

# Atmospheric Chemistry of Organic Oxidants and Their Precursors

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## MEASUREMENTS OF PANs IN MEXICO CITY

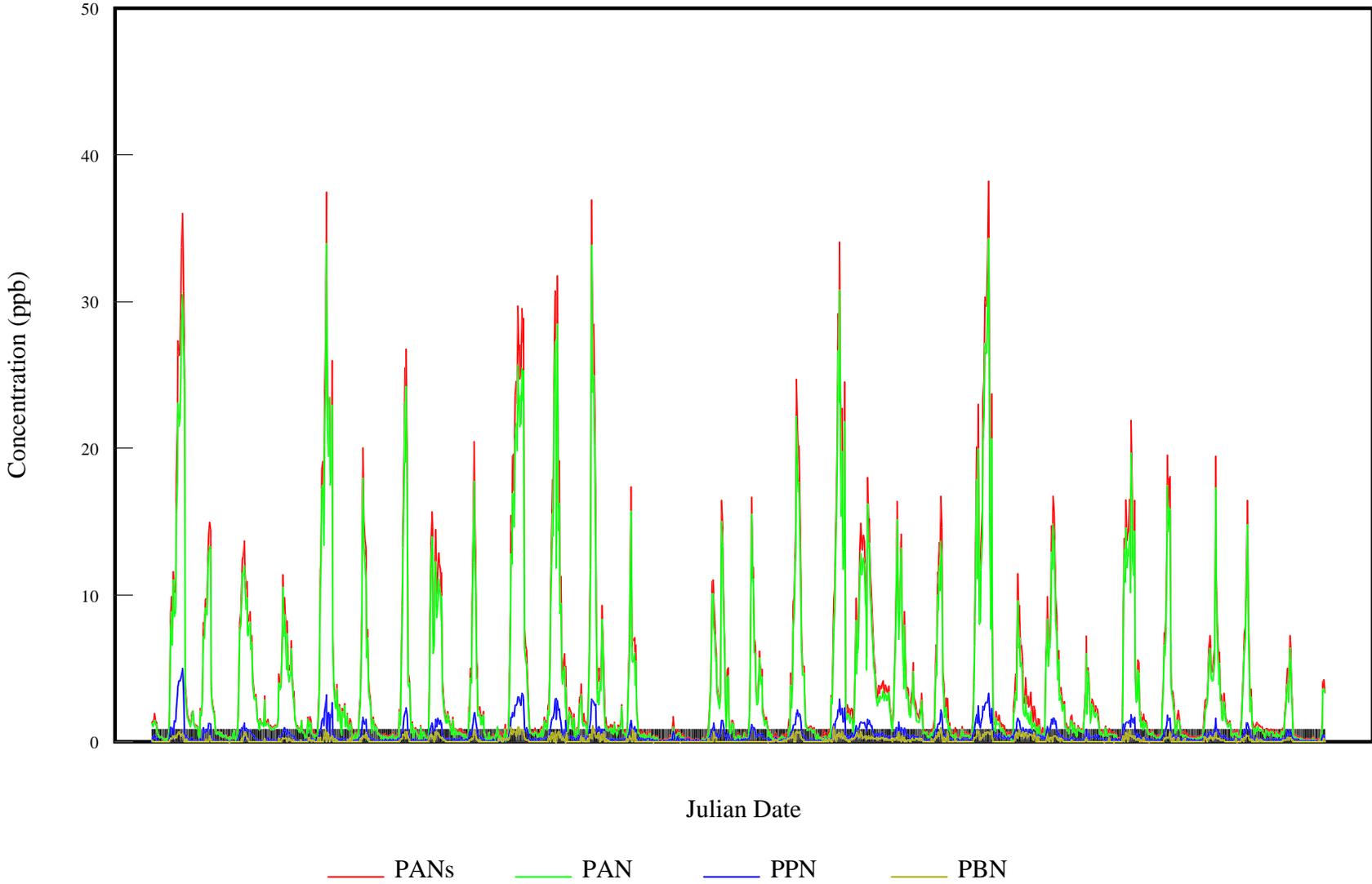
Peroxyacyl nitrates ( $\text{RCO}_3\text{NO}_2$ ) were measured in Mexico City for approx. 30 days in Feb./Mar. 1997 at the Instituto Mexicano de Petroleo (IMP). An automated gas chromatograph with an electron capture detector (GC/ECD) was used to perform the measurements at 30 minute intervals during the field campaign. Peroxyacetyl nitrate ( $\text{R} = \text{CH}_3-$ ), peroxypropionyl nitrate ( $\text{R} = \text{CH}_3\text{CH}_2-$ ), and peroxybutyryl nitrate ( $\text{R} = \text{CH}_3\text{CH}_2\text{CH}_2-$ ) were all observed at levels above 1 ppb. Peroxyacetyl nitrate levels exceeded 30 ppb during five episodes and exceeded 10 ppb during all but two days of the study. PAN/Ozone ratios were approx. 0.1 although the ratios were higher during episodes, indicating a large source of  $\text{RCO}_3\cdot$  radicals in Mexico City. Strong diurnal variations were observed indicating 1) early and rapid formation of PANs, as fast or faster than ozone, 2) very rapid loss of PANs in the mid-afternoon, again as fast or faster than ozone, and 3) little carry over from one day to the next in the air basin. Similar diurnal behavior has been recently reported for Santiago de Chile by B. Rappenglück and co-workers (Univ. München), who reported 20 ppb levels of peroxyacetyl nitrate during Nov.-Dec. 1996. Peroxyacetyl nitrate levels of 30-50 ppb were reported for the South Coast Air Basin in the late 70s by Tuazon and co-workers, who also noted a ratio of peroxyacetyl nitrate to ozone of 0.1.

Formaldehyde photolysis is most likely responsible for the observed rapid conversion of  $\text{NO}$  to  $\text{NO}_2$  via  $\text{HO}_2$  reactions leading to  $\text{OH}$  formation in the absence of  $\text{O}_3$  in the early morning. Researchers from the UNAM have reported 100 ppb levels of formaldehyde in the early morning in Mexico City. Butenes from automotive and LPG sources are the likely candidates for the PANs rapid formation, as they will form  $\text{RCO}_3\cdot$  from  $\text{OH}$  and  $\text{O}_3$  reactions. MTBE usage may be a source of formaldehyde and isobutene, as it is being added to the fuels as an octane enhancer as leaded fuels have been removed.

The late afternoon losses of PANs that are faster than ozone loss have been observed during episodes. Similar behavior has been observed in Santiago de Chile. Ozone should be reacted faster away than PANs if the loss is gas phase chemical removal by NO since the thermal decomposition of the PANs at the moderate temperatures of Mexico City (>7000 ft altitude). Recent work in our laboratory indicates that PANs react rapidly on carbonaceous soot surfaces. Both Mexico City and Santiago de Chile have very high PM-2.5 aerosol loadings, and the loss of PANs in the afternoon may

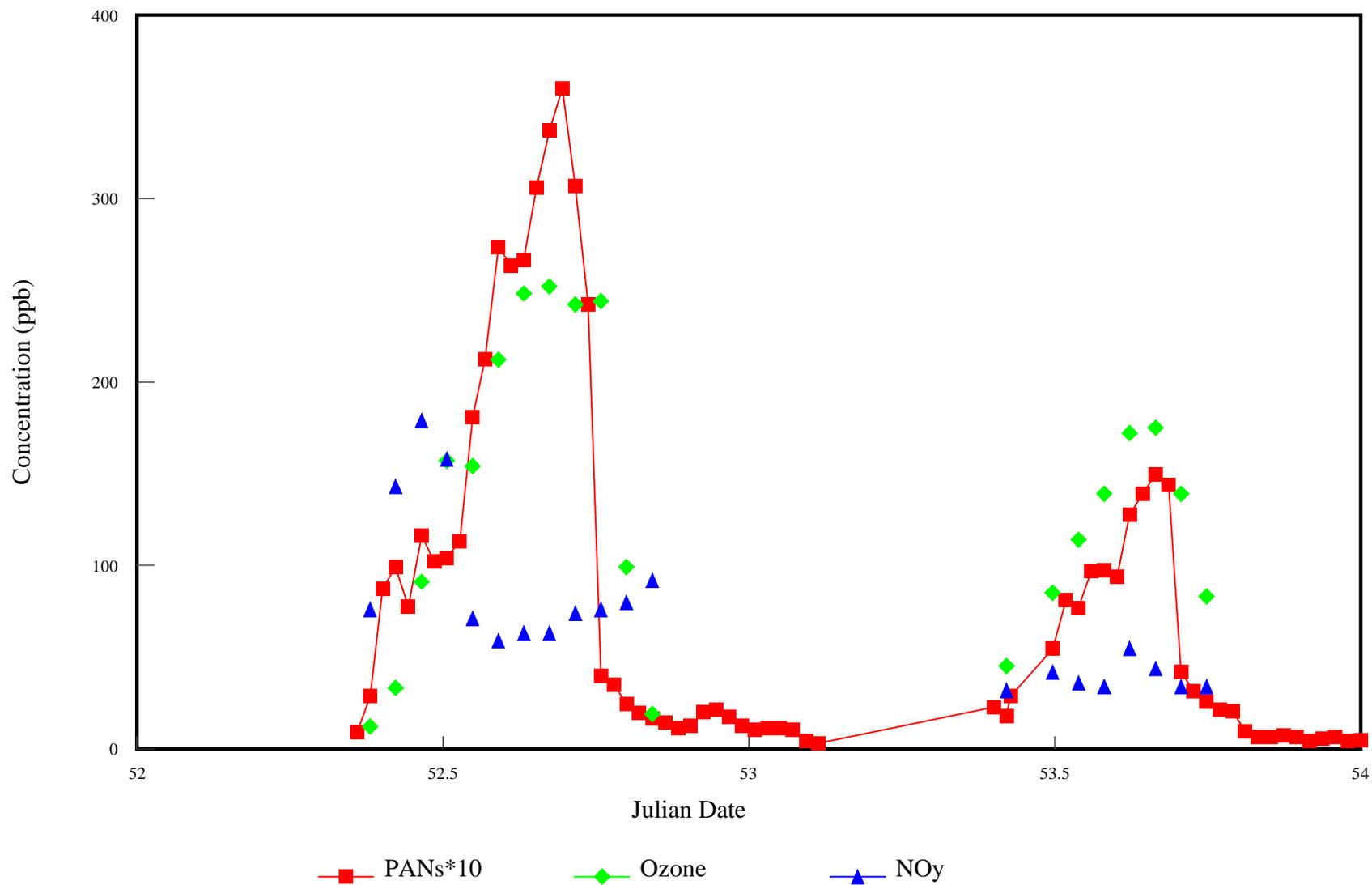
# Measurements of PANs - IMP, Mexico City

February 20-March 23, 1997



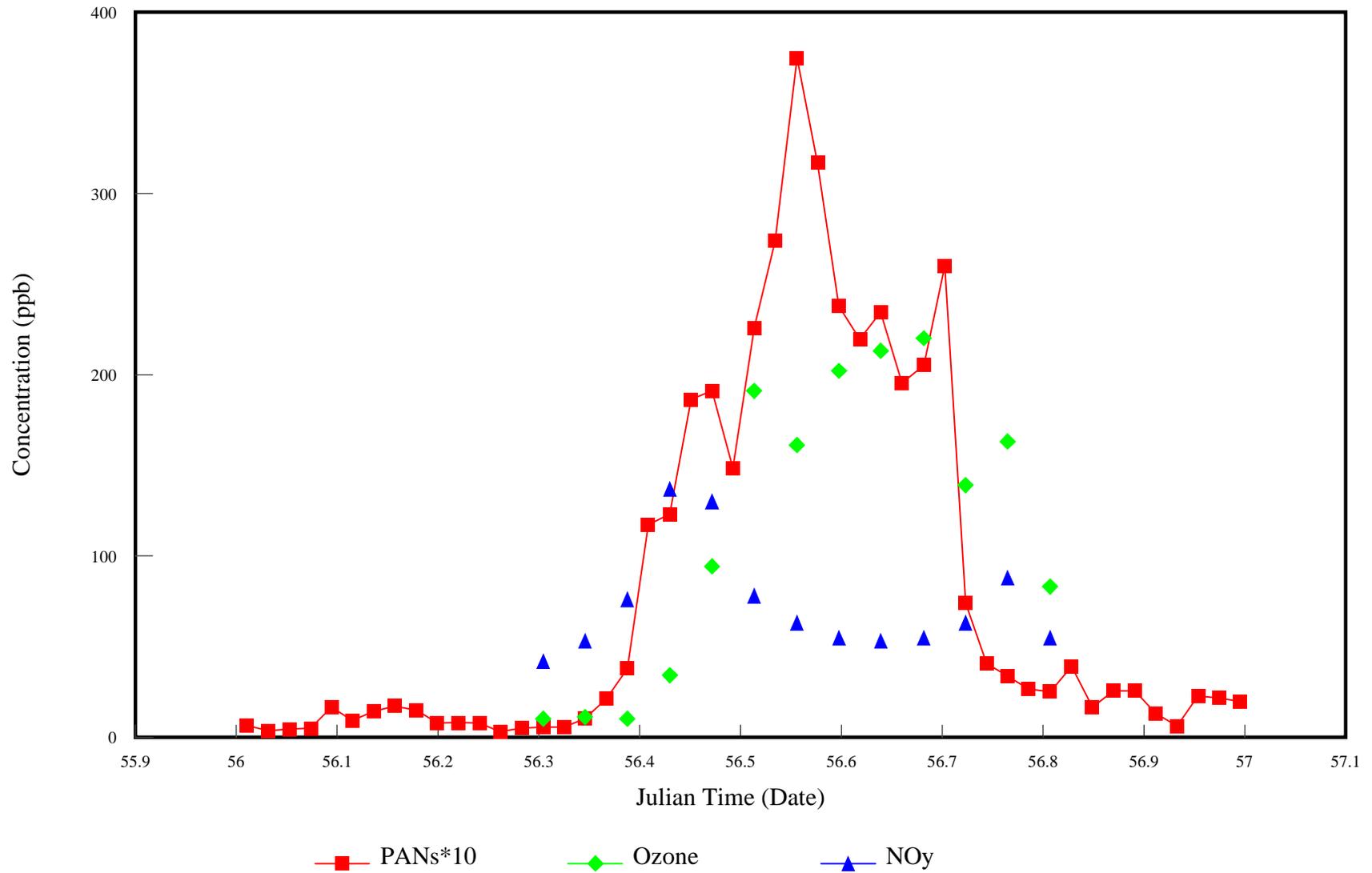
# Comparison of PANs, Ozone, and NOy

February 21-22, 1997



# Comparison of PANs, Ozon, and NOy

February 25, 1997



## Estimated Mass of Emissions in Mexico City Plume

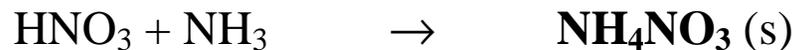
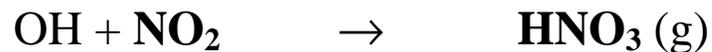
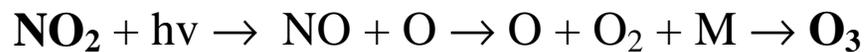
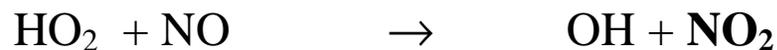
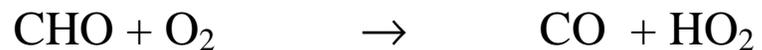
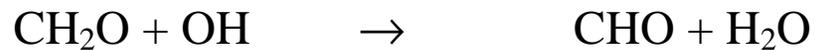
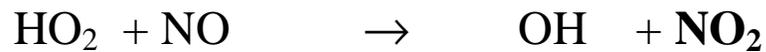
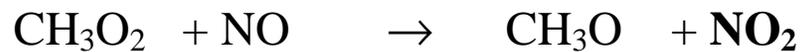
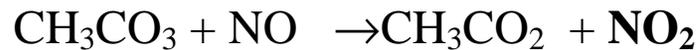
<u>Pollutant</u>	<u>Concentration</u>	<u>Metric Tons per Day</u>	<u>Mega-Tons per Year</u>
NMHC	1 ppmC	4500	1.6
CO	5 ppm	43,000	16
NO <sub>2</sub>	50 ppb	710	0.26
Ozone	200 ppb	3000	1.1
PAN	20 ppb	750	0.27
PM-2.5	50µg/m <sup>3</sup>	40,000	15

Assumptions: 770 mbar, 27 C, 2 km mixing layer, 5000 km<sup>2</sup> Metropolitan Area, no dry deposition, Air Mass is completely mixed and flushed out once a day.

# Regional Impacts of Mexico City Plume

PANs can act as source of organic radicals and  $\text{NO}_2$  in long range transport leading to formation of ozone and other oxidants, particularly peracids from  $\text{HO}_2$  reactions when  $\text{NO}$  levels become low.

## **Thermal Decomposition of PAN in the presence of $\text{NO}$ leads to the formation of Ozone and Nitrate Aerosols**



## **Under LOW $\text{NO}$ Conditions**



## WHERE IS IT GOING?

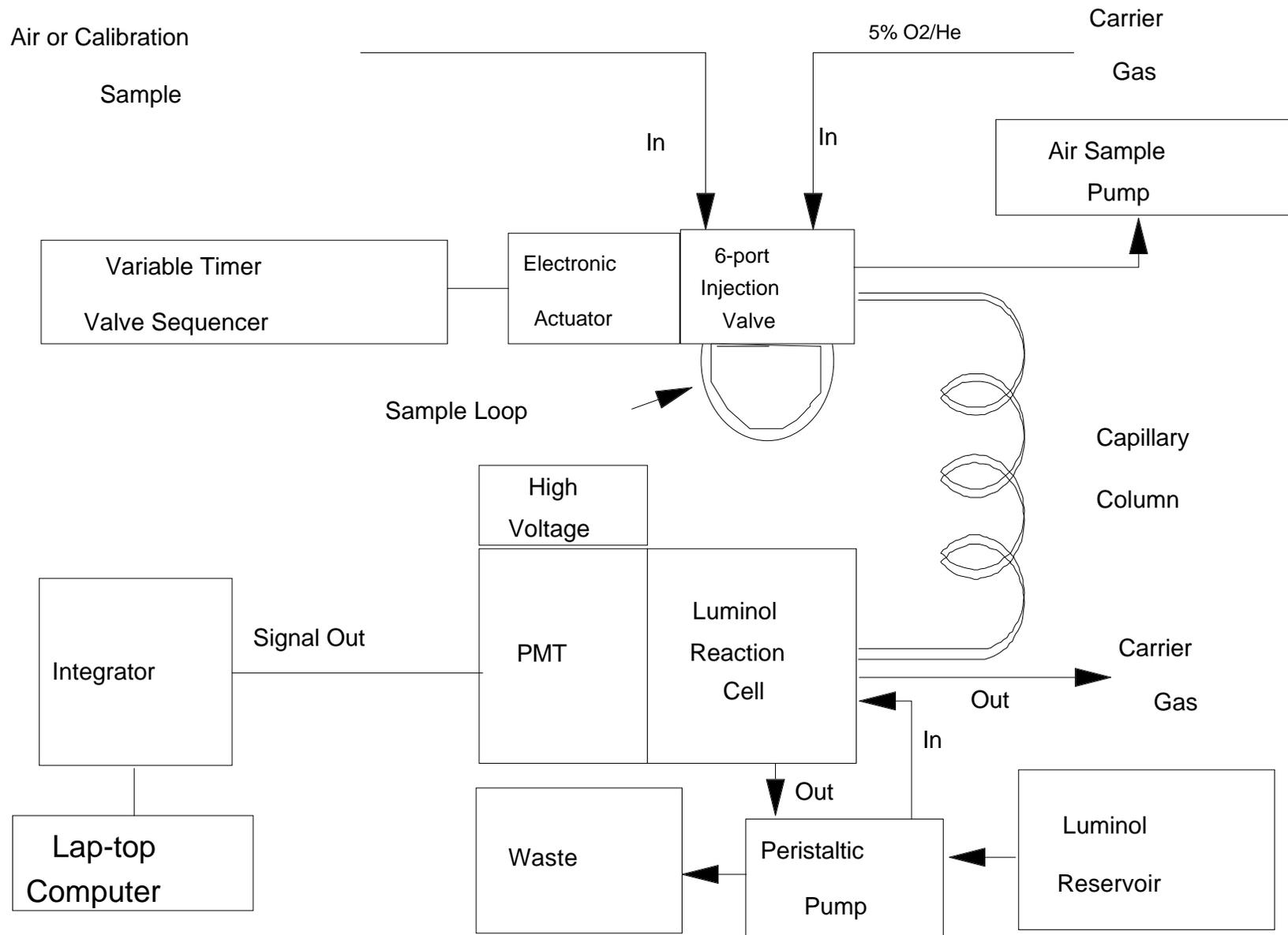
Mexico City is a very large source of air pollutants that is emitting large amounts of air pollutants on a daily basis. The apparent small carry over allows a reasonable estimate to be made of the mass of emissions that is impacting the regional and global scales from this city of 25-30 million.

Both gas phase and particulate pollutants are being carried out of Mexico City into the surrounding regions. Mexico City is at an altitude of  $>7000$  ft so that the mixed boundary layer when cleared out of the air basin is up to 10-13,000 ft. It is very likely that this polluted air mass is being transported fairly long distances in the troposphere as is indicated by the picture taken approx. 150 miles from Mexico City.

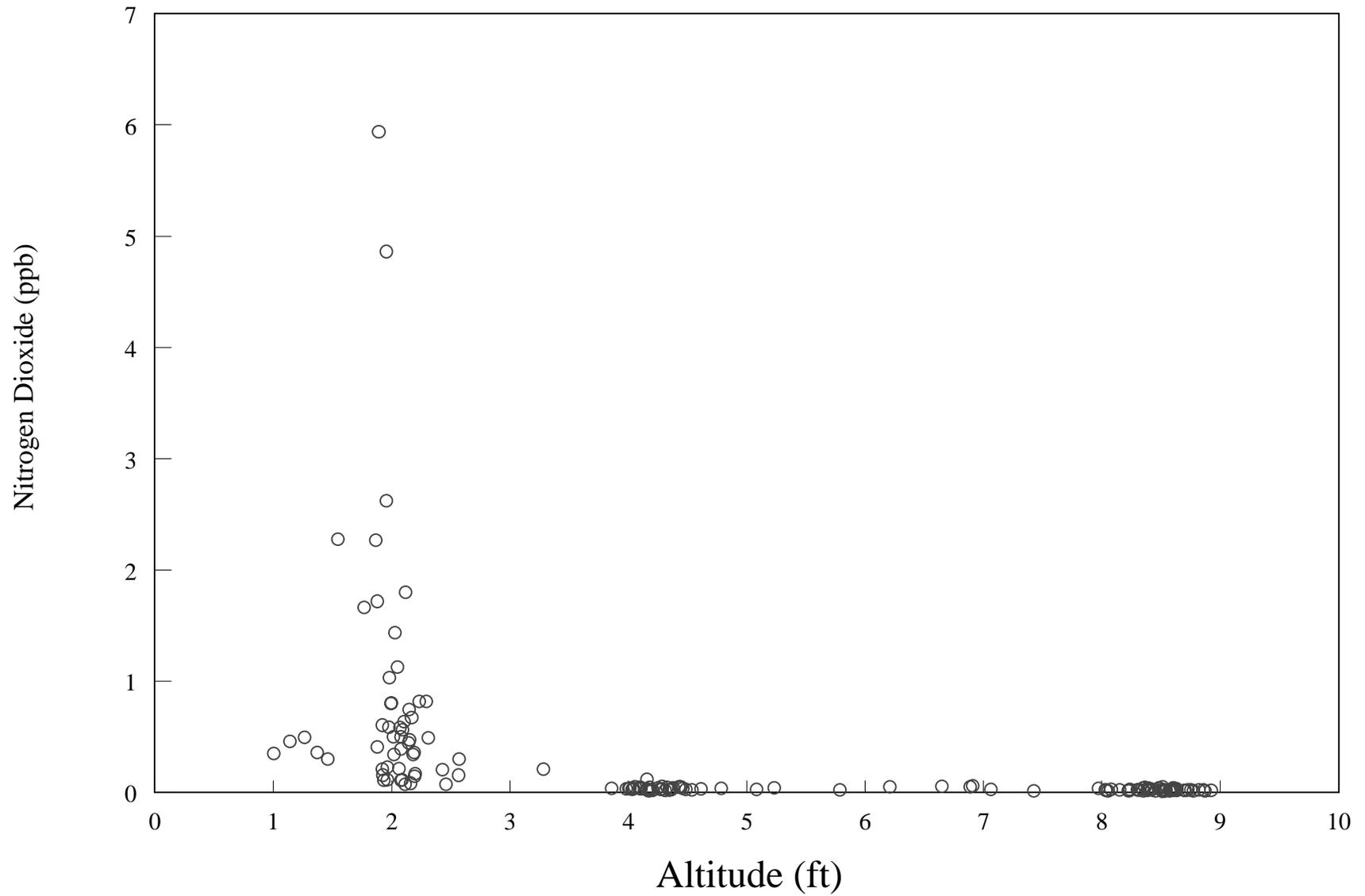
These urban air pollutants can be acting as “greenhouse gases” and as light adsorbing and scattering aerosols which will affect radiative balance on regional and global scales, as the Mexico City plume is carried from the area and mixed into the background upper tropospheric air mass. The diurnal “flushing” of the air from the basin may give a smoke signal type effect on the downwind plume allowing it to be tracked by future aircraft studies interested in Megacity plume impacts on regional scale tropospheric chemistry.

## G-1 Testing of the Luminol Based PAN/NO<sub>2</sub> Instrument

The fast capillary gas chromatographic system for rapid analysis (less than one minute) of nitrogen dioxide and peroxyacyl nitrates was modified for aircraft measurements on board the G-1 aircraft. The main modifications were the use of 5% O<sub>2</sub>/He as carrier gas to achieve essentially equivalent response for NO<sub>2</sub> and PAN, and the addition of a lap-top computer based data handling system for fast data acquisition. Test flights were successfully made near Pasco, Washington during August 1997 totaling 12 hours of flight time. Data are shown for one flight on 8/13/97 which shows the versatility of the instrument. The flight involved measurements of a nearby paper mill plume at approx. 2000 ft altitude, followed by measurements at 4000 ft where a grass-fire plume was detected, and at 8000 ft where “free troposphere” air was sampled. Temperatures during the flight were quite high, approaching 40 C in the aircraft. However, the rapid analysis time allowed PAN and NO<sub>2</sub> data to be obtained which are presented here. Assuming PAN and NO<sub>2</sub> are in equilibrium with the peroxyacetyl radical, the levels of that radical can be estimated from the instruments simultaneous measurement of these species by using the pressure and temperature data from the G-1 (see figures and table). Future improvements are planned which include a larger memory integrator for longer unattended data acquisition and modification of the capillary column mounting within the instrument to protect it from flight vibrations.

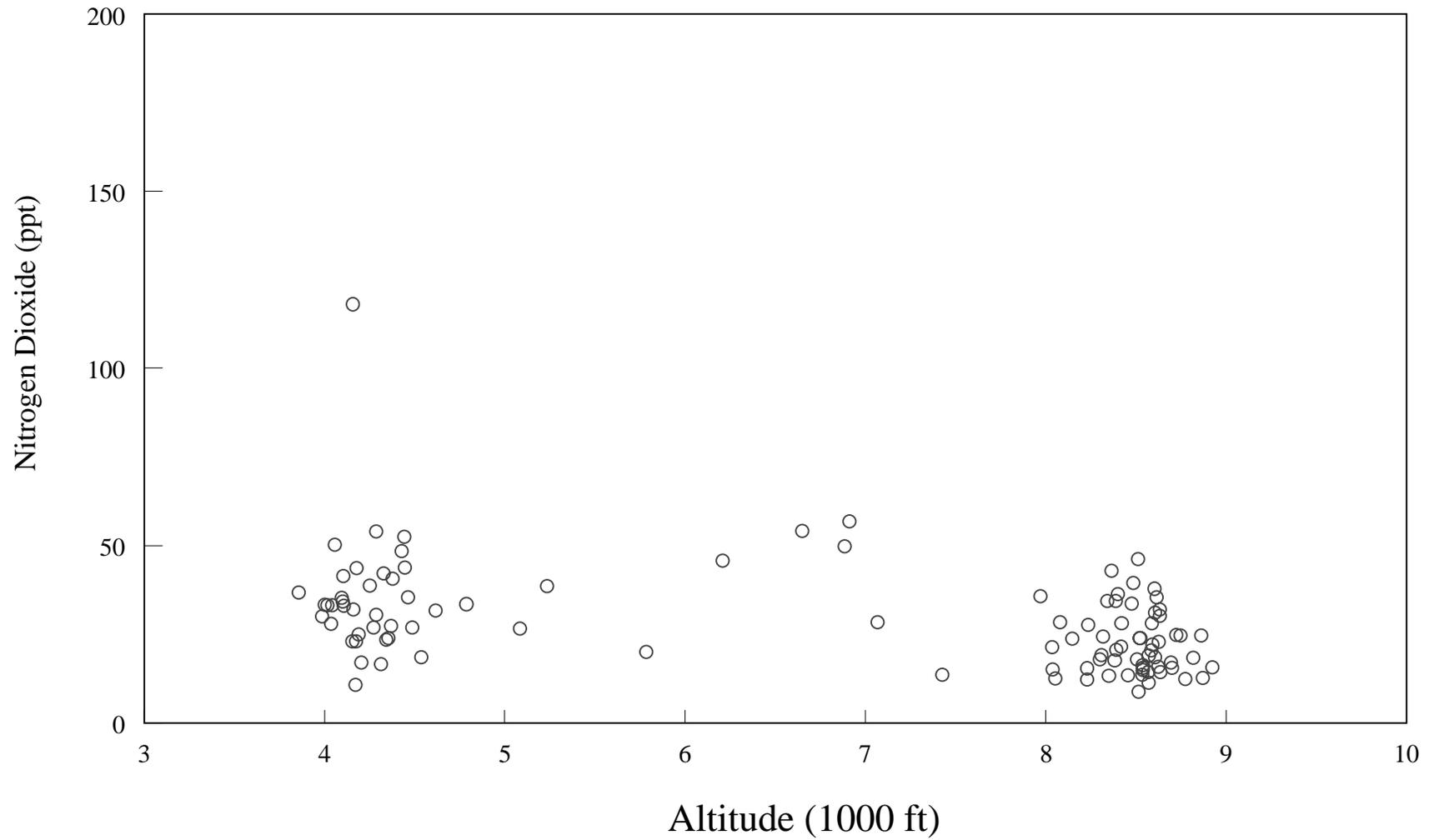


# Altitude Profile - NO<sub>2</sub> (ppb)

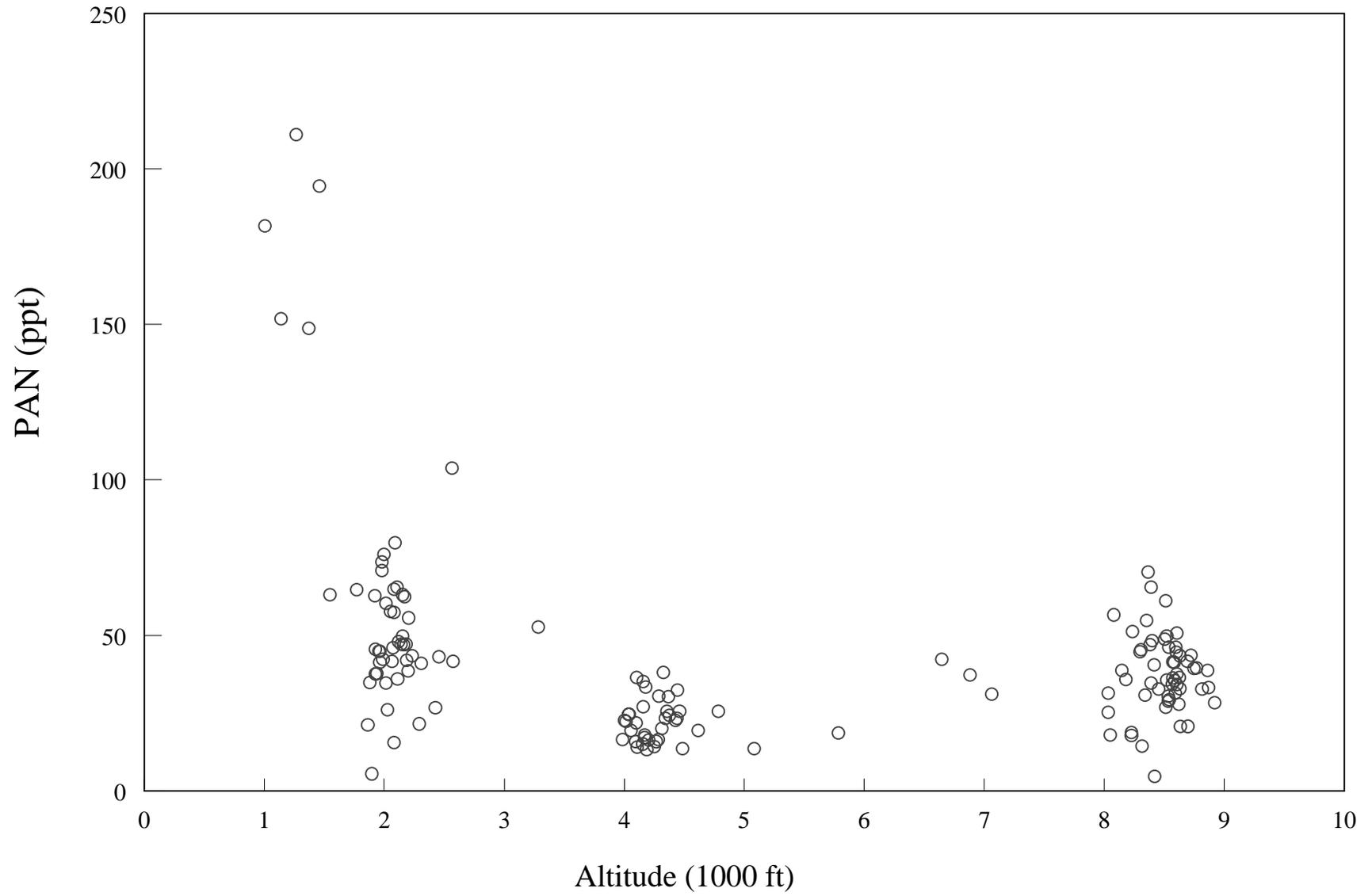


# Altitude Profile - NO2

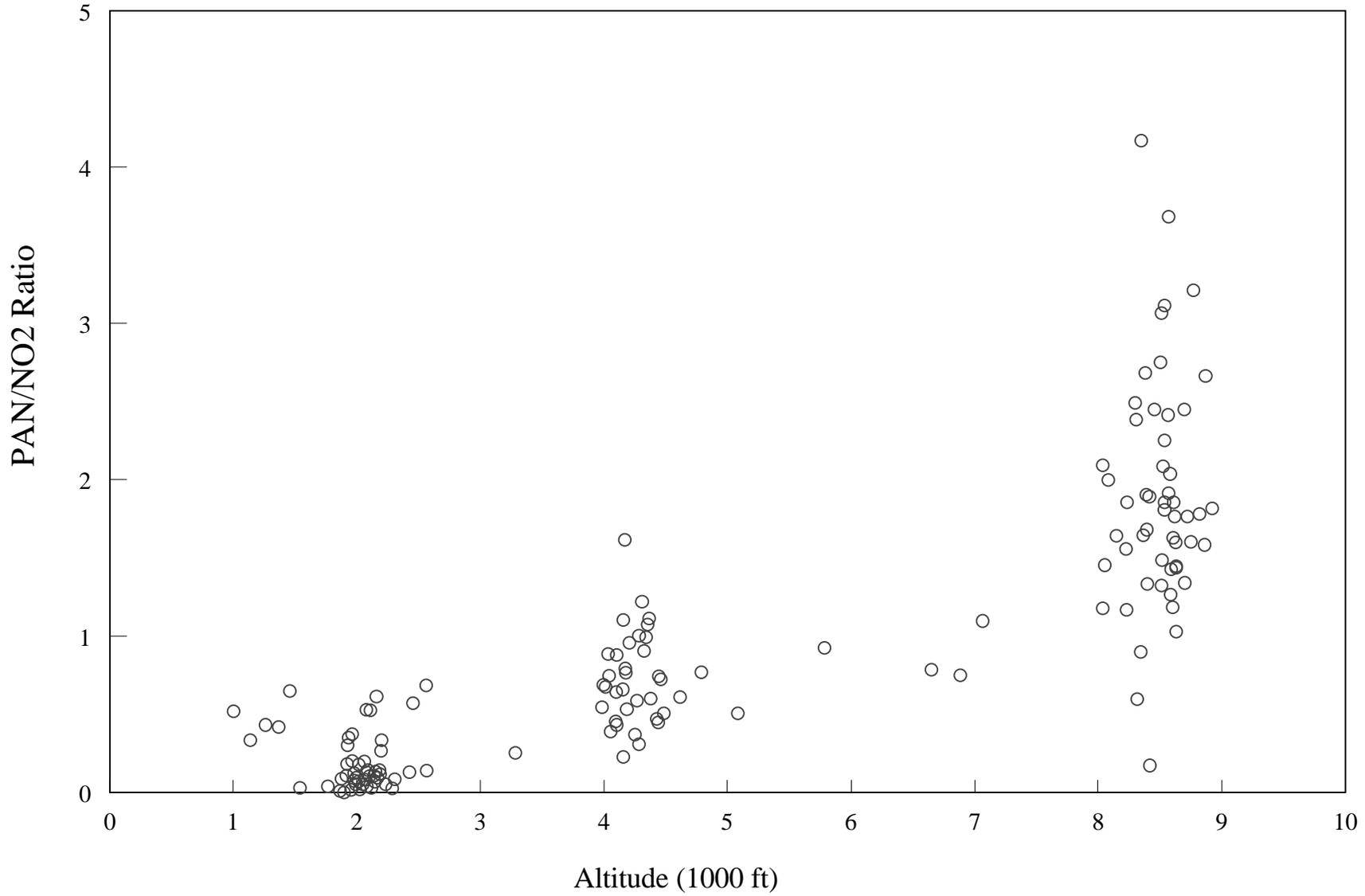
Free Troposphere?



# PAN Levels vs. Altitude



# Altitude Profile - PAN/NO2



# Peroxyacetyl Radical Concentration Estimates

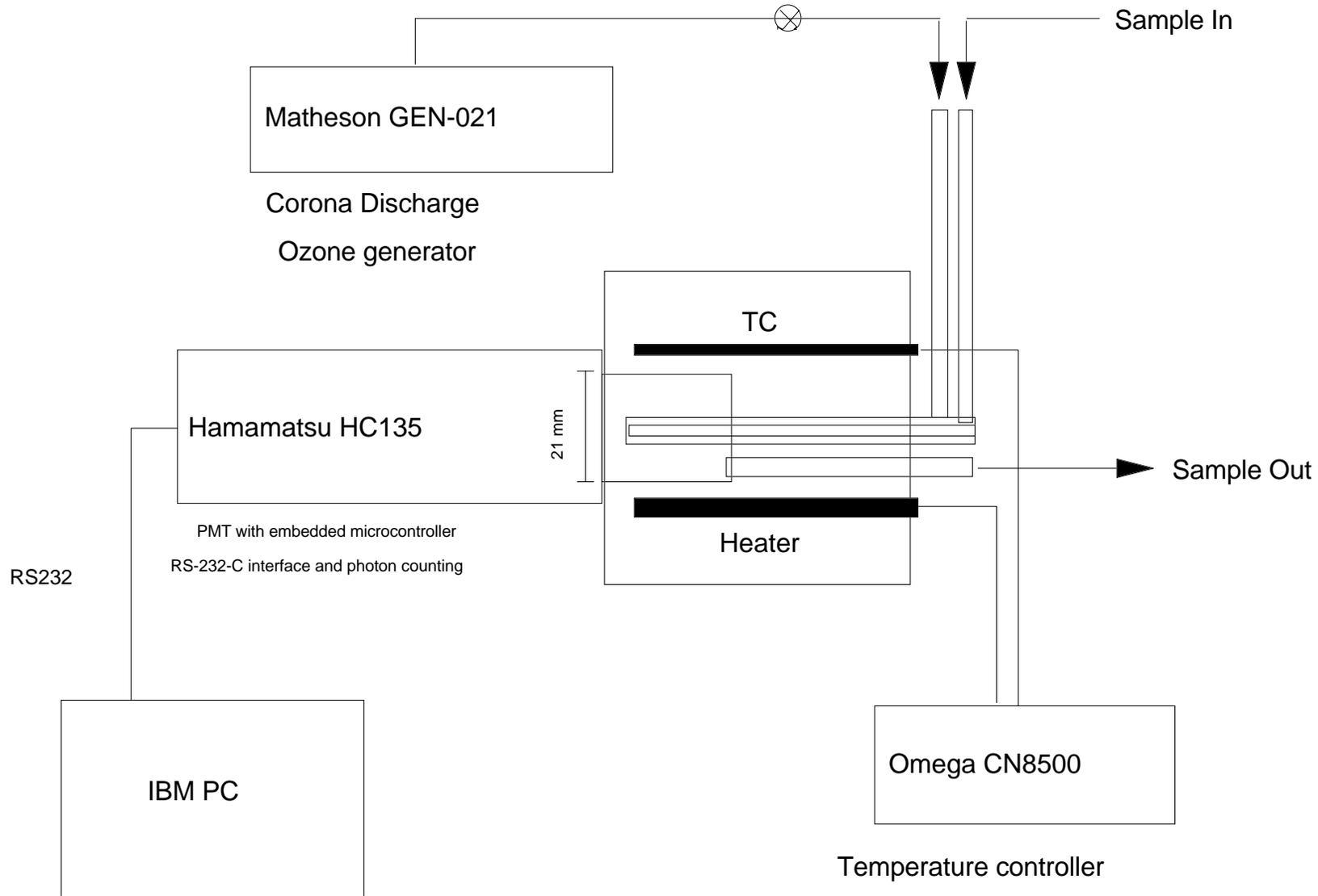
Flight over Pasco, WA - August 13, 1997

Altitude	Number of Measurements	CH <sub>3</sub> CO <sub>3</sub> · (molec/cc)*10 <sup>4</sup>	T (°C)	P (mbar)
2000	43	2.8 ± 2.9 (0.02-11.1)	28.7 ± 0.75	936.4 ± 3.3
4000	35	8.4 ± 3.1 (2.8-15.6)	26.1 ± 0.60	869.9 ± 0.63
8000	51	4.5 ± 1.7 (0.39-9.5)	16.1 ± 0.28	746.6 ± 0.50

## **OZONE-BASED HYDROCARBON ANALYZER**

We are continuing to examine the temperature dependence of the ozone chemiluminescent reactions with hydrocarbons. To date we have determined that it may be possible to improve the detection of a wide variety of hydrocarbons using ozone chemiluminescence as compared to conventional flame ionization detection. Current focus is on the development of a real-time non-methane hydrocarbon analyzer and a real-time olefin (isoprene, monoterpenes) system for applications in dry deposition studies and in the G-1 aircraft. A schematic of the proposed instrumentation along with some of the details of the photon counting based system given in the accompanying table. Application of this type of detection for chromatographic measurement of specific species is also being explored. Data for the natural monoterpenes indicates that while addition reactions predominate at room temperatures, at elevated temperatures (to 170 C) abstraction reactions can also become important, thus acting to enhance the detection sensitivities for these important atmospheric species. It is envisioned that this type of approach could yield fast response information on hydrocarbon levels in plumes which could aid in canister deployment for detailed chemical analysis in the G-1, as well as aiding in assessing the flux of hydrocarbons in eddy correlation studies of dry deposition and vegetative emissions.

# Fast Response Reactive Hydrocarbon Detector

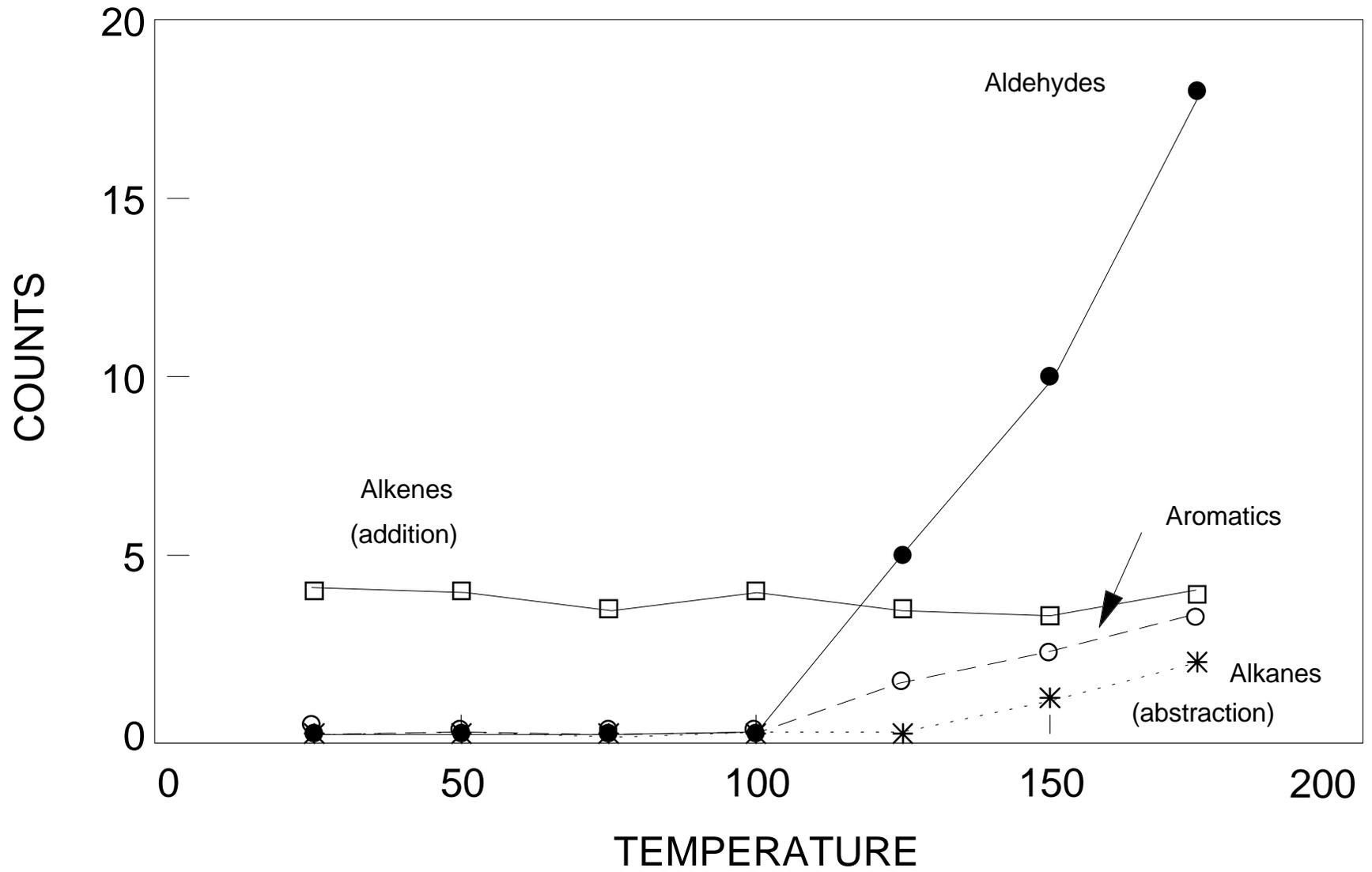


## HAMAMATSU HC135-1 PMT SENSOR MODULE

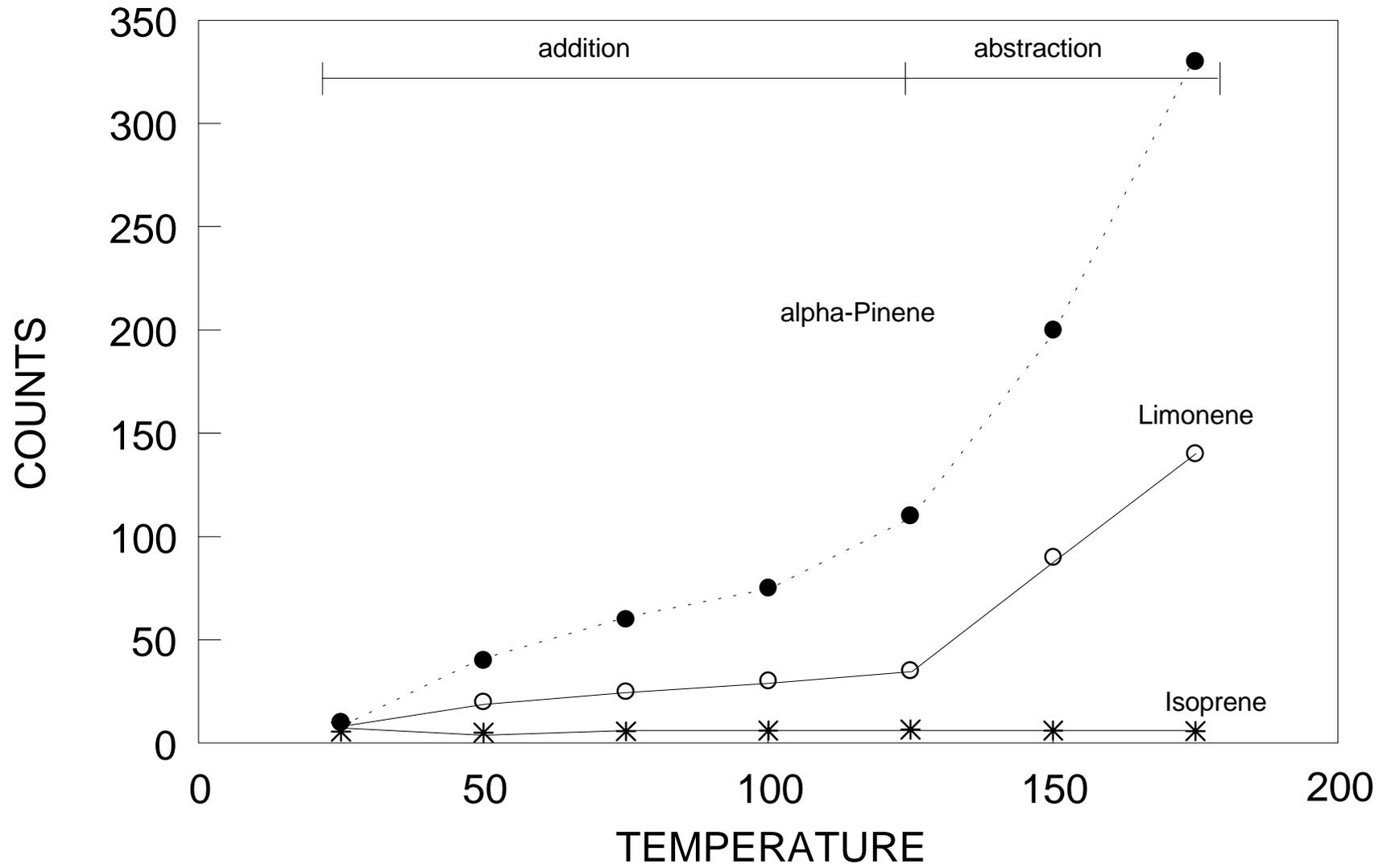
Spectral Range	300 - 650 nm
Peak Wavelength	400 nm
Dynamic Range	$2 \times 10^6$
Counting Efficiency*	22%
Spectral Sensitivity*	$4.3 \times 10^5$ CPS/pW
Maximum Light Input*	70 pW
Smallest Time Interval	10 msec
Optimum Integration Time	1 sec
Typical Dark Count	$100 \text{ sec}^{-1}$
Linearity*	0 to $2 \times 10^6$ - $\pm 1$ %
Baseline Stability*	11 %/ $^{\circ}\text{C}$
Response Stability*	$\pm 0.1$ %/ $^{\circ}\text{C}$

\* At 400 nm, 25 $^{\circ}\text{C}$ .

# TEMPERATURE DEPENDENCE OF THE OZONE CHEMILUMINESCENT REACTION



# TEMPERATURE DEPENDENCE OF THE OZONE CHEMILUMINESCENT REACTION



## **LABORATORY STUDIES**

Work continues on studies of the peroxyacyl nitrates and the corresponding peracids. Current focus is on the synthesis of methacrylperoxy nitrate (MPAN) and peroxybenzoyl nitrate (PBzN). We are attempting to refine the wet chemical synthesis to accomplish this goal for these species. MPAN is produced from the photochemical oxidation of isoprene in the presence of  $\text{NO}_2$ , while PBzN is produced from oxidation of alkylated benzenes. Comparison of the gas phase and liquid phase infrared spectra is being completed and the results are being examined to evaluate the relative importance of cyclic and linear structures for PANs. A variable long-path gas cell has been acquired from Brookhaven National Laboratory which will be modified and adapted for use with our Mattson Polaris FTIR. Studies examining the production of PANs and peracids under high and low NO conditions, respectively, are being planned for butenes and for natural monoterpenes. An UV/VIS spectrometer is also being modified to use integrating spheres to obtain absorption and light scattering data on aerosols and air pollutants. This system is being interfaced to a computer for spectral analysis and processing of the UV/VIS data. The reactions of PANs on the surfaces of standard soots will be explored and diffuse internal reflectance methods used to examine the formation of nitrated surface species from these reactions. Kinetic studies are planned using the luminol-based monitor at relevant atmospheric concentrations (1-10 ppb) to evaluate the importance of carbonaceous aerosol uptake of  $\text{NO}_2$  and PANs.