub>3</sub>, HONO, NO<sub>2</sub>, NO<sub>x</sub>, PAN, and O<sub>3</sub>. Dr. Kochy Fung of ATMAA Inc, Chatsworth, CA provided the canisters and cartridges for measurements of Hydrocarbons (C1-C12 including CH<sub>4</sub>) and Carbonyls (C1-Benzaldehyde including CO) and performed the analysis. These data were used as support information for measurements designed to determine the atmospheric concentrations of HO and HO<sub>2</sub> radicals using a third generation low-pressure laser-excited fluorescence (LEF) instrument with chemical modulation to remove ambient HO for background measurements. Additional supporting information provided by other researchers included O<sub>3</sub> profiles from Lidar measurements, organic particle speciation and integrated ground station, balloon borne and satellite Meteorological information.

This report details the measurements made by Unisearch and summarizes the canister VOC and cartridge Carbonyl measurements made by ATMAA.

An extensive data set of many of the species implicated in the production of photochemical smog and acid deposition has been acquired over a 25 day period during September 1993. Continuous data was obtained on NO<sub>2</sub>, NO<sub>x</sub>, peroxyacetyl nitrate, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, HCHO, and HONO over most of the sampling period and periodic measurements were made on NO<sub>3</sub> and HNO<sub>3</sub>. Integrated sampling techniques were employed to obtain 4 hour average measurement of carbonyls (C1-Benzaldehyde including CO) and hydrocarbons (C1-C12 including CH<sub>4</sub>). Most species were above the detection limits of the instrumentation for most of the study period.

Two episodes of high pollution were observed during the study, September 7-12 and September 22-25 when most of the species showed a marked increase in concentration over the values obtained at other times. During the first episode O<sub>3</sub> levels exceeded 200 ppbv, PAN levels reached 4 ppbv and HCHO reached 30 ppbv. H<sub>2</sub>O<sub>2</sub> and HONO also maximized during this period. A period of wet weather separated the two episodes during which the concentrations of all species were greatly reduced.

Chemiluminescence and UV-photometric measurements of O<sub>3</sub> agreed within the precision of the instrumentation. Long path differential optical absorption measurements of NO<sub>2</sub> tended to be lower than point chemiluminescence measurements. The extent to which the topography of the site influenced this difference is at present uncertain but the proximity of the point monitor to a major highway and the presence of a large depression (quarry) along the DOAS path undoubtedly had some influence.



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## 1. INTRODUCTION

During September 1994 the Los Angeles Atmospheric Free Radical Study (LAAFRS) was carried out in the greater Los Angeles area under the auspices of the State of California Air Resources Board. The overall goal of the study was to provide experimental data on HO and HO<sub>2</sub> radicals in urban air, along with other relevant atmospheric species, for use in testing photochemical models. Although the original intent was to make measurements at 3 sites, designated for upwind, downwind and source measurements, logistics only permitted measurements at the downwind site that was located in a gravel pit adjacent to the campus of Claremont College.

Dr. Robert O'Brien's group at Portland State University, under funding from the Environmental Protection Agency made measurements designed to determine the atmospheric concentrations of HO and HO<sub>2</sub> radicals using a third generation low-pressure laser-excited fluorescence (LEF) instrument with chemical modulation to remove ambient HO for background measurements. This approach is named FAGE of Fluorescence Assay with Gas Expansion

Unisearch under funding from ARB employed a variety of high quality instrumentation to provide real-time measurements of H<sub>2</sub>O<sub>2</sub>, HCHO, HNO<sub>3</sub>, HONO, NO<sub>2</sub>, NO<sub>x</sub>, PAN, and O<sub>3</sub>. Dr. Kochy Fung of ATMAA Inc, Chatsworth, CA provided the canisters and cartridges for measurements of Hydrocarbons (C1-C12 including CH<sub>4</sub>) and Carbonyls (C1-Benzaldehyde including CO) and performed the analysis. O<sub>3</sub> profiles were obtained by Lidar measurements made by Dr. Yanzeng Zhao's group and Met profiles were made Dr. John Gaynor's group, both from NOAA WPL. Dr. Glen Cass's group from Cal Tech made organic particle speciation measurements. Routine Met data was provided by SCAQMD.

This report details the measurements made by Unisearch and summarizes the canister VOC and cartridge Carbonyl measurements made by ATMAA.

Of all of the gaseous species that are released by human activity, NO<sub>x</sub> (NO + NO<sub>2</sub>) makes the largest impact on atmospheric chemistry. NO<sub>x</sub> is rapidly oxidized in the atmosphere to form HNO<sub>3</sub> and particulate nitrate which contribute directly to the problems of acid deposition. Of perhaps even greater importance is the participation of NO<sub>x</sub> in the formation of ozone and PAN. NO<sub>x</sub> is a major player in smog formation and the rate of photochemical production of O<sub>3</sub> is determined by the level of NO<sub>x</sub> present in the atmosphere. This photochemical production of ozone is of particular concern since ozone has been increasing significantly in the Northern Hemisphere, and is implicated in crop damage and forest destruction.

The measurement of PAN (peroxyacetyl nitrate) in the atmosphere is important for several reasons. It is known to be the major irritant in urban smog (Altschuller 1978), it is harmful to plants and animals, and it has been shown to be a powerful mutagenic agent, and, therefore, is implicated as a carcinogen (Kleindienst 1985). In clean air, PAN acts as an important reservoir of chemically active odd-nitrogen, and participates significantly in long-range transport.

Formaldehyde is directly emitted as part of the mix of reactive hydrocarbons generated by fossil fuel combustion. It is also a major intermediate product in the oxidation of all

hydrocarbons. Its production should therefore be higher in urban than in rural atmospheres. The major loss process is photolysis that leads to formation of HO and HO<sub>2</sub> radicals which are considered to be the most important species in atmospheric chemistry (Logan 1980). HCHO is also of interest in the oxidation of SO<sub>2</sub> in clouds because of its ability to form complexes in solution (Boyce and Hoffmann, 1984).

Recombination of HO<sub>2</sub> radicals is the principal source of hydrogen peroxide in the gas phase. Measurements of H<sub>2</sub>O<sub>2</sub> can therefore provide information about the concentration of these chain carriers. Since the concentration of HO radicals is reduced in the presence of large amounts of NO<sub>2</sub> due to their rapid reaction to form HNO<sub>3</sub>, the mixing ratios of H<sub>2</sub>O<sub>2</sub> in urban atmospheres containing large NO<sub>x</sub> to hydrocarbon ratios may be smaller than in rural areas, in contrast with the expected behavior for HCHO. H<sub>2</sub>O<sub>2</sub> is believed to be the most important oxidizer of S(IV) to S(VI) (in the aqueous phase) in the atmosphere and therefore plays an important part in acid deposition (Penkett 1979; Middleton 1980).

Continuous, real-time measurements of the gas phase concentrations of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), formaldehyde (HCHO) and nitric acid (HNO<sub>3</sub>) were made with the TAMS-150 Tunable Diode Laser Absorption Spectrometer (TDLAS) system designed for tropospheric air monitoring. Tunable diode laser absorption spectroscopy (TDLAS) offers a number of advantages for making these measurements. Its high spectral resolution provides an unequivocal identification of the measured gaseous species free from interferences of other atmospheric constituents. This specificity makes it an ideal instrument to use as a standard against which other, less definitive methods, can be compared. In addition, its high sensitivity and rapid response provides real time measurements with detection limits much better than those required for the ambient concentrations of most trace constituents under most atmospheric conditions.

Real-time measurements of H<sub>2</sub>O<sub>2</sub> were made throughout the study period beginning at 15:00 local time on September 3 and continuing through 11:00 on September 26. HCHO was measured between 15:00 September 3 through 10:00 on September 21, between 09:00 and 19:00 on September 24 and between 07:00 and 17:00 on September 26. HNO<sub>3</sub> was measured between 14:00 September 21 and 08:00 September 24 and between 19:30 September 24 and 07:00 September 26. The detection limits of the TAMS-150 system (0.2 ppbv for HCHO, 0.1 ppbv for HNO<sub>3</sub> and 0.05 ppbv for H<sub>2</sub>O<sub>2</sub>) were adequate for following the diurnal behavior during the field study. During the field study, the ambient mixing ratios of any of the three species were never below the respective detection limit for an extended period of time (more than a few hours).

Differential Optical Absorption Spectroscopy (DOAS) was employed to measure NO<sub>2</sub>, HONO and NO<sub>3</sub>. The instrument used is a transportable version of the systems that have been used in previous field studies in the Los Angeles Basin to measure key atmospheric species, including a number, such as HONO, NO<sub>3</sub> and HO which cannot be readily measured by any other method (Platt et al 1984, 1988, Biermann et al, 1988).

The DOAS was generally run with the wavelength start set to 320 nm, and the scan covered the region 320 - 372 nm. This permitted simultaneous measurements of NO<sub>2</sub> and HONO.

NO<sub>3</sub> spectra were obtained by switching the On occasion, the spectrometer was switched to the 640 nm region and NO<sub>3</sub> measurements were made.

Since HONO was the species of interest and it was expected to be highest during the evening and night, the DOAS measurements were concentrated between 20:00 and 08:00. Some data on NO<sub>2</sub> was obtained during the day in between system maintenance and data archiving procedures. Large ambient temperature fluctuations during the daylight hours coupled with inadequate cooling of the shed in which the DOAS was located and operator fatigue made acquisition of data during the mid-day period spotty and analysis of the daytime data difficult.

Measurements of HONO and NO<sub>2</sub> commenced on September 5 and continued through the evening of September 23. NO<sub>2</sub> was always well above the detection limit of 0.2 ppbv and, for most of the evening and nighttime monitoring period, HONO was also above the detection limit of 0.25 ppbv estimated from the daytime measurements. NO<sub>3</sub> was measured on five nights and the levels were well above the detection limits of 30 pptv on those occasions.

A complete suite of Luminox<sup>R</sup> chemiluminescence analyzers, modified for essentially interference free measurements, were used for the determination of the real-time concentrations of NO<sub>2</sub>, NO<sub>x</sub> (NO + NO<sub>2</sub>), NO (determined by subtracting the measured NO<sub>2</sub> from the measured NO<sub>x</sub>), peroxyacetyl nitrate (PAN), and O<sub>3</sub>. Measurements of these species started on September 1 and continued through midnight on September 24. Except for NO during high O<sub>3</sub> and O<sub>3</sub> during high NO events, all of the species were well above the detection limits (<0.1 ppbv) of the instrumentation at all times.

Hydrocarbon measurements were made by grab sampling of air parcels into stainless steel cylinders followed by speciation using high resolution capillary gas chromatography. Carbonyls were captured using the DNPH cartridge method followed by speciation using high performance liquid chromatography. The samples were obtained by Unisearch and Portland State University personnel and analyzed by ATMAA Inc. All targeted carbonyl species were at measurable levels much of the time with the exception of the aromatic aldehydes, which were detected periodically.

## **2. INSTRUMENTATION**

### **2.1 Principle of the TDLAS Method**

The TDLAS method is based on the absorption, by the target gas, of infrared radiation, at a specific wavelength in the 5 to 20 micron region. Almost all gases absorb radiation in this spectral region which makes IR absorption methods applicable, in principle, to any gas of interest. However, since many gases absorb in this region, very high spectral resolution is required to prevent interferences from other gases in the sampled air. Tunable diode lasers (TDL) have resolutions better than Doppler limited rotational-vibrational linewidths of all gases of interest.

A TDL is a small (1 mm<sup>2</sup>) Pb crystal containing variable amounts of Sn, Se, Te or S. The wavelength region at which the laser emits radiation is governed by the proportions of these

elements in the crystal. The laser operates at a low temperature in the 20 - 60 K range that is usually provided by a closed cycle helium refrigerator.

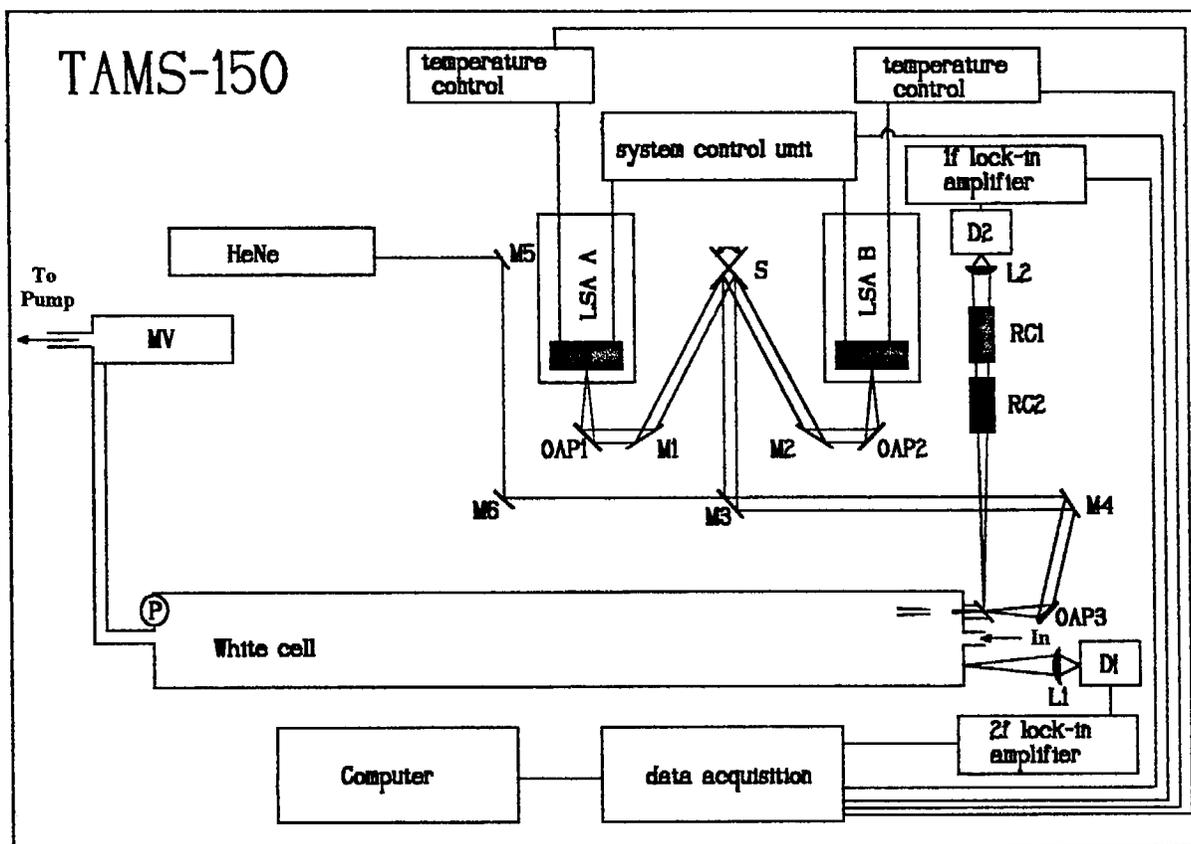
The particular wavelength at which the TDL operates depends on its temperature and the current passing through it. For a given temperature and laser current the range of wavelength emitted is extremely narrow, much smaller than that of a single rotational absorption line in the vibrational bands of the target molecule. The laser radiation can be scanned over a selected absorption line by changing the temperature of, or the current passing through, the laser. The selected absorption line can be scanned in a fraction of a second. Individual scans can be combined to provide real time analyses with response times of a fraction of a second to several minutes (depending on the gas concentration).

The technique of measuring  $\text{H}_2\text{O}_2$ , HCHO and  $\text{HNO}_3$  by TDLAS has been described in detail by (Hastie 1983 and Mackay 1993) and a full description of the TAMS-150 field instrument may be found in the Unisearch Final Report to the State of California Air Resources Board contract number A5-189-32, September 1987. A brief description of the system is provided below.

The optical system and the electronic sub-assemblies of TAMS-150 are shown in Figure 1. Two diode lasers, characterized for  $\text{H}_2\text{O}_2$ , and HCHO (or  $\text{HNO}_3$ ) respectively, are housed in laser source assemblies LSA-A and LSA-B which maintain the temperature of the lasers in the 20 to 60 K range. The frequency of the emitted radiation from each laser is a function of its composition, the temperature and the current passing through the diode. The lasers operate in cw mode and the current may be modulated at kHz frequencies so that phase sensitive detection techniques may be employed (see for example Hastie 1983).

The laser radiation from each head is collected and collimated by an  $f/2$  off-axis parabolic mirror, OAP<sub>1</sub> or OAP<sub>2</sub>, which produces a 15 mm OD parallel beam of light. Plane fold mirrors, M1 and M2, maneuver the beams onto a flip mirror, S, which is switched every three seconds to permit the beam from each diode to enter the White cell in turn. A second off axis-parabolic mirror OAP<sub>3</sub> focuses the beam into the White cell.

The White cell is a Teflon lined 1.75 m long Pyrex tube with an inside diameter of 15.2 cm. Sampled air enters through a 6 mm OD Teflon tube passing through one end plate and terminating just above, and in front of, the in-focus, White cell mirror. The gas is exhausted through a 2.5 cm ID tube in the aluminum plate at the opposite end of the cell. The mirrors are ground from Zerodur blanks to a surface quality of  $\lambda/16$ . The reflecting surfaces are gold overcoated with  $\text{MgF}_2$ . The base path length of the White cell is 150 cm. A corner cube reflector at the point where the beam would normally exit, reflects the laser radiation back through the cell, retracing its path, but translated vertically about 2 cm from the original beam (Horn and Pimentel, 1971). In this way the beam can make twice as many passes at the minimum allowable spacing between reflections on the in-focus mirror, i.e. before interference from overlap of adjacent beams becomes an important source of optical noise. With this design the incident beam makes 102 passes of the White cell for an overall path length of 153 m.



**FIGURE 1:** SCHEMATIC OF THE OPTICAL SYSTEM AND A BLOCK DIAGRAM OF THE CONTROL ELECTRONICS OF THE TAMS-150

Symbol	Description
MV	Pressure control valve
OAP <sub>1/2</sub>	f/2 off axis parabolic mirrors
OAP <sub>3</sub>	Off axis parabolic mirror with a focal length of 32 cm
M1-2	Beam directing mirrors
LSA A/B	Laser source assembly
D <sub>1/2</sub>	Infrared detectors
L <sub>1/2</sub>	BaF <sub>2</sub> lenses
S	Flip mirror
RC <sub>1/2</sub>	Reference cells for line locking
HeNe	HeNe alignment laser
TDL	Diode laser
M1-6	Beam directing mirrors
P	Baratron pressure gauge

The entrance window on the White cell is positioned at an angle of about  $45^\circ$  with respect to the laser beam and splits the beam into two parts. The majority of the laser radiation passes through the window and into the White cell. About 5% of the beam is reflected through cells, RC1 and RC2, which contain high concentrations of the monitored species and is then focused by lens L2 onto detector D2. The output of this detector is passed to a specially designed lock-in amplifier that detects the center of the absorption line due to the trace gas being monitored and sends this information to the computer for line-locking.

The beam exiting the White cell is focused by a  $\text{BaF}_2$   $f/1.5$  lens, L1, onto a liquid-nitrogen cooled, mercury cadmium telluride, infrared detector, D1. The output of this detector is fed into an oscilloscope for visual representation and to a lock-in amplifier and data acquisition/computer control system for analysis and storage.

The precision of the measurements (short term stability  $< 1$  hr) is experimentally found to be better than  $\pm 1\%$ . The accuracy depends on the ability to accurately measure the various flows and on the ability to determine the mixing ratio of the calibration standard. The computed accuracy for  $\text{H}_2\text{O}_2$ , HCHO and  $\text{HNO}_3$  is  $\pm 15\%$ .

## 2.2 Principle of the DOAS Method

The DOAS used in this study is a pre-production version of a commercial instrument under development at UNISEARCH in cooperation with the German firm of Hoffmann, who constructed the prototype. This instrument uses the spinning wheel, rapid scanning spectrometer technique described by Platt et al. (1980). The unit employs an open path with a retro-reflector situated 0.25 - 5 km from the source. It is capable of providing simultaneous measurements of  $\text{NO}_2$  (100) and HONO (30) with a time response of  $\sim 5$  minutes. Measurement of  $\text{NO}_3$  (5) is made at a different wavelength and can be done alone or in sequence with  $\text{NO}_2$  with a time response for multiple measurements of about 10 minutes. Detection limits in pptv defined as  $S/N = 1$  are given in parenthesis for a 1 km path length

The DOAS technique is based on measuring the difference between the absorbance at some wavelength ( $I_2$ ) where the species of interest has a distinct absorption feature, and two other wavelengths ( $I_1$  and  $I_3$ ) on either side of the feature as can be seen in Figure 2. Due to background noise and absorption features of other species, the true light intensity without any absorption ( $I_0$ ) can not be measured. The concentration of the pollutant species is thus determined not from the conventional  $\log(I_0/I)$  but rather from  $\log(I_0'/I)$ , where  $I_0'$  is the measured intensity at  $I_1$  and/or  $I_3$ . In practice, a reference spectrum of the species being measured is fit to the observed spectrum so that all the absorption bands due to that molecule, including their relative strength and shapes, are used in the identification and measurement.

Figure 4 is a schematic diagram of a DOAS system. High-pressure Xenon lamps or incandescent quartz-iodine lamps are typically used to produce a continuous light source (UV and visible). The prototype utilizes a 450 W high pressure xenon lamp. A spherical or parabolic mirror is used to collimate the light. The collimated parallel beam traverses the parcel of air to be monitored and is received by the collecting mirror which focuses the beam on the entrance slit of the monochromator (spectrograph).

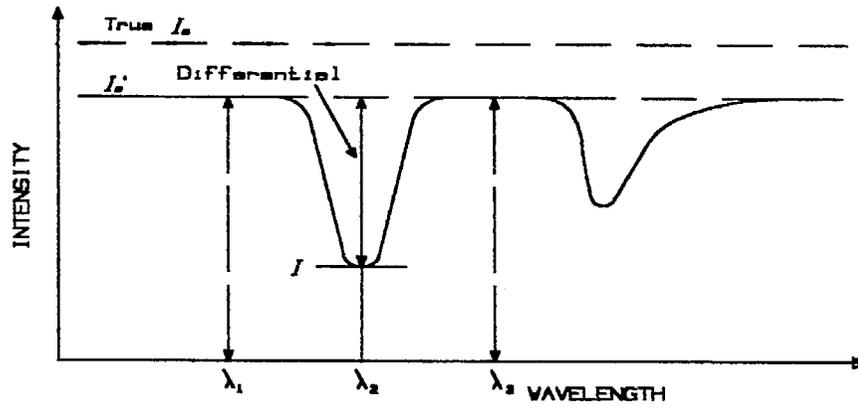


Figure 2: Basis of differential optical absorption spectroscopy

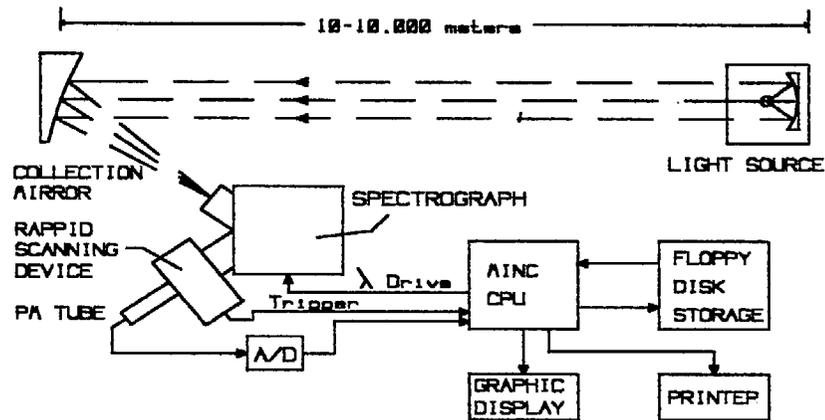


Figure 3: Schematic diagram of DOAS spectrometer

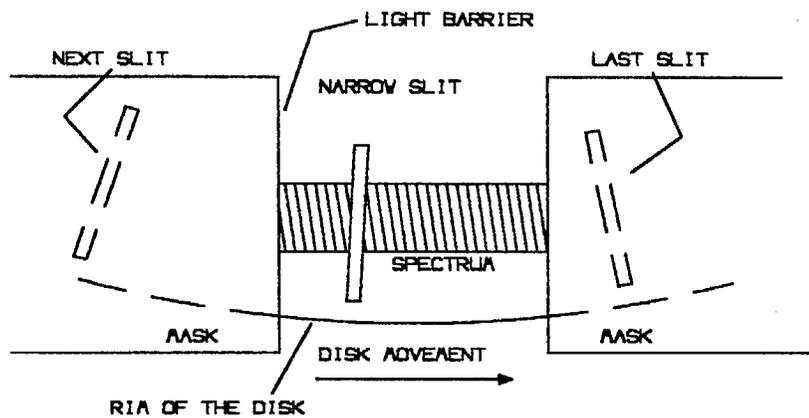


Figure 4: Schematic diagram of the slotted disk in the rapid scanning device.

The optical layout of our prototype DOAS is somewhat different. A coaxial Newtonian telescope is used for both transmitting and receiving of the xenon light. The transmitted light is reflected back by an array of cube corners, thus doubling the light path. The concave grating of the monochromator disperses the light and is adjusted such that the desired frequency range (typically 6-40 nm) is projected across the exit slit. In conventional spectroscopy the exit slit of the monochromator is usually narrow and stationary and the frequency is slowly scanned by rotating the grating. This however, is not suitable for open ambient air measurements since atmospheric turbulence with frequencies of up to 10 Hz make it desirable that the spectra be scanned at rates  $> 100$  Hz. This is achieved by replacing the exit slit of the monochromator with a rapid scanning device which is typically a rotating slotted disk with very narrow slits ( $\sim 100$  micron wide) as can be seen in Figure 3. Consequently, a single scan may require only about 10 ms and atmospheric scintillation has little if any effect on the signal. The output light is focused on a detector (photomultiplier tube) and the electrical analog signal produced is then digitized and stored in the computer ready for analytical evaluation.

The signal-to-noise (S/N) ratio of the DOAS system is improved by summing a large number of spectral records, typically 20,000 to 30,000, representing some 4 - 6 minutes signal integration time. Under the operating conditions of this study, the precision of the measurement for  $\text{NO}_2$  were found to be about  $\pm 1\%$  and the overall accuracy of the measurements, determined by instrumental stability over the long term (24 hrs) and the accuracy with which the absorption coefficients are known is assessed to be  $\pm 15\%$  for  $\text{NO}_2$  and  $\text{NO}_3$  and 20% HONO.

### 2.3 Principle of the Luminox<sup>R</sup> Method

The Luminox<sup>R</sup> technique quantifies the chemiluminescence produced when a given trace gas reacts with a given specially formulated solution. The sample air is drawn through a small chamber, over a wetted wick that is viewed by a photomultiplier tube. The output signal is adjusted for calibration and temperature effects. The principles of the various Luminox<sup>R</sup> instruments are discussed in detail in Schiff et. al.. (1986), and Drummond et. al.. (1989a,b, 1991).

#### Measurement of $\text{NO}_2$

In the case of the model LMA-3  $\text{NO}_2$  analyzer, the  $\text{NO}_2$  in the sample air that contacts a wetted wick reacts with a specially formulated solution containing luminol,  $\text{NaSO}_2$ ,  $\text{NaOH}$ , and an alcohol. The signal is proportional to the strong chemiluminescence from luminol oxidation. The basic instrument responds principally to the concentration of  $\text{NO}_2$ . The detection limit (2 sigma) of 5 pptv permits direct measurement of  $\text{NO}_2$  even in background tropospheric air. The time response (0 to 95%) for a step change of 10 ppbv  $\text{NO}_2$  is 1 s. The signal is electronically compensated for both the temperature dependence of the photomultiplier dark current, and the negative temperature dependence of  $-2\%$   $^\circ\text{C}$  of the  $\text{NO}_2$  - luminol reaction. The overall accuracy of the  $\text{NO}_2$  measurement is estimated to be  $\pm 15\%$ .

The LMA-3 has a small response to both PAN and Ozone. The instrument used had a linear response of  $\sim 10\%$  equivalent  $\text{NO}_2$  toward PAN. During the study period PAN never exceeded 5 ppbv and was usually less than 2 ppbv.  $\text{NO}_2$  was generally above 5 ppbv and

during periods of high PAN was greater than 40 ppbv. The contribution due to PAN, therefore, was less than 2% so no correction in the NO<sub>2</sub> was made.

The response to O<sub>3</sub> is more complicated. Below 1 ppbv NO<sub>2</sub> ozone gives a positive response of ~0.1% equivalent NO<sub>2</sub>. Between 1 and ~40 ppbv there is no detectable response due to O<sub>3</sub> and above 40 ppbv there is a negative response of ~0.1% equivalent NO<sub>2</sub>. For the conditions of NO<sub>2</sub> and O<sub>3</sub> prevalent during the study the ozone interference was, therefore, not significant and no correction on the NO<sub>2</sub> (and NO<sub>x</sub>) was made. On one occasion during high ozone an ozone trap capable of passing >95% of the NO<sub>2</sub> but destroying >98% of the ozone was placed at the inlet of the instrument to check the interference due to O<sub>3</sub>. No detectable difference in the signal was observed between the condition with the trap in place and without the trap when account was made for the transmission efficiency of NO<sub>2</sub>. Traps were not used continuously since the interference was negligible and the high O<sub>3</sub> levels during the middle of the day acted to reduce the lifetime of the trap to only about 24 hours making the use of O<sub>3</sub> traps very expensive.

#### Measurement of NO<sub>x</sub>

A model LNC-3 NO converter/sequencer manufactured by Scintrex/Unisearch was employed to measure NO<sub>x</sub> and, by subtraction of measured NO<sub>2</sub>, NO. This instrument uses CrO<sub>3</sub> on a substratum of Chromosorb-A to quantitatively convert NO to NO<sub>2</sub>. The sample air is first dried by means of a Nafion shell dryer (Permapur, Inc.) that removes excess humidity from the sample air without detectable loss of NO<sub>2</sub>. An outlet valve array routes the dried (5-60% relative humidity) sample stream through one of three paths. The first path goes straight through and constitutes the normal NO<sub>2</sub> mode. The second path contains the CrO<sub>3</sub> converter. A dust filter inhibits migration of the CrO<sub>3</sub> to the LMA-3 detector. The third path is via a zero trap where NO<sub>2</sub> is removed. A built-in sequencer cycles between the three modes according to the step time chosen by the operator; remote control capability is provided. The accuracy of the NO<sub>x</sub> measurement is estimated to be ± 20% while that for NO, because of the subtraction necessary, is estimated to be ± 25%.

#### Measurement of PAN

The Scintrex/Unisearch LPA-4 PAN analyzer was used to measure PAN. The instrument contains a gas chromatograph (GC) and a Luminox<sup>R</sup> detector. The original design was based on the work of Burkhardt et al. (1988). The carrier gas for the GC is generated within the instrument by scrubbing the ambient air for NO<sub>2</sub> and PAN. Every five minutes, 60 ml of ambient sample air is injected onto the column. The column consists of a 25 cm long 1/4" O.D. Teflon tube filled with Chromosorb G coated with 10% Carbowax 400. The retention time for PAN is typically 2 min. The effluent of the column is passed through a thermal converter to generate NO<sub>2</sub> from the PAN. Extra NO<sub>2</sub> is added before detection to insure that the detector remains in the linear range. A major feature of the instrument is an automatic calibration mode using the internal NO<sub>2</sub> source for calibration gas. The instrument contains its own peak integrator. The detection limit, based on a peak height of 3x baseline noise is 30 pptv. Repeatability is typically better than 5 pptv. Overall accuracy, dependent on the long term stability of the column efficiency (6 months or more) and the accuracy of the PAN reference standardization (see section 2.6) is assessed to be ± 15%.

## Measurement of Ozone

Ozone measurements were made by using a newly developed LOZ-3 portable ozone monitor and, for the last 2 weeks of the study, a Dasibi 1008-AH UV-photometric ozone analyzer. The LOZ-3 uses a solution containing Eosin-Y dye (Ray et. al., 1986). The LOZ-3 contains an automatic zeroing system that periodically removes ozone from the sample gas and automatically compensates the subsequent measurements. The signal range is 0.1 ppbv to 2.0 ppmv. The detection limit is ~0.1 ppbv. Laboratory tests indicate that the measurement is interference free (Drummond et. al., 1989a). Intermittent calibration is carried out by sampling a stream containing a known mixing ratio of ozone.

LOZ-3 instrumental noise is found to be  $\pm 0.1$  ppbv or 1% of signal and precision is usually  $\pm 0.2$  ppbv or 3% of signal, whichever is larger. Long term drift (24 hr) in the calibration is less than 10% and the overall accuracy of the measurement is assessed to be better than  $\pm 15\%$ .

## 2.4 Hydrocarbon Measurements

Hydrocarbon speciation were performed using high resolution capillary gas chromatography after cryogenic sample concentration. The technique is similar to those described previously (Singh, 1980; Grosjean and Fung, 1984), except for the use of higher resolution fused silica columns and associated changes in the oven temperature program necessitated by the properties of the newer columns. An alumina PLOT column (Chrompack) is used for the C2-C8 species and a DB-1 (J. & W. Scientific) for C8 and above. The alumina PLOT column provides excellent separations for most light hydrocarbon species, providing easy classification of alkanes and alkenes except acetylene, which tends to co-elute with n-butane for most samples. Retention time shift for acetylene seems to be dependent on the extent of deactivation of alumina by sample water.

CH<sub>4</sub> is run on a separate 2 section column consisting of SE-30 followed porapak QS packed column run at ambient temperature and the effluent is passed directly to an FID detector for measurement.

For the analysis, an average of 80 to 100 ml of air sample is concentrated using liquid argon in the absence of any drier. Detection limit of the analysis is approximately 0.01 ppbC. The precision of the analysis is within  $\pm 5\%$  for most species in ambient air. Overall accuracy of the measurements is assessed to be better than  $\pm 15\%$ .

## 2.5 Carbonyl Measurements

Carbonyls in ambient air were sampled at approximately 1 liter  $\cdot$  min<sup>-1</sup> with a C18 SepPak cartridge impregnated with purified 2,4-dinitrophenylhydrazine (DNPH) and phosphoric acid. The carbonyls are captured as the corresponding hydrazones in the cartridge, which is eluted with acetonitrile and analyzed by high performance liquid chromatography (Fung and Grosjean, 1981).

CO is run on the same 2 component column as CH<sub>4</sub> but maintained at dry ice temp. The effluent is then oxidized followed by reduction to CH<sub>4</sub> and then to the FID detector for measurement.

The method has a detection limit of approximately 1 ppbv for 60 liters of air sampled, with a precision of  $\pm 10\%$ . Carbonyls between C1 (HCHO) and benzaldehyde were speciated. The accuracy of the method as demonstrated at the Carbonaceous Species Methods Comparison Study, 1986 is about  $\pm 15\%$  for HCHO comparing to the long path spectroscopic methods used during that study (Fung and Wright, 1990).

## 2.6 Calibration Standards

The calibration standards employed in the study for each instrument are described below. On September 16, the State of California Protection Agency, Air Resources Board, Monitoring and Laboratory Division performed an audit of all  $\text{NO}_x$  and  $\text{O}_3$  analyzers at the site. The results of the audit are summarized in Table 1. Good agreement was obtained for all of the Unisearch instrumentation for calibration standard values and linearity except for the LOZ  $\text{O}_3$  analyzer that was found to have good correlation with the audit values but to be measuring 16.7% low. This error was traced to a fault in the Unisearch Dasibi that was used as the transfer standard to calibrate the LOZ. This error was corrected on September 18 and no further problems were detected. A more detailed description of the fault is provided in the sub-section Ozone below. The complete Audit analysis is provided in Appendix A.

Table 1 Quality Assurance data on Unisearch  $\text{NO}_x$  and  $\text{O}_3$  instrumentation provided by the California Air Resources Monitoring and Laboratory Division.

INSTRUMENT	AVERAGE % DIFFERENCE	STANDARD % DEVIATION	CORRELATION	COMMENTS
LNC-3 $\text{NO}_2$	1.8	4.5	0.99977	Converter efficiency 107%
LOZ-3 $\text{O}_3$	-16.7	3.9	0.99942	Offset due to Dasibi fault
DASIBI $\text{O}_3$	-3.2	2.0	0.99999	Zero fault corrected

### Nitric Oxide and Nitrogen Dioxide

$\text{NO}$ , and  $\text{NO}_2$ , calibrations are quite straight forward and calibration devices in common usage are employed to determine the sensitivity of the Luminox<sup>R</sup>. In the case of  $\text{NO}$ , gas mixtures containing NBS traceable transfer standards are obtained from a suitable manufacturer. Several mixtures are obtained and cross-calibrations are performed. These cross-calibrations are performed regularly and prior to any field study. If the agreement is not within the manufacturers quoted uncertainty additional mixtures are obtained to determine a satisfactory standard.

In the case of  $\text{NO}_2$ , permeation tubes are employed. These tubes are calibrated by weighing and by comparison with calibration gases generated by titration of  $\text{NO}$  from an NBS traceable transfer standard gas mixture with  $\text{O}_3$ . Comparison of the  $\text{NO}_2$  field standard with our lab standard system showed no measurable difference between the rate determined

before and after the field study. Furthermore, the agreement with the audit standard (see Appendix A) was within 2%. The daily calibrations with NO<sub>2</sub> performed on the NO<sub>2</sub>, NO<sub>x</sub> and PAN instruments are summarized in Table 2.

Calibrations were made against a permeation tube system providing a mixing ratio of 28.5 ppbv NO<sub>2</sub> diluted in zero air. The results provided in Table 2 are the values obtained without adjustment since the previous calibration. Once the new sensitivity of the instruments had been determined the instruments spans were adjusted to the correct mixing ratio if the measurement differed by more than 0.5 ppbv from the expected calibration value.

The CrO<sub>3</sub> converters were tested before and after the field measurements and found to have efficiencies ranging between 94% and 96% with no significant changes with time observed. NO<sub>x</sub> data was corrected for the conversion efficiency after the field study and the correction is in good agreement with the value obtained by the Audit (see Table 1) which determined a conversion efficiency of 93% (Audit calculation is for NO<sub>2</sub> to NO of 107% whereas the actual efficiency is for NO to NO<sub>2</sub>, the reciprocal of this result).

#### Peroxyacetyl Nitrate

One of the features of the LPA-4 PAN analyzer is that routine calibration consists only of ensuring that the span of the NO<sub>2</sub> detector is correct. The column/converter efficiency have only to be determined initially in the laboratory for a particular unit and that factor remains constant until the column is replaced. The instrument is calibrated using a NO<sub>2</sub> source (as done for the LMA-3) and there is no need to carry a source of PAN (which is unstable) into the field for calibration.

An internal source of NO<sub>2</sub> is used to maintain the sensitivity of the detector within 5% of calibration on a real-time basis. Confirmation of the internal reference is usually made on a daily basis (see Table 2). Column efficiency measurements, as described below, are performed before and after each field study. Our experience to date has been that the column efficiency has not changed by more than 10% over extended periods (6 months or more). The instrumental stability was amply demonstrated during the San Joaquin Air Quality Experiment (Drummond et al. 1991).

The system employed to initially determine the sensitivity of the LPA-4 towards PAN is similar to that used during the San Joaquin Valley Air Quality Experiment (Drummond 1991). The system consists of a GC that is used to purify PAN in-situ, a Teflon bag for temporary storage of the pure PAN in zero air, and an instrument for measuring NO<sub>y</sub> (NO<sub>y</sub> = NO + NO<sub>2</sub> + HNO<sub>3</sub> + PAN + etc.). Since PAN has been verified to be the only significant NO<sub>y</sub> species in the bag, the NO<sub>y</sub> instrument reports the mixing ratio of PAN.

The mixture of PAN and zero air is provided simultaneously to the LPA-4 and a Luminox<sup>R</sup> NO<sub>2</sub> analyzer-molybdenum converter/Cr<sub>2</sub>O<sub>3</sub> converter combination which has been shown to efficiently convert PAN to NO<sub>2</sub> (Blanchard et al. 1990) and the column efficiency factor adjusted so that the LPA-4 values for PAN are reported in ppbv.

Table 2 Calibration history of the LMA-3, LOZ-3 and LPA-4. All NO <sub>2</sub> measurements were referenced to a PTCS-3 permeation tube system that provided a sample of 28.5 ppbv NO <sub>2</sub> in air. The LOZ was calibrated against the Dasibi measurement						
DATE	TIME	LMA-3	LPA-4	LOZ	DASIBI	Comments
	START	NO <sub>2</sub>	NO <sub>2</sub>	O <sub>3</sub>	O <sub>3</sub>	
		(ppbv)	(ppbv)	(ppbv)	(ppbv)	
03-Sep	09:33	5.1	28.3	87	88	First calibration
04-Sep	09:31	28.3	28.5	111	105	Change zero scrubber
	18:15	31.2	28.4			
05-Sep	08:39	25.4	28.1	95	95	
	16:49	27.1	28.2			
06-Sep	08:51	31.0	27.9	91	89	
07-Sep	10:46		30.1	87	84	Lma-3 down due to peristaltic pump failure
08-Sep	12:30		28.3	98	97	Lma-3 on line 12:21 Install new pump Install new NO <sub>x</sub> converter converter
09-Sep	09:34	30.9	28.4	100	99	
10-Sep	09:08	29.3	28.3	98	97	
	10:40			53	53	O <sub>3</sub> calibration for three points
	10:45			105	100	
	10:50			177	165	
11-Sep	12:45	28.6	28.5	52	50	O <sub>3</sub> calibration for three points
	12:55			104	102	
	13:00			182	180	
12-Sep	09:15	27.6	28.0	93	94	
13-Sep	09:55	28.3	28.4	103	99	
14-Sep	10:23	27.8	27.9	98	96	
15-Sep	10:11	28.3	28.1	99	98	
16-Sep	08:23					Audit
17-Sep	09:20	28.8	28.4	118	115	
18-Sep	10:26	29.2	28.1	122	119	
19-Sep	09:23	28.8	28.3	125	121	
	10:54					Change LOZ/LMA sampling filters
20-Sep	11:47	26.6	28.0	113	111	
20-Sep	20:52	24.9	28.4			
21-Sep	07:38	28.3	28.3	114	116	
22-Sep	09:10	27.3	28.4	114	112	
23-Sep	11:17	29.8	27.8	111	109	
24-Sep	11:02	27.5	27.8	117	116	
25-Sep	07:56	28.3	27.9	117	117	
26-Sep	10:35	28.8	28.1	125	118	
27-Sep	09:00	28.5	28.0	118	117	

## Ozone

The LOZ-3 ozone analyzer was calibrated daily against a Dasibi Corporation 1008-AH photometric analyzer (see Table 2). Ozone mixtures of ~100 ppbv in zero air were used to calibrate the LOZ-3. For the period September 1 through September 16, when not being used as a calibration standard, the Dasibi was turned off to avoid contamination by potential interfering gases in ambient air. After September 16 the Dasibi was also used to monitor ambient air when not performing the calibration function.

On September 16, the ARB Monitoring and Laboratory Division performed an audit of the NO<sub>x</sub> and O<sub>3</sub> instrumentation and a fault in the Dasibi was discovered. The Dasibi zero was in error due to a faulty electronics board that overheated shortly after instrument startup but did not fail for several hours so the problem was not evident. This fault was corrected on a temporary basis by removing the cover of the Dasibi and improving the air circulation. The board was repaired on return to Unisearch and this repair had no effect on the calibration of the Dasibi other than to correct the zero error. The data obtained by the LOZ was corrected for the audit offset (see Table 1) for the period up to September 18 after which the Dasibi calibration was again reliable and no correction needed to be made.

The UNISEARCH Dasibi was calibrated prior to, and subsequent to, the field study at the Ontario Ministry of the Environment (OME) Instrument Standards Laboratory in Toronto, Ontario. They have an identical calibration system to the NIST ozone standard system against which it is compared on a yearly basis. This system is used to calibrate all of the ozone analyzers in the Ontario Ministry of the Environment monitoring network. The two calibrations of our Dasibi at OME were found to be within 2% of the standard with a constant offset of + 8 ppbv. The results are consistent with those obtained by the audit (Table 1).

## Hydrogen Peroxide, Formaldehyde and Nitric Acid

For these species, special permeation devices were developed. In the case of H<sub>2</sub>O<sub>2</sub> a permeation device was developed in which a 4 m coil of low density, polyethylene tubing, 0.32 mm OD and 0.16 mm ID is immersed in a 50% stabilized solution of H<sub>2</sub>O<sub>2</sub>. The permeation rate of this device was determined by the colorimetric TiCl<sub>4</sub> method (Slemr 1990). Periodic standardizations of the H<sub>2</sub>O<sub>2</sub> permeation source were performed during the field study. Table 3 summarizes these results.

In the case of HCHO a permeation device using paraformaldehyde permeating through a 1 m length of Teflon tubing was selected. The permeation rate from this source was determined using a colorimetric method after complexing the HCHO with chromotropic acid (Altschuller 1961). Standardization of the HCHO permeation source was performed in the laboratory before and after the field study. Table 4 summarizes the standardizations.

The nitric acid permeation device is similar to the H<sub>2</sub>O<sub>2</sub> one except that Teflon tubing is used in place of polyethylene and the active region in contact with a solution of 50% nitric acid and 50% sulfuric acid is only 2 cm long. Calibration of this device is made by pH titration against standard NaOH. The average value for the permeation rate which was used in the calibration of the TDLAS was 202 ± 3 ng/min. The results of the standardization of the

HNO<sub>3</sub> permeation device are described in detail in the Unisearch report to ARB on Measurements of Nitric Acid at the Azuza SCAQMD site (ARB 1994).

DATE	TEMP °C	TIME MINUTES	ABSORBANCE	PERM. RATE ng/min
August 24	40.0	701	1.186	523
September 4	40.1	834	1.389	513
September 11	40.0	747	1.266	523
September 19	40.1	606	1.023	<u>517</u>
			Average =	519 ± 4

DATE	TEMP (°C)	STD. CURVE SLOPE (ABS.units/M)	AVG. PERM. RATE (ng/min)
August 23	40.4	3.90E+04	472
August 24	40.4	3.90E+04	498
November 25	40.5	4.14E+04	482
		AVERAGE =	484 ± 11

Calibration of the TDLAS toward H<sub>2</sub>O<sub>2</sub>, HCHO and HNO<sub>3</sub> was performed on a routine basis. Normally, calibrations were performed every 4 hours for HCHO and once or twice a day for H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub>. Variation in the sensitivity between calibration was less than 10% for all three species throughout the study.

All permeation sources are contained in thermostated environments which maintain the temperature to within ± 0.25°C of a chosen value.

#### Hydrocarbons

Calibration of hydrocarbons is performed using the NIST SRM 1811 standard, and all hydrocarbon concentrations are referenced to benzene response.

#### Carbonyls

Liquid standards prepared by dissolving accurately weighted samples of the pure solid hydrazones are employed to calibrate the HPLC.

### 3. EXPERIMENTAL

On August 31, 1993 the Unisearch mobile laboratory containing the TAMS-150, DOAS, and Luminox<sup>R</sup> instruments arrived at the measurement site which was a quarry owned and adjacent to the Claremont College Campus in Claremont, CA. The Luminox<sup>R</sup> instruments were all up and running by mid-day of September 1 and continued measurements until midnight on September 24. The TDLAS was operational by mid-day on September 3 and operated through 18:00 on September 26. The DOAS measurements commenced at 01:00 on September 5 and stopped at 16:00 on September 23. The hydrocarbon and carbonyl sampling commenced at 12:00 on September 4 and end at 22:00 on September 26.

Except for the DOAS system, all of the investigator instrumentation was located in a 20 by 20 meter area approximately 50 m north of the quarry rim and about 20 m south of Foothill Blvd. The site was about 5 m below the Foothill Blvd. road level. The TDLAS and the Luminox<sup>R</sup> instruments were housed in the Unisearch mobile laboratory. The DOAS was located in a shed about 20 m west from the Unisearch mobile lab. This location provided a good line of sight to a retro-reflector located on the far side of a quarry some 768 meters south yielding a total analytical path of 1436 meters. Hydrocarbon and carbonyl samplers were located approximately 5 m north of the Unisearch mobile lab and 5 m west of the Portland State mobile lab.

#### 3.1 TDLAS Sampling and Calibration Procedures

Sample air was drawn through a 6 mm OD, 0.75 mm wall, FEP type Teflon tube approximately 3 m long. Particles were removed from the air by a 1.2 micron pore size Teflon filter located at the tubing entrance. The Teflon filter was replaced each day. A Teflon needle valve located 1 m downstream of the inlet maintained the flow into the White cell at 10 standard liters per minute (SLM). The inlet line was at ambient temperatures.

The air traverses the inlet line in a few tenths of a second while the residence time in the White cell is about 5 seconds. The flow of air entering the White cell is monitored with a calibrated mass flowmeter just prior to each calibration and is adjusted by the needle valve as necessary. A motorized valve, which is referenced to a MKS Baratron pressure gauge, controls the pressure in the White cell at 25 Torr.

The sensitivity of the TAMS-150 toward  $\text{H}_2\text{O}_2$ , HCHO and  $\text{HNO}_3$  is determined by introducing a 'spike' of known concentration of the target gas to the air stream where it is sampled into the system, immediately upstream of the particle filter. The concentration of the spike is chosen to provide mixing ratios similar to that of the constituent in the sampled air. In this way, any surface effects that may occur will be the same for the sampled and spiked air and should, therefore, cancel. A complete description of sampling integrity testing performed on  $\text{H}_2\text{O}_2$ , HCHO and  $\text{HNO}_3$  is given, respectively, in Slemr et al, (1986), Harris et al, (1988) and Mackay (1987).

In the case of HCHO the calibration gases flowed continuously through the addition lines up to a 3-way solenoid valve located close to the sampling gas inlet. When not required for calibration, the gas mixture was exhausted far away from the inlet. During a calibration the

solenoid valve closed the exhaust line and admitted the calibration gas mixture to the sampled air stream. The addition lines were sufficiently short that negligible loss of the trace constituent occurred in the lines and little delay is observed before stabilization of the measured calibration mixing ratio. Calibrations were performed automatically under computer control. For  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$  calibrations were performed manually. When calibrating, the addition line was inserted into the sampling line several minutes prior to acquiring a calibration spectrum. This delay was required for  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$  as they are sticky gases and longer times are required to reach equilibrium mixing than is the case for  $\text{HCHO}$ .

The minimum detection limit, MDL, defined as a signal-to-noise ratio of 1, was determined experimentally at the selected laser operating conditions and absorption feature. Scrubbed ambient air ( $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$ ) or clean bottled air ( $\text{HCHO}$ ) was introduced at the sampling inlet and the laser current scanned over the range of the absorption feature to obtain a background noise level,  $S_n$ . A known mixing ratio,  $MR$ , in ppbv of trace constituent is then added and the signal,  $S_s$  measured. The ratio of  $S_n/S_s \times MR$  provides the MDC in ppbv, which was about 0.2 ppbv for  $\text{HCHO}$ , 0.05 ppbv for  $\text{H}_2\text{O}_2$  and 0.1 ppbv for  $\text{HNO}_3$ .

The following description of the sequence of events during an automatic ambient air monitoring experiment illustrates how laser control, as well as data analysis, are achieved. The procedures are the same for  $\text{H}_2\text{O}_2$ ,  $\text{HCHO}$  and  $\text{HNO}_3$  except for the type and frequency of the background spectra acquisition.

Information for the operating parameters selected for the  $\text{H}_2\text{O}_2$  measurements are input to the computer. The software then operates the system automatically. It first obtains a background spectrum by sampling scrubbed ambient air at the inlet so that the White cell is free of  $\text{H}_2\text{O}_2$ . The background spectrum is obtained and archived. Next, calibration gas is added at the sampling inlet and, after a suitable stabilization period (60 seconds), a calibration-reference spectrum is obtained. The reference spectrum is also archived in its untreated form as are all subsequent spectra of ambient air. The background spectrum is subtracted (channel by channel) from the reference spectrum and the result normalized to the mean value of the untreated reference spectrum. This procedure essentially removes the frequency dependent structure present in the background from the reference spectra.

Once the calibration-background procedure has been completed the software resets the solenoid valves to admit ambient air and, after an appropriate delay (60 seconds for both species) to achieve steady conditions, an ambient air spectrum is acquired. The background structure is subtracted and the result digitally smoothed. The smoothing algorithm employs least squares fitting of the best quadratic or cubic function to a running window of seventeen channels and replaces the data in the central channel of the group with the value of the function at that point. This algorithm is very effective in suppressing high frequency noise without distorting line shapes if the number of channels per line width (i.e., the scan range) is appropriately chosen. The ambient air spectrum is then compared to the calibration spectrum using a least squares fitting procedure. Since the mean values of the calibration spectrum and the ambient air spectrum may differ due to potentially varying broad band transmittance of ambient air outside the White cell and since the mean value of the ambient

spectrum contains no useful information, the calibration spectrum is adjusted to have a zero mean value before fitting. Thus, the intensity of the absorption line in the ambient air spectrum is obtained as a fraction of the calibration line intensity.

A sampling sequence is made up of a background measurement, one or more ambient measurements and a second background measurement. Because the above described analysis procedure depends on the background remaining constant during a sampling sequence the minimum detection limit will depend on the stability of the background structure during this period. Variability in the atmospheric conditions can act to degrade the detection limits when the composition of the sampled air mass is rapidly changing.

The TAMS-150 simultaneously obtained a 1 minute average data point for each species ( $\text{H}_2\text{O}_2$  and HCHO or  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$ ) every 3 minutes. The raw data were stored on floppy diskettes for future analysis in the laboratory and the real time measurements were printed out to the computer monitor and printer at 3 minute intervals.

Calibration of  $\text{H}_2\text{O}_2$  (and  $\text{HNO}_3$  when monitored) was performed manually once a day, usually between 06:00 and 08:00. The sensitivity of the instrument toward  $\text{H}_2\text{O}_2$  (and  $\text{HNO}_3$ ) was observed to have a day-to-day stability of better than 10%. HCHO was calibrated automatically approximately every four hours. The sensitivity variation was less than 10% between calibrations.

Background spectra for formaldehyde were obtained by adding bottled zero air at the sampling inlet to flush the system of ambient HCHO. Since the HCHO levels were always more than an order of magnitude above the detection limits background spectra were only obtained every few hours.

Hydrogen peroxide background spectra were obtained by inserting a charcoal scrubber in the sampling line that efficiently removed the  $\text{H}_2\text{O}_2$  with a minimum perturbation the  $\text{H}_2\text{O}$  concentration.  $\text{H}_2\text{O}$  is the major interfering species in the absorption region employed for detection of  $\text{H}_2\text{O}_2$  and, therefore, it is important to retain any perturbation of the background spectra due to this species so that it may be subtracted from the ambient measurement.

Since the ambient  $\text{H}_2\text{O}_2$  levels were often close to the detection limit, changes in the background due to fluctuations in the humidity could significantly degrade the detection limit. To minimize this source of noise the ambient measurement sequence used was to alternately take background and ambient spectra. The actual sequence of events was: 1) turn on scrubber and allow 30 seconds of stabilization, 2) measure background for 60 seconds, 3) turn off scrubber and allow 30 seconds of stabilization, 4) measure ambient for 60 seconds, 5) turn on scrubber and allow 30 seconds of stabilization, 6) measure background for 60 seconds, and so on. Therefore, one ambient data point was obtained every 3 minutes.

Nitric acid background spectra were obtained by inserting a 2  $\mu\text{m}$  pore size Nylon filter in the inlet air stream to scrub the air of  $\text{HNO}_3$  while leaving all other gaseous species untouched. Since nitric acid is a sticky molecule, the air was scrubbed for 3 minutes prior to obtaining a background signal.  $\text{HNO}_3$  was always well above the detection limit so background spectra were only recorded every 4 hours and were not subtracted from the

measurement except at nighttime when the ambient level fell below 4 ppbv. Additional details on the method of sampling, calibration and data handling can be found in Mackay 1994.

The accuracy of the measurements is estimated to be  $\pm 15\%$ . The major source of calibration error for both species is the colorimetric calibration procedure which has an uncertainty assessed at  $\pm 5\%$ . Additional uncertainties of  $\pm 2\%$  are caused by temperature variations of the permeation device,  $\pm 2\%$  from the measurement of the carrier gas flow,  $\pm 1\%$  for the precision of the measurements and  $\pm 5\%$  for the variation in the sensitivity between calibrations. The carrier gas flowmeter (Tylan, model FM36 1-20SLM) was checked against a bubble flowmeter prior to the study.

For the entire study, except for one occasion arising from a power failure, data coverage was 98% for  $\text{H}_2\text{O}_2$ , 96% for  $\text{HCHO}$  and 100% for  $\text{HNO}_3$  (for the limited time measured) with down times associated with the calibration periods for the most part. On September 11 a power failure at 01:00, which required that the TDLAS system be completely set up again, gave rise to a 17 hour period (01:00-18:00) in which no data was recorded.

### 3.2 DOAS Sampling and Calibration Procedures

The instrument was installed in a small wooden shed about 50 meters from the lip of the quarry. The retro-reflectors (2) were installed on the opposite wall of the quarry 768 meters away (west by south-west, 5 degrees declination) yielding a total analytical path of 1436 meters.

In the early days of operations at Claremont it had been observed that the standard automatic data evaluation procedures yielded poor results. Upon investigation it was concluded that this was due to spectral drift induced by low quality 220V AC power supplied and very variable ambient temperatures. The temperature in the wooden shed often exceeded  $100^\circ\text{F}$  at mid day and dropped to as low as  $60^\circ\text{F}$  during the night. This affected several aspects of the DOAS system. Thermally induced distortion of the instrument caused the coaxial telescope to go out-of-focus affecting both the transmitted beam and, more importantly, the focus and the angle of input beam as it entered the spectrograph. This causes a shift with a range of about 10 nm as a function of the time of day. Consequently, the instrument required perpetual "tweaking" between 7 am and 8 PM. In addition the high temperature fluctuation also affected the scanning disk in the spectrograph. Often during the day variation in disk speed caused ghost spectra rendering the spectra unreliable and at times useless.

Fortunately, both  $\text{HONO}$  and  $\text{NO}_3$  are night species. Between 8 PM and 7 am the system was relatively stable and good data could be acquired.

While the system itself was operated continuously (24 hrs/day), continuous supervision was maintained during the periods 1800 to 0030 and 0430 to 1130 but with only regular spot checks during the day. Data acquisition was stopped daily at around 11:30 for download of data and house keeping (down for about 2 hours). Two major discontinuities in data acquisition were caused by site power failure, Sept. 10-11, and the failure of a high voltage

rectifier in the xenon lamp power supply on Sept. 15. All other discontinuities in the evaluated data, are due to fog, rain, and optical drift due to thermal problems.

Data points were obtained approx. every 4.5 min. Each data point was an average of 20,000 scans. The raw data was automatically stored along side with the evaluated results. The data was re-evaluated in the laboratory to provide hour average values

The output of the DOAS spectrometer is a raw spectrum, divided into 670 segments or 'channels'. Initially, a high order (9th) polynomial is fitted to the spectrum to remove the large scale features that are due primarily to the spectrum of the xenon lamp. Each channel in the spectrum is divided by the corresponding channel in the polynomial to produce a normalized spectrum. In such a spectrum, the value of each channel in the absence of an absorption feature equals unity.

In order to correlate the incoming spectrum with reference gas spectra, the indicated wavelengths in each spectrum over the region of interest must coincide. In general, this will not be the case since the indicated wavelengths of the DOAS spectrometer may not agree exactly with the instrument used for the values in the literature. One of the spectra, either the observed or the reference, may have to be shifted and/or squeezed to rectify any differences.

In the case of the measurements in Claremont, the NO<sub>2</sub> contribution was always sufficient to yield clear absorption bands. A reference NO<sub>2</sub> spectrum (Bass et. al., 1976) was shifted to match the observed NO<sub>2</sub> absorption bands. A similar treatment was applied to the HONO reference spectrum (Stockwell and Calvert 1978).

The corrected synthetic spectra were then fitted to the raw spectrum, using a linear least-squares fitting routine. The fit coefficients, together with the differential absorption coefficients (Platt and Perner, 1980) for specific bands, were used to calculate concentrations of gases over the observed path length.

The DOAS software allows these data processing steps to be included in an ASCII script file that defines an automatic data acquisition procedure. During the Claremont field period, data was processed and made available as 'real-time' hard copy. Because of the severe diurnal temperature changes at Claremont, corrections to the reference spectra were needed on at least an hourly basis. The data was post-processed at Claremont with new correction values estimated and applied batchwise to the data, a very tedious process.

A new function was written to track automatically the strong NO<sub>2</sub> absorption feature at approximately 364 nm. The function then stretched the incoming spectrum so that the position of the feature agreed exactly with the corresponding feature in the synthetic spectrum. All the NO<sub>2</sub>/HONO data presented in this report has been processed using this function.

Better correlation coefficients were obtained for HONO if the NO<sub>2</sub> contribution was fitted and stripped before fitting the HONO reference spectrum, as compared to a simultaneous fitting procedure.

We can derive an accuracy for DOAS measurements from the estimated errors in the following components:

1)	Length of optical path	1%
2)	Determination of absorption cross-sections	5%
3)	Wavelength normalization/polynomial fitting	1%
4)	Wavelength shifts and fitting coefficients	5%
5)	Random system/electronic noise	3%
	<b>Total</b>	<b>15%</b>

We have estimated detection limits for the other gases based on their differential absorption cross-sections relative to  $\text{NO}_2$ . Thus, we estimate the approximate detection limits for HONO and  $\text{NO}_3$  to be 30 pptv and 5 pptv respectively. For these less abundant species, which can be only analyzed after stripping any major species from the raw spectra, the variability of item 4 of the major species would be added to the variability of determination of the minor species to give an overall figure of ~20%.

### 3.3 Luminox<sup>R</sup> $\text{NO}_2$ , $\text{NO}_x$ , PAN and $\text{O}_3$ Sampling and Calibration Procedures

The Luminox<sup>R</sup> analyzers and the Dasibi  $\text{O}_3$  monitor were located in the Unisearch mobile laboratory along with the TDLAS system. Air was sampled through Teflon lines at the rear of the mobile lab at roof level at the same point as the TDLAS sampled. Separate sampling lines were used for each instrument type, one for  $\text{NO}_2/\text{NO}_x$ , one for the LOZ and Dasibi  $\text{O}_3$  analyzers and one for PAN. 5  $\mu\text{m}$  pore size filters were placed at the inlets to each instrument to remove particles. A common filter was used for the LOZ and Dasibi  $\text{O}_3$  analyzers to ensure they were both sampling the same air mass.

A common data acquisition/control system which averaged the instantaneous inputs from each analyzer was used to collect and store the information as one minute data points. For the PAN and both  $\text{O}_3$  instruments the data system simply averaged and stored the calibrated voltages provided by the instruments as the equivalent mixing ratios. In the case of the  $\text{NO}_2$  and  $\text{NO}_x$  measurements, the control system dictated the mode of operation so that in each one minute period, one 15 sec average  $\text{NO}_2$  value and one 15 second  $\text{NO}_x$  value was obtained. The control system caused a valve in the LNC-3 controller to switch so that the sampled air could either pass directly to the LMA-3  $\text{NO}_2$  analyzer (for a measurement of  $\text{NO}_2$ ) or pass through a converter that converted  $\text{NO}$  into  $\text{NO}_2$  (for a measurement of  $\text{NO}_x$ ) prior to injection into the LMA-3. After each valve switch, a 15 second delay was invoked to ensure that the air sampled was not contaminated by the previous mode. Once every 15 minutes a second valve was switched in which scrubbed the ambient air of  $\text{NO}_2$  so that a background measurement could be made.

Each instrument was calibrated daily as described in section 2.6. Calibrations were performed through the inlet filters to ensure that any losses would be accounted for by the

calibration procedure. All of the instruments with the exception of the Dasibi were measuring ambient air by 00:00 on September 1. The Dasibi analyzer was only used for calibrations prior to September 16 after which it also sampled ambient air. The instruments continued to operate with essentially no data loss (except for 01:00-05:00 on September 11 during the power failure) until 24:00 September 24 when they were turned off.

The detection limits of the LMA-3 for  $\text{NO}_2$ , (3x the noise) have been determined experimentally to be  $\sim 5$  pptv. The LPA-4 PAN analyzer has a computed detection limit of 30 pptv and the LOZ detection limit is estimated to be  $\sim 100$  pptv. The accuracy of the  $\text{NO}_2$ ,  $\text{NO}_x$  and PAN measurements can be calculated from the following parameters, 5% for the permeation device uncertainty, 2% for the temperature variation in the permeation tube temperature control, 2% for the flow measurement, 1% for the measurement precision and 5% for the variation in the sensitivity between calibrations. This gives an estimated accuracy for  $\text{NO}_2$  of 15%. The  $\text{NO}_x$  and PAN measurements have the additional uncertainty of the efficiency of the converter (column in the case of PAN) over the measurement period which is assessed at 5% and gives a total accuracy for  $\text{NO}_x$  and PAN of 20%.

The LOZ is calibrated against the Dasibi  $\text{O}_3$  analyzer which itself is calibrated against the NIST absolute  $\text{O}_3$  standard via the Ontario Ministry of the Environment equivalent absolute standard. The variation in the Dasibi standard was found to be less than 3% between calibrations and the LOZ had a drift of less than 5% between calibrations so we estimate that the overall accuracy to be 10% or better.

### 3.4 Carbonyls

Carbonyl compounds in air are collected by drawing air through a cartridge impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH). The resulting products (hydrazones) are measured in the laboratory using high performance liquid chromatography to determine the levels of the carbonyl compounds originally present in air.

Automated carbonyl sequential samplers were used in the program. The sampler was equipped with timers to allow automatic multiple transfers to take place sequentially. Channel 1, 2 and 3 were independent, and they were programmed to sample over specific time period. To collect a parallel sample, Channel 4 was used. It was designed to collect a sample simultaneously with Channel 2 if the toggle switch was set to the Duplicate position. With the toggle at the Blank position, Channel 4 would collect a field blank. The sampling flow rate through the cartridge was regulated by differential flow controllers to approximately 800 ml per minute. The carbonyl samplers were entirely reliable throughout the study with no loss of data due to malfunction.

Cartridges were loaded daily into the sampler and were exposed according to the sampling schedule. Four four-hour integrated samples were collected each day. Periodically, blanks or duplicates were also taken. For each cartridge sample, information on the sampling date and time, cartridge number, sampler and channel number were recorded in a log sheet. Exposed cartridges were retrieved by field personnel the same day after exposure and stored refrigerated inside a sealed metal container. Exposed cartridges were returned at three to four day intervals to

the laboratory for extraction and analysis using high performance liquid chromatography. A total of 91 cartridges were analyzed.

An exposed cartridge was eluted with three milliliters of acetonitrile. An aliquot (~10  $\mu$ l) of the extract was injected using an autosampler into a Shimadzu LC 6 high performance liquid chromatograph for separation and UV detection (365 nm) of the carbonyl hydrazones using reverse phase (C18) chromatography with gradient elution. Carbonyl species measured included formaldehyde, acetaldehyde, acetone, propanal, crotonaldehyde, methylethyl ketone, butanal, C5, C6, C7 aliphatic carbonyls, benzaldehyde and tolualdehyde.

### 3.5 Hydrocarbons

Ambient air samples were integrated over a four hour period into six liter passivated (SUMMA polished) stainless steel canisters using a hydrocarbon sampler, which allowed sequential timed collection of two samples. An outlet pressure regulated Viton diaphragm pumped ambient air into the canister. The discharge rate of the pump was controlled by a stainless steel differential flow controller to allow steady pressurization of the canister to about 15 psig over the four hour period. However, unlike the carbonyl sampler, the hydrocarbon sampling unit was not entirely reliable, on occasion resulting in too rapid or too slow filling. Nevertheless, no data was lost due to these malfunctions, and, for these samples, only the integration time was uncertain but this did not invalidate the measurements. Hydrocarbon sampling followed the same schedule as carbonyl. Canister samples were returned to the laboratory at the same time with the carbonyl samples.

An aliquot of air sample in a canister was concentrated in a glass-bead packed freeze-out loop immersed in liquid Ar. The condensed volatile organic species in the loop was revolatilized using boiling hot water and injected into a Hewlett Packard 5890 Series II gas chromatograph upon switching the sampling valve from the LOAD to INJECT position. A 50-m, 0.2 mm ID PONA column (Hewlett Packard) with crosslinked methyl silicone stationary phase was used for the separation of C2-C12 hydrocarbons using temperature programming. The conditions were -55°C for 3 min., 15°/min to 40°, then 4°/min to 150°, and isothermal at 150° for 10 minutes. Detection was by flame ionization. The gas chromatograph was calibrated using NIST SRM 1666b (9.4 ppmv propane). Concentrations of the hydrocarbon species were expressed on a ppbC (parts-per-billion carbon) referencing to the propane standard. Identification of the hydrocarbon species in a sample was based on retention indices established from analysis of multiple standard mixtures from various sources, including Scott Specialty Gases, Supple, as well as standards prepared by AtmAA from neat compounds.

Methane was analyzed by gas chromatography using an eight-foot Porapak Q packed column and detected by FID. Carbon monoxide was also analyzed likewise with the column at dry ice temperature. In the case of CO, the column effluent was directed to a catalytic column containing In catalyst in hydrogen. CO was converted to CH<sub>4</sub> for detection using FID. A sample was injected using a fixed volume injection loop. The methane and CO mixed calibration standard was from Scott Specialty Gases.

## 4. RESULTS AND DISCUSSION

The data obtained for each group of species along with quality assurance information has been provided to ARB in spreadsheet format as hard copy and on floppy diskettes. All continuous data was provided as one hour average values along with standard deviations about the average value. Integrated samples were provided as interval average values.

The magnitude of the data sets does not permit complete reproduction here and only summaries or excerpt for example are provided. The one hour average TDLAS, DOAS and Luminox<sup>R</sup> measurements made during the study period are summarized in Appendix B. The carbonyl measurements are summarized in Appendix C and an example of the hydrocarbon analysis for one canister is provided in Appendix D. Qualitative observations for each species, or group of measurements in the case of the carbonyls and hydrocarbons, is provided below. No detailed interpretation of the data is presented here as it is outside the scope of this report.

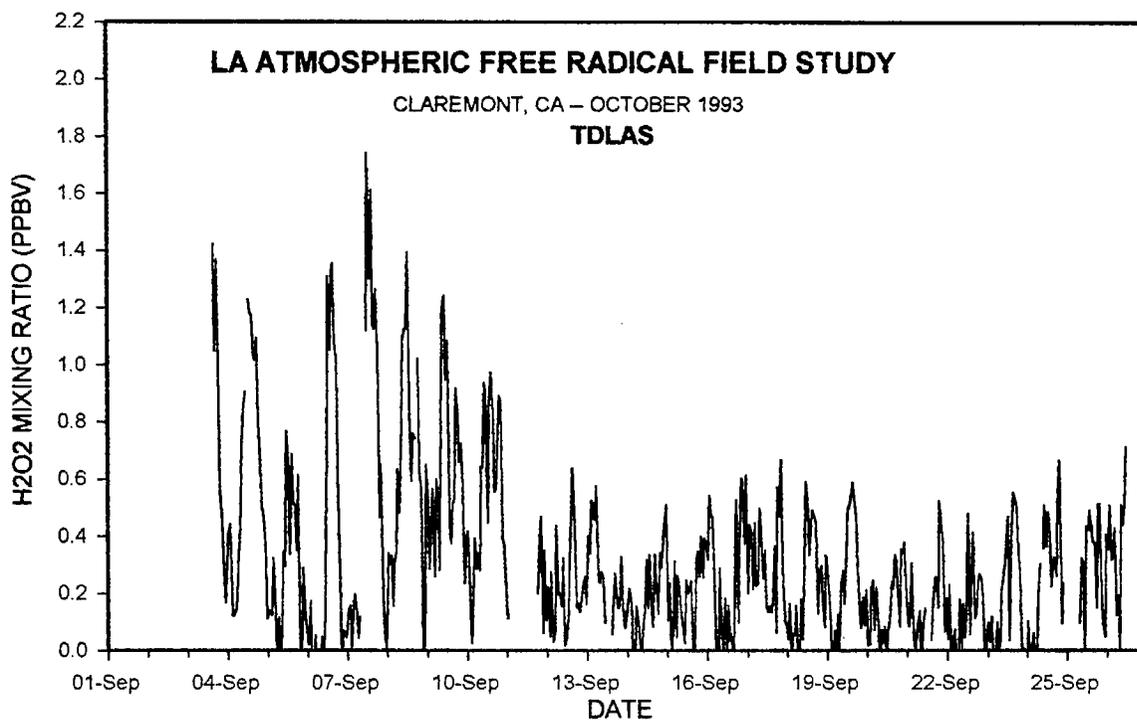
### 4.1 TDLAS H<sub>2</sub>O<sub>2</sub>, HCHO and HNO<sub>3</sub>

The H<sub>2</sub>O<sub>2</sub>, HCHO and HNO<sub>3</sub> averages were determined from the slope of a least squares fit of a calibration spectrum to the average of the ambient spectra acquired over a one hour period and calculated at the point situated in the middle of the time period; i.e. the data point at 10:30 includes all spectra acquired in the time period 10:00 through 11:00.

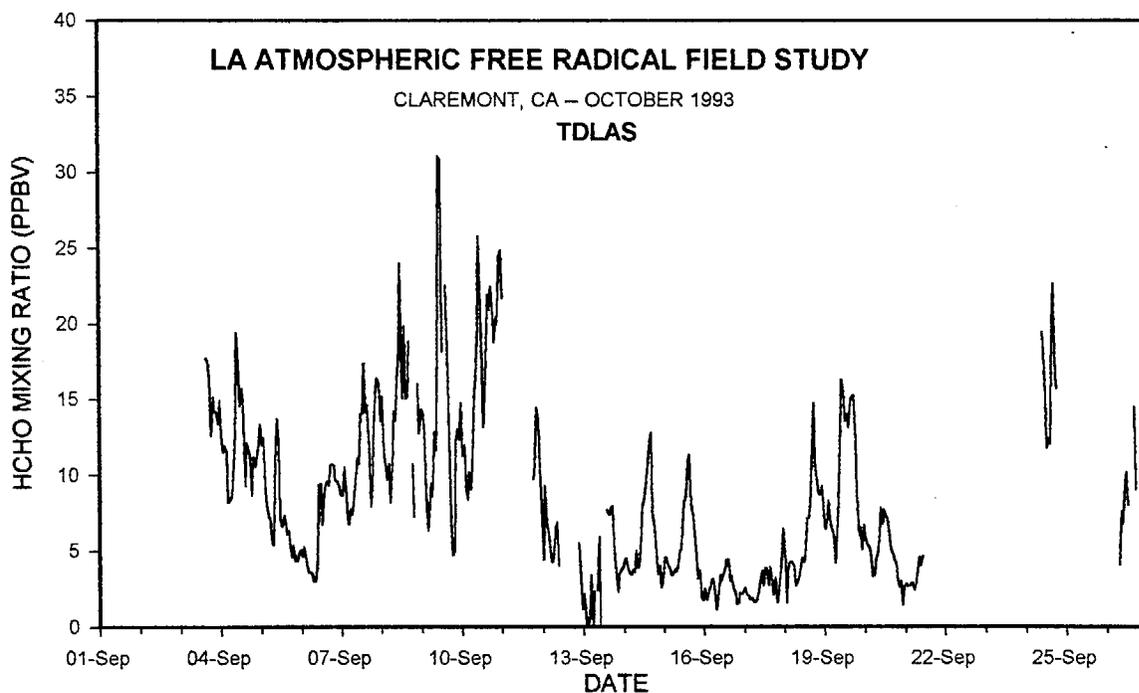
Figure 5 shows the diurnal behavior of H<sub>2</sub>O<sub>2</sub> during the study period. The variation is quite regular with daily maxima occurring between 11:00 and 15:00. The results are quite similar to those observed during the summer 1987 SCAQS at Claremont (Mackay 1988). The highest hour average measured occurred on September 7 when the value reached 1.8 ppbv. Between September 9 and September 13 the H<sub>2</sub>O<sub>2</sub> daily maximum decreased from 1.2 ppbv to ~0.6 ppbv where it remained essentially constant for the remainder of the study period. Prior to September 10 the weather at the site was hot and dry. After September 11, fog or light drizzle was often encountered in the night or early morning that may have accounted for the decrease in the daytime H<sub>2</sub>O<sub>2</sub> maxima. Nighttime values usually were below 0.1 ppbv and often below the detection limit of 0.05 ppbv throughout the study.

Figure 6 shows the diurnal behavior of HCHO during the study period. HCHO also usually showed a mid-day maximum, however, the behavior was not regular during the early part of the study (through September 11) largely due to high nighttime values which often exceeded 5 ppbv. After September 11, the diurnal behavior was more regular and nighttime values were generally below 0.5 ppbv. The extent to which the topography of the site determined the HCHO levels is not certain but the variability is quite dissimilar to the results obtained during the summer 1987 SCAQS (Mackay 1988) at a site less than 1/2 mile to the west of the present location.

The highest daily maximum occurred on September 10, two days later than the maximum in H<sub>2</sub>O<sub>2</sub>. A rapid decrease in the daily maxima occurred on September 13, several days later but consistent with the H<sub>2</sub>O<sub>2</sub> observations. Except for September 24, HCHO was generally lower after September 12. On only one occasion, the night of September 13, when it rained at the site, did the measured HCHO mixing ratio decrease below the detection limit of 0.2 ppbv. At all other times HCHO was 2 ppbv or greater.



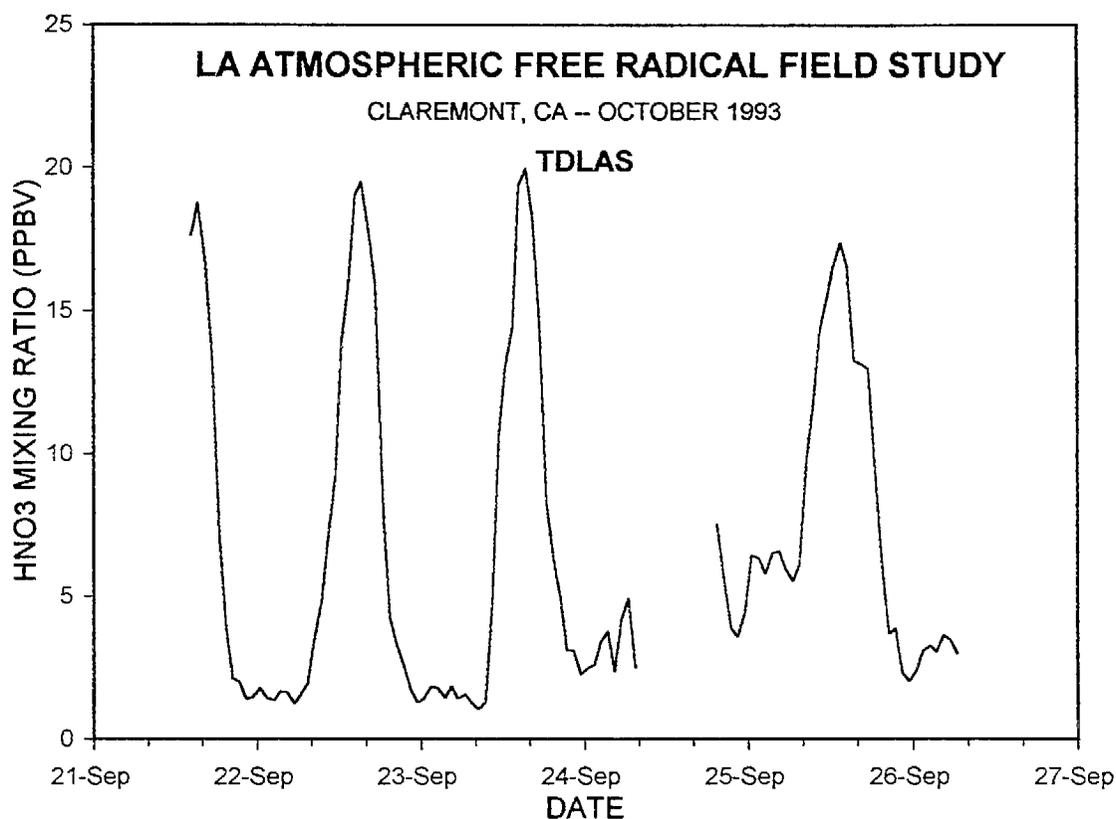
**FIGURE 5:** Diurnal behavior of the 1 hour averaged H<sub>2</sub>O<sub>2</sub> mixing ratio measured by the tunable diode laser absorption spectrometer during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993.



**FIGURE 6:** Diurnal behavior of the 1 hour averaged HCHO mixing ratio measured by the tunable diode laser absorption spectrometer during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993.

On many of the measurement days at both sites a double maximum in the HCHO signal was observed. The first occurred during the morning, ~08:00-11:00, and the second peak occurred in the afternoon, 12:00-16:00. The results are similar to those first recorded during the Carbonaceous Species Methods Comparison Study at Glendora, CA in 1986 (Lawson et. al. (1988)) where the morning peak was found to correlate well with directly injected pollutants such as  $\text{NO}_x$  and particulate black carbon concentrations and the afternoon peak was associated with arrival of photochemically produced ozone.

$\text{HNO}_3$  was measured simultaneously with  $\text{H}_2\text{O}_2$  during the period September 21 through September 26 with nighttime only values on September 24 and 26. As shown in figure 7, the diurnal variation of  $\text{HNO}_3$  is as expected with daytime maxima ~20 ppbv and nighttime minima of ~2 ppbv. These results are consistent with previous measurements of  $\text{HNO}_3$  in the LA basin (Mackay 1986).

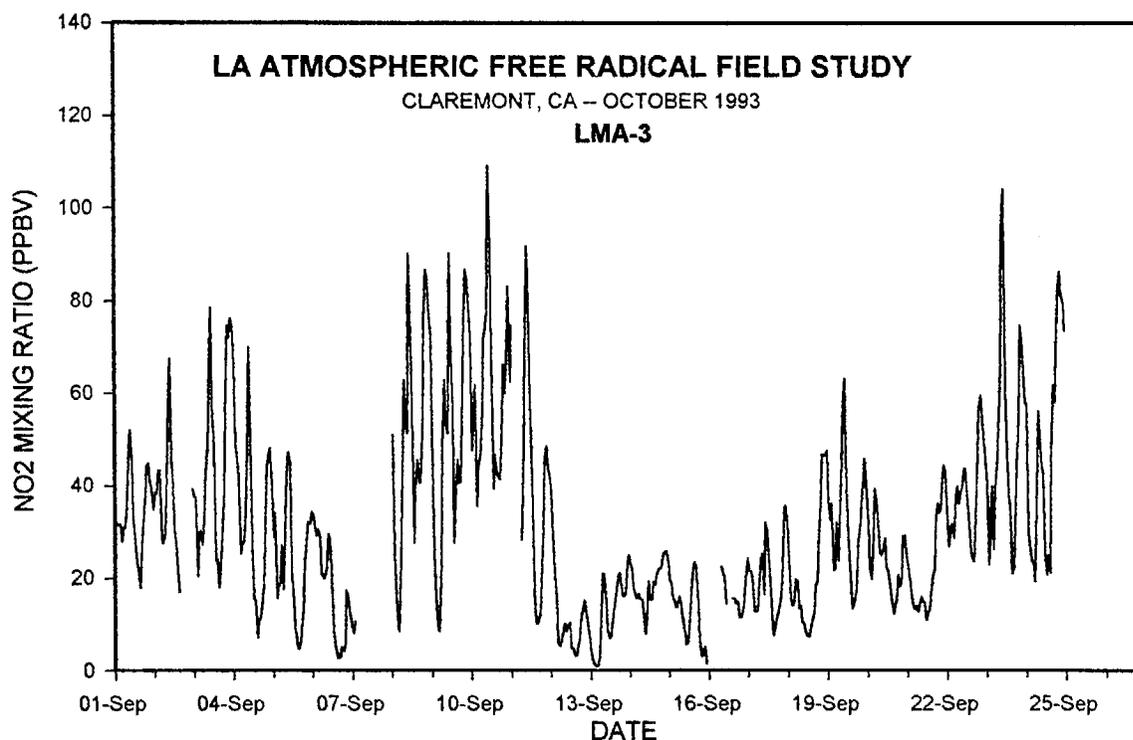


**FIGURE 7:** Diurnal behavior of the 1 hour averaged  $\text{HNO}_3$  mixing ratio measured by the tunable diode laser absorption spectrometer during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993.

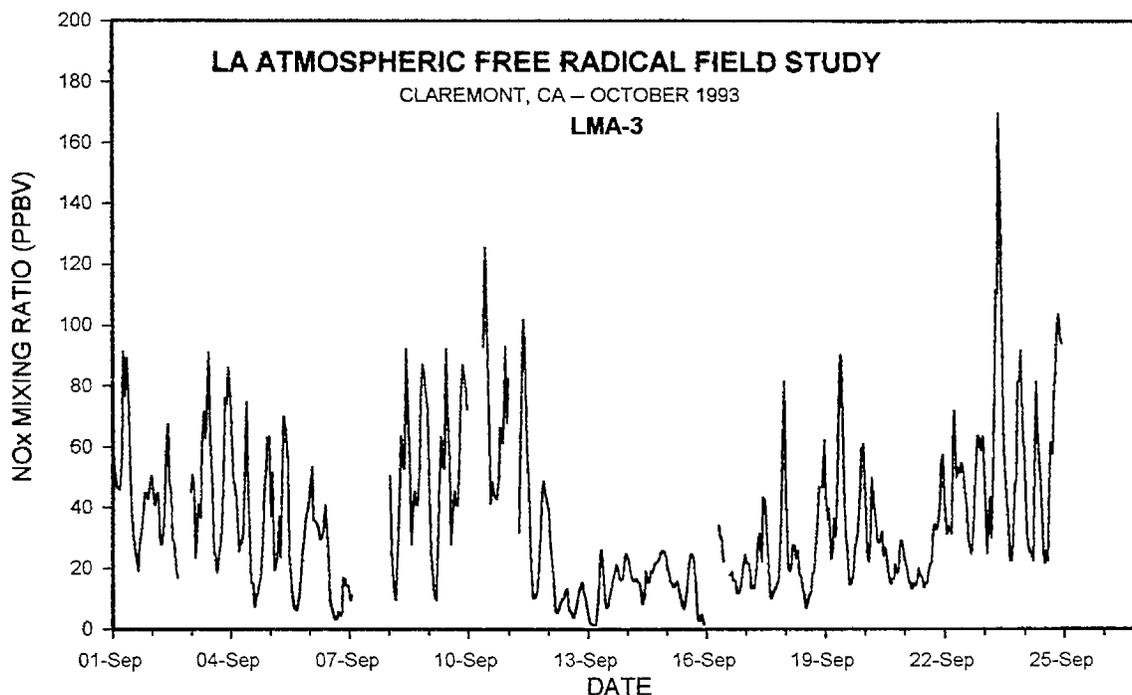
#### 4.2 Luminox<sup>R</sup> NO<sub>2</sub>, NO<sub>x</sub>, PAN and O<sub>3</sub>

NO<sub>2</sub> and NO<sub>x</sub> (and NO) show behavior expected at the site with maximum values over 100 ppbv on occasion with values generally in the 20 to 50 ppbv range. Two maxima were usually observed each day which correlated with the morning and evening traffic density. NO was observed to decrease to zero (as expected) in the middle of the day when O<sub>3</sub> maximized. NO<sub>2</sub> was highest during the periods September 8-11 and September 23-25 and lowest between September 12 and September 18. The highest value (~110 ppbv) was recorded on the evening of September 11. NO was highest during the period September 18 through September 25 with the highest value (~70 ppbv) recorded on September 23. These variations correlated with periods of hot-dry and cool-damp weather respectively.

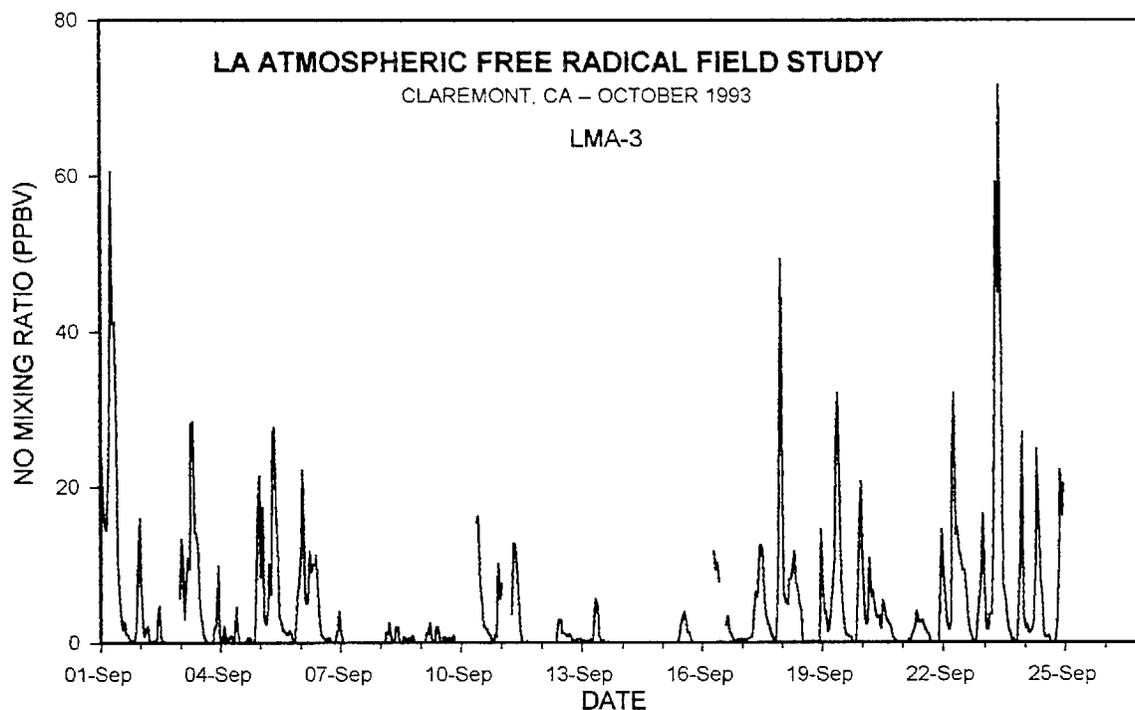
The PAN mixing ratios shown in Figure 11 exhibited similar behavior to NO<sub>2</sub> except that daily maxima generally occurred at mid-afternoon. The highest values again occurred during two periods of dry-warm weather, September 8-11 and September 23-25. The highest value was recorded on September 8 when the one hour averaged PAN levels reached 4.2 ppbv. During most of the rest of the study period the PAN maximum values ranged between 1 and 2 ppbv. Nighttime values were in the 100-300 pptv range except for the period of wet weather between September 12 and 18 when the nighttime values dropped below the detection limit of 30 pptv. Daytime values during this period often did not exceed 300 pptv.



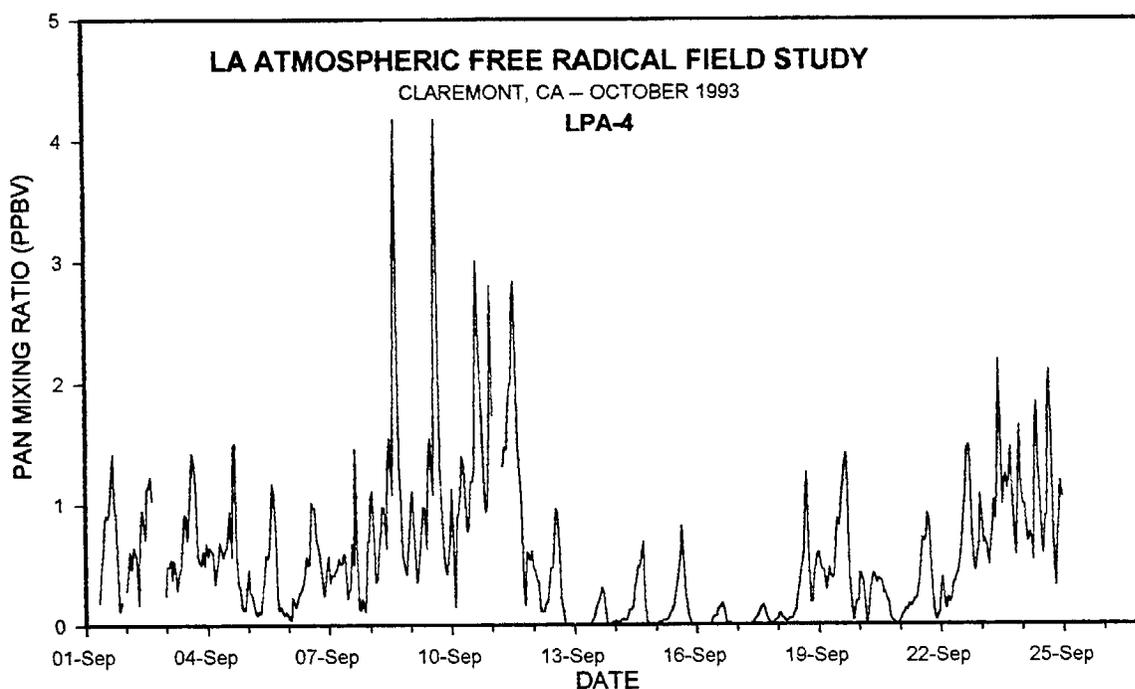
**FIGURE 8:** Diurnal behavior of the 1 hour averaged NO<sub>2</sub> mixing ratio measured by a Luminox<sup>R</sup> LNC-3 converter/sequencer combined with a LMA-3 NO<sub>2</sub> analyzer during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993.



**FIGURE 9:** Diurnal behavior of the 1 hour averaged NO<sub>x</sub> mixing ratio measured by a Luminox<sup>R</sup> LNC-3 converter/sequencer combined with a LMA-3 NO<sub>2</sub> analyzer during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993.



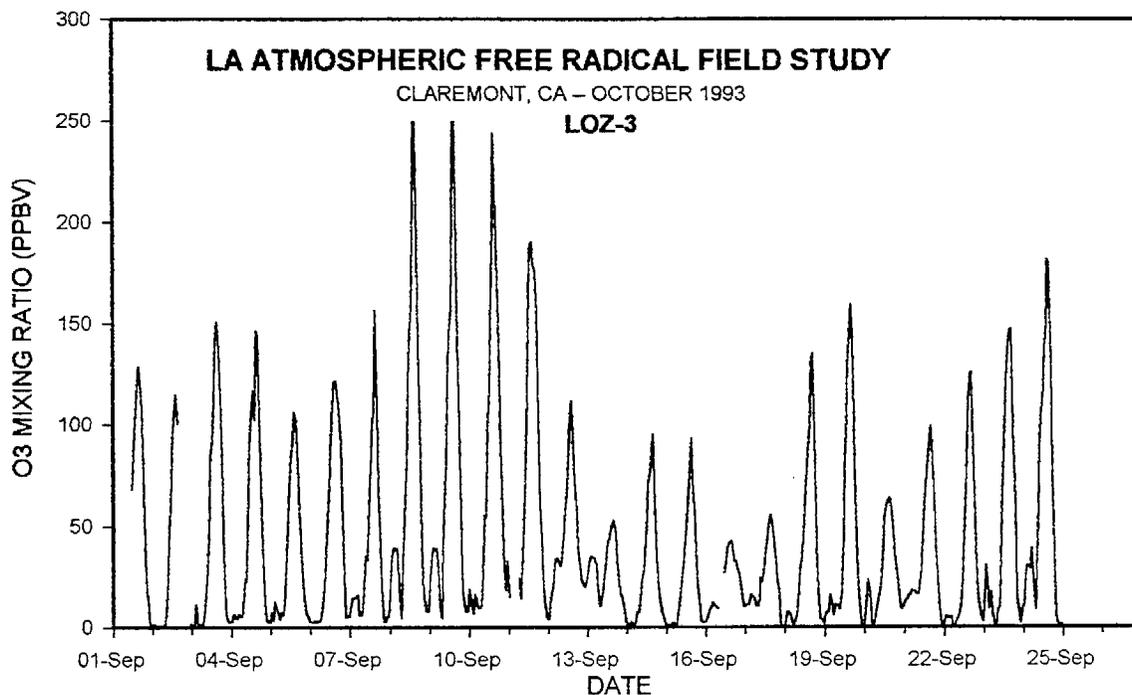
**FIGURE 10:** Diurnal behavior of the 1 hour averaged NO mixing ratio determined by subtracting the NO<sub>2</sub> measurement from the NO<sub>x</sub> measurement made by a Luminox<sup>R</sup> LNC-3 converter/sequencer combined with a LMA-3 NO<sub>2</sub> analyzer during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993.



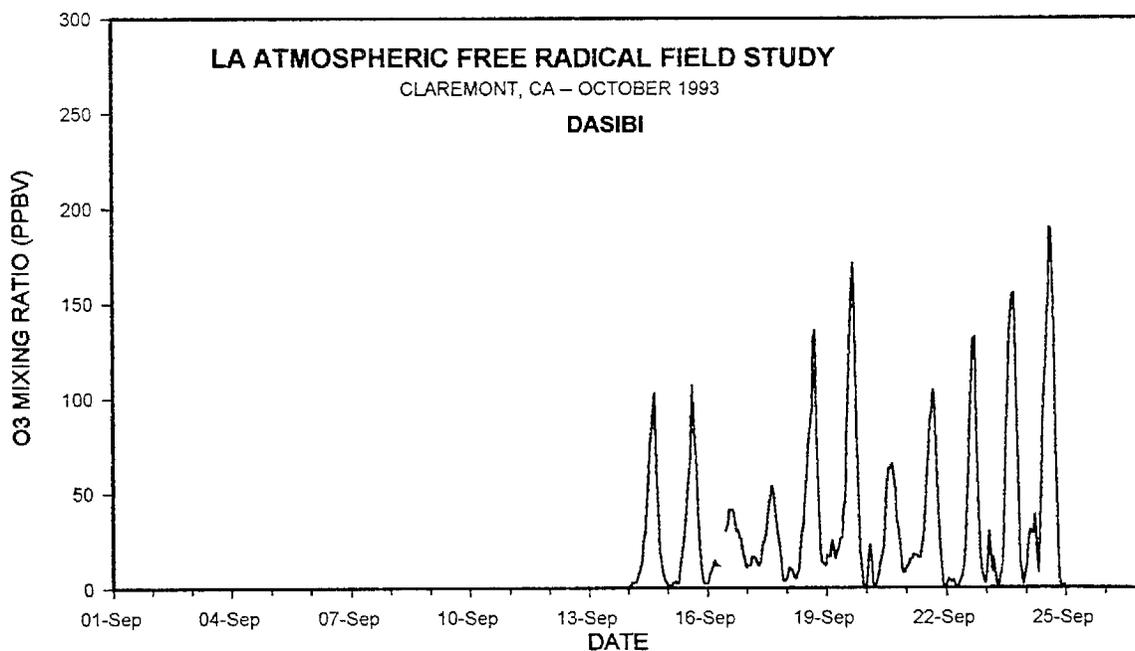
**FIGURE 11:** Diurnal behavior of the 1 hour averaged peroxyacetyl nitrate mixing ratio determined by the Luminox<sup>R</sup> LPA-4 PAN analyzer during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993.

The diurnal variation in ozone mixing ratio as measured by the Luminox<sup>R</sup> LOZ-3 during the study period is displayed in Figure 12. The results are typical of those expected in the LA basin with daytime maxima occurring in mid-afternoon. Maximum values were typically ~100 ppbv except for the period September 8-12 when values of almost 250 ppbv (September 8 and 9) were recorded. Nighttime mixing ratios usually were below a few ppbv except during the highest daytime period when nighttime values between 10 and 20 ppbv were recorded. This is not unexpected as NO levels during this period were very low.

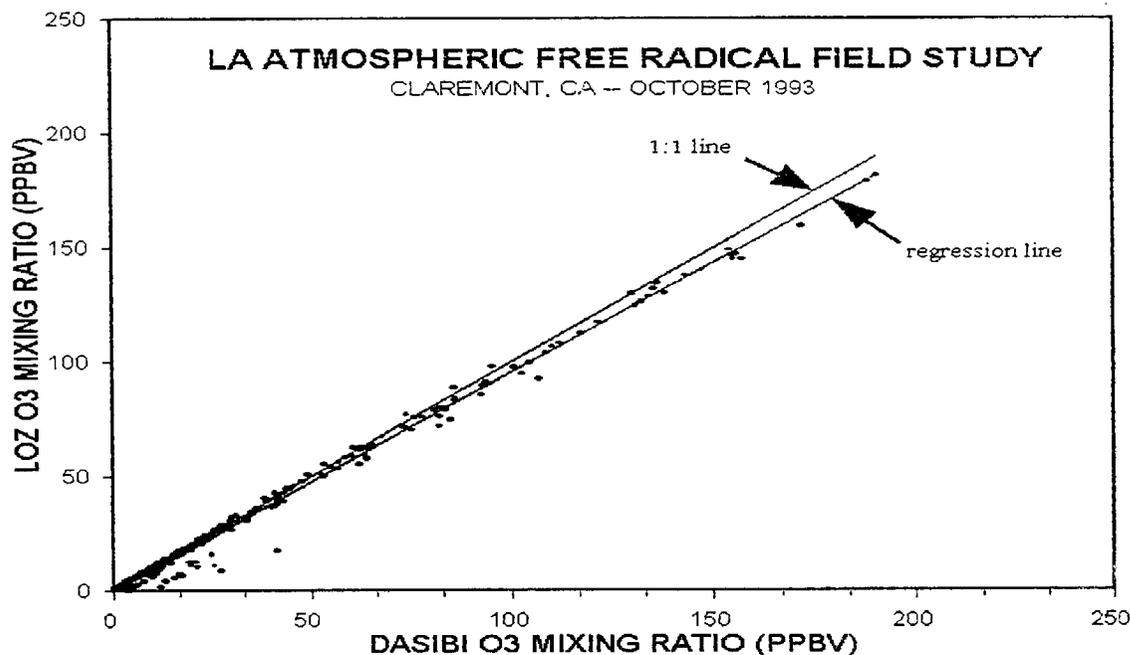
From the period September 14 through September 25, O<sub>3</sub> was also measured using a Dasibi UV-photometric analyzer. These results are shown in figure 13. The agreement between the two instruments is excellent. A correlation plot of the data obtained by the two instruments is shown in Figure 14. The regression analysis of 261 points obtained during the study period provides a slope = 0.96, intercept of -0.16 ppbv and a correlation coefficient of 0.993. The LOZ results are slightly lower than the Dasibi measurement although the deviation at 200 ppbv is only 10 ppbv (5%), well within the estimated uncertainty of the two instruments. A few outliers were observed at low O<sub>3</sub> mixing ratios when the Dasibi measured significantly higher than the LOZ-3. These occasions were at night and associated with high NO<sub>x</sub> levels during the day. This observation has been reported earlier (Drummond 1989b) and attributed to Dasibi scrubber contamination.



**FIGURE 12:** Diurnal behavior of the 1 hour averaged ozone mixing ratio determined by the Luminox<sup>®</sup> LOZ-3 O<sub>3</sub> analyzer during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993.



**FIGURE 13:** Diurnal behavior of the 1 hour averaged ozone mixing ratio determined by the Dasibi UV-photometric O<sub>3</sub> analyzer during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993.



**FIGURE 14:** Correlation plot of the 1 hour averaged ozone mixing ratio determined by the LOZ-3 chemiluminescence O<sub>3</sub> analyzer and the Dasibi UV-photometric O<sub>3</sub> analyzer during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993. Regression analysis provides: Slope = 0.96, Intercept = -0.16 ppbv and R<sup>2</sup> = 0.993

### 4.3 DOAS HONO, NO<sub>2</sub> and NO<sub>3</sub>

Examples of field spectra for NO<sub>2</sub>, HONO and NO<sub>3</sub> are shown in Figures 15-17, together with the corresponding reference spectra. Note that the HONO spectrum has already been stripped of NO<sub>2</sub>, which otherwise would completely obscure the HONO bands at 342, 354 and 368 nm.

The spectral window used (320 - 340 nm) covered some of the many HCHO absorption bands. Figure 18 contains an example of an HCHO calibration spectrum generated by inserting a cell containing HCHO vapor into the optical path. HCHO bands from atmospheric absorption have been observed in the spectra at Claremont but quantitative results require further processing and are not presented in this report.

The NO<sub>3</sub> absorption band at 662 nm has been observed (Figure 17) at Claremont but is partially obscured by other features in this spectral region. The source of these other bands is presently unknown, however, recent DOAS publications have indicated that poorly resolved water vapor bands may be present.

The overall shape of the spectrum in the 600 nm region in the current DOAS instrument shows sharp discontinuities, possibly as a result of vignetting at the exit aperture of the spectrometer. The extraneous bands seen in the fitted data may be due to oscillations induced in the fitting of the polynomial to the raw spectrum.

Since the  $\text{NO}_2$  level at Claremont was highly variable but rarely fell below 5 ppbv, it is difficult to predict a detection limit for  $\text{NO}_2$  based on the current data. From earlier work in the summer at a site in Southern Ontario, where the  $\text{NO}_2$  level rarely exceeded 1 ppbv, we have estimated a detection limit based on a 2000 m path length (round trip) to be 100 pptv for the 6 min integration period used for these measurements.

As noted above, the calculation of gas concentrations is based on fitting a reference spectrum to the observed spectrum. The depth of a standard feature in the fitted spectrum is then measured and used together with a literature value for the absorption cross section to determine the concentration of gas along the path length viewed. The fitting procedures are based on least squared error routines in which the differences in each channel between the sum of the fitted contributions and the observed level are minimized. The presence of unknown species, features due to the lamp spectrum and random noise will alter the fitting coefficients. As the width of the spectrum fitted increases, more features of the reference gas are included improving, in principle, the selectivity. As the bandwidth increases, one could expect that the fitting coefficients might vary on either side of the 'true' values but, in practice, the coefficients always seem to decrease.

Figures 19 through 21 display the diurnal variation in the  $\text{NO}_2$ , HONO and  $\text{NO}_3$  measurements made by the DOAS during the field study. The results for  $\text{NO}_2$  are similar to those obtained by the Luminox<sup>R</sup> point monitor for  $\text{NO}_2$  levels below about 40 ppbv. Above that level the Luminox<sup>R</sup> values are generally higher than the DOAS measurements except on September 20 when for two short periods of time the long path measurement was significantly higher than the point measurement. The narrowness of the high spike in the DOAS measurement might be indicative of an error in the analysis although this was not readily apparent from an inspection of the data files.

The correlation of the long-path DOAS  $\text{NO}_2$  measurements with the point LMA-3 measurements is shown in Figure 22 for two sets of overnight data spanning a period of heavy pollution. The slope of the regression line through the data is 0.56, indicating that the long-path measurements are significantly lower than the point measurements. This is in contrast to measurements made using the same instrument at a rural site where there were no significant local sources of  $\text{NO}_2$  (Nadler 1992). At the latter site, the agreement between the point monitor and the DOAS was excellent with the regression analysis providing a slope = 0.92, an intercept of 0.2 ppbv and  $R^2 = 0.98$ . In light of these observations, the possibility exists that the discrepancy may be due to actual differences in the air mass monitored and due to the topography of the site, the integrated values over the quarry were lower than the point measurements which were made close to a busy highway. This may have some implications in the interpretation of the HONO data discussed below.

The HONO measurements obtained by the DOAS appear to be consistent with values measured previously in the LA basin. The peak in the mixing ratio occurs around midnight and HONO is generally below the detection limit of the instrument (30 pptv) during the daylight hours. The highest HONO value was measured during the early morning of September 10 when it reached a level of almost 2.5 ppbv. This is the same period of high pollution noted for the other species. During the majority of the study the HONO nighttime

maxima were in the 1 to 1.5 ppbv range with the exception of the cool damp period from September 13 -18.

NO<sub>3</sub> was measured on four occasions, the nights of September 13-14, 19-20, 20-21 and 22-23. The measurements were made only to get information on the ambient mixing ratio periodically during the latter part of the study and no effort was made to follow the diurnal variation. For this reason only 2-5 hours of data were acquired during each measurement period. The measurements indicate that the NO<sub>3</sub> levels were between 80 and 200 pptv in the hours about midnight at the site.

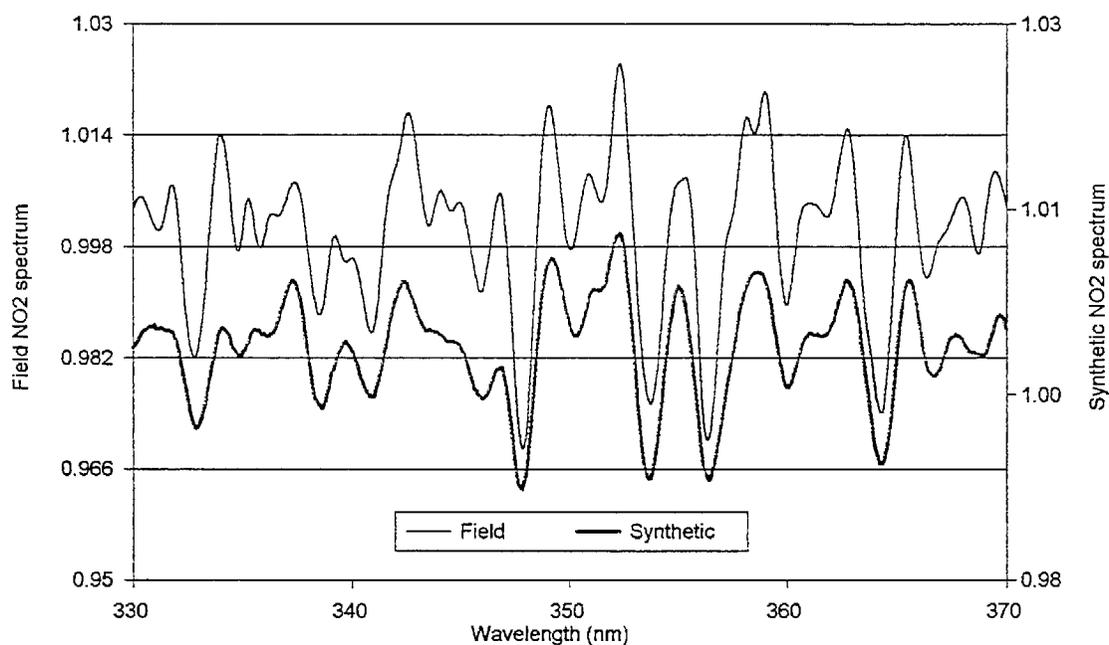
#### 4.4 Carbonyl Measurements

All targeted carbonyl species were at measurable levels much of the time except for the aromatic aldehydes, which were detected periodically. Summary statistics along with the complete data set are presented in Appendix C. In general, the predominant carbonyl species were formaldehyde, acetaldehyde, acetone and methylethyl ketone. Daytime levels tended to be higher than nighttime. The highest concentrations occurred on the afternoon and evening of September 10, with a gradual build-up which started from the afternoon of September 7. Formaldehyde reached approximately 31 ppbv. There were some moderately elevated levels noted around the fourth week of September. Otherwise the HCHO levels were fairly flat modulating between approximately 2 to 6 ppbv. The diurnal profiles of the other carbonyls mimicked formaldehyde closely. Because four hour integrated samples were taken during this study, the usual early morning and late afternoon peaks were less apparent in this study.

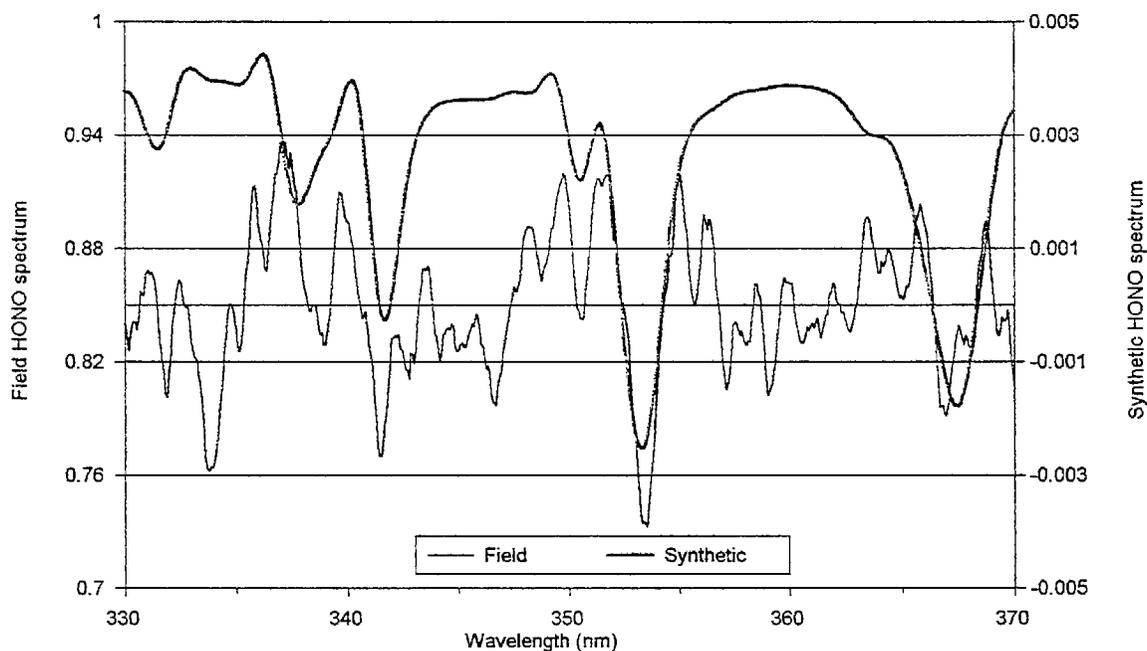
#### 4.5 Hydrocarbon Measurements

Approximately 150 species, accounting for about 70 to 80% of the VOC in the sample were identified. An example of the analysis for one canister is provided in Appendix D. There were some very large tailing peaks, presumably from polar/oxygenated compounds, in almost all of the samples from approximately the first 2 weeks of the study. These peaks were likely alcohols or acetonitrile (from other sampling activities at the test site).

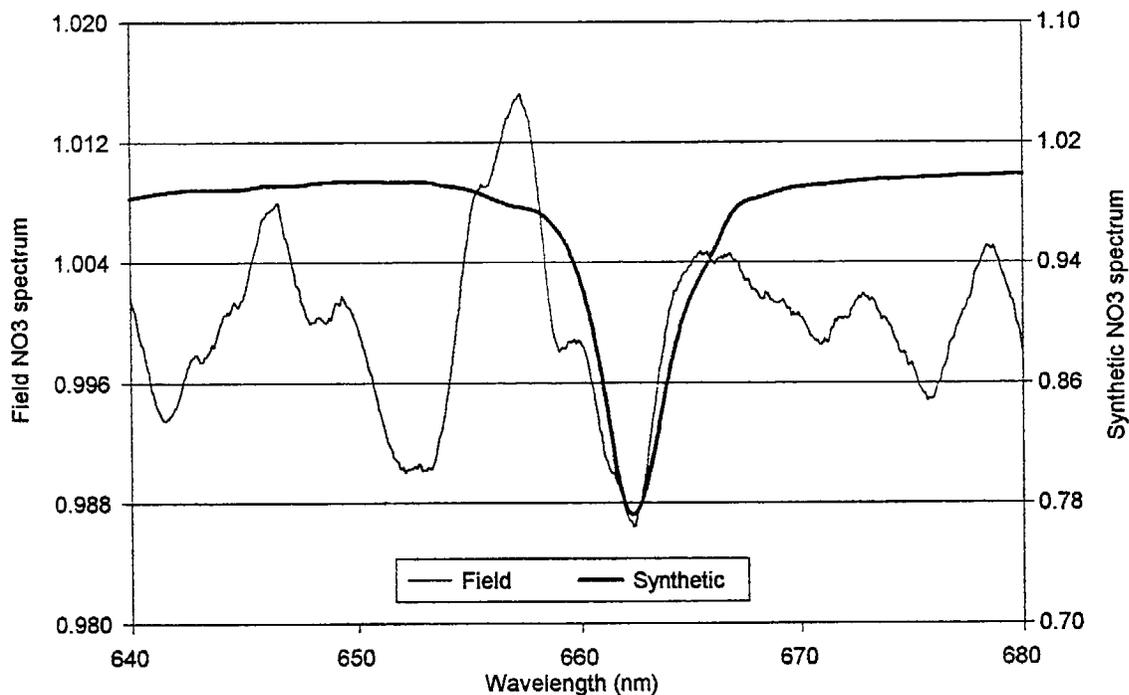
There were not too many high VOC days during this study. Except for one sample (a suspect), no others had total non-methane hydrocarbons (TNMHC) greater than 1 ppmC. The lowest TNMHC was about 100 ppbC for the midnight sample on September 13. The variation of HC and carbonyl levels appeared to track each other at a first approximation. Methane and Carbon Monoxide measurements are summarized in Appendix E. Methane levels ranged from approximately 1.6 to 2 ppmv. CO levels were lower than 1 ppmv for many of the samples. A detailed analysis of the VOC data will be needed to determine the significance of this data set in comparison with prior data base such as those from the Southern California Air Quality Study conducted in 1987.



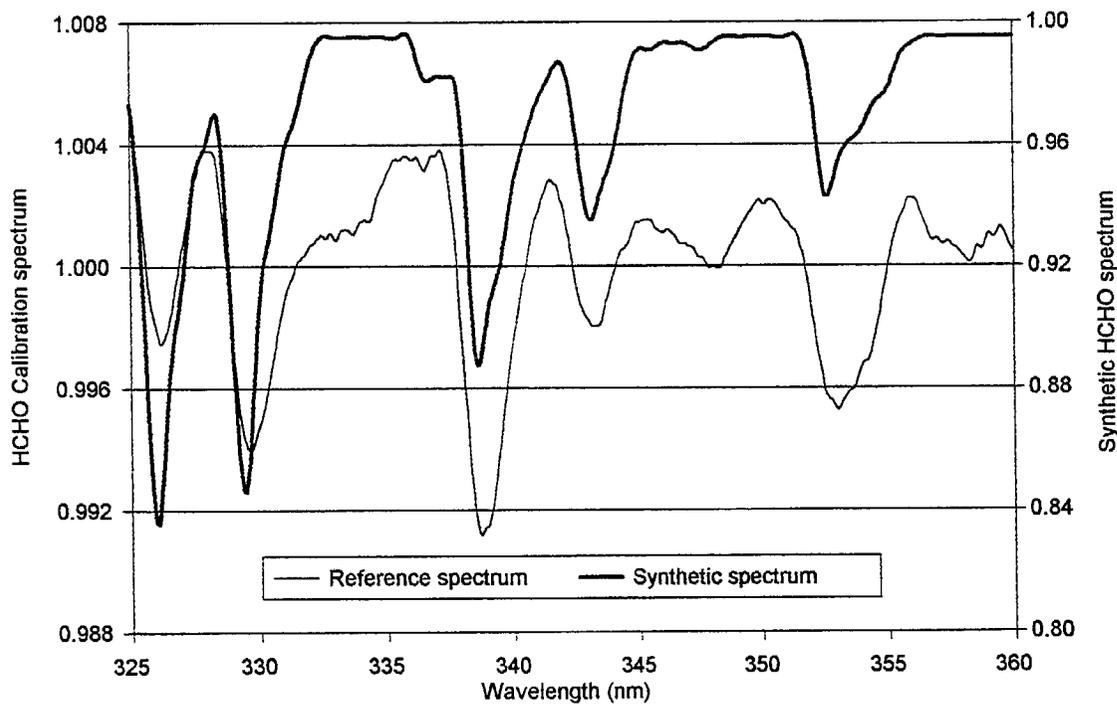
**FIGURE 15:** Typical differential optical absorption spectrometer spectra of  $\text{NO}_2$  obtained during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993. The lower trace is the synthetic spectrum.



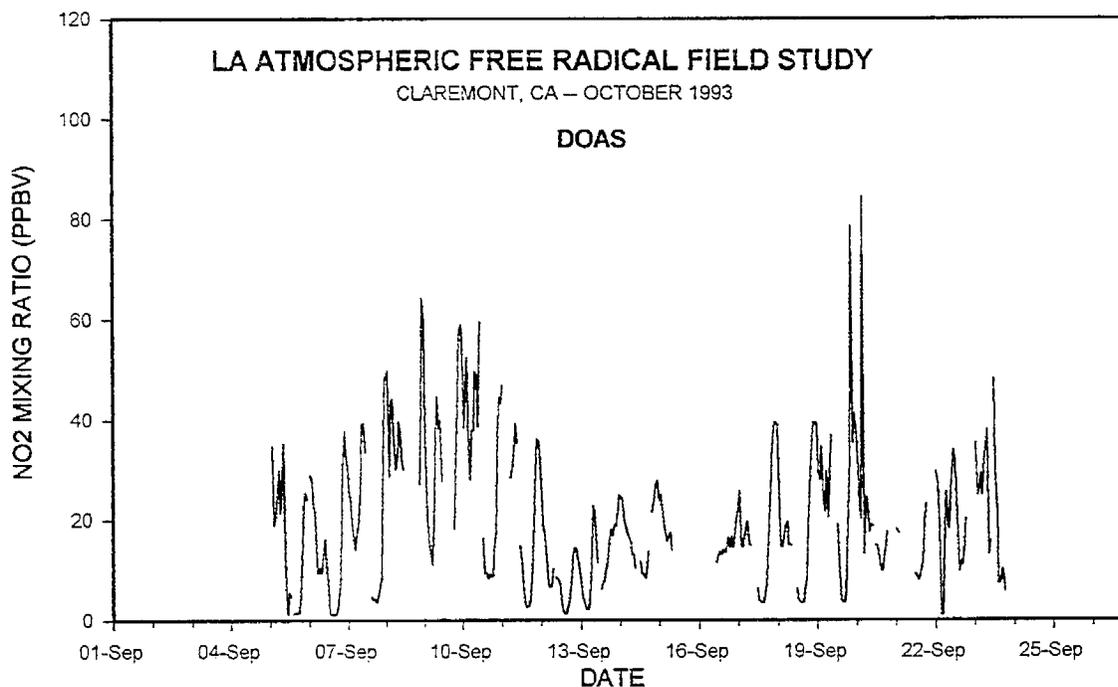
**FIGURE 16:** Typical residual differential optical absorption spectrometer spectra of HONO after  $\text{NO}_2$  has been removed which were obtained during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993. The upper trace is the synthetic spectrum.



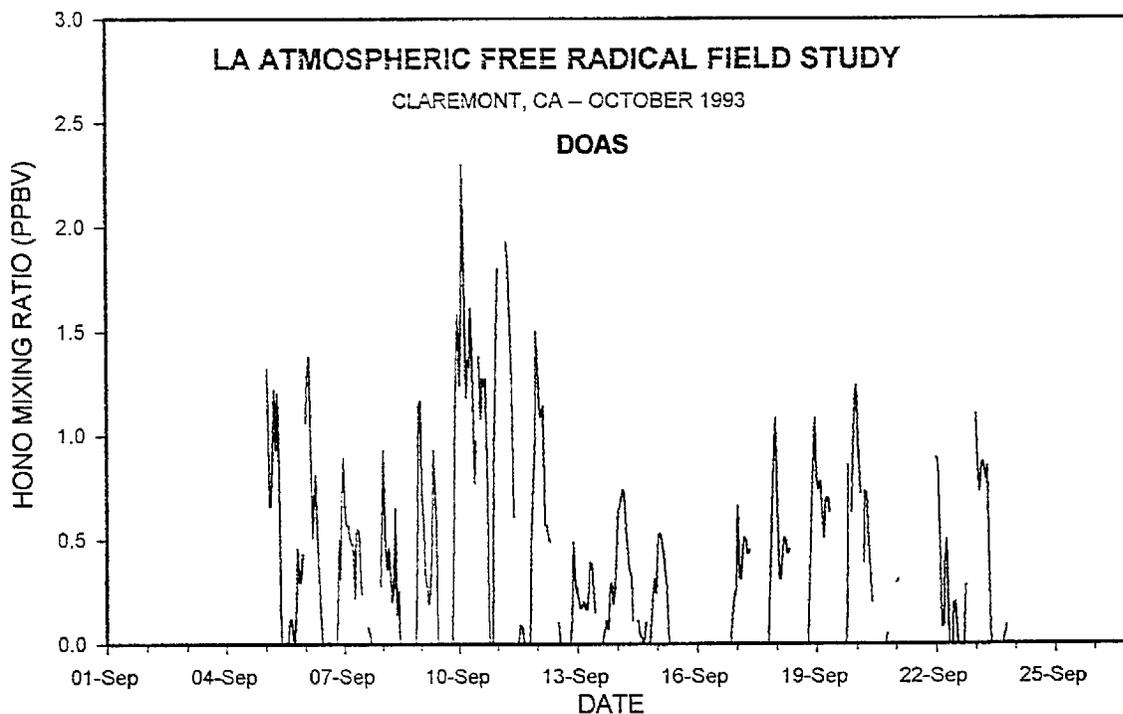
**FIGURE 17:** Typical differential optical absorption spectrometer spectra of  $\text{NO}_3$  obtained during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993. The upper trace is the synthetic spectrum



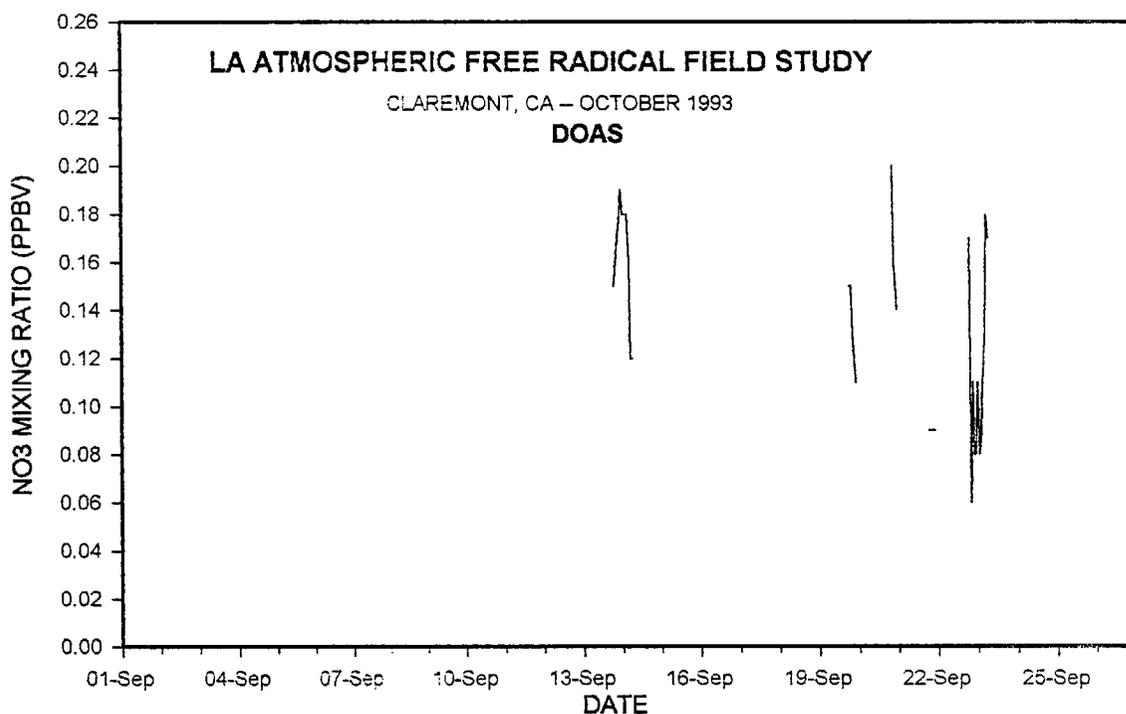
**FIGURE 18:** Typical differential optical absorption spectrometer spectra of HCHO obtained from a reference cell containing a high concentration of gaseous HCHO. The upper trace is the synthetic spectrum.



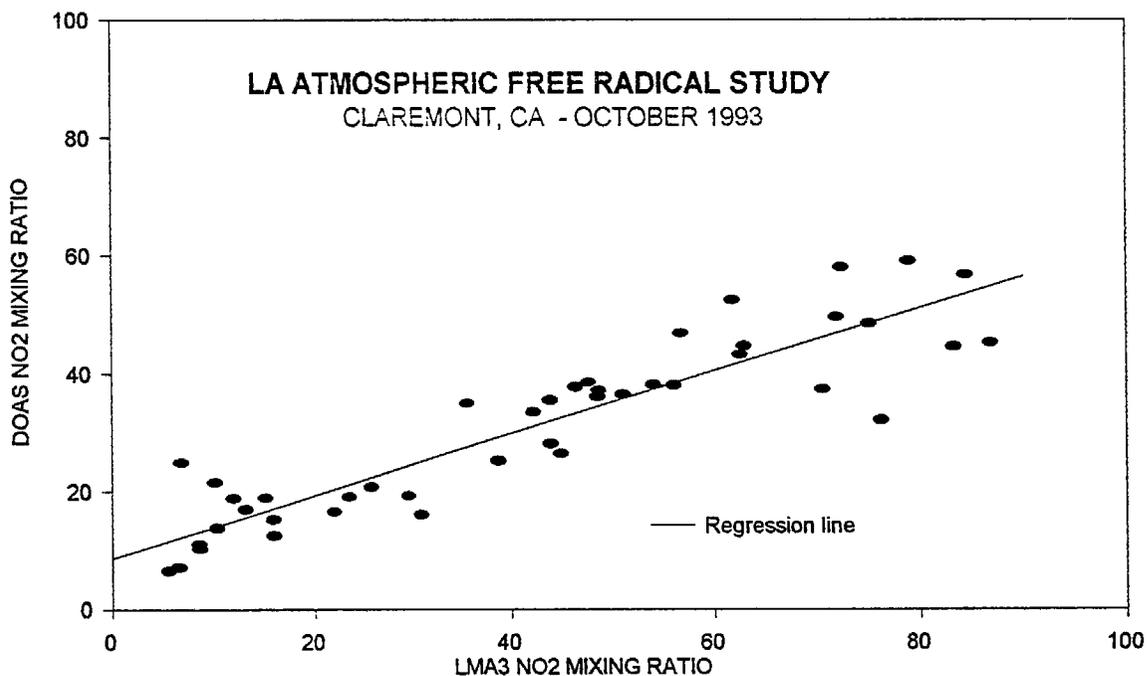
**FIGURE 19:** Diurnal behavior of the 1 hour averaged NO<sub>2</sub> mixing ratio measured by the differential optical absorption spectrometer during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993.



**FIGURE 20:** Diurnal behavior of the 1 hour averaged HONO mixing ratio measured by the differential optical absorption spectrometer during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993.



**FIGURE 21:** Diurnal behavior of the 1 hour averaged  $\text{NO}_3$  mixing ratio measured by the differential optical absorption spectrometer during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993.



**FIGURE 22:** Correlation plot of the 1 hour averaged  $\text{NO}_2$  mixing ratio determined by the LMA-3 chemiluminescence  $\text{NO}_2$  analyzer and the DOAS during the LA Atmospheric Free Radical Field Study at Claremont, CA during September, 1993. Regression analysis provides: Slope = 0.53, Intercept = 8.7 ppbv and  $R^2 = 0.83$

## 5. CONCLUSIONS

An extensive data set of many of the species implicated in the production of photochemical smog and acid deposition has been acquired over a 25 day period during September 1993. Continuous data was obtained on  $\text{NO}_2$ ,  $\text{NO}_x$ , peroxyacetyl nitrate,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , HCHO, and HONO over most of the sampling period and periodic measurements were made on  $\text{NO}_3$  and  $\text{HNO}_3$ . Integrated sampling techniques were employed to obtain 4 hour average measurement of carbonyls (C1-Benzaldehyde including CO) and hydrocarbons (C1-C12 including  $\text{CH}_4$ ). Most species were above the detection limits of the instrumentation for most of the study period.

Two episodes of high pollution were observed during the study, September 7-12 and September 22-25 when most of the species showed a marked increase in concentration over the values obtained at other times. During the first episode  $\text{O}_3$  levels exceeded 200 ppbv, PAN levels reached 4 ppbv and HCHO reached 30 ppbv.  $\text{H}_2\text{O}_2$  and HONO also maximized during this period. A period of wet weather separated the two episodes during which the concentrations of all species were greatly reduced.

Chemiluminescence and UV-photometric measurements of  $\text{O}_3$  agreed within the precision of the instrumentation. Long path differential optical absorption measurements of  $\text{NO}_2$  tended to be lower than point chemiluminescence measurements. The extent to which the topography of the site influenced this difference is a present uncertain but the proximity of the point monitor to a major highway and the presence of a large depression (quarry) along the DOAS path undoubtedly had some influence.

## 6. REFERENCES

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APPENDIX A  
QUALITY ASSURANCE DATA  
PROVIDED BY  
THE CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY  
AIR RESOURCES BOARD  
MONITORING AND LABORATORY DIVISION



CALIFORNIA AIR RESOURCES BOARD

FINAL PERFORMANCE AUDIT

BY

QUALITY ASSURANCE SECTION  
 MONITORING AND LABORATORY DIVISION  
 Manager: Alice Westerinen Ph: (916) 324-6191

Printout Date: 11/08/93

\*\*\*\*\*  
 Site: CLAREMONT-B ARB Site #: 70997 Audit Date: 09/16/93  
 \*\*\*\*\*

Final Audit Results For O3

Instrument #: EPA #: 056  
 Make & Model: DASIBI 1008AH

	Station Response	Station Net Resp.	True Value	Percent Difference
Zero:	0.006			
	0.405	0.399	0.406	-1.7
	0.184	0.178	0.181	-1.7
	0.075	0.069	0.072	-4.2

Average % Diff.	Standard % Dev.	Correlation	95% Probability Limits	
-2.5	1.4	.99999	Upper= 0	Lower= -5

Remarks: DAILY CALIBRATIONS. 4TH AUDIT PT W/TRUE VALUE OF 0.026 SHOWED % DIFFERENCE OF 0%.

Printout Date: 11/08/93

\*\*\*\*\*  
Site: CLAREMONT-B ARB Site #: 70997 Audit Date: 09/16/93  
\*\*\*\*\*

### Van Ozone Response

Barometric Display (Volts) = 0.8084  
Barometric Pressure (mmHg) = 727.558  
Altitude Correction Factor = 1.0445

Response	Chart	True
Pre Zero	= -0.100	
High	= 38.600	0.406
Medium	= 17.100	0.181
Low	= 6.700	0.072
Post Zero	= -0.200	

---

No Van Audit Level Concentrations

Printout Date: 11/08/93

\*\*\*\*\*  
Site: CLAREMONT-B ARB Site #: 70997 Audit Date: 09/16/93  
\*\*\*\*\*

Standards Van No.: B Year: 93 Quarter: 3 Version: 0

Superblend Cylinder Number: CC50758  
CO = 14860.00 THC = 6246.00  
CH4= 6246.00 NO = 347.20  
NOX= 347.20 SO2 = 150.50

H2S Superblend Cylinder Number: CC28237  
CO = 14010.00 H2S = 293.40

Cylinder	Conc.	ID Number
Ultra Pure Air =	0.000	CC56480
Low CO Cyl =	7.230	CC12921
High CO Cyl =	45.200	CC12145
O3 Corr Factor =	1.0203 +	-0.0012 08000
PM10 Corr Factor =	36.7000	0517
Dichot System Property Number = 2502		
Dichot System Total Slope =	0.984	Total Intercept = 0.106
Dichot System Coarse Slope =	0.997	Coarse Intercept = 0.012
Barometric Pressure System Property Number = 178105		
Barometric Pressure Slope =	406.339	Intercept = 399.074
Presentation Line Loss =	1.71%	
Meterological Equipment:		
Temp ID	%RH (Hygro.) ID	Wind direct ID
slope 0.00	%RH (Psych.) ID	Horiz Wind ID
inter 0.00		Vert Wind ID

**SITE INFORMATION**

Site Name: CLAREMONT-B

Site Number: 70997  
Agency Number: 63 Agency: PRIVATE STUDY  
Site Altitude: 383.7 Meters ( 1259 Feet)  
Station Tech: GERVASE MACKAY  
No Residence Time  
Audit Date: 09/16/93 Year: 93 Quarter: 3  
ARB Auditors: WARREN CRECY  
MIKE MIGUEL  
Van Number: B SOUTHWIND II  
Standards Version: 0  
Last Audit Date: / /  
Remarks: RESEARCH DIVISION SPECIAL STUDY.

CALIFORNIA AIR RESOURCES BOARD

FINAL PERFORMANCE AUDIT

BY

QUALITY ASSURANCE SECTION  
MONITORING AND LABORATORY DIVISION

Manager: Alice Westerinen

Ph: (916) 324-6191

Printout Date: 11/03/93

\*\*\*\*\*  
Site: CLAREMONT ARB Site #: 70999 Audit Date: 09/16/93  
\*\*\*\*\*

Final Audit Results For O3

Instrument #: EPA #:  
Make & Model: SCINTREX LOZ3

Station Response	Station Net Resp.	True Value	Percent Difference
Zero: 0.000			
0.320	0.320	0.406	-21.2
0.154	0.154	0.181	-14.9
0.062	0.062	0.072	-13.9

Average % Diff.	Standard % Dev.	Correlation	95% Probability Limits	
-16.7	3.9	.99942	Upper= -9	Lower= -24

Remarks: DAILY CALIBRATIONS. 4TH AUDIT PT W/TRUE VALUE 0.026 SHOWED % DIFFERENCE OF -7.7%

Final Audit Results For NO2

Instrument #: EPA #:  
Make & Model: SCINTREX LNC-3

Station Response	True Value	Percent Difference
0.107	0.110	-2.7
0.056	0.055	1.8
0.017	0.016	6.3

Average % Diff.	Standard % Dev.	Correlation	95% Probability Limits	
1.8	4.5	.99977	Upper= 11	Lower= -7

Average Converter Efficiency: 107.8 %

Remarks: DAILY CALIBRATION

Printout Date: 11/03/93

\*\*\*\*\*  
Site: CLAREMONT ARB Site #: 70999 Audit Date: 09/16/93  
\*\*\*\*\*

Van Ozone Response

Barometric Display (Volts) = 0.8084  
Barometric Pressure (mmHg) = 727.558  
Altitude Correction Factor = 1.0445

Response	Chart	True
Pre Zero	= -0.100	
High	= 38.600	0.406
Medium	= 17.100	0.181
Low	= 6.700	0.072
Post Zero	= -0.200	

Van Audit Level Concentrations

Level	Chart	Co	CH4	THC	NO	NOX	SO2	Dilution
1	0.0	0.0	0.00	0.00	0.000	0.000	0.000	0.00000
2	7.9	7.9	3.33	3.33	0.185	0.185	0.080	0.00053
3	6.5	6.5	2.74	2.74	0.152	0.152	0.066	0.00044
4	5.4	5.4	2.27	2.27	0.126	0.126	0.055	0.00036
5	3.8	3.8	1.60	1.60	0.089	0.089	0.039	0.00026

Van CO Analyzer Slope = 0.998156 Intercept = -.016671 Corr = 1.00000

		AADCO	Ultra Pure	Low CO	High CO
Pre	=	0.000	0.000	7.200	45.100
Post	=	0.000	0.000		45.100

Printout Date: 11/03/93

\*\*\*\*\*  
Site: CLAREMONT ARB Site #: 70999 Audit Date: 09/16/93  
\*\*\*\*\*

Standards Van No.: B Year: 93 Quarter: 3 Version: 0

Superblend Cylinder Number: CC50758  
CO = 14860.00 THC = 6246.00  
CH4= 6246.00 NO = 347.20  
NOX= 347.20 SO2 = 150.50

H2S Superblend Cylinder Number: CC28237  
CO = 14010.00 H2S = 293.40

Cylinder	Conc.	ID Number
Ultra Pure Air =	0.000	CC56480
Low CO Cyl =	7.230	CC12921
High CO Cyl =	45.200	CC12145
O3 Corr Factor =	1.0203 +	-0.0012 08000
PM10 Corr Factor =	36.7000	0517
Dichot System Property Number = 2502		
Dichot System Total Slope =	0.984	Total Intercept = 0.106
Dichot System Coarse Slope =	0.997	Coarse Intercept = 0.012
Barometric Pressure System Property Number = 178105		
Barometric Pressure Slope =	406.339	Intercept = 399.074
Presentation Line Loss = 1.71%		
Meterological Equipment:		
Temp ID	%RH (Hygro.) ID	Wind direct ID
slope 0.00	%RH (Psych.) ID	Horiz Wind ID
inter 0.00		Vert Wind ID

**SITE INFORMATION**

Site Name: CLAREMONT  
  
Site Number: 70999  
Agency Number: 63 Agency: PRIVATE STUDY  
Site Altitude: 383.7 Meters ( 1259 Feet)  
Station Tech: GERVASE MACKAY  
No Residence Time  
Audit Date: 09/16/93 Year: 93 Quarter: 3  
ARB Auditors: WARREN CRECY  
MIKE MIGUEL  
Van Number: B SOUTHWIND II  
Standards Version: 0  
Last Audit Date: / /  
Remarks: RESEARCH DIVISION SPECIAL STUDY

CALIFORNIA AIR RESOURCES BOARD

FINAL PERFORMANCE AUDIT

BY

QUALITY ASSURANCE SECTION  
MONITORING AND LABORATORY DIVISION

Manager: Alice Westerinen

Ph: (916) 324-6191

Printout Date: 11/03/93

\*\*\*\*\*  
Site: CLAREMONT #2 ARB Site #: 70998 Audit Date: 09/16/93  
\*\*\*\*\*

Final Audit Results For O3

Instrument #: 325719

EPA #: 047

Make & Model: TECO 49

	Station Response	Station Net Resp.	True Value	Percent Difference
Zero:	0.003			
	0.409	0.406	0.407	-0.2
	0.184	0.181	0.183	-1.1
	0.073	0.070	0.071	-1.4

Average % Diff.	Standard % Dev.	Correlation	95% Probability Limits	
-0.9	0.6	.99999	Upper= 0	Lower= -2

Remarks: LAST CALIBRATED 3/93. STATION RESPONSES TAKEN FROM INSTRUMENT.



Printout Date: 11/03/93

\*\*\*\*\*  
Site: CLAREMONT #2 ARB Site #: 70998 Audit Date: 09/16/93  
\*\*\*\*\*

Standards Van No.: B Year: 93 Quarter: 3 Version: 0

Superblend Cylinder Number: CC50758  
CO = 14860.00 THC = 6246.00  
CH4= 6246.00 NO = 347.20  
NOX= 347.20 SO2 = 150.50

H2S Superblend Cylinder Number: CC28237  
CO = 14010.00 H2S = 293.40

Cylinder	Conc.	ID Number
Ultra Pure Air =	0.000	CC56480
Low CO Cyl =	7.230	CC12921
High CO Cyl =	45.200	CC12145
O3 Corr Factor =	1.0203 +	-0.0012 08000
PM10 Corr Factor =	36.7000	0517
Dichot System Property Number = 2502		
Dichot System Total Slope =	0.984	Total Intercept = 0.106
Dichot System Coarse Slope =	0.997	Coarse Intercept = 0.012
Barometric Pressure System Property Number = 178105		
Barometric Pressure Slope =	406.339	Intercept = 399.074
Presentation Line Loss =	1.71%	
Meterological Equipment:		
Temp ID	%RH (Hygro.) ID	Wind direct ID
slope 0.00	%RH (Psych.) ID	Horiz Wind ID
inter 0.00		Vert Wind ID

**SITE INFORMATION**

Site Name: CLAREMONT #2

Site Number: 70998  
Agency Number: 63 Agency: PRIVATE STUDY  
Site Altitude: 383.7 Meters ( 1259 Feet)  
Station Tech: YANZENG ZHAO  
No Residence Time  
Audit Date: 09/16/93 Year: 93 Quarter: 3  
ARB Auditors: MIKE MIGUEL  
WARREN CRECY

Van Number: B SOUTHWIND II  
Standards Version: 0  
Last Audit Date: / /

Remarks: AUDIT DONE FOR ARB- RD. AUDIT PERFORMED THRU SAMPLE INLET.

Final Report  
07/01/93 To 09/30/93

AUDIT DATE	SITE NUMBER	AGENCY NUMBER	AGENCY DESCRIPTION	POLLUTANT	INSTRUMENT	PROPERTY NUMBER	STATION TYPE	AVERAGE % DIFFERENCE
** SITE #: 70997 SITE NAME: CLAREMONT-B								
09/16/93	70997	63	PRIVATE STUDY	O3	DASIBI 1008AH	9999	SPM	-2.5
** SITE #: 70998 SITE NAME: CLAREMONT #2								
09/16/93	70998	63	PRIVATE STUDY	O3	TECO 49	325719	SPM	-0.9
** SITE #: 70999 SITE NAME: CLAREMONT								
09/16/93	70999	63	PRIVATE STUDY	O3	SCINTREX LOE3	9999	SPM	-16.7
09/16/93	70999	63	PRIVATE STUDY	NO2	SCINTREX LNC-3	9999	SPM	1.8

ALL STATIONS  
07/01/93 To 09/30/93  
AIR QUALITY DATA ACCURACY ESTIMATES-BY SITE

AUDIT DATE	SITE #	AGENCY	POLLUTANT	AVE % DIFF	STANDARD DEVIATION	95% PROBABILITY LIMITS		BEST FIT LINEAR REGRESSION	
						UPPER	LOWER	SLOPE	INTERCEPT
** SITE #: 70997		SITE NAME: CLAREMONT-B		AGENCY: PRIVATE STUDY					
09/16/93	70997	63	03	-2.5	1.4	0.3	-5.3	0.9872	-0.0015
** SITE #: 70998		SITE NAME: CLAREMONT #2		AGENCY: PRIVATE STUDY					
09/16/93	70998	63	03	-0.9	0.6	0.3	-2.1	1.0006	-0.0015
** SITE #: 70999		SITE NAME: CLAREMONT		AGENCY: PRIVATE STUDY					
09/16/93	70999	63	03	-16.7	3.9	-8.9	-24.4	0.7673	0.0101
09/16/93	70999	63	NO2	1.8	4.5	10.6	-7.0	0.9555	0.0024

ALL STATIONS  
07/01/93 To 09/30/93  
AIR QUALITY DATA ACCURACY ESTIMATES-BY AUDIT TEST LEVEL

POLLUTANT	NUMBER OF AUDITS	EPA AUDIT RANGE	RANGE OF AUDIT POINTS	AVERAGE % DIFFERENCE	STANDARD DEVIATION	95 % PROBABILITY LIMITS	
						UPPER	LOWER
NO2	1	0.03 - 0.08 PPM	0.0160 -- 0.0160 *	6.2500	---	---	---
NO2	1	0.15 - 0.20 PPM	0.0550 -- 0.0550 *	1.8182	---	---	---
NO2	1	0.35 - 0.45 PPM	0.1100 -- 0.1100 *	-2.7273	---	---	---
O3	3	0.03 - 0.08 PPM	0.0710 -- 0.0720	-6.4880	6.5560	6.3619	-19.3379
O3	3	0.15 - 0.20 PPM	0.1810 -- 0.1830	-5.8892	7.8235	9.4450	-21.2233
O3	3	0.35 - 0.45 PPM	0.4060 -- 0.4070	-7.7174	11.6844	15.1840	-30.6187

\* - Data out of EPA range

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ALL STATIONS  
07/01/93 To 09/30/93  
AIR QUALITY DATA ACCURACY ESTIMATES-BY POLLUTANT

POLLUTANT	NUMBER OF ANALYZERS AUDITED	AVERAGE OF THE AVERAGE PERCENT DIFFERENCE	STANDARD DEVIATION	95% PROBABILITY LIMITS	
				UPPER %	LOWER %
NO2	1	1.7803	4.4888	10.5783	-7.0177
O3	3	-6.6982	2.4488	-1.8985	-11.4978



## APPENDIX B

Summary of the hour average mixing ratios measured by the TDLAS, DOAS and Luminox<sup>R</sup> instruments during the LA Atmospheric Free radical field study at Claremont, CA during September 1993.



LA ATMOSPHERIC FREE RADICAL FIELD STUDY

LOCATION: CLAREMONT, CALIFORNIA  
 SOURCE: UNISEARCH ASSOCIATES INC

DATE	START TIME	AVERAGE INTERVAL (HRS)	SPECIES:	HONO DOAS (ppbV)	NO2 DOAS (ppbV)	NO3 DOAS (ppbV)	NO LMA-3 (ppbV)	NO2 LMA-3 (ppbV)	NOx LMA-3 (ppbV)	O3 DASIBI (ppbV)	O3 LOZ-3 (ppbV)	PAN LPA-4 (ppbV)	H2O2 TDLAS (ppbV)	HCHO TDLAS (ppbV)	HNO3 TDLAS (ppbV)	
01-Sep	00:00	01:00					24.65	32.53	57.13							
01-Sep	01:00	01:00					18.65	31.61	50.30							
01-Sep	02:00	01:00					15.32	31.54	46.88							
01-Sep	03:00	01:00					14.39	31.75	46.22							
01-Sep	04:00	01:00					18.21	27.78	46.00							
01-Sep	05:00	01:00					26.41	31.02	57.40							
01-Sep	06:00	01:00					60.64	30.78	91.38							
01-Sep	07:00	01:00					40.96	35.56	76.74							
01-Sep	08:00	01:00					41.30	47.92	89.32							
01-Sep	09:00	01:00					26.66	52.06	78.63							
01-Sep	10:00	01:00					10.87	45.72	56.55							
01-Sep	11:00	01:00					5.57	33.10	38.55		67.90					
01-Sep	12:00	01:00					3.77	27.85	31.55		85.05					
01-Sep	13:00	01:00					1.69	23.59	25.46		101.25					
01-Sep	14:00	01:00					2.74	21.34	24.09		115.13					
01-Sep	15:00	01:00					1.05	17.94	19.12		128.70					
01-Sep	16:00	01:00					1.10	26.86	27.93		124.41					
01-Sep	17:00	01:00					0.32	31.85	32.26		108.43					
01-Sep	18:00	01:00					0.10	37.91	38.14		89.16					
01-Sep	19:00	01:00					0.24	44.27	44.62		42.11					
01-Sep	20:00	01:00					0.37	44.82	45.14		18.30					
01-Sep	21:00	01:00					1.55	41.25	42.77		13.95					
01-Sep	22:00	01:00					8.47	38.72	47.15		0.71					
01-Sep	23:00	01:00					16.04	34.85	50.87		0.00					
02-Sep	00:00	01:00					8.22	38.44	46.70		1.37					
02-Sep	01:00	01:00					2.39	38.25	40.65		1.63					
02-Sep	02:00	01:00					0.84	43.29	44.19		1.01					
02-Sep	03:00	01:00					1.82	43.31	45.12		0.27					
02-Sep	04:00	01:00					2.17	28.64	30.63		1.17					
02-Sep	05:00	01:00					0.07	27.49	27.70		0.31					
02-Sep	06:00	01:00					0.05	29.71	29.70		0.18					
02-Sep	07:00	01:00					0.25	37.55	37.99		1.51					
02-Sep	08:00	01:00					0.32	57.01	57.48		5.92					
02-Sep	09:00	01:00					0.02	67.55	67.51		22.46					
02-Sep	10:00	01:00					3.63	45.99	49.32		48.57					
02-Sep	11:00	01:00					4.75	39.72	44.41		62.24					
02-Sep	12:00	01:00					-0.15	30.16	29.94		94.57					
02-Sep	13:00	01:00					0.27	27.42	27.73		106.13					
02-Sep	14:00	01:00					-0.07	19.98	19.85		115.00					
02-Sep	15:00	01:00					-0.06	16.96	16.84		100.79					
02-Sep	16:00	01:00														
02-Sep	17:00	01:00														
02-Sep	18:00	01:00														
02-Sep	19:00	01:00														
02-Sep	20:00	01:00														
02-Sep	21:00	01:00														
02-Sep	22:00	01:00														
02-Sep	23:00	01:00														
							5.75	39.38	45.13		1.79					0.25

LA ATMOSPHERIC FREE RADICAL FIELD STUDY

LOCATION: CLAREMONT, CALIFORNIA  
 SOURCE: UNISEARCH ASSOCIATES INC

DATE	START TIME	AVERAGE INTERVAL	SPECIES:	HONO	NO2	NO3	NO	NO2	NOx	O3	O3	LOZ-3	PAN	H2O2	HCHO	HNO3
DD-MM	HH:MM	(HRS)	TECHNIQUE:	DOAS	DOAS	DOAS	LMA-3	LMA-3	LMA-3	DASIBI	LOZ-3	LPA-4	TDLAS	TDLAS	TDLAS	TDLAS
				(ppbV)												
03-Sep	00:00	01:00		13.36			37.48	50.84	0.04			0.49				
03-Sep	01:00	01:00		9.06			37.48	46.56	0.39			0.49				
03-Sep	02:00	01:00		3.01			20.49	23.40	11.76			0.54				
03-Sep	03:00	01:00		7.30			29.86	37.26	2.41			0.38				
03-Sep	04:00	01:00		10.92			30.08	41.03	0.92			0.53				
03-Sep	05:00	01:00		9.45			27.24	36.64	1.85			0.43				
03-Sep	06:00	01:00		28.10			32.35	60.51	0.24			0.29				
03-Sep	07:00	01:00		28.47			42.95	71.53	3.90			0.42				
03-Sep	08:00	01:00		14.26			48.44	62.82	15.68			0.48				
03-Sep	09:00	01:00		13.87			60.75	74.51	23.31			0.66				
03-Sep	10:00	01:00		12.60			78.60	91.22	44.69			0.92				
03-Sep	11:00	01:00		4.84			57.42	62.11	81.91			0.91				
03-Sep	12:00	01:00		3.69			48.49	51.69	92.40			0.70				
03-Sep	13:00	01:00		1.60			23.84	25.29	112.00			0.92		1.46		15.93
03-Sep	14:00	01:00		0.77			24.19	25.02	140.91			1.28				
03-Sep	15:00	01:00		0.33			18.14	18.57	150.78			1.42		1.42		17.74
03-Sep	16:00	01:00		-0.25			22.48	22.37	142.77			1.31		1.05		17.47
03-Sep	17:00	01:00		-0.40			29.48	27.81	122.76			1.07		1.37		16.44
03-Sep	18:00	01:00		-0.50			38.89	35.46	84.14			0.58		0.86		12.64
03-Sep	19:00	01:00		-0.50			55.68	51.35	45.92			0.53		0.56		15.16
03-Sep	20:00	01:00		1.79			74.59	76.32	10.01			0.50		0.46		14.23
03-Sep	21:00	01:00		2.29			71.83	74.18	5.22			0.61		0.33		14.16
03-Sep	22:00	01:00		9.91			76.19	86.09	2.83			0.50		0.17		13.37
03-Sep	23:00	01:00		1.49			74.67	76.25	2.72			0.68		0.31		14.95
04-Sep	00:00	01:00		0.03			66.19	66.10	3.16			0.57		0.40		12.66
04-Sep	01:00	01:00		0.13			48.58	48.55	6.56			0.65		0.44		11.50
04-Sep	02:00	01:00		2.19			45.96	48.16	5.28			0.62		0.12		11.92
04-Sep	03:00	01:00		-0.25			42.23	41.84	4.33			0.60		0.12		11.54
04-Sep	04:00	01:00		0.08			25.43	25.50	6.77			0.35		0.14		8.20
04-Sep	05:00	01:00		0.80			27.14	27.95	5.50			0.43		0.15		8.37
04-Sep	06:00	01:00		0.90			28.14	29.04	5.68			0.56		0.34		8.69
04-Sep	07:00	01:00		0.08			31.30	31.42	11.64			0.69		0.42		10.05
04-Sep	08:00	01:00		0.34			47.41	48.05	24.28			0.62		0.72		12.69
04-Sep	09:00	01:00		4.62			70.07	74.68	22.74			0.56		0.85		19.39
04-Sep	10:00	01:00		1.83			50.30	51.89	64.90			0.62		0.91		17.35
04-Sep	11:00	01:00		-0.10			27.77	27.47	90.12			0.65				14.56
04-Sep	12:00	01:00		-0.16			15.78	15.46	105.78			0.79		1.23		15.70
04-Sep	13:00	01:00		-0.02			15.13	14.98	117.00			0.94		1.19		14.83
04-Sep	14:00	01:00		0.16			7.21	7.40	102.52			1.17		1.17		9.30
04-Sep	15:00	01:00		0.06			10.97	11.17	146.67			1.48		1.04		12.19
04-Sep	16:00	01:00		0.69			11.70	12.32	143.40			1.50		1.02		11.81
04-Sep	17:00	01:00		0.72			14.33	15.07	93.78			0.56		1.10		11.13
04-Sep	18:00	01:00		0.26			18.34	18.79	58.11			0.32		0.80		8.69
04-Sep	19:00	01:00		-0.08			31.91	31.94	39.72			0.33		0.69		11.21
04-Sep	20:00	01:00		0.53			44.51	44.99	12.74			0.16		0.50		10.55
04-Sep	21:00	01:00		6.77			46.44	53.31	4.56			0.13		0.49		11.04
04-Sep	22:00	01:00		15.11			48.10	63.19	2.82			0.13		0.39		12.07
04-Sep	23:00	01:00		21.42			42.11	63.46	3.07			0.29		0.11		13.38

LA ATMOSPHERIC FREE RADICAL FIELD STUDY

LOCATION: CLAREMONT, CALIFORNIA  
SOURCE: UNISEARCH ASSOCIATES INC

DATE	START TIME	AVERAGE INTERVAL	SPECIES	HONO	NO2	NO3	NO	NO2	NOx	O3	PAN	H2O2	HC1O	HNO3
DD-MM	HH:MM	(HRS)	TECHNIQUE:	DOAS	DOAS	DOAS	I.M.A.-3	I.M.A.-3	I.M.A.-3	DASIBI	LPA-4	TDLAS	TDLAS	TDLAS
				(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)
05-Sep	00:00	01:00					8.39	28.85	37.15	7.63	0.46	0.14	11.98	
05-Sep	01:00	01:00		1.32	34.64		17.47	34.19	51.68	3.47	0.28	0.13	12.46	
05-Sep	02:00	01:00		0.66	18.91		3.48	15.71	19.20	12.94	0.25	0.13	9.42	
05-Sep	03:00	01:00		0.67	21.13		2.30	18.06	20.35	9.35	0.17	0.32	8.06	
05-Sep	04:00	01:00		0.92	24.25		4.30	19.22	23.61	7.80	0.12	0.15	7.17	
05-Sep	05:00	01:00		1.22	29.98		10.17	27.10	37.17	3.92	0.09	-0.04	7.19	
05-Sep	06:00	01:00		0.93	21.46		6.11	17.66	23.62	7.71	0.12	0.11	5.60	
05-Sep	07:00	01:00		1.20	29.32		26.85	28.73	55.71	5.88	0.10	-0.06	5.37	
05-Sep	08:00	01:00		0.82	35.29		27.71	42.38	70.19	12.70	0.23	0.09	11.00	
05-Sep	09:00	01:00		-0.16	7.26		18.22	47.17	65.27	29.39	0.40	0.35	13.76	
05-Sep	10:00	01:00		-0.35	1.14		10.19	45.09	55.30	49.14	0.58	0.29	12.20	
05-Sep	11:00	01:00		-0.09	5.58		3.50	21.84	25.17	74.71	0.55	0.77	7.14	
05-Sep	12:00	01:00		0.01	4.81		2.56	15.35	17.77	83.71	0.60	0.62	6.63	
05-Sep	13:00	01:00		0.00			1.58	9.49	11.06	93.65	0.94	0.34	7.37	
05-Sep	14:00	01:00		0.11	1.43		1.41	6.17	7.52	106.46	1.17	0.69	6.96	
05-Sep	15:00	01:00		0.12	1.54		1.24	4.81	6.06	101.66	1.03	0.52	6.09	
05-Sep	16:00	01:00		0.06	1.41		0.96	5.50	6.47	88.06	0.75	0.51	6.36	
05-Sep	17:00	01:00		-0.02	1.77		1.58	9.39	10.96	57.94	0.24	0.35	5.34	
05-Sep	18:00	01:00		0.18	3.13		1.00	13.23	14.30	39.19	0.13	0.62	4.59	
05-Sep	19:00	01:00		0.46	12.33		0.04	23.48	23.62	25.43	0.16	-0.03	5.37	
05-Sep	20:00	01:00		0.29	22.38		-0.01	29.34	29.36	14.56	0.12	0.05	4.36	
05-Sep	21:00	01:00		0.32	25.50		3.09	32.15	35.25	7.63	0.09	0.29	4.45	
05-Sep	22:00	01:00		0.43	24.08		6.46	31.86	38.33	5.78	0.11	0.12	4.85	
05-Sep	23:00	01:00					7.76	34.38	42.13	3.12	0.09	0.09	5.08	
06-Sep	00:00	01:00		1.06	29.08		12.93	33.53	46.45	2.74	0.06	0.02	4.64	
06-Sep	01:00	01:00		1.27	27.63		22.21	31.26	53.41	3.22	0.05	0.18	5.29	
06-Sep	02:00	01:00		1.38	23.76		6.84	29.26	36.12	3.22	0.23	-0.08	4.68	
06-Sep	03:00	01:00		1.10	20.41		5.02	30.57	35.61	2.95	0.17	-0.06	3.96	
06-Sep	04:00	01:00		0.51	9.46		5.37	28.81	34.10	3.32	0.16	0.06	3.55	
06-Sep	05:00	01:00		0.69	9.57		11.74	21.09	32.79	2.96	0.22	-0.08	3.65	
06-Sep	06:00	01:00		0.81	10.56		9.04	20.47	29.49	5.01	0.27	-0.06	3.53	
06-Sep	07:00	01:00		0.54	9.41		10.06	19.91	29.97	10.87	0.29	-0.07	2.99	
06-Sep	08:00	01:00		0.33	13.06		9.90	22.47	32.39	21.90	0.32	0.05	3.08	
06-Sep	09:00	01:00		0.15	16.30		11.29	29.56	40.86	31.78	0.41	-0.01	4.30	
06-Sep	10:00	01:00		-0.03	11.18		6.51	28.42	34.91	49.93	0.56	0.13	9.41	
06-Sep	11:00	01:00		-0.20	6.49		2.89	19.69	22.52	70.10	0.50	0.69	9.44	
06-Sep	12:00	01:00		-0.04	1.36		1.17	8.80	9.91	87.47	0.52	1.31	6.75	
06-Sep	13:00	01:00		0.01	1.24		0.73	5.78	6.43	109.53	1.01	1.05	8.86	
06-Sep	14:00	01:00		0.01	1.14		0.43	3.54	3.94	120.90	0.98	1.33	9.46	
06-Sep	15:00	01:00		-0.01	1.09		0.40	2.77	3.14	121.68	0.97	1.36	9.64	
06-Sep	16:00	01:00		-0.11	1.69		0.71	3.21	3.83	112.33	0.72	1.08	9.34	
06-Sep	17:00	01:00		-0.04	2.69		0.57	5.13	5.57	107.53	0.66	1.01	10.68	
06-Sep	18:00	01:00		0.00	6.90		0.01	4.37	4.30	91.43	0.58	0.63	10.71	
06-Sep	19:00	01:00		0.04	16.44		-0.24	5.80	5.55	62.40	0.42	0.27	10.68	
06-Sep	20:00	01:00		0.50	30.49		-0.06	17.37	17.01	27.21	0.24	-0.07	9.72	
06-Sep	21:00	01:00		0.31	37.60		0.66	15.85	16.51	5.15	0.30	0.07	9.57	
06-Sep	22:00	01:00		0.71	33.38		1.86	12.94	14.32	5.98	0.49	0.06	9.16	
06-Sep	23:00	01:00		0.89	30.78		4.06	10.20	14.20	5.24	0.57	0.05	8.68	

LA ATMOSPHERIC FREE RADICAL FIELD STUDY

LOCATION: CLAREMONT GROUND SITE  
SOURCE: UNISEARCH ASSOCIATES INC

DATE	START TIME	INT	SPEC: TECH:	HONO DOAS (ppbV)	NO2 DOAS (ppbV)	NO3 DOAS (ppbV)	NO LMA-3 (ppbV)	NO2 LMA-3 (ppbV)	NOx LMA-3 (ppbV)	O3 DAS (ppbV)	LOZ (ppbV)	PAN LPA-4 (ppbV)	H2O2 TDLAS (ppbV)	HCHO TDLAS (ppbV)	HNO3 TDLAS (ppbV)
DD-MM	HH:MM	(HRS)													
07-Sep	00:00	01:00		0.68	24.97		1.25	8.17	9.46		9.00	0.35	0.14	8.70	
07-Sep	01:00	01:00		0.57	24.68		0.26	10.65	11.14		14.94	0.42	0.16	10.53	
07-Sep	02:00	01:00		0.57	19.61						14.75	0.41	-0.02	9.84	
07-Sep	03:00	01:00		0.32	16.41						15.01	0.44	0.17	7.26	
07-Sep	04:00	01:00		0.48	14.07						16.49	0.47	0.20	6.73	
07-Sep	05:00	01:00		0.48	18.34						6.38	0.55	0.14	7.78	
07-Sep	06:00	01:00		0.22	18.38						6.03	0.51	0.05	7.45	
07-Sep	07:00	01:00		0.53	26.14						6.91	0.51	0.12	8.44	
07-Sep	08:00	01:00		0.55	39.06						21.23	0.59		9.94	
07-Sep	09:00	01:00		0.53	39.41						35.62	0.57		11.14	
07-Sep	10:00	01:00		0.24	33.76						33.14	0.22		10.77	
07-Sep	11:00	01:00									59.74	0.29		14.05	
07-Sep	12:00	01:00									79.09	0.31		14.12	
07-Sep	13:00	01:00									101.05	0.67	1.12	17.39	
07-Sep	14:00	01:00		0.08	4.78						107.17	0.50	1.30	14.15	
07-Sep	15:00	01:00		0.05	4.10						156.70	1.46	1.61	14.15	
07-Sep	16:00	01:00		0.01	4.38						107.91	1.13	1.14	14.64	
07-Sep	17:00	01:00		-0.15	3.56						68.22	0.16	1.27	7.99	
07-Sep	18:00	01:00		-0.33	4.36						40.17	0.13	1.04	9.28	
07-Sep	19:00	01:00		-0.50	6.18						19.56	0.21	0.47	13.30	
07-Sep	20:00	01:00			8.84						2.82	0.15	0.65	15.86	
07-Sep	21:00	01:00			26.76						2.82	0.12	0.19	16.43	
07-Sep	22:00	01:00		0.28	47.96						5.79	0.69	0.10	16.03	
07-Sep	23:00	01:00		0.68	48.47						5.34	0.70	0.31	13.56	
08-Sep	00:00	01:00		0.93	49.85						5.03	0.56	-0.01	15.18	
08-Sep	01:00	01:00		0.44	28.84						24.95	0.47	0.32	11.49	
08-Sep	02:00	01:00		0.36	43.02						8.00	0.18	0.33	10.51	
08-Sep	03:00	01:00		0.46	44.19						5.31	0.30	0.16	9.72	
08-Sep	04:00	01:00		0.32	37.96						12.37	0.39	0.31	10.73	
08-Sep	05:00	01:00		0.20	30.32						14.12	0.49	0.35	8.21	
08-Sep	06:00	01:00		0.27	32.84						6.14	0.51	0.64	10.58	
08-Sep	07:00	01:00		0.65	39.62						7.34	0.48	0.48	14.25	
08-Sep	08:00	01:00		0.14	37.31						22.66	0.37	0.79	13.56	
08-Sep	09:00	01:00		0.25	32.13						39.47	0.30	1.09	16.35	
08-Sep	10:00	01:00		0.00	30.20						56.88	0.41	1.12	18.43	
08-Sep	11:00	01:00									75.09	0.58	1.13	24.01	
08-Sep	12:00	01:00									91.43	0.33	1.39	15.10	
08-Sep	13:00	01:00									89.15	0.48	0.85	19.86	
08-Sep	14:00	01:00									104.66	0.65	0.59	15.08	
08-Sep	15:00	01:00									116.58	0.95	0.76	15.34	
08-Sep	16:00	01:00									144.61	2.09	0.74	18.86	
08-Sep	17:00	01:00									134.19	2.28			
08-Sep	18:00	01:00									83.58	0.80	1.02	10.77	
08-Sep	19:00	01:00									43.54	0.56	0.63	7.26	
08-Sep	20:00	01:00		0.01	27.22						15.19	0.87	0.57		
08-Sep	21:00	01:00		0.41	42.73						5.48	1.24	-0.02	16.04	
08-Sep	22:00	01:00		1.14	64.21						3.67	1.13	0.03	12.80	
08-Sep	23:00	01:00		1.17	60.03						10.56	0.99	0.65	14.38	

LA ATMOSPHERIC FREE RADICAL FIELD STUDY

LOCATION: CLAREMONT, CALIFORNIA  
SOURCE: UNISEARCH ASSOCIATES INC

DATE	START TIME	AVERAGE INTERVAL	SPECIES:	HONO	NO2	NO3	NO	NO2	NOx	O3	PAN	H2O2	HO10	HNO3
DD-MM	HH:MM	(HRS)	TECHNIQUE:	DOAS (ppbV)	DOAS (ppbV)	DOAS (ppbV)	LMA-3 (ppbV)	LMA-3 (ppbV)	LMA-3 (ppbV)	LOZ-3 (ppbV)	LPA-4 (ppbV)	TDLAS (ppbV)	TDLAS (ppbV)	TDLAS (ppbV)
09-Sep	00:00	01:00		0.74	36.55		-0.38	50.97	50.41	21.59	1.06	0.51	14.22	
09-Sep	01:00	01:00		0.55	20.84		-0.13	25.79	25.54	35.17	1.10	0.28	13.21	
09-Sep	02:00	01:00		0.34	15.29		0.08	15.86	15.90	39.44	0.67	0.50	8.69	
09-Sep	03:00	01:00		0.27	13.83		1.34	10.24	11.64	38.00	0.36	0.57	6.36	
09-Sep	04:00	01:00		0.19	11.08		1.10	8.52	9.61	39.26	0.39	0.26	7.55	
09-Sep	05:00	01:00		0.25	19.16		2.62	23.52	26.38	28.94	0.61	0.60	9.49	
09-Sep	06:00	01:00		0.41	37.23		0.60	48.62	49.16	11.29	0.79	0.54	8.60	
09-Sep	07:00	01:00		0.93	44.67		0.06	62.90	63.43	4.60	0.98	0.28	12.89	
09-Sep	08:00	01:00		0.82	38.15		0.18	54.02	54.01	40.83	0.97	0.97	11.60	
09-Sep	09:00	01:00		0.56	39.97		2.05	51.40	52.64	69.37	0.64	1.20	18.10	
09-Sep	10:00	01:00		-0.10	27.91		1.99	90.29	92.27	81.45	1.26	1.24	31.04	
09-Sep	11:00	01:00					-0.05	71.82	71.56	132.64	1.54	0.95	30.85	
09-Sep	12:00	01:00					-0.72	56.29	55.27	145.54	1.31	1.09	18.19	
09-Sep	13:00	01:00					0.76	27.68	27.68	157.25	1.08	0.44		
09-Sep	14:00	01:00					0.72	39.50	39.14	228.38	3.00	0.38	22.52	
09-Sep	15:00	01:00					0.19	45.64	45.41	278.80	4.20	0.51	18.18	
09-Sep	16:00	01:00					0.56	40.63	40.54	208.26	2.64	0.53	12.55	
09-Sep	17:00	01:00					0.71	41.00	40.79	138.99	1.34	0.92	7.02	
09-Sep	18:00	01:00		-0.43	18.35		0.39	54.17	54.53	100.15	1.00	0.84	4.71	
09-Sep	19:00	01:00		0.06	32.18		0.94	76.19	75.70	42.27	0.59	0.66	5.08	
09-Sep	20:00	01:00		0.50	45.28		0.14	86.78	86.91	17.40	0.50	0.73	12.25	
09-Sep	21:00	01:00		1.09	56.81		-0.05	84.37	84.01	10.04	0.42	0.57	13.02	
09-Sep	22:00	01:00		1.42	59.18		-0.03	78.88	78.80	7.67	0.59	0.24	12.33	
09-Sep	23:00	01:00		1.58	58.04		-0.03	72.36	72.12	8.74	0.76	0.35	14.75	
10-Sep	00:00	01:00		1.24	38.51			47.64		19.02	0.50	0.42	11.24	
10-Sep	01:00	01:00		1.63	46.92			56.74		12.02	0.50	0.27	12.01	
10-Sep	02:00	01:00		2.30	52.53			61.82		6.82	0.16	0.03	9.33	
10-Sep	03:00	01:00		1.76	35.01			35.62		16.43	0.89	0.13	8.40	
10-Sep	04:00	01:00		1.18	28.18			43.91		14.42	0.93	0.39	10.19	
10-Sep	05:00	01:00		1.36	37.82			46.40		10.19	1.10	0.28	9.07	
10-Sep	06:00	01:00		1.33	38.08			56.06		9.18	1.40	0.34	12.27	
10-Sep	07:00	01:00		1.61	49.61			71.90		11.53	1.31	0.28	15.12	
10-Sep	08:00	01:00		1.33	48.54			75.02		26.71	1.10	0.64	16.45	
10-Sep	09:00	01:00		0.77	38.71		15.38	77.66	92.91	55.48	0.78	0.64	19.87	
10-Sep	10:00	01:00		0.97	59.55		16.29	109.13	125.51	54.38	0.84	0.94	25.80	
10-Sep	11:00	01:00					7.65	91.37	98.59	98.89	1.18	0.89	20.97	
10-Sep	12:00	01:00		1.38	16.43		5.54	67.41	72.70	117.18	1.18	0.45	13.15	
10-Sep	13:00	01:00		1.08	9.24		2.24	39.36	41.30	151.20	1.28	0.85	14.24	
10-Sep	14:00	01:00		1.27	9.66		1.99	46.68	48.58	196.60	2.04	0.97	18.85	
10-Sep	15:00	01:00		1.24	8.48		1.73	42.66	44.41	244.25	3.01	0.83	21.94	
10-Sep	16:00	01:00		1.27	9.33		1.34	41.94	43.23	202.86	2.30	0.56	20.90	
10-Sep	17:00	01:00		0.73	8.88		1.00	41.57	42.60	182.52	2.07	0.57	22.51	
10-Sep	18:00	01:00		0.14	9.04		0.44	50.60	51.11	139.77	1.51	0.77	21.14	
10-Sep	19:00	01:00		-0.28	14.26		-0.08	66.16	66.21	89.68	1.12	0.89	18.79	
10-Sep	20:00	01:00		-0.09	17.98		1.10	59.81	61.25	58.54	0.94	0.88	20.42	
10-Sep	21:00	01:00		0.82	37.36		0.77	70.53	71.13	29.20	1.02	0.40	19.98	
10-Sep	22:00	01:00		1.16	44.61		10.08	83.28	93.13	18.38	1.86	0.36	24.41	
10-Sep	23:00	01:00		1.50	43.27		5.63	62.55	67.68	32.67	2.81	0.17	24.86	



LA ATMOSPHERIC FREE RADICAL FIELD STUDY

LOCATION: CLAREMONT, CALIFORNIA  
SOURCE: UNISEARCH ASSOCIATES INC

DATE	START TIME	AVERAGE INTERVAL	SPECIES	TECHNIQUE	HONO	NO2	NO3	NO	NO2	NOx	O3	O3	O3	PAN	H2O2	H110	HNO3
DD-MM	HH:MM	(HRS)			DOAS (ppbV)	DOAS (ppbV)	DOAS (ppbV)	LMA-3 (ppbV)	LMA-3 (ppbV)	LMA-3 (ppbV)	LOZ-3 (ppbV)	DASIBI (ppbV)	LOZ-3 (ppbV)	LPA-4 (ppbV)	TDLAS (ppbV)	TDLAS (ppbV)	TDLAS (ppbV)
13-Sep	00:00	01:00			0.21	7.08		0.32	4.04	4.33	27.45		27.45	0.01	0.40	2.13	
13-Sep	01:00	01:00			0.17	4.48		0.24	1.92	2.17	33.42		33.42	0.01	0.34	0.17	
13-Sep	02:00	01:00			0.18	3.10		0.24	1.31	1.55	35.04		35.04	0.01	0.53	-0.20	
13-Sep	03:00	01:00			0.20	2.31		0.30	0.86	1.16	34.72		34.72	0.01	0.49	0.68	
13-Sep	04:00	01:00			0.17	2.17		0.19	1.12	1.31	34.35		34.35	0.01	0.46	3.38	
13-Sep	05:00	01:00			0.16	3.63		0.45	2.97	3.48	31.27		31.27	0.01	0.58	-1.09	
13-Sep	06:00	01:00			0.26	10.48		0.29	10.63	11.21	22.18		22.18	0.00	0.25	2.34	
13-Sep	07:00	01:00			0.39	22.99		2.86	21.04	23.91	10.50		10.50	0.00	0.24		
13-Sep	08:00	01:00			0.38	21.41		5.58	20.76	26.25	11.75		11.75	0.01	0.28	2.39	
13-Sep	09:00	01:00			0.29	16.47		4.60	14.99	19.58	18.13		18.13	0.01	0.25	5.94	
13-Sep	10:00	01:00			0.15	11.58		1.04	8.77	9.81	25.68		25.68	0.03	0.10	-3.14	
13-Sep	11:00	01:00						0.06	6.95	7.01	32.13		32.13	0.06			
13-Sep	12:00	01:00			0.00	6.24		0.36	7.83	7.97	42.02		42.02	0.13			
13-Sep	13:00	01:00			0.00	7.38		0.05	10.97	11.06	44.04		44.04	0.17			
13-Sep	14:00	01:00			-0.02	8.25		-0.03	13.62	13.64	48.48		48.48	0.20			
13-Sep	15:00	01:00			0.03	9.69		0.12	16.05	16.19	51.95		51.95	0.26			
13-Sep	16:00	01:00			0.07	11.72		-0.01	18.83	18.71	52.74		52.74	0.31			
13-Sep	17:00	01:00			0.11	15.91		0.09	21.19	21.29	46.94		46.94	0.26			
13-Sep	18:00	01:00			0.07	18.25		-0.03	19.88	19.87	32.72		32.72	0.12			
13-Sep	19:00	01:00			0.28	17.00		0.03	16.40	16.46	21.86		21.86	0.01			
13-Sep	20:00	01:00			0.29	18.98		0.17	16.10	16.12	17.28		17.28	0.01			
13-Sep	21:00	01:00			0.19	18.88		0.02	16.97	17.04	14.48		14.48	0.01			
13-Sep	22:00	01:00			0.28	21.61		0.08	23.01	23.15	8.07		8.07	0.02			
13-Sep	23:00	01:00			0.39	24.94		0.03	24.96	24.97	3.73		3.73	0.02			
14-Sep	00:00	01:00			0.64	24.42		0.02	23.19	23.21	3.73		3.73	0.04			
14-Sep	01:00	01:00			0.65	24.36		-0.01	21.88	21.88	0.26		0.26	0.02			
14-Sep	02:00	01:00			0.70	20.25		-0.05	17.75	17.66	2.83		2.83	0.03			
14-Sep	03:00	01:00			0.74	18.64		-0.01	16.28	16.25	2.15		2.15	0.04			
14-Sep	04:00	01:00			0.71	17.46		0.08	15.54	15.63	3.14		3.14	0.05			
14-Sep	05:00	01:00			0.55	16.78		-0.03	16.68	16.64	2.81		2.81	0.04			
14-Sep	06:00	01:00			0.40	15.80		0.07	15.59	15.70	4.22		4.22	0.04			
14-Sep	07:00	01:00			0.36	13.26		0.06	15.36	15.43	7.92		7.92	0.05			
14-Sep	08:00	01:00			0.32	13.01		-0.24	12.07	11.83	7.44		7.44	0.09			
14-Sep	09:00	01:00			0.11	10.32		0.02	8.10	8.11	14.61		14.61	0.12			
14-Sep	10:00	01:00						-0.19	11.74	11.59	24.08		24.08	0.13			
14-Sep	11:00	01:00						-0.12	19.27	19.24	28.71		28.71	0.16			
14-Sep	12:00	01:00			0.11	11.78		-0.06	15.62	15.53	37.64		37.64	0.30			
14-Sep	13:00	01:00			0.05	9.19		0.02	15.35	15.37	54.06		54.06	0.37			
14-Sep	14:00	01:00			0.03	9.34		0.02	19.23	19.28	71.09		71.09	0.49			
14-Sep	15:00	01:00			0.01	8.47		0.04	18.58	18.53	82.37		82.37	0.47			
14-Sep	16:00	01:00			0.03	9.83		0.16	20.57	20.77	92.74		92.74	0.56			
14-Sep	17:00	01:00			0.10	13.70		-0.01	21.95	21.94	102.73		102.73	0.69			
14-Sep	18:00	01:00						0.02	22.23	22.26	60.08		60.08	0.24			
14-Sep	19:00	01:00			0.01	21.73		0.06	22.80	22.81	34.60		34.60	0.04			
14-Sep	20:00	01:00			0.11	23.78		-0.04	25.22	25.15	19.92		19.92	0.00			
14-Sep	21:00	01:00			0.23	26.48		0.02	25.58	25.58	11.71		11.71	0.00			
14-Sep	22:00	01:00			0.31	27.93		-0.02	25.81	25.76	8.28		8.28	0.00			
14-Sep	23:00	01:00			0.24	23.85		-0.02	23.45	23.43	4.64		4.64	0.00			
14-Sep											2.79		2.79	0.00			

LA ATMOSPHERIC FREE RADICAL FIELD STUDY

LOCATION: CLAREMONT, CALIFORNIA  
SOURCE: UNISEARCH ASSOCIATES INC

DATE	START TIME	AVERAGE INTERVAL	SPECIES: TECHNIQUE:	HONO DOAS	NO2 DOAS	NO3 DOAS	NO LMA-3	NO2 LMA-3	NOx LMA-3	O3 DASIBI	O3 LOZ-3	PAN LPA-4	H2O2 TDLAS	HCHO TDLAS	HNO3 TDLAS
DD-MM	HH:MM	(HRS)		(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)
15-Sep	00:00	01:00		0.51	25.23		-0.03	19.84	19.80	0.74	0.48	0.02	0.11	4.50	
15-Sep	01:00	01:00		0.53	22.56		0.00	18.51	18.51	1.56	1.17	0.02	0.24	4.59	
15-Sep	02:00	01:00		0.51	20.27		0.05	15.70	15.74	1.94	1.13	0.03	-0.01	4.11	
15-Sep	03:00	01:00		0.44	17.60		-0.02	14.93	14.96	2.98	2.20	0.03	0.08	3.80	
15-Sep	04:00	01:00		0.40	15.79		0.00	13.75	13.75	3.33	2.47	0.04	0.31	3.42	
15-Sep	05:00	01:00		0.27	16.86		0.04	14.99	15.03	2.25	1.18	0.04	0.05	3.49	
15-Sep	06:00	01:00		0.15	17.51		-0.10	16.04	15.93	2.61	1.24	0.05	0.26	3.78	
15-Sep	07:00	01:00		-0.06	14.04		-0.24	14.04	13.79	8.23	7.32	0.06	0.21	3.62	
15-Sep	08:00	01:00					-0.56	10.90	10.29	16.89	16.10	0.10	0.12	4.11	
15-Sep	09:00	01:00					0.02	8.34	8.28	22.57	21.41	0.12	0.09	4.97	
15-Sep	10:00	01:00					0.84	5.81	6.65	31.45	30.60	0.17	0.03	5.17	
15-Sep	11:00	01:00					2.39	6.56	8.99	40.52	37.50	0.26	0.25	7.32	
15-Sep	12:00	01:00					3.12	9.95	13.11	53.70	50.59	0.34	0.20	8.24	
15-Sep	13:00	01:00					3.96	17.36	21.42	64.44	58.19	0.44	0.22	8.71	
15-Sep	14:00	01:00					2.62	21.82	24.35	85.11	75.29	0.60	0.24	10.85	
15-Sep	15:00	01:00					1.30	23.36	24.69	107.01	93.47	0.82	0.00	11.32	
15-Sep	16:00	01:00					1.32	22.32	23.64	82.49	72.51	0.52	-0.07	8.05	
15-Sep	17:00	01:00					0.32	14.48	14.65	62.31	55.90	0.26	0.30	7.32	
15-Sep	18:00	01:00					-0.42	6.59	6.08	41.68	38.39	0.16	0.35	6.15	
15-Sep	19:00	01:00					-0.45	3.19	2.74	22.28	20.94	0.08	0.26	4.16	
15-Sep	20:00	01:00					-0.37	3.56	3.15	10.78	10.22	0.02	0.40	3.20	
15-Sep	21:00	01:00					-0.37	5.21	4.88	3.60	3.56	0.00	0.26	3.70	
15-Sep	22:00	01:00					-0.18	1.55	1.46	2.12	2.28	0.00	0.39	1.98	
15-Sep	23:00	01:00								2.17	2.61	0.00	0.38	1.76	
16-Sep	00:00	01:00								3.15	3.65	0.00	0.32	2.54	
16-Sep	01:00	01:00								6.57	6.88	0.00	0.54	1.78	
16-Sep	02:00	01:00								8.99	8.50	0.01	0.48	2.08	
16-Sep	03:00	01:00								11.73	10.83	0.01	0.47	2.67	
16-Sep	04:00	01:00								14.45	12.40	0.02	0.25	3.11	
16-Sep	05:00	01:00								12.32	10.69	0.01	-0.01	3.14	
16-Sep	06:00	01:00								11.91	10.71	0.01	-0.05	2.26	
16-Sep	07:00	01:00					11.72	22.46	34.17	11.48	9.46	0.01	0.29	1.13	
16-Sep	08:00	01:00					9.34	21.09	30.47			0.02	0.11	1.95	
16-Sep	09:00	01:00					10.33	20.33	30.59			0.06	-0.00	3.38	
16-Sep	10:00	01:00					7.74	14.61	22.46			0.07	0.19	2.99	
16-Sep	11:00	01:00								30.09	26.98	0.07	-0.04	3.52	
16-Sep	12:00	01:00		0.00	11.49					33.73	31.29	0.13	0.16	3.96	
16-Sep	13:00	01:00		-0.07	13.81					41.22	40.87	0.15	0.03	4.43	
16-Sep	14:00	01:00		-0.08	13.12					41.42	41.78	0.17	0.06	4.40	
16-Sep	15:00	01:00		-0.05	13.54		2.21	15.59	17.80	41.42	42.98	0.18	-0.05	3.01	
16-Sep	16:00	01:00		-0.01	14.31		3.44	15.53	18.87	40.96	40.89	0.12	0.10	3.42	
16-Sep	17:00	01:00		-0.14	16.57		1.49	14.55	16.06	38.36	32.58	0.02	0.53	2.54	
16-Sep	18:00	01:00		-0.13	14.47		1.25	14.87	16.09	30.15	32.58	0.02	0.10	2.33	
16-Sep	19:00	01:00		-0.11	16.86		0.50	11.44	11.95	30.55	32.91	0.02	0.36	1.52	
16-Sep	20:00	01:00		0.03	14.58		0.30	11.73	12.04	27.14	29.06	0.02	0.60	1.62	
16-Sep	21:00	01:00		0.17	15.79		0.05	12.75	12.87	25.32	26.90	0.02	0.59	2.25	
16-Sep	22:00	01:00		0.22	20.19		0.37	14.30	14.70	21.12	22.01	0.01	0.38	2.12	
16-Sep	23:00	01:00		0.27	22.60		0.46	20.24	20.80	15.39	14.97	0.00	0.38	2.12	
16-Sep							0.44	24.24	24.66	10.77	9.97	0.00	0.61	2.36	

LA ATMOSPHERIC FREE RADICAL FIELD STUDY

LOCATION: CLAREMONT, CALIFORNIA  
SOURCE: UNISEARCH ASSOCIATES INC

DATE	START TIME	AVERAGE INTERVAL	SPECIES:	HONO	NO2	NO3	NO	NO2	NOX	O3	O3	O3	PAN	H2O2	IK110	INO3
DD-MM	HH:MM	(HRS)	TECHNIQUE:	DOAS (ppbV)	DOAS (ppbV)	DOAS (ppbV)	LMA-3 (ppbV)	LMA-3 (ppbV)	LMA-3 (ppbV)	DASIBI (ppbV)	LOZ-3 (ppbV)	LPA-4 (ppbV)	LPA-4 (ppbV)	TDLAS (ppbV)	TDLAS (ppbV)	TDLAS (ppbV)
17-Sep	00:00	01:00		0.66	25.84		0.39	21.64	22.02	11.72	11.12	0.00	0.20	0.20	2.56	
17-Sep	01:00	01:00		0.32	15.02		0.31	21.50	21.81	11.86	11.24	0.00	0.44	0.44	2.13	
17-Sep	02:00	01:00		0.31	14.63		0.47	20.17	20.60	12.48	11.57	0.00	0.41	0.41	2.07	
17-Sep	03:00	01:00		0.44	16.55		0.52	13.02	13.48	16.70	16.40	0.00	0.22	0.22	1.83	
17-Sep	04:00	01:00		0.51	18.77		0.65	12.76	13.48	16.12	15.40	0.00	0.45	0.45	1.94	
17-Sep	05:00	01:00		0.49	19.80		0.72	13.14	13.84	15.76	14.89	0.00	0.23	0.23	1.64	
17-Sep	06:00	01:00		0.43	15.24		1.28	19.12	20.42	12.46	11.06	0.00	0.24	0.24	1.63	
17-Sep	07:00	01:00		0.45	14.92		4.64	23.64	28.31	11.90	10.38	0.00	0.50	0.50	1.84	
17-Sep	08:00	01:00					6.47	25.23	31.64	14.08	13.68	0.01	0.42	0.42	2.21	
17-Sep	09:00	01:00					5.86	16.52	22.11	23.58	24.83	0.03	0.25	0.25	2.97	
17-Sep	10:00	01:00					11.40	31.96	43.49	24.11	22.55	0.05	0.35	0.35	3.65	
17-Sep	11:00	01:00		-0.05	6.41		12.64	30.02	42.57	28.60	27.61	0.06	0.16	0.16	2.70	
17-Sep	12:00	01:00		-0.06	3.74		11.90	24.67	36.46	35.88	35.51	0.10	0.14	0.14	3.91	
17-Sep	13:00	01:00		-0.11	3.49		5.34	17.64	22.94	44.38	44.87	0.13	0.15	0.15	3.69	
17-Sep	14:00	01:00		-0.17	3.80		3.79	9.67	13.43	49.68	50.81	0.15	0.13	0.13	2.74	
17-Sep	15:00	01:00		-0.21	3.80		2.39	7.67	10.07	53.71	55.78	0.17	0.19	0.19	3.93	
17-Sep	16:00	01:00		-0.25	6.02		2.13	10.23	12.31	49.23	51.16	0.13	0.37	0.37	2.98	
17-Sep	17:00	01:00		-0.17	9.03		1.18	11.47	12.63	41.09	43.39	0.07	0.06	0.06	2.09	
17-Sep	18:00	01:00		-0.08	18.87		0.63	13.38	14.07	31.31	33.33	0.04	0.57	0.57	3.22	
17-Sep	19:00	01:00		0.17	29.23		-0.07	16.18	16.10	23.04	24.25	0.02	0.47	0.47	1.61	
17-Sep	20:00	01:00		0.41	34.89		0.29	19.81	20.18	18.52	18.56	0.02	0.67	0.67	2.21	
17-Sep	21:00	01:00		0.74	39.50		7.71	34.39	42.22	4.67	1.31	0.02	0.29	0.29	3.40	
17-Sep	22:00	01:00		0.86	39.56		20.45	35.70	56.09	3.64	0.00	0.04	0.11	0.11	4.63	
17-Sep	23:00	01:00		1.08	38.94		49.34	32.16	81.47	4.38	0.00	0.04	0.09	0.09	6.46	
18-Sep	00:00	01:00		0.66	25.84		19.60	23.47	42.90	6.24	3.09	0.08	0.04	0.04	4.36	
18-Sep	01:00	01:00		0.32	15.02		6.24	15.63	21.89	10.65	8.11	0.10	0.16	0.16	1.62	
18-Sep	02:00	01:00		0.31	14.63		5.21	14.07	19.22	10.03	7.15	0.07	-0.02	-0.02	4.17	
18-Sep	03:00	01:00		0.44	16.55		4.93	15.18	20.10	9.40	6.43	0.06	0.06	0.06	4.28	
18-Sep	04:00	01:00		0.51	18.77		8.10	19.81	27.89	6.27	2.52	0.04	0.06	0.06	4.00	
18-Sep	05:00	01:00		0.49	19.80		8.15	19.39	27.52	5.13	1.24	0.03	0.16	0.16	4.00	
18-Sep	06:00	01:00		0.43	15.24		9.77	13.43	23.14	7.80	4.46	0.06	-0.06	-0.06	2.68	
18-Sep	07:00	01:00		0.45	14.92		11.73	14.08	25.84	10.06	6.24	0.05	0.01	0.01	2.91	
18-Sep	08:00	01:00					7.75	10.62	18.32	19.75	18.01	0.06	0.18	0.18	3.18	
18-Sep	09:00	01:00					6.90	10.44	17.26	29.20	28.79	0.10	0.04	0.04	3.70	
18-Sep	10:00	01:00					5.12	8.24	13.39	34.87	34.81	0.13	0.32	0.32	4.56	
18-Sep	11:00	01:00		-0.05	6.41		4.00	7.78	11.81	47.82	48.02	0.23	0.59	0.59	4.25	
18-Sep	12:00	01:00		-0.06	4.02		-0.12	7.28	7.01	60.82	63.03	0.34	0.50	0.50	4.74	
18-Sep	13:00	01:00		-0.11	3.74		0.03	8.55	8.61	74.12	77.73	0.44	0.34	0.34	7.14	
18-Sep	14:00	01:00		-0.17	3.49		-0.16	11.09	10.97	85.87	89.41	0.49	0.45	0.45	7.19	
18-Sep	15:00	01:00		-0.21	3.80		0.24	12.59	12.80	95.33	98.92	0.60	0.49	0.49	8.12	
18-Sep	16:00	01:00		-0.25	6.02		-0.17	19.48	18.19	130.14	130.85	1.14	0.47	0.47	10.84	
18-Sep	17:00	01:00		-0.17	9.03		0.07	19.37	19.57	136.25	135.35	1.26	0.45	0.45	14.79	
18-Sep	18:00	01:00		-0.08	18.87		0.24	27.08	27.33	82.50	80.79	0.49	0.13	0.13	10.72	
18-Sep	19:00	01:00		0.17	29.23		0.00	35.78	35.83	43.15	39.53	0.19	0.28	0.28	9.53	
18-Sep	20:00	01:00		0.41	34.89		0.17	46.79	46.96	19.17	12.95	0.21	0.30	0.30	8.84	
18-Sep	21:00	01:00		0.74	39.50		0.15	46.69	46.77	12.97	4.76	0.41	0.18	0.18	8.70	
18-Sep	22:00	01:00		0.86	39.56		0.37	46.55	46.94	13.06	4.12	0.53	0.08	0.08	9.29	
18-Sep	23:00	01:00		1.08	38.94		14.50	47.66	62.10	11.88	1.73	0.59	0.33	0.33	7.42	

LA ATMOSPHERIC FREE RADICAL FIELD STUDY

LOCATION: CLAREMONT, CALIFORNIA  
 SOURCE: UNISEARCH ASSOCIATES INC

DATE	START TIME	AVERAGE INTERVAL	SPECIES	HONO	NO2	NO3	NO	NO2	NOx	O3	O3	LOZ-3	PAN	H2O2	HCHO	HNO3
DD-MM	HH:MM	(HRS)	TECHNIQUE:	DOAS (ppbV)	DOAS (ppbV)	DOAS (ppbV)	LMA-3 (ppbV)	LMA-3 (ppbV)	LMA-3 (ppbV)	DASIBI (ppbV)	LOZ-3 (ppbV)	LPA-4 (ppbV)	TDLAS (ppbV)	TDLAS (ppbV)	TDLAS (ppbV)	TDLAS (ppbV)
19-Sep	00:00	01:00		0.80	29.69		7.32	36.78	43.90	17.24	6.87	0.60	0.28	6.42		
19-Sep	01:00	01:00		0.74	28.03		3.70	32.43	36.14	16.36	7.79	0.49	0.15	7.15		
19-Sep	02:00	01:00		0.78	34.63		3.93	36.10	39.80	16.97	7.58	0.46	-0.05	8.33		
19-Sep	03:00	01:00		0.66	24.22		1.38	21.72	23.02	24.93	16.21	0.45	-0.04	6.79		
19-Sep	04:00	01:00		0.51	21.76		1.88	22.50	24.52	20.79	12.72	0.29	0.07	6.42		
19-Sep	05:00	01:00		0.68	29.85		4.55	31.94	36.53	15.50	5.92	0.33	-0.04	5.94		
19-Sep	06:00	01:00		0.70	20.60		6.74	23.76	30.63	19.51	11.51	0.48	0.13	4.22		
19-Sep	07:00	01:00		0.69	29.49		10.69	32.16	42.94	21.14	10.85	0.41	0.01	6.92		
19-Sep	08:00	01:00		0.63	36.85		23.08	44.93	68.29	25.67	11.29	0.39	0.24	8.24		
19-Sep	09:00	01:00					32.17	57.88	90.21	27.33	8.88	0.42	0.28	13.16		
19-Sep	10:00	01:00					24.90	63.25	88.10	41.49	17.63	0.77	0.17	16.30		
19-Sep	11:00	01:00					8.51	40.01	48.32	45.85	46.00	0.88	0.35	15.46		
19-Sep	12:00	01:00		-0.18	19.10		4.31	29.50	33.90	78.27	76.00	0.83	0.50	13.59		
19-Sep	13:00	01:00		-0.27	9.27		2.15	22.76	24.84	108.75	103.65	1.02	0.51	14.06		
19-Sep	14:00	01:00		-0.18	4.06		1.19	13.45	14.60	138.27	130.03	1.15	0.55	13.11		
19-Sep	15:00	01:00		-0.19	3.63		0.88	14.23	15.16	154.97	144.76	1.30	0.59	14.93		
19-Sep	16:00	01:00		-0.21	3.67		0.85	15.98	16.83	171.52	159.50	1.42	0.53	15.14		
19-Sep	17:00	01:00		-0.10	5.82		0.70	17.63	18.32	157.17	144.78	1.31	0.46	15.29		
19-Sep	18:00	01:00		0.15	18.76		-0.58	28.35	27.85	83.90	79.38	0.42	0.29	12.33		
19-Sep	19:00	01:00		0.86	11.00		-1.30	31.77	30.53	43.05	42.86	0.16	0.15	8.59		
19-Sep	20:00	01:00			78.66		-0.25	36.21	36.01	20.04	20.68	0.04	0.08	6.03		
19-Sep	21:00	01:00		0.63	35.50		5.60	41.42	47.07	7.71	8.66	0.10	0.19	6.53		
19-Sep	22:00	01:00		0.95	41.46		13.13	45.83	58.92	-0.14	0.34	0.20	0.09	5.08		
19-Sep	23:00	01:00		1.16	38.38		20.70	40.41	61.06	-0.27	0.02	0.19	0.21	6.71		
20-Sep	00:00	01:00		1.24	32.70		11.74	31.81	43.45	4.19	4.93	0.43	0.02	5.96		
20-Sep	01:00	01:00		0.98	23.43		3.74	22.20	25.85	16.72	17.70	0.43	0.02	5.43		
20-Sep	02:00	01:00		0.72	20.31		2.29	19.82	22.13	22.88	23.84	0.36	0.21	5.27		
20-Sep	03:00	01:00			84.48		2.87	25.56	28.54	16.74	17.06	0.25	0.25	4.89		
20-Sep	04:00	01:00		0.39	13.38		10.89	39.25	50.12	-0.61	0.18	0.00	0.07	3.32		
20-Sep	05:00	01:00		0.73	24.64		5.80	36.70	42.48	0.52	1.55	0.11	0.22	3.35		
20-Sep	06:00	01:00		0.72	23.96		6.78	32.07	38.79	3.11	4.09	0.24	0.14	4.45		
20-Sep	07:00	01:00		0.49	17.67		4.80	25.63	30.43	7.90	9.13	0.38	-0.19	4.77		
20-Sep	08:00	01:00		0.36	19.07		3.53	25.08	28.68	12.62	14.00	0.43	0.07	6.08		
20-Sep	09:00	01:00		0.20	18.89		3.24	26.13	29.03	17.64	18.79	0.41	0.03	7.82		
20-Sep	10:00	01:00					3.52	28.54	32.06	21.63	22.54	0.35	0.08	6.77		
20-Sep	11:00	01:00		-0.01	15.10		1.82	22.56	24.36	39.31	39.65	0.39	-0.07	7.73		
20-Sep	12:00	01:00		-0.02	14.77		5.44	21.29	26.75	55.25	54.12	0.37	0.07	7.29		
20-Sep	13:00	01:00		-0.04	12.97		4.24	19.28	23.48	62.57	61.15	0.36	0.11	7.13		
20-Sep	14:00	01:00		-0.04	10.51		3.23	14.87	17.94	63.53	62.41	0.27	0.24	6.19		
20-Sep	15:00	01:00		-0.05	9.81		2.60	12.30	14.86	65.52	64.10	0.28	0.22	5.17		
20-Sep	16:00	01:00		-0.01	11.91		2.34	14.26	16.62	60.46	59.20	0.22	0.34	4.81		
20-Sep	17:00	01:00		0.01	14.98		1.57	15.37	16.90	52.20	51.43	0.18	0.31	4.53		
20-Sep	18:00	01:00		0.05	17.73		0.64	20.68	21.35	36.16	35.98	0.08	0.21	4.14		
20-Sep	19:00	01:00				0.20	0.27	18.20	18.41	29.44	29.84	0.04	0.08	3.09		
20-Sep	20:00	01:00				0.16	0.14	20.19	20.46	21.96	22.40	0.03	0.35	2.60		
20-Sep	21:00	01:00				0.15	0.14	29.05	29.16	10.47	11.45	0.00	0.34	2.99		
20-Sep	22:00	01:00				0.14	0.01	29.24	29.20	8.02	9.14	0.01	0.38	1.43		
20-Sep	23:00	01:00					-0.08	25.88	25.79	9.55	10.66	0.02	0.20	1.61		

LA ATMOSPHERIC FREE RADICAL FIELD STUDY

LOCATION: CLAREMONT, CALIFORNIA  
 SOURCE: UNISEARCH ASSOCIATES INC

DATE	START TIME	AVERAGE INTERVAL	SPECIES	HONO	NO2	NO3	NO	NO2	NOx	O3	O3	LOZ-3	PAN	H2O2	HCl/O	HNO3
DD-MM	HH-MM	(HRS)	TECHNIQUE:	DOAS (ppbv)	DOAS (ppbv)	DOAS (ppbv)	LMA-3 (ppbv)	LMA-3 (ppbv)	LMA-3 (ppbv)	DASIBI (ppbv)	LOZ-3 (ppbv)	LPA-4 (ppbv)	TDLAS (ppbv)	TDLAS (ppbv)	TDLAS (ppbv)	TDLAS (ppbv)
21-Sep	00:00	01:00		0.29	18.27		-0.27	22.47	22.18	11.31	12.54	0.04	0.09	2.83		
21-Sep	01:00	01:00		0.31	17.40		-0.27	19.86	16.59	13.07	14.11	0.08	0.09	2.65		
21-Sep	02:00	01:00					-0.22	16.73	16.47	15.10	16.16	0.10	0.31	2.74		
21-Sep	03:00	01:00					0.50	14.27	14.78	15.61	16.58	0.14	0.08	2.88		
21-Sep	04:00	01:00					-0.02	13.29	13.27	17.77	18.55	0.13	0.00	2.89		
21-Sep	05:00	01:00					1.03	13.93	14.94	17.22	18.13	0.17	0.05	2.42		
21-Sep	06:00	01:00					1.43	12.75	14.18	17.22	18.05	0.16	0.09	3.01		
21-Sep	07:00	01:00					2.13	14.35	16.42	16.06	16.34	0.17	0.14	3.73		
21-Sep	08:00	01:00					4.05	16.01	20.09	15.81	16.56	0.21	-0.04	4.58		
21-Sep	09:00	01:00					2.67	15.03	17.82	21.82	22.48	0.22	0.07	4.03		
21-Sep	10:00	01:00					2.56	14.72	17.27	27.66	28.26	0.25	0.15	4.66		
21-Sep	11:00	01:00		-0.12	9.24		2.94	10.93	13.85	44.84	44.75	0.38				
21-Sep	12:00	01:00		-0.12	9.02		2.49	12.63	15.15	57.20	56.24	0.54				
21-Sep	13:00	01:00		-0.12	8.12		1.82	13.41	15.21	73.51	71.58	0.72				
21-Sep	14:00	01:00		-0.14	8.42		1.13	17.01	18.13	86.33	83.32	0.69				17.62
21-Sep	15:00	01:00		-0.15	10.36		1.14	20.53	21.64	93.18	89.59	0.74				18.77
21-Sep	16:00	01:00		-0.15	12.38		0.14	22.24	22.37	104.54	99.63	0.92				16.83
21-Sep	17:00	01:00		-0.22	19.92		-0.47	32.70	32.36	94.93	90.26	0.87				13.52
21-Sep	18:00	01:00		-0.24	23.28		-1.41	36.08	34.64	64.99	62.90	0.48				7.23
21-Sep	19:00	01:00					-1.19	34.10	32.87	41.92	41.57	0.27				3.89
21-Sep	20:00	01:00					-0.39	34.80	34.45	22.36	23.04	0.09				2.14
21-Sep	21:00	01:00					-0.00	41.80	41.86	8.55	9.66	0.04				2.00
21-Sep	22:00	01:00					0.09	44.38	54.20	1.48	2.27	0.07				1.40
21-Sep	23:00	01:00					14.49	43.00	57.44	-0.43	0.30	0.12				1.48
22-Sep	00:00	01:00		0.89	29.65		8.88	34.04	42.82	2.46	3.42	0.35				1.77
22-Sep	01:00	01:00		0.88	27.06		4.60	26.88	31.40	4.92	5.70	0.40				1.43
22-Sep	02:00	01:00		0.53	18.65		2.64	31.28	33.94	4.19	5.32	0.20				1.36
22-Sep	03:00	01:00		0.08	0.99		1.59	31.68	33.27	3.17	4.33	0.13				1.69
22-Sep	04:00	01:00		0.10	1.30		2.72	28.71	31.38	4.34	5.44	0.23				1.64
22-Sep	05:00	01:00		0.38	18.60		23.30	37.58	60.98	0.37	0.75	0.19				1.25
22-Sep	06:00	01:00		0.50	25.61		32.15	39.82	71.97	-0.15	0.09	0.23				1.59
22-Sep	07:00	01:00		0.00	18.78		13.82	36.14	49.94	2.35	3.31	0.34				1.97
22-Sep	08:00	01:00		0.00	18.40		14.82	38.34	53.17	3.70	4.61	0.37				3.48
22-Sep	09:00	01:00		0.00	27.98		11.72	39.78	51.44	6.48	7.36	0.41				4.77
22-Sep	10:00	01:00		0.19	34.04		10.93	43.84	54.82	11.90	12.69	0.44				7.00
22-Sep	11:00	01:00		0.20	33.05		9.21	43.56	52.71	21.59	22.82	0.56				9.27
22-Sep	12:00	01:00		0.07	27.44		9.29	36.24	45.43	43.95	44.77	0.71				13.84
22-Sep	13:00	01:00		-0.10	19.92		7.45	33.41	40.86	62.78	62.20	0.89				15.93
22-Sep	14:00	01:00		-0.14	9.87		3.48	26.06	29.42	93.89	90.90	1.09				19.06
22-Sep	15:00	01:00		-0.13	12.03		1.78	24.58	26.38	117.58	112.33	1.43				19.51
22-Sep	16:00	01:00		-0.12	11.14		1.19	23.66	24.84	131.09	124.84	1.48				17.70
22-Sep	17:00	01:00		0.28	15.35		0.29	32.88	33.27	132.47	126.18	1.43				15.93
22-Sep	18:00	01:00		0.28	20.37		-0.40	42.65	42.14	81.40	78.65	0.77				7.99
22-Sep	19:00	01:00					0.17	56.00	56.18	39.64	39.78	0.51				4.28
22-Sep	20:00	01:00					0.06	59.55	63.68	16.78	17.70	0.45				3.38
22-Sep	21:00	01:00					0.11	55.91	62.09	8.07	8.73	0.57				2.59
22-Sep	22:00	01:00		0.08	49.35		0.08	49.35	58.83	5.44	6.39	0.69				1.82
22-Sep	23:00	01:00		0.11	16.53		0.11	46.88	63.44	2.52	2.84	1.08				1.27

LA ATMOSPHERIC FREE RADICAL FIELD STUDY

LOCATION: CLAREMONT, CALIFORNIA  
SOURCE: UNISEARCH ASSOCIATES INC

DATE	START TIME HH:MM	AVERAGE INTERVAL (HRS)	SPECIES:	HONO DOAS (ppbV)	NO2 DOAS (ppbV)	NO3 DOAS (ppbV)	NO LMA-3 (ppbV)	NO2 LMA-3 (ppbV)	NOx LMA-3 (ppbV)	O3 DASIBI (ppbV)	O3 LOZ-3 (ppbV)	PAN LPA-4 (ppbV)	H2O2 TDLAS (ppbV)	HCHO TDLAS (ppbV)	HNO3 TDLAS (ppbV)
23-Sep	00:00	01:00		1.10	35.44	0.08	7.09	40.52	47.45	9.21	10.41	0.89	0.10		1.43
23-Sep	01:00	01:00		0.79	25.08	0.09	1.74	30.01	24.81	29.68	30.93	0.68	0.03		1.85
23-Sep	02:00	01:00		0.73	25.86	0.11	1.82	30.81	32.65	22.33	23.35	0.71	0.12		1.78
23-Sep	03:00	01:00		0.86	29.25	0.13	3.68	39.94	43.53	8.47	9.48	0.64	-0.18		1.45
23-Sep	04:00	01:00		0.87	25.12	0.18	3.72	26.23	30.00	16.11	17.69	0.50	-0.07		1.84
23-Sep	05:00	01:00		0.84	32.08	0.17	12.46	39.55	52.04	6.36	7.13	0.63	0.10		1.42
23-Sep	06:00	01:00		0.79	34.90		32.49	45.95	78.50	1.66	1.81	0.80	-0.02		1.56
23-Sep	07:00	01:00		0.85	37.97		59.30	52.12	111.51	1.48	1.68	1.03	0.04		1.27
23-Sep	08:00	01:00		0.16	13.28		45.03	65.22	110.27	6.96	8.53	0.87	0.21		1.03
23-Sep	09:00	01:00		-0.11	15.93		74.11	95.39	169.87	9.71	10.39	1.21	0.27		1.29
23-Sep	10:00	01:00					34.54	104.16	138.42	23.38	24.35	2.19	0.31		4.70
23-Sep	11:00	01:00		-0.09	48.11		7.54	60.95	67.74	67.98	67.28	1.83	0.37		10.56
23-Sep	12:00	01:00		-0.25	29.96		5.98	47.55	53.46	86.44	84.27	0.99	0.47		12.94
23-Sep	13:00	01:00		-0.27	21.90		3.45	38.46	41.76	112.09	108.07	1.19	0.04		14.40
23-Sep	14:00	01:00		-0.37	7.34		1.79	34.28	36.10	134.39	128.56	1.24	0.39		19.36
23-Sep	15:00	01:00		-0.29	7.95		1.47	20.92	22.30	147.31	140.25	1.13	0.55		19.95
23-Sep	16:00	01:00		0.02	10.15		0.04	22.47	22.23	154.68	146.48	1.26	0.53		18.32
23-Sep	17:00	01:00		0.06	8.64		0.50	31.64	32.22	155.52	147.06	1.47	0.51		14.67
23-Sep	18:00	01:00		0.09	5.91		-0.58	47.84	47.25	100.91	97.68	1.01	0.35		8.30
23-Sep	19:00	01:00					-0.50	50.04	49.53	62.81	62.60	0.68	0.28		6.32
23-Sep	20:00	01:00					5.69	74.80	80.74	14.04	14.52	0.58	-0.02		5.00
23-Sep	21:00	01:00					10.79	71.61	82.31	5.50	6.56	1.23	0.01		3.08
23-Sep	22:00	01:00					27.05	64.63	91.70	1.79	2.18	1.64	-0.01		3.09
23-Sep	23:00	01:00					3.78	58.17	61.97	8.90	9.91	1.21	-0.18		2.28
24-Sep	00:00	01:00					1.82	57.49	59.11	10.29	11.27	1.01	0.10		2.50
24-Sep	01:00	01:00					2.39	29.83	32.08	24.82	25.35	0.99	-0.02		2.61
24-Sep	02:00	01:00					1.25	25.68	27.01	30.46	30.54	0.85	-0.03		3.44
24-Sep	03:00	01:00					1.43	24.10	25.30	29.85	30.16	0.69	0.06		3.79
24-Sep	04:00	01:00					1.71	23.17	24.97	28.63	28.96	0.76	-0.02		2.35
24-Sep	05:00	01:00					3.04	19.34	22.27	38.81	39.16	0.71	-0.02		4.20
24-Sep	06:00	01:00					10.90	40.32	51.64	24.01	23.92	0.54	0.20		4.93
24-Sep	07:00	01:00					24.99	56.33	81.21	8.35	8.84	1.60	0.30		2.48
24-Sep	08:00	01:00					15.84	50.17	65.75	27.72	28.80	1.84		19.44	
24-Sep	09:00	01:00					8.26	44.42	52.80	59.07	58.60	1.33	0.36		18.80
24-Sep	10:00	01:00					5.87	42.77	48.19	86.26	88.66	1.07	0.51		15.29
24-Sep	11:00	01:00					1.36	25.76	26.90	110.36	106.58	0.66	0.36		11.79
24-Sep	12:00	01:00					0.69	20.79	21.49	121.46	117.33	0.59	0.48		12.42
24-Sep	13:00	01:00					0.67	25.08	25.82	143.23	137.83	0.90	0.46		12.06
24-Sep	14:00	01:00					0.93	21.33	22.24	153.94	148.92	0.90	0.23		17.19
24-Sep	15:00	01:00					-0.46	47.42	47.49	190.09	181.60	1.99	0.31		22.61
24-Sep	16:00	01:00					-0.53	61.88	61.20	187.82	179.03	2.10	0.33		16.50
24-Sep	17:00	01:00					-0.45	58.15	57.58	135.41	132.02	1.29	0.26		15.72
24-Sep	18:00	01:00					0.41	73.75	74.20	76.28	75.69	0.68	0.51		
24-Sep	19:00	01:00					1.94	82.93	85.08	26.51	27.14	0.32	0.66		7.52
24-Sep	20:00	01:00					10.05	86.50	96.49	5.46	5.96	0.71	0.10		5.57
24-Sep	21:00	01:00					22.32	81.30	103.51	-0.24	0.04	0.90	0.24		3.89
24-Sep	22:00	01:00					16.33	79.55	95.83	1.38	1.40	1.18			3.58
24-Sep	23:00	01:00					20.53	73.71	94.00	1.69	1.84	1.06	0.42		4.45

LA ATMOSPHERIC FREE RADICAL FIELD STUDY

LOCATION: CLAREMONT, CALIFORNIA  
 SOURCE: UNISEARCH ASSOCIATES INC

DATE	START TIME	AVERAGE INTERVAL	SPECIES	HONO DOAS	NO2 DOAS	NO3 DOAS	NO LMA-3	NO2 LMA-3	NOx LMA-3	O3 DASIBI	O3 LOZ-3	PAN LPA-4	H2O2 TDLAS	HCHO TDLAS	HNO3 TDLAS
DD-MM	HH:MM	(HRS)	TECHNIQUE:	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)	(ppbV)
25-Sep	00:00	01:00													6.44
25-Sep	01:00	01:00													6.35
25-Sep	02:00	01:00													5.82
25-Sep	03:00	01:00													6.54
25-Sep	04:00	01:00													6.59
25-Sep	05:00	01:00													5.98
25-Sep	06:00	01:00													5.55
25-Sep	07:00	01:00											0.10		6.12
25-Sep	08:00	01:00											0.32		9.81
25-Sep	09:00	01:00											0.31		11.76
25-Sep	10:00	01:00											-0.03		14.29
25-Sep	11:00	01:00											0.43		15.34
25-Sep	12:00	01:00											0.42		16.54
25-Sep	13:00	01:00											0.49		17.37
25-Sep	14:00	01:00											0.43		16.55
25-Sep	15:00	01:00											0.39		13.25
25-Sep	16:00	01:00											0.37		13.13
25-Sep	17:00	01:00											0.15		12.96
25-Sep	18:00	01:00											0.51		9.44
25-Sep	19:00	01:00											0.51		6.08
25-Sep	20:00	01:00											0.19		3.67
25-Sep	21:00	01:00											0.10		3.89
25-Sep	22:00	01:00											0.05		2.33
25-Sep	23:00	01:00											0.41		2.03
26-Sep	00:00	01:00											0.35		2.41
26-Sep	01:00	01:00											0.51		3.08
26-Sep	02:00	01:00											0.32		3.27
26-Sep	03:00	01:00											0.34		3.05
26-Sep	04:00	01:00											0.43		3.64
26-Sep	05:00	01:00											0.12		3.45
26-Sep	06:00	01:00											0.19		3.00
26-Sep	07:00	01:00											-0.03	4.12	
26-Sep	08:00	01:00											0.51	7.62	
26-Sep	09:00	01:00											0.44	6.82	
26-Sep	10:00	01:00											0.51	9.20	
26-Sep	11:00	01:00											0.71	10.21	
26-Sep	12:00	01:00												8.03	
26-Sep	13:00	01:00													
26-Sep	14:00	01:00													
26-Sep	15:00	01:00													
26-Sep	16:00	01:00													
26-Sep	17:00	01:00													
26-Sep	18:00	01:00													
26-Sep	19:00	01:00													
26-Sep	20:00	01:00													
26-Sep	21:00	01:00													
26-Sep	22:00	01:00													
26-Sep	23:00	01:00													
													0.67	14.55	9.10



## APPENDIX C

Summary statistics along with the complete data set for Carbonyl Species measured during the LA Atmospheric Free Radical Field Study at Claremont, CA during September 1993.





Carbonyl Data: OH. Study, Claremont

Compound Identity from 1 to 12:  
 formaldehyde, acetaldehyde, acetone, propanal, C4 carbonyls (crotonaldehyde, methyl ethyl ketone, butanal), benzaldehyde, C5 carbonyls (pentanones & pentanal), m-tolaldehyde, C6 carbonyls (hexanones and hexanal), and C7 carbonyls.  
 Negative values = less than blank, or non-detected.

Sample #	Date	Start	Stop	Duration	1 HCHO	2 CH3CHO	3 Acetone	4 Propanal	5 Crotonal	6 MEK	7 Butanal	8 Bzal	9 C5	10 m-Tolual	11 C6	12 C7
181	09/04/93	12:31	15:31	03:00	8.72	8.88	6.95	0.57	0.08	2.08	0.66	-0.04	0.83	-0.02	1.76	3.83
181R	09/04/93	12:31	15:31	03:00	8.48	8.49	6.93	0.59	0.88	1.24	0.54	-0.04	0.60	-0.02	3.17	4.20
154	09/04/93	15:33	18:33	03:00	6.20	6.76	4.97	0.68	0.00	1.52	0.59	-0.04	0.55	-0.02	2.40	8.68
212	09/05/93	05:59	08:58	02:59	7.11	5.76	5.17	0.49	0.00	0.77	0.58	-0.04	-0.06	-0.02	1.09	3.30
214	09/05/93	08:59	11:59	03:00	8.86	8.03	5.74	0.79	0.00	1.22	0.44	-0.04	0.58	-0.02	1.52	4.34
204	09/05/93	08:59	11:59	Blank												
206	09/05/93	12:02	16:02	04:00	11.03	5.39	5.08	0.42	0.82	0.75	0.28	-0.03	0.43	0.03	1.24	2.93
195	09/05/93	16:06	20:07	04:01	10.12	3.36	2.59	0.34	0.66	1.14	0.45	-0.02	-0.04	-0.01	0.62	1.25
197	09/05/93	16:06	20:07	04:01	10.01	3.49	2.45	0.40	0.00	-0.00	0.00	-0.02	0.51	-0.01	0.80	1.40
220	09/06/93	06:00	09:00	03:00	5.37	4.36	4.36	0.35	0.21	0.87	0.39	-0.04	-0.06	-0.02	0.89	3.10
210	09/06/93	09:00	12:00	03:00	9.01	7.12	5.12	0.71	0.41	1.09	0.58	-0.04	0.48	-0.02	1.00	3.57
186 R	09/06/93	12:00	16:00	04:00	10.92	5.53	6.86	0.69	0.90	1.00	0.56	0.13	1.77	0.17	1.18	2.97
194	09/06/93	16:00	20:00	04:00	10.87	5.55	6.84	0.69	0.89	1.01	0.53	0.05	2.32	0.20	1.99	3.06
188	09/07/93	03:00	06:00	03:00	6.44	5.92	6.20	0.87	0.85	1.07	0.64	0.24	1.91	0.18	1.38	3.17
219	09/07/93	06:00	09:00	03:00	7.37	5.56	6.89	0.63	0.31	0.88	0.31	0.11	1.13	0.07	1.17	4.05
159	09/07/93	09:00	12:00	03:00	9.47	6.26	7.24	0.65	0.42	1.01	0.30	0.10	1.50	0.10	2.11	5.37
196	09/07/93	12:00	16:00	04:00	9.36	8.83	9.75	1.15	0.62	1.58	0.67	0.34	2.35	0.19	2.11	7.69
215	09/07/93	16:00	20:00	04:00	15.09	8.23	8.38	1.07	0.98	1.40	0.70	0.23	2.61	0.20	1.98	4.60
170	09/08/93	00:00	04:00	04:00	15.19	6.23	6.52	0.88	0.61	1.12	0.52	0.13	1.59	0.13	1.55	4.27
218	09/08/93	07:18	11:18	04:00	8.76	6.71	8.29	0.85	0.35	1.21	0.38	0.11	1.46	0.07	1.70	5.27
227	09/08/93	12:00	16:00	04:00	15.54	4.97	5.12	0.58	0.33	0.89	0.34	0.07	1.69	0.10	1.11	4.76
211	09/08/93	18:00	22:00	04:00	16.47	8.21	10.11	1.23	0.94	1.67	0.75	0.30	3.47	0.24	2.39	6.03
211R	09/08/93	18:00	22:00	04:00	11.64	9.47	10.56	1.36	0.78	1.95	0.63	0.26	2.64	0.17	2.82	6.07
224	09/09/93	00:00	04:00	04:00	11.40	9.07	10.19	1.33	0.79	1.91	0.67	0.24	1.83	0.14	2.77	6.32
226	09/09/93	06:00	10:00	04:00	8.18	6.20	9.09	0.72	0.51	1.43	0.36	0.12	2.12	0.12	2.59	4.08
193	09/09/93	12:00	16:00	04:00	11.50	7.06	9.70	0.78	0.51	1.57	0.46	0.17	2.41	0.10	1.71	5.93
202	09/09/93	18:00	22:00	04:00	21.38	13.65	18.71	1.72	1.69	3.00	1.07	0.39	5.10	0.24	3.42	6.62
189	09/09/93	18:00	22:00	04:00	24.51	8.78	9.96	1.35	0.82	1.83	0.69	0.27	2.66	0.15	2.79	5.65
198	09/10/93	00:00	04:00	04:00	21.19	7.92	9.00	1.19	0.72	1.69	0.55	0.24	2.35	0.13	2.65	5.32
217	09/10/93	06:00	10:00	04:00	10.77	7.70	11.62	0.88	0.61	1.94	0.41	0.20	1.55	0.09	2.04	5.25
269	09/10/93	12:00	16:00	04:00	15.88	10.69	15.37	1.20	0.64	2.50	0.56	0.36	2.54	0.14	3.54	8.17
268	09/10/93	18:00	22:00	04:00	23.95	14.20	16.39	1.82	1.56	2.86	1.12	0.38	5.60	0.27	3.80	6.77
272	09/10/93	18:00	22:00	04:00	28.84	10.86	13.11	1.55	1.11	2.47	0.77	0.34	2.43	0.16	3.42	5.88
272R	09/10/93	18:00	22:00	04:00	30.69	11.25	13.67	1.60	1.10	2.48	0.77	0.33	2.38	0.15	3.09	5.39
229	09/11/93	00:30	04:00	03:30	31.09	11.53	13.73	1.62	1.13	2.42	0.74	0.34	2.18	0.12	3.00	5.30
192	09/11/93	06:00	10:00	04:00	13.69	15.46	17.28	1.33	0.73	2.62	0.65	0.25	2.59	0.13	4.13	8.10
200	09/11/93	12:35	16:00	03:25	11.02	10.86	15.13	1.50	1.52	2.31	0.92	0.30	3.62	0.22	3.08	7.27
222	09/11/93	18:00	22:00	04:00	10.79	7.61	10.75	1.11	0.79	1.38	0.53	0.19	1.41	0.12	1.62	4.33
283	09/12/93	00:00	04:00	04:00	7.53	5.98	8.25	0.87	0.43	1.18	0.39	0.13	0.72	0.07	0.95	3.57
251	09/12/93	06:00	10:00	04:00	5.91	4.72	6.80	0.68	0.46	0.89	0.39	0.10	0.86	0.09	0.93	2.85
201	09/12/93	12:00	16:00	04:00	5.90	5.34	7.35	0.70	0.78	0.95	0.50	0.12	1.75	0.12	1.26	3.54

Carbonyl Data: OH. Study, Claremont

Compound Identity from 1 to 12:  
 formaldehyde, acetaldehyde, acetone, propanal, C4 carbonyls (crotonaldehyde, methyllethyl ketone, butanal), benzaldehyde, C5 carbonyls  
 (pentanones & pentanal), m-tolualdehyde, C6 carbonyls (hexanones and hexanal), and C7 carbonyls.  
 Negative values = less than blank, or non-detected.

Sample #	Date	Start	Stop	Duration	1 HCHO	2 CH3CHO	3 Acetone	4 Propanal	5 Crotonal	6 MEK	7 Butanal	8 Bzal	9 C5	10 m-Tolual	11 C6	12 C7
208	09/12/93	18:00	22:00	04:00	2.53	2.47	3.59	0.34	0.26	0.35	0.20	0.06	0.42	0.05	0.33	2.02
187	09/12/93	18:00	22:00	04:00	3.03	2.18	2.53	0.38	0.18	0.32	0.27	0.09	0.46	0.05	0.39	2.72
216	09/13/93	00:00	04:00	04:00	1.89	1.64	2.17	0.30	0.27	0.31	0.21	0.04	0.45	0.04	0.34	1.73
216 R	09/13/93	00:00	04:00	04:00	1.97	1.69	2.28	0.32	0.27	0.30	0.21	0.03	0.42	0.03	0.26	1.58
205	09/13/93	06:00	10:00	04:00	2.49	1.80	2.30	0.28	0.18	0.32	0.17	0.04	0.36	0.02	0.30	2.35
213	09/13/93	12:00	16:00	04:00	4.49	4.12	4.20	0.56	0.41	0.70	0.33	0.07	0.95	0.07	0.66	2.24
207	09/13/93	18:00	22:00	04:00	3.14	2.40	3.07	0.34	0.23	0.43	0.20	0.05	0.47	0.03	0.36	1.92
209	09/14/93	00:00	04:00	04:00	3.78	2.90	3.73	0.35	0.24	0.51	0.18	0.07	0.32	0.02	0.31	2.19
286	09/14/93	06:00	10:00	04:00	4.08	3.30	3.16	0.46	0.25	0.57	0.24	0.08	0.48	0.03	0.42	2.69
249	09/14/93	12:00	16:00	04:00	7.00	6.65	6.21	0.89	0.68	1.01	0.50	0.12	1.66	0.09	1.25	3.42
245	09/14/93	18:00	22:00	04:00	3.98	3.17	2.93	0.44	0.26	0.52	0.24	0.06	0.48	0.04	0.35	2.07
271	09/15/93	00:00	04:00	04:00	3.46	4.00	4.37	0.39	0.21	0.62	0.19	0.06	0.38	0.12	0.18	1.34
263	09/15/93	06:00	10:00	04:00	3.78	2.75	3.07	0.34	0.24	0.48	0.19	0.04	0.36	0.02	0.22	1.57
252	09/15/93	12:00	16:00	04:00	6.86	6.37	6.71	0.89	0.72	1.19	0.51	0.12	1.47	0.09	1.21	3.00
252 R	09/15/93	12:00	16:00	04:00	6.65	6.16	6.47	0.88	0.65	1.13	0.49	0.11	1.59	0.84	1.14	2.76
234	09/15/93	18:00	22:00	04:00	4.25	3.03	3.56	0.49	0.29	0.59	0.23	0.06	0.60	0.03	0.43	1.89
274	09/15/93	18:00	22:00	04:00	4.38	2.99	3.46	0.48	0.28	0.59	0.25	0.05	0.58	0.04	0.42	1.78
226	09/16/93	00:00	04:00	04:00	2.99	2.01	2.73	0.28	0.19	0.42	0.15	0.02	0.25	0.22	0.10	1.29
250	09/16/93	06:00	10:00	04:00	3.62	2.64	3.16	0.34	0.20	0.42	0.18	0.04	0.28	0.28	0.28	1.52
221	09/16/93	12:00	16:00	04:00	4.44	3.97	3.80	0.57	0.34	0.60	0.32	0.05	0.73	0.05	0.50	2.13
280	09/16/93	18:00	22:00	04:00	2.17	1.80	2.29	0.29	0.21	0.31	0.19	0.03	0.37	0.17	0.24	1.56
223	09/16/93	18:00	22:00	04:00	2.23	1.83	2.05	0.29	0.22	0.28	0.20	0.02	0.33	0.18	0.22	1.52
270	09/17/93	00:00	04:00	04:00	2.41	2.12	2.50	0.28	0.18	0.44	0.17	0.05	0.36	0.14	0.13	1.37
255	09/17/93	06:00	10:00	04:00	3.05	2.38	2.58	0.31	0.19	0.42	0.19	0.09	0.35	0.03	0.18	2.07
255 R	09/17/93	06:00	10:00	04:00	2.92	2.28	2.43	0.29	0.17	0.39	0.18	0.10	0.35	0.03	0.23	1.80
237	09/17/93	12:00	16:00	04:00	3.47	2.89	3.08	0.48	0.33	0.55	0.30	0.07	0.79	0.07	0.47	2.33
239	09/17/93	18:00	22:00	04:00	2.75	1.76	2.17	0.29	0.19	0.33	0.18	0.03	0.36	0.03	0.36	1.62
228	09/17/93	18:00	22:00	04:00	2.58	2.05	2.49	0.30	0.20	0.36	0.19	0.04	0.40	0.04	0.35	1.69
242	09/18/93	00:00	04:00	04:00	3.21	2.32	3.42	0.32	0.18	0.49	0.19	0.04	0.39	0.03	0.26	2.37
242 R	09/18/93	00:00	04:00	04:00	3.03	2.22	3.23	0.32	0.17	0.45	0.17	0.02	0.33	0.02	0.26	1.90
235	09/18/93	06:00	10:00	04:00	3.24	2.45	2.51	0.33	0.17	0.44	0.23	0.03	0.47	0.05	0.32	2.12
258	09/18/93	12:00	16:00	04:00	4.18	4.41	5.14	0.63	0.48	0.81	0.42	0.09	1.94	0.11	1.28	4.41
256	09/18/93	18:00	22:00	04:00	8.76	6.18	5.30	0.75	0.44	0.93	0.38	0.08	1.50	0.09	1.04	4.51
247	09/19/93	00:00	04:00	04:00	6.20	5.11	6.55	0.70	0.31	0.96	0.34	0.09	0.71	0.06	0.81	3.33
267	09/19/93	06:00	10:00	04:00	8.16	5.84	6.49	0.87	0.39	1.01	0.44	0.12	0.99	0.06	1.28	4.23
279	09/19/93	12:00	16:00	04:00	7.83	7.56	8.96	1.06	0.89	1.38	0.69	0.19	2.30	0.16	1.99	4.20
264	09/19/93	18:00	22:00	04:00	9.72	7.22	7.45	1.04	0.55	1.21	0.54	0.15	1.18	0.09	1.74	5.09
261	09/20/93	00:00	04:00	04:00	5.51	4.57	6.47	0.64	0.31	0.85	0.35	0.07	0.73	0.07	0.81	2.95
232	09/20/93	06:00	10:00	04:00	2.66	1.81	2.15	0.27	0.13	0.35	0.15	0.02	0.31	0.01	0.28	2.62
253	09/20/93	12:00	16:00	04:00	4.53	4.42	4.64	0.66	0.46	0.84	0.39	0.08	1.43	0.10	1.43	4.16
253 R	09/20/93	12:00	16:00	04:00	4.54	4.41	4.65	0.65	0.46	0.81	0.38	0.12	1.35	0.08	1.49	3.78
230	09/20/93	18:00	22:00	04:00	3.63	2.45	3.13	0.39	0.28	0.53	0.22	0.05	0.51	0.05	0.48	2.45

Carbonyl Data: OH. Study, Claremont

Compound Identity from 1 to 12:  
 formaldehyde, acetaldehyde, acetone, propanal, C4 carbonyls (crotonaldehyde, methyl ethyl ketone, butanal), benzaldehyde, C5 carbonyls  
 (pentanones & pentanal), m-tolualdehyde, C6 carbonyls (hexanones and hexanal), and C7 carbonyls.  
 Negative values = less than blank, or non-detected.

Sample #	Date	Start	Stop	Duration	1 HCHO	2 CH3CHO	3 Acetone	4 Propanal	5 Crotonal	6 MEK	7 Butanal	8 Bzal	9 C5	10 m-Tolual	11 C6	12 C7	
273	09/20/93	18:00	22:00	04:00	3.34	2.43	3.32	0.88	0.28	0.53	0.21	0.05	0.48	0.04	0.46	2.93	
231	09/21/93	00:00	04:00	04:00	3.24	3.10	4.01	0.47	0.23	0.63	0.23	0.06	0.47	0.04	0.47	1.94	
265	09/21/93	06:00	10:00	04:00	3.71	3.34	4.61	0.49	0.27	0.68	0.23	0.06	0.62	0.04	0.64	2.19	
246	09/21/93	12:00	16:00	04:00	6.98	5.78	6.48	0.77	0.62	0.98	0.42	0.11	1.75	0.08	1.40	2.41	
284	09/21/93	18:00	22:00	04:00	8.18	4.98	6.08	0.78	0.40	0.98	0.39	0.13	0.94	0.05	0.97	1.79	
266	09/22/93	00:00	04:00	04:00	4.22	4.21	5.61	0.49	0.26	0.87	0.21	0.07	0.43	0.02	0.40	1.16	
248	09/22/93	06:00	10:00	04:00	6.34	5.49	6.21	0.65	0.34	1.02	0.26	0.10	0.49	0.02	0.65	1.22	
244	09/22/93	12:00	16:00	04:00	10.05	6.00	7.67	0.95	0.78	1.28	0.63	0.27	1.65	0.08	1.56	2.49	
277	09/22/93	18:00	22:00	04:00	6.95	6.20	9.58	0.88	0.44	1.48	0.46	0.12	1.19	0.06	1.44	3.03	
277 R	09/22/93	18:00	22:00	04:00	6.78	6.06	9.27	0.82	0.42	1.41	0.41	0.13	1.14	0.06	1.39	2.56	
238	09/23/93	00:00	04:00	04:00	7.85	6.34	9.81	0.88	0.44	1.49	0.45	0.14	0.77	0.57	1.44	2.16	
281	09/23/93	06:00	10:00	04:00	11.78	8.10	9.56	1.01	0.56	1.39	0.41	0.23	0.77	0.73	2.19	2.61	
236	09/23/93	12:00	16:00	04:00	11.45	8.27	12.31	1.26	1.05	1.72	0.66	0.22	0.78	1.39	2.54	3.71	
285	09/23/93	18:00	22:00	04:00	11.50	11.43	12.97	1.47	0.79	2.00	0.62	0.22	1.66	0.07	1.91	2.83	
243	09/24/93	00:00	04:00	04:00	8.77	6.61	10.54	0.94	0.47	1.67	0.48	0.14	1.27	0.05	1.75	2.70	
283	09/24/93	06:00	10:00	04:00	9.75	6.88	9.72	0.87	0.44	1.34	0.41	0.15	0.81	0.95	1.99	3.71	
278	09/24/93	12:00	16:00	04:00	12.10	6.58	9.59	1.27	0.95	1.49	0.66	0.15	0.57	1.12	2.14	3.14	
275	09/24/93	18:00	22:00	04:00	12.00	10.71	11.33	1.46	0.73	1.80	0.57	0.22	1.59	0.05	1.90	2.80	
254	09/25/93	00:00	04:00	04:00	7.83	5.83	9.28	0.75	0.40	1.29	0.37	0.13	0.74	0.74	1.99	2.83	
262	09/25/93	06:00	10:00	04:00	11.49	4.88	6.49	0.59	0.27	0.75	0.33	0.09	0.65	0.66	1.17	3.57	
262 R	09/25/93	06:00	10:00	04:00	11.66	4.99	6.59	0.57	0.28	0.79	0.36	0.07	0.37	0.97	1.20	4.06	
282	09/25/93	12:00	16:00	04:00	8.70	4.66	5.87	0.62	0.55	0.73	0.44	0.11	1.18	0.11	0.87	2.02	
260	09/25/93	18:00	22:00	04:00	9.14	7.47	9.53	1.10	0.62	1.30	0.52	0.16	1.74	0.09	2.18	1.89	
124	09/26/93	00:00	04:00	04:00	5.92	5.83	7.05	0.66	0.30	0.82	0.34	0.09	1.41	0.04	1.37	4.02	
125	09/26/93	06:00	10:00	04:00	5.67	3.59	4.85	0.44	0.28	0.57	0.32	0.06	1.11	0.07	0.92	3.50	
119	09/26/93	12:00	16:00	04:00	6.88	7.65	10.36	1.11	0.83	1.16	0.65	0.15	2.06	0.17	1.94	3.44	
143	09/26/93	18:00	22:00	04:00	11.24	8.83	10.19	1.03	0.54	1.23	0.57	0.16	1.81	0.11	2.11	8.58	
O'Brian's Samples																	
257	09/21/93	13:38	14:38	01:00	1.25	3.30	3.20	0.02	0.09	0.51	0.13	-0.11	0.26	0.09	-0.21	3.94	
240	09/23/93	12:09	13:12	01:03	13.13	10.37	10.53	1.55	0.72	1.60	0.90	0.18	3.02	0.14	2.25	8.20	
276	09/23/93	14:00	15:06	01:06	12.53	10.18	12.38	1.66	0.95	2.03	1.05	0.18	2.90	0.17	2.51	7.72	
241	09/24/93	10:58	12:18	01:20	7.12	6.16	8.32	0.93	0.55	1.32	0.63	0.17	2.15	0.11	1.95	7.85	
259	09/24/93	15:00	16:00	01:00	14.82	11.24	14.95	2.09	1.11	3.35	1.24	0.31	6.00	0.09	5.58	-0.04	
Avg Blank.																	
					HCHO	CH3CHO	Acetone	Propanal	Crotonal	MEK	C4	Bzal	C5	m-Tolual	C6	C7	0
					0.08	0.057	0.421	0.028	0	0	0	0	0.011	0	0.062	0	0

## APPENDIX D

Example of the results obtained for the Hydrocarbon Speciation from canister samples measured during the LA Atmospheric Free Radical Field Study at Claremont, CA during September 1993.



Date	09/06/93		11.XLS
Start Time	09:46		
Stop Time	11:45		
Total ppbC	505.15		
Iden. ppbC	452.15		
	Carbon #	Class	ppbC
Ethane	2	a	9.93
Propane	3	a	19.07
2MPropane	4	a	7.48
Butane	4	a	15.34
i-Pentane	5	a	30.64
Pentane	5	a	12.00
CyPentane	5	a	1.28
2,2DMButane	6	a	0.57
2,3DMButane	6	a	2.42
2MPentane	6	a	8.95
3MPentane	6	a	6.67
Hexane	6	a	6.69
MCyPentane	6	a	5.23
2,2DMPentane	7	a	0.69
2,4DMPentane	7	a	1.80
2,2,3TMButane	7	a	1.26
2MHexane	7	a	2.98
2,3DMPentane	7	a	2.57
3MHexane	7	a	3.80
Heptane	7	a	2.26
2,2,3TMPnta	8	a	5.58
2,5DMHxa/TMPnta	8	a	1.06
2,4DMHxa	8	a	0.04
2,3,4TMPnta	8	a	1.88
2,3DMHexane	8	a	0.14
2MHptane	8	a	1.02
4MHpta/3M3EPnta	8	a	0.57
3,4DMHxa	8	a	0.16
3MHpta/DMCyHxa	8	a	1.17
Octane	8	a	1.29
2,3,5TMHxa	9	a	0.14
2,2DMHpta	9	a	0.14
4,4DMHpta	9	a	0.21
2,6DMHpta	9	a	0.40
3,3& 3,5DMHpta	9	a	0.18
DMHeptanes	9	a	0.55
4- & 2MOtanes	9	a	0.30
3MOctane	9	a	1.10
Nonane	9	a	1.32
2,2DMOcta	10	a	0.05

Date	09/06/93		11.XLS
Start Time	09:46		
Stop Time	11:45		
Total ppbC	505.15		
Iden. ppbC	452.15		
	Carbon #	Class	ppbC
3,3DMOcta	10	a	0.12
2,3DMOcta	10	a	0.48
2MNona	10	a	0.50
3EOcta	10	a	0.19
3MNona	10	a	0.32
Decane	10	a	2.28
C11 Alkane	11	a	0.25
C11 Alkane	11	a	0.53
Undecane	11	a	1.02
Dodecane	12	a	0.52
3-Carene	10	b	0.23
d-Limonene	10	b	0.49
g-Terpinene	10	b	0.27
F22	1	c	0.17
F12	1	c	0.21
F11	1	c	0.04
F113	2	c	0.29
Ethylene	2	e	9.62
Propene	3	e	2.98
i-Butene	4	e	1.70
1,3-Btadiene	4	e	0.27
t2-Butene	4	e	0.08
c2-Butene	4	e	0.22
3M1Butene	5	e	0.21
t2Pentene	5	e	0.24
c2Pentene	5	e	0.15
1Hexene	6	e	0.72
t3Hexene	6	e	0.13
c3Hexene	6	e	0.17
t2Hexene	6	e	0.15
3Mt2Pentene	6	e	0.42
2M2Pentene	6	e	1.09
c2Hexene	6	e	0.02
3Mc2Pentene	6	e	1.01
2M2Hexene	7	e	0.07
3Mt3Hexene	7	e	0.09
2,4,4TM1Pnte	8	e	0.82
1-Octe	8	e	0.14
t2-Octene	8	e	0.20
c2-Octe	8	e	0.07

Date	09/06/93		11.XLS
Start Time	09:46		
Stop Time	11:45		
Total ppbC	505.15		
Iden. ppbC	452.15		
	Carbon #	Class	ppbC
t3-None	9	e	0.78
t2-None	9	e	0.73
c2-None	9	e	0.14
1-Decene	10	e	0.11
MCl	1	h	0.74
MBr	1	h	0.09
DCIMethane	1	h	0.16
ECl	2	h	0.11
t1,2DCIEte	2	h	0.53
CvHexane	6	n	1.56
1,1DMCyPentane	7	n	1.25
c1,3DMCyPnta	7	n	1.15
t1,3DMCyPnta	7	n	1.15
MCyHxa/DMCyPnta	7	n	1.69
ECyPntane	7	n	1.28
TMCyPta/2,2DMHxa	8	n	0.31
1t2c4TMCyPnta	8	n	0.47
1t2c3TMCyPnta	8	n	0.24
1,1,2TMCyPnta	8	n	0.84
c1,3DMCyHxa	8	n	0.44
t1,4DMCyHxa	8	n	3.21
1,1DMCyHxa	8	n	0.53
c1,3EMCyPnta	8	n	0.34
t1,2EMCyPnta	8	n	0.18
t1,2DMCyHxa	8	n	0.13
iPrCyPnta/TMHxa	8	n	0.18
c1,2DMCyHxa	8	n	0.77
ECyHxa	8	n	0.36
nPrCyPnta	8	n	0.33
1,1,3TMCyHxa	9	n	0.29
C9 Nphthene	9	n	0.12
iBuCyPnta	9	n	0.09
nBuCyPnta	9	n	0.27
Benzene	6	r	11.91
Toluene/TMPnta	7	r	25.59
EBzn	8	r	4.40
m-Xylene	8	r	7.27
p-Xylene	8	r	3.43
Styrene	8	r	0.34
o-Xyl/TMCyHxa	8	r	6.94

Date	09/06/93		11.XLS
Start Time	09:46		
Stop Time	11:45		
Total ppbC	505.15		
Iden. ppbC	452.15		
	Carbon #	Class	ppbC
iPrBzn	9	r	0.25
nPrBzn	9	r	1.01
m-EToluene	9	r	2.68
p-EToluene	9	r	1.61
1,3,5TMBzn	9	r	0.44
o-EToluene	9	r	1.17
1,2,4TMBzn	9	r	2.64
tBuBzn	9	r	3.33
1,2,3TMBzn	9	r	0.90
sBuBzn	10	r	0.60
1M3iPrBzn	10	r	0.04
1M4iPrBzn	10	r	0.58
p-DEBzn	10	r	0.20
1M4nPrBzn	10	r	0.80
C4-Bzn	10	r	0.30
o-DEBzn	10	r	0.56
nBuBzn	10	r	0.46
1,3DM2EBzn	10	r	0.74
C4-Bzn	10	r	7.20
t1Bu2MBzn	11	r	0.12
Naphthalene	12	r	3.49
Acetylene	2	v	13.14
Propyne	3	v	0.52
1-Butyne	4	v	0.08
Oxy-HC			6.88
Oxy-HC			6.20
Oxy-HC			38.14
Oxy-HC			0.08
Oxy-HC			12.18
Oxy-HC			49.68
Oxy-HC			14.69
Oxy-HC			7.27
Oxy-HC			1.90
Oxy-HC			4.23
Oxy-HC			0.17

## APPENDIX E

Carbon monoxide and methane values obtained from canister samples measured during the LA Atmospheric Free Radical Field Study at Claremont, CA during September 1993.



LA Atmospheric Free Radical Field Study: Methane & Carbon Monoxide Levels							
Sample #	Date	Start Time	End Time	Methane, ppm		CO, ppm	
					Repeat		Repeat
OB#2	09/23/93	12:45	12:50	1.99	2.05	2.56	2.40
OB#3	09/23/93	14:37	14:41	2.17		1.03	
OB#4	09/24/93	11:39	11:44	2.12		1.35	
OB#5	09/24/93	15:30	15:35	2.10		1.75	1.74
OB#6	09/25/93	11:30	11:35	1.79		1.82	
OB#7	09/25/93	22:30		1.79	1.85	2.67	
OB#8	09/27/93	09:50		1.69		1.02	
OB#9	09/28/93	14:53		1.68		1.43	
OB#10	09/30/93	05:40		1.74		2.11	1.95
OB#11	10/04/93	14:31		2.12		1.32	
58	09/19/93	06:00	10:00	2.03	2.01	1.02	
59	09/19/93	12:00	16:00	2.04		0.98	
60	09/19/93	18:00	22:00	1.89		0.63	
61	09/20/93	00:00	04:00	1.93		0.82	
62	09/20/93	06:00	10:00	1.97		0.73	
63	09/20/93	12:00	16:00	1.79	1.84	0.80	0.68
64	09/20/93	18:00	22:00	1.75		0.41	
65	09/21/93	00:00	04:00	1.76	1.71	0.54	
66	09/21/93	06:00	10:00	1.77		0.61	
67	09/21/93	12:00	16:00	1.75		0.95	
68	09/21/93	18:00	22:00	1.71		0.72	
69	09/22/93	00:00	04:00	1.88		0.69	
70	09/22/93	06:00	10:00	1.96		0.73	0.76
71	09/22/93	12:00	16:00	1.80	1.82	0.96	
72	09/22/93	18:00	22:00	1.84		1.00	
73	09/23/93	00:00	04:00	1.94		1.05	
74	09/23/93	06:00	10:00	2.04		1.70	
75	09/23/93	12:00	16:00	2.01		1.21	1.25
76	09/23/93	18:00	22:00	1.99		1.11	
77	09/24/93	00:00	04:00	1.82		0.84	
78	09/24/93	06:00	10:00	1.80		1.23	
79	09/24/93	12:00	16:00	1.83		0.82	
80	09/24/93	18:00	22:00	1.93		1.42	1.39
81	09/25/93	00:00	04:00	1.88		1.02	
82	09/25/93	06:00	10:00	1.83		0.69	
83	09/25/93	12:00	16:00	1.59	1.43	0.34	
84	09/25/93	18:00	22:00	1.82		1.28	
85	09/26/93	00:00	04:00	1.69		0.72	0.74
86	09/26/93	06:00	10:00	1.70		0.33	
87	09/26/93	12:00	16:00	1.66		0.41	
88	09/26/93	18:00	22:00	1.61		0.76	0.76

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