Development of a Direct, Low Pressure, Laser-Induced Fluorescence Measurement Technique for NO2., Ambient Measurements and Urban NOx Chemistry

Linda Acha George
Portland State University

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This Dissertation is brought to you for free and open access. It has been accepted for inclusion in Dissertations and Theses by an authorized administrator of PDXScholar. Please contact us if we can make this document more accessible: pdxscholar@pdx.edu.
DEVELOPMENT OF A DIRECT, LOW PRESSURE, LASER-INDUCED FLUORESCENCE MEASUREMENT TECHNIQUE FOR NO₂ AMBIENT MEASUREMENTS AND URBAN NOₓ CHEMISTRY

by LINDA ACHA GEORGE

A dissertation submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in ENVIRONMENTAL SCIENCES AND RESOURCES: CHEMISTRY

Portland State University 1991

Title: Development of A Direct, Low Pressure, Laser-Induced Fluorescence Measurement Technique for NO₂, Ambient Measurements and Urban NOₓ Chemistry.

APPROVED BY THE MEMBERS OF THE DISSERTATION COMMITTEE:

Robert J. O'Brien, Chair
Thomas M. Hard
David K. Roe
Pavel K. Smejtek
Randy D. Zelick

Nitrogen oxides control the global formation of ozone in the lower atmosphere and
influence the much higher levels of ozone formed in areas subjected to photochemical air pollution. As an important member of the nitrogen oxide family, NO₂ plays a significant role in serving as the only known source of ozone (through photolysis) in the lower atmosphere and as sink for HO via the formation of nitric acid. Ozone can be destroyed by reaction with another member of the nitrogen oxide family, nitric oxide (NO), to reform NO₂. This cycle between NO, NO₂ and O₃ is known as the NOₓ-O₃ photostationary state (PSS). Imbalances in this cycle have been used to calculate ambient levels of oxidants (such as RO₂ and HO₂) responsible for ozone production. Consequently, accurate NO₂ measurements are critical to making meaningful measurements of the imbalances in the NOₓ-O₃ photostationary states (PSS).

A low pressure laser-excited fluorescence technique (FAGE) for the direct determination of atmospheric NO₂ has been developed. This technique has been explored with both a Nd-YAG laser (1.4 W, 532nm, 30Hz) and a Cu-vapor (1.2 W, 511nm, 5.6kHz) laser. The detection limits for these instruments, under laboratory conditions and a signal collection time of 20s (10s each signal and background), have been determined to be 450 and 350pptv NO₂, respectively. In these systems, the background was measured by chemically reducing NO₂ with FeSO₄·7H₂O.

Ambient measurements of the NOₓ-O₃ photostationary state (PSS) were undertaken on a rooftop monitoring site in downtown Portland, Oregon. NO₂ was monitored with the Cu-vapor system. Nitric oxide and ozone were monitored with standard instruments. Data for three days in 1990 are presented. Overall these data sets clearly show that despite daily changes in concentration of NO, NO₂ and O₃ of factors of 4-10 each, the
PSS remains relatively constant to within ~50%. This is in itself strong confirmation of the primary importance of the NO$_x$-O$_3$ photostationary state in controlling the concentrations of these species at these levels. In addition, these experiments also serve to demonstrate that the monitoring instruments, including FAGE-NO$_2$, are not subject to serious interferences or artifacts at these concentration levels.
TO THE OFFICE OF GRADUATE STUDIES:

The members of the Committee approve the dissertation of Linda Acha George presented March 8, 1991.

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DEDICATION

Dedicated to the memory

of my father, E.V.George.
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<tr>
<th>Abbreviation</th>
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<tr>
<td>A/D</td>
<td>Analog to Digital Converter</td>
</tr>
<tr>
<td>CL</td>
<td>Chemiluminescence Instrument</td>
</tr>
<tr>
<td>CSTR</td>
<td>Continuous Stirred Tank Reactor</td>
</tr>
<tr>
<td>ERTC</td>
<td>Atmospheric Mechanism Developed by ERTC Corporation and the Environmental Protection Agency</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron-Spin Resonance</td>
</tr>
<tr>
<td>FAGE</td>
<td>Fluorescence Assay with Gas Expansion</td>
</tr>
<tr>
<td>FPC</td>
<td>Fluorescence Photon Collection</td>
</tr>
<tr>
<td>FYP</td>
<td>Fluorescence Yield of Photons</td>
</tr>
<tr>
<td>hv</td>
<td>Energy of a Photon of Light with Frequency $v$, $h=\text{Planck’s Constant}$</td>
</tr>
<tr>
<td>HC</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>LEF</td>
<td>Laser-Excited Fluorescence (synonymous with LIF)</td>
</tr>
<tr>
<td>LIF</td>
<td>Laser-Induced Fluorescence (synonymous with LEF)</td>
</tr>
<tr>
<td>Nd-YAG</td>
<td>Neodymium-Yttrium Aluminum Garnet</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>Sum of NO (nitric oxide) and NO$_2$ (nitrogen dioxide)</td>
</tr>
<tr>
<td>O$_x$, OX</td>
<td>Oxidant</td>
</tr>
<tr>
<td>PAN</td>
<td>Peroxyacetyl Nitrate</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier Tube</td>
</tr>
<tr>
<td>ppb,ppbv</td>
<td>Parts-Per-Billion by Volume</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>ppm, ppmv</td>
<td>Parts-Per-Million by Volume</td>
</tr>
<tr>
<td>ppt, pptv</td>
<td>Parts-Per-Trillion by Volume</td>
</tr>
<tr>
<td>PSS</td>
<td>NO$_x$-O$_y$ Photostationary State</td>
</tr>
<tr>
<td>QVT</td>
<td>LeCroy (Model QVT3001) multichannel analyzer. This instrument was used in the gated charge integration mode unless otherwise noted.</td>
</tr>
<tr>
<td>SNR</td>
<td>Signal-to-Noise Ratio</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet portion of the electromagnetic spectrum</td>
</tr>
<tr>
<td>UVMRD</td>
<td>Home-made Photodiode Device Sensitive to the 300-400nm Portion of the Solar Radiation</td>
</tr>
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CHAPTER I

INTRODUCTION

Accurate measurements of global nitrogen oxide distributions are critical in assessing the impact of human activity on the troposphere. Although reliable, sensitive techniques for the direct measurement of nitric oxide (NO) have been developed, available direct techniques for the measurement of nitrogen dioxide (NO₂) suffer from interferences and/or lack of sensitivity. This investigation examines the utility of an analytic technique known as FAGE, fluorescence assay with gas expansion, in the development of a sensitive, direct method of measuring low levels of tropospheric NO₂.

IMPORTANCE OF NITROGEN OXIDES IN THE ATMOSPHERE

Nitrogen oxides play a critical role in the chemistry of the clean and polluted atmosphere. The most abundant and chemically active of the nitrogen oxides in the troposphere are NO and NO₂. Their sum concentration in the atmosphere is known as NOₓ. Together, they are in large part responsible for controlling the concentration of photochemical oxidants in the atmosphere.

Photochemical oxidation of natural and anthropogenic emissions is the means by which the atmosphere maintains a near constant atmospheric composition. Evidence that increasing emissions of anthropogenic substances [Crutzen and Gidel, 1983; Khalil and
Rasmussen, 1990a, Khalil and Rasmussen, 1990b] are beginning to change this balance brings greater urgency for understanding the chemistry of the atmosphere. NO$_x$ compounds are important in controlling the concentrations of the two primary oxidants of the troposphere, hydroxyl radical (HO) and ozone (O$_3$) (Figure 1).

The hydroxyl radical is the chief agent in preventing the buildup of hydrocarbons and other compounds in the troposphere. Hydrocarbon removal is usually initiated by oxidation with HO via:

$$\text{RH} + \text{HO} \rightarrow \text{R} + \text{H}_2\text{O}$$  \hspace{1cm} \text{R1}$$

where RH is a hydrocarbon. In the presence of sunlight and further reaction with HO and other compounds, oxidized hydrocarbons either are removed from the atmosphere as soluble organic compounds by wet or dry deposition or are completely oxidized to CO$_2$.

Ozone also initiates the oxidation of some hydrocarbons, particularly some alkenes. It is also critical in forming HO in the clean atmosphere via reactions 2 and 3.

$$\text{O}_3 + \text{hv (}\lambda<310\text{nm)} \rightarrow \text{O (}^1\text{D)} \hspace{1cm} \text{R2}$$

$$\text{O (}^1\text{D)} + \text{H}_2\text{O} \rightarrow 2\text{OH} \hspace{1cm} \text{R3}$$

One of the chief environmental issues concerning tropospheric ozone is its apparent increase in remote areas of the boundary layer [Feister and Warmbt, 1987; Volz and Kley,
Figure 1. Simplified nitrogen oxide reaction scheme.
Elevated levels of ozone are detrimental to human and vegetative health as ozone causes destructive oxidation of human and plant cell tissue [Folinsbee et al., 1988; Heck et al., 1982].

Nitrogen oxides are released into the atmosphere both naturally and by human activity. The largest source of nitrogen oxides is nitrous oxide (N₂O) which is emitted via microbial processes in soil and natural waters. Nitrous oxide is not chemically active in the troposphere but it is an important agent in controlling stratospheric ozone.

NOₓ is the principal form of chemically active nitrogen oxides in the troposphere. High temperature combustion of fossil fuel and biomass burning constitutes about 70% of the total inventoried emission sources for NOₓ of which ~95% is NO and ~5% is NO₂ [Logan, 1983]. The remaining sources of NOₓ emissions are due to microbial activity in soils and production of NOₓ in lightning discharges [Logan, 1983]. Some recent estimates conclude that lightning could be the single largest contributor of nitrogen oxides in the global N budget [Liaw et al., 1990].

Ozone in the troposphere is formed via the photolysis of NO₂ and the subsequent reaction of the released O atom with O₂. Ozone can then react with the NO newly generated or already present to reform NO₂ and O₂.

\[
\begin{align*}
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \quad \text{R4} \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M} \quad \text{R5} \\
\text{(M=third body collider)} \\
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{R6}
\end{align*}
\]
This cycle is known as the NOx-O3 Photostationary State (PSS) and has been the subject of much study and controversy [Calvert and Stockwell, 1983; Parrish et al., 1986; Calvert, 1976; O’Brien, 1974; Fehsenfeld et al., 1988]. The occurrence of significant side reactions such as R7 or R8 involving NOx or O3 can alter the above null cycle resulting in the net production (R7 + R8) or loss of ozone (ozone + alkene ---> products). Thus measurement of the imbalance of the PSS due to side reactions is critical in understanding ozone chemistry in the troposphere.

\[
\begin{align*}
\text{RO}_2 + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 \quad \text{R7} \\
\text{HO}_2 + \text{NO} & \rightarrow \text{HO} + \text{NO}_2 \quad \text{R8}
\end{align*}
\]

NOx is primarily removed from the troposphere via the production of nitric acid (HNO3):

\[
\text{HO} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \quad \text{R9}
\]

This is followed by the wet or dry deposition of HNO3. Dry deposition of NO2 can also contribute significantly to NOx loss processes [Logan, 1983]. NOx is removed by these processes on the order of hours to days [Logan, 1983]. Nitric acid impacts the environment in two ways: first, its formation by R9 results in the consumption of a hydroxyl radical, which reduces hydrocarbon consumption rates and secondly, the removal
of nitric acid itself, by wet or dry deposition from the atmosphere onto land, vegetation or water, can produce environmentally undesirable results.

Although emission sources of NO$_x$ are centered in urban areas, the production of organic nitrates via reactions such as:

$$\text{RO}_2 + \text{NO} \rightarrow \text{RONO}_2 \text{(alkyl nitrate)}$$

$$\text{RO}_2 + \text{NO}_2 \rightarrow \text{ROONO}_2 \text{(alkyl peroxynitrate)}$$

have been recognized to provide a means of long range transport of reactive nitrogen from polluted to unpolluted regions [Singh and Hanst, 1981]. Peroxyacetyl nitrate (PAN) is the most abundant organic nitrate in the troposphere and contributes significantly to the total tropospheric abundance of reactive nitrogen oxides NO$_y$ (NO$_x$, HNO$_3$, NO$_3$, organic nitrate, NO$_3$, N$_2$O$_5$, ... ) [Singh et al., 1985; Singh, 1987; Buhr et al., 1990]. With the proper meteorological conditions, transport of NO$_y$ compounds in the range of 100’s of kilometers has been observed [Hov, 1984; Moxim, 1990]. NO$_y$ reservoir species can be converted to NO and NO$_2$ by the processes shown below.

$$\text{N}_2\text{O}_5 + \text{hv} \rightarrow \text{NO}_2 + \text{NO}_3$$

$$\text{RO}_2\text{NO}_2 \rightarrow \text{RO}_2 + \text{NO}_2$$

$$\text{NO}_3 + \text{hv} \rightarrow \text{NO}_2 + \text{O}$$

$$\text{NO}_3 + \text{hv} \rightarrow \text{NO} + \text{O}_2$$
If these NO\textsubscript{y} reservoir species have been transported from a polluted region, these processes can lead to tropospheric ozone production as NO\textsubscript{2} is photolyzed to form O\textsubscript{3}, in regions remote from NO\textsubscript{x} sources.

Concentrations of NO\textsubscript{x} present in a given area are a strong function of the season, latitude and type of source components important there, be they anthropogenic, natural or due to transport. This results in NO\textsubscript{x} concentrations that can vary over 4-5 orders of magnitude from mixing ratios of $10^{-12}$ in "very clean" environments to polluted air levels of over $10^{-8}$. Increasing NO\textsubscript{x} levels in remote areas impacted by urban emissions can have dramatic effects on remote ozone levels [Sillman et al., 1990]. Consequently, accurate measurements of global tropospheric NO\textsubscript{x} distribution are critical for predicting potential ozone production due to increasing NO\textsubscript{x} emissions. Although reliable direct measurements of low concentrations of NO have been achieved in the last few years, direct detection of NO\textsubscript{2} at low mixing ratios remains a research challenge.

**MEASUREMENT TECHNIQUES FOR NO\textsubscript{2}**

Tropospheric measurement of NO\textsubscript{2} has generally been accomplished using techniques based on NO determination. NO\textsubscript{x} chemiluminescence (NO\textsubscript{x}-CL) instruments, for example, monitor NO\textsubscript{2} by first converting the species to NO by photolytic or chemical means [Kley and McFarland, 1980; Kelly et al., 1980; Ridley et al., 1988a]. Nitric oxide is then measured by reacting it with excess O\textsubscript{3} and measuring the chemiluminescence emitted by NO\textsubscript{2} generated in an excited state. Nitric oxide chemiluminescence (NO-CL)
is an accurate, rapid, sensitive analytical technique which compares very well [Hoell et al., 1987, Gregory et al., 1990a] with more sophisticated 2-photon laser excited fluorescence (LEF) techniques [Bradshaw et al., 1985]. However, NO-CL does require the subtraction of an artifact signal which is determined at night [Parrish et al., 1990].

Although comparably sensitive to NO\textsubscript{2} and NO, CL measurement of NO\textsubscript{2} as NO suffers from uncertainties in the conversion efficiency, with the possibility that other members of the extensive NO\textsubscript{y} family are partially converted as well [Fehsenfeld et al., 1988; Ridley et al., 1988b]. NO\textsubscript{2} has recently been measured [Sandholm et al., 1990] by first photolyzing the molecule to produce NO, which is then measured by 2-photon LEF (utilizing three lasers) [Bradshaw et al., 1985]. Direct measurement of NO\textsubscript{2} by other techniques (such as optical absorption, matrix-isolation/ESR) has been accomplished, but requires either long temporal [Biermann et al., 1988; Mackay et al., 1988; Schiff et al., 1983, Mihelcic et al., 1990] or spatial [Kolsch et al., 1989; Platt et al., 1979] averaging. Suitable averaging times are dependent on the processes being studied and on the environment in which the measurements are being made. Measurements of equilibrium atmospheric chemistry should be made with averaging times (or distances) shorter than time in which different air parcels are encountered. In urban environments this can be on the order of seconds. In order to study the kinetics of perturbation from the equilibrium state the relaxation time of the system will determine a suitable averaging time.

A recently published intercomparison of airborne NO\textsubscript{2} instruments [Gregory et al., 1990b] compared indirect techniques, NO-chemiluminescence [Ridley et al., 1988b]
and NO-LEF [Sandholm et al., 1990], and one direct technique, tunable diode-laser spectroscopy (TDLAS) [Schiff et al., 1990]. The intercomparison reports that there is a 30-40% level of agreement between these techniques for concentrations above 100pptv but "when the data were restricted to mixing ratios of <50pptv, little correlation among the measurements was observed". Correlations between the two indirect techniques were better than between either one with the direct technique for all concentrations reported. A recent ground-based intercomparison [Fehsenfeld et al., 1990] of NO₂ measurement techniques (NO-chemiluminescence and TDLAS-NO₂), concluded that these instruments agree only for [NO₂]>400pptv. Clearly the development of an additional direct NO₂ technique would be beneficial in understanding the discrepancies between the direct and indirect NO₂ techniques.
CHAPTER II

DEVELOPMENT OF FAGE-NO₂

FAGE PRINCIPLE

FAGE, Fluorescence Assay by Gas Expansion, is a technique that has been developed to enhance signal-to-noise ratios (SNR) for trace gas detection in the atmosphere [Hard et al., 1984]. This technique involves the low pressure excitation of the target species by a light source to an upper electronic state. Excitation of the target species at low pressure reduces collisional quenching and thereby lengthens the fluorescence lifetime. To understand the superiority of this technique over ambient pressure fluorescence techniques it is beneficial to discuss the characteristics of the signal (S) and background (B).

For a fluorescence technique, the signal is due to the emission of photons of the target species after it has been excited by incident light of the appropriate wavelength(s). This signal is designated the gross signal as it includes the signal due the target species as well as the background signal. A measurement of the background is achieved by removing by some means the signal due the target species. The background signal derives from a number of sources that can be categorized into electrical, scattered photons and fluorescence of species other than the target. Interferences result when the gross signal contains significant contributions due to some source other than the target species
which is also modulated by the background subtraction technique or if the background subtraction technique corrupts the "true" background signal.

One goal of any analytic technique is to optimize the operating parameters of the system to maximize the signal-to-noise ratio (SNR) of the instrument.

\[
\text{SNR} = \frac{S}{\sigma_s}
\]

(1)

S is the signal and \(\sigma_s\) is the uncertainty in measuring S. For an instrument based on photon counting, the lower limit uncertainty of the measurement is given by Poisson statistics, where:

\[
\sigma_{\text{PHOTONS}} = \sqrt{\text{PHOTONS}}
\]

(2)

Greater uncertainty can arise due to variation in analyte concentration, fluctuations in detector response, etc. However, systems operating under relatively low signal photon arrival rates operate with an internal variance limited by Poisson uncertainty [Currie, 1989]. A measurement of the signal (S) is made by subtracting the background (B) from the gross signal (S+B), where S and B represent the number of photons due to the signal and background respectively.

\[
\text{net signal} = \text{gross signal} - \text{background}
\]

\[
S = (S + B) - B
\]

(3)
The uncertainty of the measurement is a function of the total number of photons collected.

In order to measure the concentrations of analyte that may have relatively low optical densities and/or fluorescence yields, high photon excitation rates are required. This is easily achievable by laser sources. Unfortunately this results in a large background pulse due to Raleigh, Raman and Mie scattering of the constituents of sample as well as the scattering of photons off of the components of the detection cell. Discrimination of fluorescence photons from scattered photons is difficult when the ratio of excitation photons to fluorescence photons is extremely high - resulting in poor SNR ratios. Saturation of the detection optics, such as photomultipliers, during the laser pulse is a common phenomenon further limiting SNR ratios.

FAGE takes advantage of the different temporal characteristics of the scattering and fluorescence processes. Scattered photons are emitted essentially simultaneously with the laser pulse but the fluorescence lifetime of the target species can be extended by operating at reduced pressure. By operating at lower pressure the detection system can be turned "on" some time after the laser fires. At this point the background due to scattering is greatly reduced while the signal due to fluorescence of the desired species persists. In addition, photomultiplier saturation effects are lowered due to the proportional decrease in Rayleigh and Mie scattering with pressure. Thus an effective discrimination between scattered and fluorescence photons can be achieved.

Operation at reduced pressure also proportionally decreases analyte concentration but this effect is offset, within limitations, by the change in fluorescence yield with
pressure. For a given concentration of a species in an excited state $A^*$, a simple fluorescence decay involves two processes:

$$A^* \longrightarrow hv \quad (k_r)$$

$$A^* + M \longrightarrow A + M \quad (k_q)$$

where $k_r$ is the rate constant for fluorescence emission, $k_q$ is the quenching rate constant of the emitting state and $M$ is the concentration of the quencher. The fluorescence yield of photons (FYP) from a given initial concentration of $X^*$ can be shown to be:

$$FYP = k_r/(k_r+k_qM) \quad (4)$$

The concentration of the excited species can be written as a mole fraction, $x_{A^*}$, times the total concentration, $M$, which gives:

$$FYP = k_r/(k_r+k_qM) \times x_{A^*} M \quad (5)$$

Since the processes considered here are in the gas-phase, pressure and concentration are directly proportional to one another. Figure 2 shows the relationship of FYP (normalized to 1) and the fluorescence lifetime to the quenching pressure. The rate coefficients for $k_r$ and $k_q$ used in this figure are for NO$_2$. Clearly as long as $k_qM\gg k_r$, the number of emitting photons is independent of quencher concentration (or pressure) and linearly
Figure 2. Fluorescence yield and lifetime vs. quenching pressure.
dependent on the mole fraction of excited state. Thus FAGE decreases the rate of photon emission so as to achieve optimal photon recovery after the laser fires but does not decrease the total number of photons emitted.

Theoretical enhancements of SNR with FAGE can be demonstrated assuming an exponential decay for the fluorescence signal and an exponential decay plus a constant (which reflects any approximately constant background such as the dark current of the PMT or ambient (stray) light) for the background.

\[
S(t) = S_0 \exp(-k_s t) \quad (6)
\]
\[
B(t) = B_0 \exp(-k_b t) + D \quad (7)
\]

S(t) and B(t) represent the signal and background as function of time. \(S_0, k_s\) and \(B_0, k_b\) are the intensities at \(t=0\) and the decay rates of the signal and exponentially decaying part of the background, respectively. For a simple fluorescence process \(k_s\) would have the form of the denominator in equation 5. D simulates the dark current of the detection device which is assumed to be constant with respect to time.

If the signal is much lower than the background at \(t=0\) and the signal decays slower that the background, optimal signal recovery would be enhanced with a delay with respect to \(t=0\). If the delay is too long the exponentially decaying effects of both the signal and background will have degraded the SNR (see Figure 3a). To achieve full signal recovery, an integration gate width, \(t_g\), of infinite width would seem optimal. However, in any real detection system the signal will decay into the noise of the detection
Figure 3. Maximizing SNR with $t_g$ and $t_d$. 
device (represented by D). At this point the signal recovery is improving much more slowly than the increase in noise due to the influence of integrated dark current, D (see Figure 3b). Thus a finite gate width is warranted.

The integrated signal and background for time $t_d$ (delay time) to $t_d+t_g$ (delay plus gate width) is:

$$S_{\text{int}} = S_0/k_s[\exp(-k_s t_d) - \exp(-k_s(t_d+t_g))]$$

$$B_{\text{int}} = B_0/k_b[\exp(-k_b t_d) - \exp(k_b(t_d+t_g))] + D t_g$$

Based on definitions in equations 1 and 2 and the propagation of error through equation 3,

$$\text{SNR} = S_{\text{int}}/(S_{\text{int}} + 2B_{\text{int}})^{0.5}$$

For a given set of experimental conditions, $S_0$, $B_0$, $k_s$ and $k_b$, the delay and gate width settings for maximum SNR can be predicted by setting the partial derivatives of equation 10 with respect to $t_g$ and $t_d$ equal to zero and solving simultaneously. $\text{SNR}_{\text{max}}$ is calculated by substituting the optimal gate parameters, $t_g$ and $t_d$, back into equation 10. (See Appendix A for details of calculations.)

$\text{SNR}_{\text{max}}$ is a function of the absolute values of each of the parameters, $S_0$, $B_0$, $k_s$, $k_b$ and D. However by keeping $B_0$, D and $k_b$ constant while varying $S_0$ and $k_s$ the effect of the ratios $k_b/k_s$ and $B_0/S_0$ on $\text{SNR}_{\text{max}}$ can be evaluated. As expected, the higher SNR's
are achieved when signal is stronger than background \((S_0/B_0 > 1)\) and the background decays much faster than the signal \((k_b/k_s > 1)\). This is seen in the steep rise in SNR\(_{\text{max}}\) in the lower right-hand quadrant of Figure 4. To compare FAGE SNR with SNR of fluorescence techniques made at atmospheric pressure (short fluorescence lifetime), SNR is calculated with full recovery of signal and background. To achieve this, \(t_d\) is set equal to zero and since lifetimes are short at atmospheric pressure, \(t_g\) need not be long. Since \(t_g\) is assumed to be short, the contribution of dark current to the total background is assumed to be negligible and set equal to zero. The net effect is to set the quantities within the brackets in equations 8 and 9 to 1. It is assumed that in order to make this comparison that equations 8 and 9 are independent of pressure. That is, the pressure difference between the high and low pressure simulation does not significantly reduce the fluorescence yield.

When signal and background conditions are favorable \((B_0/S_0 \ll 10)\), SNR enhancement, defined as the ratio of SNR\(_{\text{max}}\) computed by optimal gating to SNR without optimal gating (1 atmosphere case), is slightly greater or equal to one. On the other hand, when conditions are unfavorable \((B_0/S_0 \gg 10)\), lengthening of fluorescent lifetimes and use of optimal gating can increase SNR significantly (upper half of Figure 5). In practical terms, an enhanced SNR ratio of 5 translates into a reduction in signal averaging times of 25 to achieve the same SNR.

Summarizing, FAGE offers two important advantages over atmospheric fluorescence techniques. First, by lowering pressure for excitation, the fluorescence photon arrival rate is reduced which allows for effective temporal discrimination against
Figure 4. SNR as a function of the ratios $k_b/k_s$ and $B_0/S_0$. 
Figure 5. Enhancement of SNR achieved with optimal gating as a function of $k_d/k_s$ and $B_0/S_0$. 
a huge scattering pulse due the laser source. In practice this is the largest factor in improving SNR ratio. However, SNR can be further enhanced via optimal gating when background photons are higher in intensity but have faster decays than signal photons. For instance, from Figure 5, for $B_0=1000S_0$, and $k_o=50 k_s$, SNR enhancement ratio is about 4 thus indicating that a 16 times shorter averaging time can be used to achieve the same SNR. In principle, all laser-induced-fluorescence measurements that can be operated in a reduced fluorescence quenching environment should benefit from the first effect. In addition, target species with long natural lifetimes should benefit with the use of optimal gating to discriminate against unwanted fluorescence.

APPLICATION OF FAGE TO NO$_2$

Nitrogen dioxide absorbs in the UV and visible portion of the electromagnetic spectrum. It has a largely continuum absorption spectrum with some banded features (Figure 6). Quantum mechanical calculations predict a linear $^2B_1$ and a low-lying bent $^2B_2$ excited state [Gillespie et al., 1975] (see Figure 7). Transitions involving these states and the ground state $^2A_1$ are complex and have been studied extensively [Donnelly and coworkers 1976,1978,1979;Hardwick, 1985] but assignment of emission lines to particular states has not been completely accomplished. There is general agreement that excitation at wavelengths above 500nm result in the electronic transition $^2B_2 <^2A_1$ [Hiraoka et al., 1987, Schmiedl et al., 1977]. The radiative lifetime of emission from the $^2B_2$ state based on the integrated absorption coefficient is about two orders of magnitude shorter than the
Figure 6. NO₂ absorption spectrum.
Figure 7. NO₂ energy level diagram.
observed lifetime (30-100µs) [Schofield, 1977]. This type of behavior is indicative of a mechanism involving forbidden transitions and energy transfer mechanisms. This effect, which has been studied extensively, results from a complicated mechanism involving perturbation of upper vibrational levels of the ground state, $^2A_1$, and radiationless transitions between vibronic states [Donnelly et al, 1979]. Consequently, NO$_2$ has fluorescence properties that are a strong function of excitation wavelength, pressure and spectral detection region. Although the anomalous excited energy state transitions of NO$_2$ make it difficult to fully characterize its fluorescence properties, the extended radiative lifetime of NO$_2$ makes FAGE a particularly suitable analytic technique for measuring NO$_2$ concentration as described in the previous section.

An expression for signal recovery for FAGE-NO$_2$ can be derived for the measurement of NO$_2$. By explicitly including all known contributions to signal recovery this exercise is useful in the development of the instrument. Fluorescence photon collection is written as

$$F_{PC} = L_p \times D_e \times F_e \times C_x$$  \hspace{1cm} (11)

where, $L_p$ is the number of laser photons per laser pulse at the excitation wavelength, $D_e$ is the optical efficiency of the detection system, $F_e$ is yield of fluorescence and $C_x$ is the concentration of NO$_2$.

$$L_p = \frac{\text{average power(Watts)} \times \text{wavelength(meters)}}{(\text{pulse repetition rate, Hz}) \times 3 \times 10^8 \text{(m/sec)} \times 6.63 \times 10^{-34} \text{(J \cdot s)}}$$  \hspace{1cm} (12)
\[
D_e = \frac{(\text{radius of optics})^2}{4 \pi (\text{distance from optics to fluorescence region})^2} \cdot (Q_{ei} F_e) \cdot R
\] (13)

\[
F_e = \sigma \lambda (\text{cm}^2) \cdot l (\text{cm}) \cdot k_p / \left( k_r + \Sigma (k_{qi} M_j) \right)
\]

\[
[\exp(-k_r + \Sigma (k_{qi} M_j) t_d) - \exp(-k_r + \Sigma (k_{qi} M_j)(t_d + t_g))] \] (14)

The number of laser photons, \( L_p \), is readily calculated from the average power, wavelength and pulse repetition frequency of the laser. \( D_e \) is estimated based on the solid angle of collection, photomultiplier quantum efficiency \( Q_{ei} \) over the region of emission, spectral filter overlap \( F_i \) over the region of emission, and percent reflection losses on surfaces, \( R \). \( F_e \) is determined by the absorption coefficient at the excitation wavelength \( \sigma \), path length \( l \), and fluorescence yield \( F_{YP} \) including the integration gate width and delay.

For the FAGE-NO\(_2\) systems, \( D_e \) is 1/16 and the length of the detection zone, \( l \), is 3 cm. \( Q_{ei} \) was determined to be 0.02 based on the quantum efficiency of the photomultiplier tube given by the manufacturer (EMI Photomultiplier Catalog, 1986) over the detected wavelength region. Reflection losses and misalignment losses give an estimated value of \( R \) of .33. The spectral filter overlap \( F_i \) was calculated to be 70% based on filter transmission and the normalized fluorescence spectrum of NO\(_2\) measured by Donnelly and co-workers, 1979. These quantities have been used to calculate a theoretical calibration factor for the systems developed. These factors as well as other quantities pertaining to the actual FAGE systems are tabulated in Table II in Chapter IV.
CHAPTER III

DESCRIPTION OF INSTRUMENTS

INTRODUCTION

Three different laser systems were involved in the development of FAGE-NO$_2$. The first two systems (Figure 8), FAGE1 and FAGE2, were based on Neodymium-Yttrium Aluminum Garnet (Nd-YAG) lasers and the most recently designed instrument, FAGE3, was developed around a Cu-vapor laser. Each system contributed to a greater understanding of the limitations and potential improvements that could be made. Most of the development work was done with FAGE1. Modifications necessary and improvements made for FAGE2 and FAGE3 are elucidated below.

FAGE1

The first laser employed was a 15 year old 6Hz Nd-YAG laser (General Photonics, Model YAG-TWO-70A) used earlier in the ambient FAGE-HO measurements [Hard et al., 1984]. The Nd-YAG crystal emits at 1.06μm which is frequency doubled within the laser head to emit about 30% of its power at 532nm. Typical green power of the FAGE1 laser was ~200 mW. The original detection cell was an uncoated aluminum block with 2 inch diameter ports on 5 sides to accommodate beam entrance and exit arms, vacuum and sample nozzle ports, and photomultiplier (PMT) port (see
Figure 8. FAGE1 and FAGE2 experimental setup.
Figure 8). Since the FAGE technique delays signal acquisition until some time after the laser fires, it was thought that an uncoated (semi-reflective) cell would enhance signal recovery compared to a cell which had been coated for minimum reflectivity to minimize collection of scattered light from the laser beam. Coating for maximum reflectivity is particularly effective in signal limited chemiluminescence systems [Mehrabzadeh et al., 1984]. However the intensity of scattering caused by passage of the laser beam through the cell effectively saturated the PMT and its recovery was noted to last several microseconds. This was a lesson in the importance of the scattering background on the PMT even with time delayed gating. It was clear that in order to achieve an acceptable SNR, reducing the background due to scattering would be a major challenge.

One large source of scattering signal at reduced pressure comes from the laser light scatter off of the entrance and exit windows. The intensity of the scatter is a function of the laser intensity, quality of window material used and any imperfections (scratches, bubbles, etc.) or dirt on it. This light can be detected as background signal if it enters the detection cell and reflects off of the walls of the detection cell into the detection zone. The amount of window scatter reaching the detection zone was reduced by positioning baffles with circular apertures within the window arms. The size of the aperture is a compromise between the desire to minimize the scatter reaching the detection zone (reducing baffle size) and minimizing the possibility of the laser beam hitting the baffle (increasing baffle size). Likewise the position of the baffle is a compromise between reducing scattering signal reaching the detection zone (placing
baffle close to the detection region) and reducing the effect of surfaces likely to reflect back scatter into the detection region (placing baffle further away from detection region). The optimal baffle placement and size for the Nd-Yag laser (Figure 9) were determined by peering into the detection cell at the detection port with the room lights turned off and at low cell pressure while various configurations of baffle size and placements were tried.

Optical imaging was also used to reduce the detection of wall-scattered photons and increase signal recovery. The design of the cell limited the minimum distance of the PMT to 3.5 inches away from the detection zone. The calculated volume collection efficiency is then 2.0%. By placing a 2 inch diameter lens 2 inches away from the detection zone the signal can be imaged onto the PMT photocathode, using a second focussing lens, to increase collection efficiency to 6.25% (equation 13). With the detection zone imaged above the cell a rectangular mask was used to further limit the amount of the scattering reaching the detector from walls outside the desired field of view (Figure 10).

While the above techniques greatly reduced the amount of unwanted scattering reaching the detection zone, spectral filters were necessary to further reduce the scattered laser photons collected. Since NO₂ fluorescence emission is red-shifted from the laser line a red cut-on filter was desirable. Wratten gel filters (No. 21,.1% transmission @532nm, Wratten filter catalog, Kodak Corp.) were initially tried but they did not have sufficient attenuation and transmission properties. We found that several
Figure 9. Optimal baffle placement.
Figure 10. Detection optics.
Schott filters (OG570) with an attenuation of $10^{-5}$ at 532nm placed in series (thus multiplicative attenuations) were suitable for this system.

The photon detection device was a EMI 9816QB photomultiplier tube (PMT) operating at 1900 Volts. Current from the PMT was sent to a gated charge integrator (LeCroy QVT3001) (QVT) whose binary output was connected to a home-made QVT interface device (Appendix B) which was then connected to a IBM-compatible computer. Signal acquisition was synchronized with the laser firing via a MRD trigger photodiode. A variable delay, $t_d$, time between laser firing and start of signal acquisition and a variable integration gate width, $t_g$, was accomplished using coaxial cable and the internally generated adjustable gate width of the QVT (Figure 11).

The binary output of the QVT is collected via a parallel I/O card (Metrabyte, PIO-12) in the microcomputer. The data acquisition software (Appendix C) waits for a signal from the I/O card before beginning transfer. The number transferred from the QVT is a number proportional to the charge collected from the photomultiplier for that laser shot (the proportionality constant is supplied by the manufacturer). Conversion of charge, in units of coulombs, to the number of photons was accomplished by two methods. First a histogram of the signal from the PMT with low-level light illumination is recorded. The channel with the highest number of counts is taken as the average for a single photon event. Second, a calculation was made by converting the voltage vs. time trace of the most intense curve (i.e. highest arrival rate) of a single photon observed on a 400MHz oscilloscope to charge. Since these two methods come into reasonable agreement, it is expected that direct conversion of integrated charge to
Laser pulse detected by photodiode (MRD 500)

Generated by delay coils (FAGE1) or delay generator (FAGE2, FAGE3)

Figure 11. Timing diagram for signal acquisition.
number of photons is a valid procedure. Laser power was monitored with a digital power meter (Scientech, Model 365) and recorded by the microcomputer.

FAGE2

The experimental design of FAGE2-NO₂ was very similar to FAGE1 (Figure 8). The second Nd-YAG laser (Quantel Series YG-580) operated with a repetition rate of 30Hz and an average power of about 1.2 Watts @532nm. Improvements were made in baffle design by using adjustable metal irises for baffle apertures. This was a necessary modification since the higher power of the laser caused the paper baffles to burn within the cell. In addition the sharper edge of the metal aperture proved superior in reducing scatter (compared to the rough fibrous edge of paper) and also allowed for greater ease in optimizing baffle size. For a larger range of tₜ and tₑ, a home-made delay generator coupled with a pulse generator (Tektronix, PG502) was used to provide the external gate width for the gated charge integrator.

FAGE3

For FAGE3 (Figure 12) a Cu-vapor laser (Cooper Lasersonics, Model 251) was used. A larger cell was used in this setup in anticipation of the development of simultaneous measurement of other quantities of atmospheric interest. The Cu-vapor laser has a pulse frequency of 5.6kHz and a pulse width of about 30ns. Copper vapor lasers emit at two wavelengths, 578nm and 510.6nm. Laser power at 510.6nm is about 40-60% of the total emission depending on the operating pressure of the laser. The
Figure 12. FAGE3 experimental setup.
578nm and 510.6nm beams are separated via a dichroic mirror. The 578nm beam is used to pump a dye-laser system for use in the HO₃-FAGE apparatus.

The relatively large copper vapor laser beam diameter (~3.8cm) makes it unsuitable for use in the detection cell for a number of reasons. A large beam requires a greater field of view for the detection system and reduces the ability to physically mask undesired scattering present at the walls of the cell. In addition, a large beam also requires large entrance windows which increase the susceptibility of the detection optics to ambient light. A Galilean type telescope followed by long focal length field lenses was found to be best suited for reducing the beam diameter (Figure 12). Unfortunately super-radiant lasers, such as a Cu-vapor laser, have poor divergence characteristics which are proportionally magnified by the reduction in beam size. Therefore while every effort was made to produce a small collimated beam, an unfortunate reduction in laser power and beam stability resulted.

After telescoping, the beam is sent via reflectance coated mirrors to the FAGE cell. Baffles with adjustable irises are placed within both arms of the cell to minimize detection of light scattered by entrance and exit windows. The unavoidable expanding nature of the beam necessitated additional apertures constructed of razor blades which were placed within the main detection cell before the detection region. The baffle immediately after the detection zone was constructed with pieces cut up from a Wratten gel filter. This radiation absorbing material was found to be superior to black absorbing paper, adjustable irises or razor blades for the purposes of this baffle.
Current from the PMT is sent to the QVT capable of 3-mode analysis in the form a charge integration (Q-mode), time-to-digital conversion (T-mode) and voltage peak measurements (V-mode). T-mode data collection is most desirable since it can directly provide the number of photons collected as well as a histogram of when they arrived at the detector. This provides a simple and efficient method of determining the temporal characteristics of the signal and background. However, this mode is constrained to be only valid in environments of low photon arrival rates. Although statistical corrections can be applied, an upper limit of validity for this correction is around a 20% arrival rate. Despite this limitation T-mode data collection is a valuable tool in ascertaining the sources of background signals. When photon arrival rates are higher than can be corrected, charge integration (Q-mode) is used.

The high repetition rate of the FAGE3 laser system presented some unique problems. The data collection frequency of FAGE3 is 200 times faster than FAGE2 and 1000 times faster than FAGE1. For the same amount of net signal per unit time due to NO₂, FAGE3 measures approximately constant background events, such as ambient light, proportionally more often. In other words, the integration sampling window is 1000-200 times longer than either FAGE1 or FAGE2. Thus background events, such as photons due to ambient light, contribute proportionally more to the gross signal than either FAGE2 or FAGE1. However, in contrast to FAGE3-HOₓ [Chan et al., 1990] exposure of a nozzle system to ambient light, necessary to minimize HOₓ sampling loss, is not necessary to sample the relatively stable NO₂ molecule. Consequently, FAGE-NO₂ is immune from stray light entering through the nozzle into the detection cell. On
the other hand, since the measured fluorescence is visible light, room light entering through the entrance and exit windows can increase measured background signal. Acceptable reduction in the effect of room light was accomplished by attaching a long tube constructed of velvetized black paper over the exit window arm and placing an adjustable iris in front of the entrance window.

The circuitry of the QVT generates a constant current which is integrated along with the signal being measured. This provides a means of determining the zero point of the integration (called a pedestal) which is offset from zero coulombs on the QVT output. Thus each time the laser fires the measured signal from the QVT includes the current due to the pedestal of the QVT. This pedestal current is not completely constant and seems to vary as a function of instrument temperature. A drift of 1-4 QVT counts is not unusual during the course of a day, especially during field studies where temperature fluctuations are significant. In addition sudden pedestal shifts of 1-2 QVT counts were noticeable, perhaps due to electrical pickup.

Shifts in pedestal current were not particularly a problem with either FAGE1 or FAGE2 since signal due to the laser was much higher than the pedestal current. For FAGE3 the signal due to the laser is at a level much closer to the pedestal current and, since the integration sampling window is much larger, the pedestal current represents a much higher proportion of the total gross current measured. Thus drifts in the pedestal current can cause spurious signals. This problem was largely solved by introducing a baffle attached to computer-controlled stepper motor before the laser beam entered the cell. By blocking the beam periodically (every five minutes) a measurement
of the pedestal itself could be made. This modification was found to be effective in eliminating spurious signals due to pedestal drift.

The low repetition rate of FAGE1 allowed the use of a simple interpreted programming language TBASIC (Transera Corp., Provo, Utah) while the higher repetition lasers used in FAGE2 and FAGE3 demanded the use of faster compiled code. Software based on combination of QuickC (Microsoft Corp.) with inline assembly language was written for the latter two systems (Appendix C).
CHAPTER IV

INSTRUMENT OPTIMIZATION, LINEARITY AND SENSITIVITY

FAGE1

The primary goals in the development of FAGE1 were to reduce the background and to enhance net signal recovery to the extent that reasonable concentrations of NO₂ could be detected with small averaging times. The former was accomplished primarily by optimizing baffling and detection optics as discussed in the previous chapter. The latter was accomplished by exploring various NO₂ modulation techniques.

Relatively high concentrations of NO₂ were generated, for instrument development purposes, with home-made permeation tubes. These devices consisted of a pyrex bulb with a neck of glass tubing serving as a liquid NO₂ (actually N₂O₄) reservoir with a piece of Teflon tube connecting the reservoir and a pyrex cap made of tubing. The permeation rate is a function of the size of the gap between reservoir and cap, type of teflon used and temperature. A dilution system was devised with the use of mass flow controllers [Goldan et al., 1986]. The linearity of the calibration system was demonstrated with the use of a chemiluminescence NO₂ analyzer (Thermoelectric, Model 14). The approximate NO₂ permeation rate could be determined by this technique.

Four different NO₂ modulation techniques were tried. Three of them were based on photolysis of NO₂ using light sources available in the lab: a flash lamp, a high
powered mercury lamp and a black light. Reduction of NO₂ to NO by photolysis is used by NO-detection instruments to measure total NOₓ [Kley and McFarland, 1980; Sandholm et al., 1990]. At wavelengths below 398nm NO₂ is photolyzed to NO and O atom with near unity quantum efficiency. The overall efficiency of photolyzing NO₂ contained in a given air parcel is determined by the photon flux of appropriate wavelength, the exposure time of the air parcel to the light source and pressure in the photolysis cell. The residence time of the photolysis cell was on the order of 6s. Aluminum foil surrounded the photolysis cell and light source to enhance energy transfer to the photolysis cell.

Flash lamp photolysis was the only photolytic technique to achieve a measurable modulation of the NO₂ signal. Flash lamp pulse width was measured to be ~ 20μs. Various configurations were tried to achieve maximum modulation. It was thought that by synchronizing the flash lamp firing to the laser pulse with the appropriate delay for the passage of the photolyzed air parcel, maximum modulation efficiency could be achieved. Unfortunately neither the flash lamp circuitry nor laser circuitry would accommodate synchronization. Triggering the laser with the photolysis flash lamp resulted in instabilities in the laser flash lamp trigger circuit resulting in laser shut down. Instead, the flash lamp was operated at a rate which maximized modulation independent of laser firing.

The data collection cycle for this system was to measure the NO₂ signal for 200 laser shots, turn the flash lamp on with a computer-controlled relay switch, delay for 10 seconds, then collect background for another 200 shots, turn lamp off and then delay another 10 seconds before the next collection cycle. A linearity test of the system was
performed and is shown in Figure 13. The upper data points represent the average for several repetitions of the above cycle for the gross signal phase. Similarly, the points just below the gross signal represent the average with the flash lamp firing. The net average difference is multiplied by ten for clarity and is also plotted. The error bars are the standard error of the mean. Although the data indicates that the system is generally linear, deficiencies with this system are evident.

The primary concern is the low modulation efficiency of less than 10%. Modulation efficiency is given by equation 15.

\[
\frac{\text{gross signal} - \text{modulated signal}}{\text{gross signal} - \text{background ("zero" NO}_2\text{)}} = (15)
\]

Much larger modulations are necessary to reach acceptable detection limits. The significantly negative intercept could be explained by light from the lamp leaking into the detection zone during the photolysis mode. This would raise the background with respect to the signal and result in a negative offset. Calculated signal photon collection is \(-3\) photons/ppb NO₂ for a 1.1min averaging time. Signal-to-noise ratios were on the order of 5 for about 300ppb NO₂.

With further examination of the data (Figure 14) large fluctuations in the net signal are evident. This may be an indication that potentially higher modulation efficiencies are possible with proper synchronization of the laser and flash lamp. Each point here represents the signal and background summed for 200 laser shots. The
Figure 13. FAGEI linearity with photolysis modulation.
Figure 14. Raw data from Figure 13.
averages of these points are plotted in Figure 13. The high and low modulations could be a result of a sometimes fairly good but usually poor synchronization. Another possible explanation for the "noise" in the data is interaction of electrical noise from the flashlamp with the PMT. In fact, during experiments with the flashlamp, the computer would, on occasion, "hang up" resulting in the loss of all data acquired. Because of the above considerations photolysis as modulation technique was not pursued.

Modulation of NO₂ by chemical and surface reduction to NO was widely used in CL instruments until recently [Kelly et al., 1987]. These techniques include passing the sample through heated stainless steel tubing, molybdenum metal or ferrous sulfate. However chemical reduction schemes for NO₂ tend to reduce other members of the extensive NOₓ family to NO as well. For this reason they are not suitable for use in instruments measuring NO [Fehsenfeld et al., 1988]. Hydrated ferrous sulfate (FeSO₄·H₂O) is reported to have the highest conversion efficiency for NO₂ to NO, upwards of 99%. Conversion of other species to NO is unimportant for this instrument since FAGE-NO₂ is spectrally specific for NO₂ and not NO.

A linearity test with FeSO₄ as the modulating agent was done in a experiment similar to the one utilized above. The NO₂ permeation device used in these experiments was bought commercially (VICI-Metronics) and the permeation rate certified by the manufacturer (105ng/min @30C) was used. The permeation rate was verified within 10% by constant temperature weighings over a period of one month. The cycle here was to collect gross signal for 200 laser shots, switch a three-way valve to allow air passage through a filter capsule filled with ~ 170g of FeSO₄, wait 10 seconds, then collect
background signal for 200 laser shots. The average laser power in these experiments was
~200mW. The pressure in the fluorescence cell was 1.5 torr. In contrast to Figure 14,
the background in Figure 15 is random with respect to concentration reflecting excellent
conversion of NO₂. Thus with FeSO₄, unlike the photolysis experiments, the background
does not appear to be limited by the conversion efficiency. Much of the variation of the
background with time was due to laser beam drift and the consequent misalignment of
the beam through the cell. The frequency doubler of the laser was affected by small
changes in temperature which demanded frequent tuning of the crystal during an
experiment as well as beam realignment.

The slope of the line through the average net signal in Figure 15 is 38.4±1.6
photons/ppbv, the standard error in y is equivalent to 0.6ppbv, and the intercept is
equivalent to -0.6 ± 0.6ppbv NO₂. The error bars in the Figure are twice the standard error
in the mean. This implies a detection limit of around 0.6ppbv with a 1.1 minute
averaging time. The calibration factor for FAGEI based on the above quantities is 345
photons/(ppb min watt).

Signals from the FAGEI system were compared with data from a NOₓ-CL
analyzer in an experiment carried out in a continuous stirred tank reactor (CSTR) [Hard
et al., 1984]. Nitric oxide and mesitylene flowed into the teflon-film CSTR which was
surrounded by UV fluorescent light. The NOₓ-CL analyzer (ThermoElectron Model 14)
was equipped with a heated stainless steel NOₓ converter. Ozone was measured by its
absorption at 254nm (Dasibi ozone analyzer). Data from the latter commercial
Figure 15. FAGE1 linearity with FeSO₄ modulation.
instruments were transferred in binary form or converted with an A/D converter to the FAGE1 computer.

Figure 16 shows NO, NO₂ and O₃ data for two cycles of photolysis and darkness. FAGE-NO₂ is plotted on this graph after application of a calibration factor determined from a linear regression of FAGE-NO₂ net photon count vs. NO₂ concentration measured by the CL instrument. The FAGE-NO₂ data is shown with a 1.1 min averaging time. The calibration factor determined in the linearity test in Figure 17 could not be used here because the signal recovery was attenuated (by reducing gate width, t₇) in this experiment to accommodate the relatively high concentrations involved. Although NOₓ-Cl instruments with stainless steel converter are known to have interference in the presence of alkyl nitrites such as PAN (peroxyacetyl nitrate) a deviation from good correlation in Figure 17 is not expected in this experiment. A rough simulation of aromatic photooxidation indicates that PAN represents only about 5% of the NO₂ concentration and thus would not cause a noticeable difference between the two sets of data. This is in contrast to measurements in the remote troposphere, where low NO₂ relative to PAN is a frequent occurrence [Singh et al., 1985].

**FAGE2**

FAGE2 involved the use of the higher-powered, more reliable Quantel Nd-YAG laser. The frequent down time and lack of beam stability limited the ability of FAGE1 to optimize FAGE-NO₂. One of the means of optimizing SNR using the FAGE technique is with optimal gating as discussed in Chapter II. Experimental optimization of the
Figure 16. FAGE1 bag calibration data.
**Figure 17.** Linearity of bag calibration data.
system was studied by varying the two controlling parameters of signal collection: $t_d$ and $t_g$. As previously discussed, they are, respectively, the delay between the laser firing and time at which the gated charge integrator was turned on and the width of the integration gate. Average power in these experiments was around 1.4 Watts and cell pressure ~0.25 torr.

With gate width fixed at 2000ns, delay time was varied from 800ns to 7000ns. An NO$_2$ concentration of 42ppbv was used for these experiments and the PMT output was summed for 10s (300 laser shots) during each signal and background phase, with a seven second delay between each phase. Variation in SNR with $t_d$ is shown in Figure 18 for two experiments. SNR was calculated based on equation 2. Error bars are the standard deviation of several repetitions of the same conditions. SNR is fairly constant in the region of 1000 to 1500ns but drops off beyond 1500ns. Triggering the integration gate before 1000ns results in steep decline of SNR. Triggering at times <750ns resulted in an overflow condition of the QVT, indicating the presence of a significant portion of the tail of the scattered laser pulse. Figure 19 shows the variation of SNR with respect to $t_g$. The optimal SNR could not be achieved by increasing $t_g$ due to the limitations of the QVT. Increasing $t_g$, increases the zero point (or the QVT pedestal, as discussed in the previous Chapter) of the QVT which limits the dynamic range for measurements and sets an upper limit for usable $t_g$ values. However, with the best achievable value of the parameters, $t_g$ and $t_d$, using 42ppbv NO$_2$, signal and background counts were 950 and 412cps respectively. This represents almost a factor of 3 improvement in calibration factor over FAGE1. This was achieved by a combination of effects, including optimization of $t_g$ and
Figure 18. SNR versus $t_d$. 

Signal-to-Noise Ratio

Trigger Delay ($t_d$), ns
Figure 19. SNR versus $t_g$. 
t, improved alignment of cell optics and lower cell pressure (reducing PMT saturation). Since the fluctuations in signal intensity were found to be consistent with Poisson photon counting statistics a detection limit can be extrapolated, where \( \text{SNR} = S/(S+2B)^{1/2} \) is calculated as unity. This calculation generates a detection limit of 450pptv for the 30s integration time employed in the experiment. Greater sensitivity would result from longer averaging times, with the improvement in SNR expected to increase as the square root of the averaging time.

These series of experiments demonstrated that the FAGE-NO\(_2\) responds in a manner consistent with the theory presented in Chapter II. In addition, experimental optimization of gating resulted in a reasonably good calculated detection limit with a small averaging time. However, limitations of the system were also noted. The QVT-based detection system was designed for systems with low photon arrival rates per pulse and short integration gates. High photon arrival rates per pulse, as in FAGE2 (and FAGE1), integrated with a QVT, limit the effective dynamic measurement range of the instrument. In addition Figure 19 demonstrates that longer integration gates are desirable to achieve greater sensitivity.

Sensitivity is also enhanced by operating at lower cell pressures. Since the intensity of Rayleigh and Mie scattering is inversely proportional to cell pressure, decreasing pressure will reduce PMT saturation and/or recovery time (in effect, it decreases the lifetime of the background signal). The effect of cell pressure on background is seen in Figure 20. These data were taken by measuring the background signal with respect to trigger gate time. The gate width used here was kept low (250ns)
Figure 20. Background vs. cell pressure.
so that the time dependence of the signal is clear. Clearly the decay processes in the background signal are not simple and involve at least two and perhaps three different decays. Nevertheless, as expected, the decay rate is fastest at the lowest pressure. This is consistent with the idea that decreasing pressure reduces the intensity of Rayleigh scattering which decreases PMT recovery time. If a fluorescence process susceptible to collisional quenching were a major component of the background, then an decrease in fluorescence decay rate with decreasing pressure would be expected.

Optimal SNR will occur at some value of the reduced pressure if the lifetime of NO$_2$ increases with decreasing pressure and the lifetime of the background increases more slowly or decreases with pressure. One limit in reducing cell pressure is reached when a significant fraction of the emitting target molecules radiate (rate constant $k_r$) vs. undergoing quenching (rate constant $k_q$). This limit is related to the half-quenching pressure of the target species ($[M]_0 = k_q/k_r$) (Figure 2), at which pressure half the excited molecules fluoresce while half are quenched. At this point the fluorescence signal has dropped by 1/2 relative to its value at atmospheric pressure.

Thus one parameter in the sensitivity of FAGE-NO$_2$ is related to $k_q$ and $k_r$. Since the effective fluorescence lifetime of NO$_2$ is a strong function of excitation wavelength, spectral detection region and pressure regime a measurement of $k_q$ and $k_r$ under the operating conditions of the current system is desirable. This was accomplished by measuring the signal and background of a fairly high concentration of NO$_2$ ($\sim$150ppb) at various pressures as a function of trigger delay. The signal and background were acquired for 200 laser shots each with a delay of 10 seconds between phases. Multiple
measurements were made at each delay setting. FeSO₄ was used as the modulating agent. Trigger delay was measured with a 400MHz oscilloscope (Tek 2465A). As an example, the data for gross signal and background is shown in Figure 21 for the experiment done at 1 torr cell pressure.

Assuming a single exponential fluorescence decay, the net integrated signal intensity due to NO₂ from the time tₜ to the time tₜ + tᵢ is given by:

\[
\frac{S}{(k_r + k_q M)} \{ \exp[-(k_r + k_q M) tₜ] - \exp[-(k_r + k_q M) (tₜ + tᵢ)] \}
\]

where S is essentially a proportionality constant which is a function of NO₂ concentration, kᵣ, and signal recovery efficiency and M is the pressure of the quencher (N₂). If the fluorescence decay rate, kᵣ, is defined as kᵣ = (kᵣ + k_q M) then equation 16 can be expressed as:

\[
\text{net signal} = \frac{S}{kᵣ} \{ \exp[-kᵣ tₜ] - \exp[-kᵣ (tₜ + tᵢ)] \}
\]

Equation 17 is the model equation with which quenching data was fitted. Each data set at a given pressure was fit using a commercial (MINSQ, MicroMath Corp.) parameter fitting (Levenberg-Marquadt algorithm) program with kᵣ and S as the fitted parameters. Table I gives the results of the parameter fitting. The excellent correlation of the model with the data indicates that the above model based on a single exponential fluorescence
Figure 21. Net signal and background at 1 torr.
### TABLE I

RESULTS OF FITTING QUENCHING DATA TO EQUATION 17

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>$S$ (photons)</th>
<th>Fitted values</th>
<th>$k_f$ (nsec$^{-1}$)</th>
<th>$\sigma$ error</th>
<th>$\sigma$ error</th>
<th>$r^2 corr$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>9.9</td>
<td>0.48</td>
<td>2.6e-4</td>
<td>4e-6</td>
<td>.998</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>78.1</td>
<td>1.4</td>
<td>1.2e-3</td>
<td>7e-6</td>
<td>.999</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>183.8</td>
<td>0.8</td>
<td>5.3e-4</td>
<td>3e-6</td>
<td>.999</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>562.2</td>
<td>7.1</td>
<td>1.9e-3</td>
<td>2e-5</td>
<td>.999</td>
<td></td>
</tr>
</tbody>
</table>
decay is appropriate for the operating conditions of FAGE2. This is consistent with detailed studies of NO₂ fluorescence characteristics which indicate that single exponential decays are observed at high pressures while biexponential fluorescence decays are observed at much lower pressures (P<0.01 torr) [Donnelly et al., 1979]. The results in Table I of decreasing decay rate of NO₂ fluorescence intensity with decreasing pressure are in contrast to Figure 20 where decreasing pressure increases the rate of background decay.

If the fluorescence properties of NO₂ were simple, a fluorescence quenching plot of k_f or (1/τ, where τ=fluorescence lifetime) vs P (Figure 22) would yield both k_r (intercept) and k_q (slope). However extrapolation of a fluorescence quenching plot obtained at relatively high pressures to zero does not give a meaningful determination of k_r for NO₂. The negative intercept (implying a negative value for k_r) of Figure 22 has been observed by others making similar measurements at comparable pressures [Kirzinis et al., 1984]. Consequently, the experimental results shown in Figure 22 can only be used to determine k_q under the operating conditions of FAGE2. A linear regression of the points in Figure 22 gives k_q = 4.0±0.1 x 10⁻¹¹ cm³s⁻¹. Using the measured k_q value and reported values for k_r, [M]₀ is calculated to be in the range of 26 to 5mTorr. This suggests that optimum SNR can be achieved by operating in the mTorr pressure range.

However, a second criterion in choosing an operating pressure for efficient measurement of a species with long fluorescence lifetimes requires that the emitting species remain in the detection region long enough for fluorescence to occur. This
Figure 22. Quenching of NO$_2$ fluorescence in N$_2$. 
criterion can be met by suitable adjustment of flow parameters in concert with cell pressure [Mehrabzadeh, et al. 1984]. Figure 23 illustrates the relationship of the time the emitting species spends in the detection zone (assuming plug flow) with the fluorescence lifetime of NO₂ with respect to operating pressure. At a pressure of .1 torr, in Figure 23, given an initially excited parcel of air, 99.95% (10 fluorescent lifetimes) of this excited population is deactivated (either by radiating or by quenching) before leaving the detection zone. For the flow rates used in FAGE2 the two pressure limitations (half-pressure and fluorescent lifetime) occur at comparable pressures.

A linear increase in signal recovery is anticipated from equation 11 unless saturation effects occur. As laser intensity is increased the rate of populating the excited state also increases. Saturation occurs when the rate of populating the excited state approaches the rate of depopulating the excited state by stimulated emission. Thus increasing laser intensity at this point results in a decreased response for each excitation photon. Saturation of the excited state is potentially a concern in terms of achieving maximum signal to noise ratio. Thus saturation reduces the efficiency of the absorption - fluorescence processes and causes deviations from the implicit linearity of response with laser power. This is an important consideration for extrapolating sensitivities based on low power measurements to higher power measurements. It also necessary to understand the influence of laser power in order to normalize response variations in laser power.

Gross changes in laser power were readily controlled in FAGE2 by varying the voltage applied to the oscillator flash lamps. Small fluctuations in laser power (~5%) were present at any given setting. Figure 24 shows the effect of laser power on signal
Figure 23. Fluorescence lifetime and detection zone lifetime vs. cell pressure.
Figure 24. Signal and background vs. laser power.
recovery and the concomitant effect on the background intensity. Data collection cycle was 100 shots each for signal and background with a several second delay between them. After each change in voltage on the flash lamps, laser power was allowed to come into rough equilibrium before new data was acquired. Signal integration gate width and trigger delay were both set to 2000ns. A concentration of ~30ppb of NO₂ was generated with the VICI permeation tube for this experiment.

The fluorescence signal due to NO₂ appears to be linear with laser intensity in Figure 24 with a linear regression correlation of .999 and a slope of 1190 photons/W of laser power. A small positive offset of 11.5 is well within the 1-sigma standard error of Y of 36.8 and therefore cannot be considered a significant offset of the instrument. The log-log plot of data in Figure 25 results in a slope of 1.01 which confirms the linear correlation calculated from Figure 24. This seems indicates that over the laser power ranges used, NO₂ fluorescence is not saturated.

Figures 24 and 25 also show the relationship of the background signal to laser power. Clearly the background is not a simple linear function of laser power. The best fit line in Figure 25 gives a slope of 1.26 for the background. With a slope less than two, the contribution of two-photon processes must be minimal, if any. A slope greater than one suggests a connection between a linear scattering function and photomultiplier tube saturation.

One means of increasing sensitivity is to increase excitation power. An important limitation in this regard results from non-linear effects in either signal or background with laser power. When non-linear effects, such as slope \( \text{log}(S) \ vs \ \text{log} \text{power} < 1 \) (excited state
Figure 25. LOG-LOG plot of data in Figure 24.
saturation) and/or slope_{log B vs. log power} > 1 (photomultiplier tube saturation), are apparent, SNR does not improve predictably or may degrade with laser power. High pulse power can also increase photochemical interference effects (discussed in Chapter VI). These effects can be minimized by reducing the laser energy per pulse while increasing average laser powers suggesting the use of a high repetition rate laser (FAGE3).

FAGE3

FAGE3 was developed with a Cu-vapor laser operating at a 5.6 kHz pulse repetition rate. The present implementation of the system was designed to make ambient measurements from the rooftop of Science Building II at Portland State University. At this point the operating parameters of the system have not been fully optimized but sensitivity was more than adequate for the ambient levels of NO₂ encountered. Calibration was achieved by the same system described earlier. A calibration factor of 292 ± 5 photons/ppb was determined with a standard error in Y of 40 photons computed with laser power of 1.2 Watts (Figure 26). One sigma error bars are plotted as horizontal bars.

Compared to FAGE2 the energy per pulse is reduced by a factor of 200 while still maintaining close to the same overall average laser power. Controlled variation in laser power is not easily achievable with the Cu-vapor laser but some characteristics of the background were determined. Using the T-mode of the QVT the effect of pressure on the background could be easily be determined. By varying the cell pressure from .14 torr to ~760 torr, the background lifetime changed from 7µs to 3µs. It is important to note
Figure 26. FAGE3 calibration.
that this is reversed from the situation in FAGE2 where the background decay was longer at higher pressures. The low quenching efficiency of the background implies that a gas phase background fluorescence process is not the principal background source. One possible contributor is fluorescence of the components of the detection cell resulting from excitation by Rayleigh scattered photons. However, the pressure dependence in this regard is difficult to understand. Optimization of this system will necessitate further investigation of the source of the background and the possible means of removing it.

Ambient measurements made with FAGE3 are described in the following chapter. The sensitivity of the current configuration of the system was more than adequate for making measurements in the urban environment. Typically, signal to noise ratios were in the range of 30-60 for 10s averaging time (34s cycle time). The operating characteristics of all three laser systems are summarized in Table II.
TABLE II
OPERATING CHARACTERISTICS OF FAGE1, FAGE2 AND FAGE3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>FAGE1</th>
<th>FAGE2</th>
<th>FAGE3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser</td>
<td>Nd-YAG</td>
<td>Nd-YAG</td>
<td>Cu-vapor</td>
</tr>
<tr>
<td>Excitation Wavelength (nm)</td>
<td>532</td>
<td>532</td>
<td>511</td>
</tr>
<tr>
<td>Pulse Repetition Rate (Hz)</td>
<td>6</td>
<td>30</td>
<td>5600</td>
</tr>
<tr>
<td>Beam Diameter (mm)</td>
<td>6</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Average Power (Watt)</td>
<td>0.20</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Pulse Energy (mJ)</td>
<td>33</td>
<td>47</td>
<td>.21</td>
</tr>
<tr>
<td>Detection Cell Pressure (Torr)</td>
<td>1.6</td>
<td>.25</td>
<td>.35</td>
</tr>
<tr>
<td>NO₂ absorption coeff. (a) ((10^{19} \text{ cm}^2))</td>
<td>1.47</td>
<td>1.47</td>
<td>2.46</td>
</tr>
<tr>
<td>Measured NO₂ Calibration Factor (b) ((\text{photons}/(W \cdot \text{ppb NO}_2)))</td>
<td>5.8</td>
<td>16</td>
<td>24</td>
</tr>
<tr>
<td>Theoretical NO₂ Calibration Factor (b) ((\text{photons}/(W \cdot \text{ppb NO}_2)))</td>
<td>12</td>
<td>23</td>
<td>39</td>
</tr>
<tr>
<td>Detection Limit ((\text{ppb NO}_2, 20s averaging time)) (c)</td>
<td>2.3(a), 1.7(d)</td>
<td>.45(d)</td>
<td>.35(e), .37(d)</td>
</tr>
</tbody>
</table>

\(a\) from Schneider et al., 1987, \(b\) derived from equation 11 and the quantities in this table, \(c\) determined by calibration, \(d\) calculated from Poisson statistics.
CHAPTER V

ANALYSIS OF INTERFERENCES AND BACKGROUNDS

POTENTIAL INTERFERENCES

Interferences in this system are possible if the gross fluorescence signal responds to atmospheric constituents other than NO₂ and is modulated by FeSO₄ or if the modulation technique alters the "true" background signal. A review of the literature indicates that no known gas phase constituent of the troposphere both absorbs near 532 or 511nm and fluoresces [Schofield, 1977; Okabe, 1978; Finlayson-Pitts and Pitts, 1986].

The largest potential source of interference is aerosols. This was a limiting factor in previous attempts to measure NO₂ with laser-induced fluorescence at atmospheric pressure [Gelbwachs and Birnbaum, 1973]. To a large extent, aerosols should be discriminated by the temporal and spectral specificity of the FAGE system since aerosols must absorb at 532 or 511nm and fluorescence with microsecond lifetimes in order to present significant interference to the FAGE-NO₂ system. However, with heavy aerosol loading, the passage of air over the FeSO₄ crystals could potentially alter the true background fluorescence by acting as particulate filter, resulting in an interference of a positive sign. Interference problems such as these are recognizable if they alter the measured signal fluorescence lifetime relative to the known value for NO₂. (With the low photon arrival rates associated with Cu-vapor pumping, fluorescence lifetimes may be
determined directly during ambient measurements by operating the gated charge integrator in the time mode at low NO₂ levels. It is unlikely that the fluorescence lifetime of any potential aerosol interference is pressure dependent, although this should be experimentally verified. Conversely, the fluorescence lifetime of NO₂ can be easily manipulated via the operating cell pressure. Should this approach prove unsuccessful, another (less desirable) approach would be the use of an aerosol filter before entering the sampling manifold [Tucker et al., 1975]. Or it may be necessary to utilize the spectral NO₂ modulation techniques described in the literature [Kley and McFarland, 1980; Sandholm et al., 1990].

Another potential source of interference is the photolysis of ambient NO₃ to NO₂ within the laser beam. NO₃ is photolyzed to NO₂ (+ O atom) with near unity quantum yield at wavelengths between 470 to 580 nm [Magnotta and Johnston, 1980]. This will result in an interference if the NO₂ produced is detected by the same or subsequent laser pulse(s). The relative magnitude of this interference will depend on the fraction of NO₃ detected as NO₂ and the relative contribution of detected NO₃ to the NO₂ signal.

NO₃ is a minor constituent of the atmosphere during the daytime as it rapidly photodissociates to form either NO₂ (90%) or NO (10%). Nighttime concentrations of NO₃ range from 9 to 500 pptv in urban areas and 6 to 30 pptv in remote environments [Finlayson-Pitts and Pitts, 1986]. In urban air where typical NO₂ concentrations are in the range of 10 to >100 ppb, the conversion of NO₃ to NO₂ will not produce a significant interference. However, at night in the remote troposphere, [NO₃] is expected to be 50-70% of [NO₂] [Logan, 1983] and therefore could potentially produce a significant
interference. Since NO₃ would increase the signal measured in the signal mode and would be presumably be reduced by FeSO₄, NO₃ would be a positive interference to FAGE-NO₂.

A simple photochemical model of the processes occurring within the laser pulse was developed to simulate NO₃ interference (see Table III). Using the values in table II, calculations indicate that the high pulse energy of the FAGE2 laser (Nd-YAG) will photolyze more than 50% of the NO₃ in the sample to produce NO₂, 90% of which will then be detected during the same laser pulse. In the configuration of FAGE2, with a 30Hz laser, the linear velocity of the flow is sufficiently high (>1000 cm/s), that NO₂ produced, via NO₃ photolysis, by one pulse will be removed from the excitation region before the next pulse arrives. These calculations indicate that the FAGE2 system would not be suitable for nighttime clean air measurements without reductions in pulse energy. This may be accomplished by reducing overall laser power (reducing sensitivity) or by expanding the beam diameter (possibly increasing scatter off of cell windows).

Calculations done with the parameters of the Cu-vapor laser indicate that about 3% of NO₃ will be converted to NO₂. Less than 40% of these NO₂ molecules will absorb and fluoresce within the first laser pulse. At the current operating conditions of FAGE3, based on a plug flow model, about 1/2 of the region excited by the first pulse will be traversed by the second pulse. However, even if all of the NO₂ produced via NO₃ photolysis is detected with the second pulse, the upper bound of this process represents a small interference. This small interference can be easily reduced by lowering cell
TABLE III

A SIMPLIFIED PHOTOCHEMICAL MODEL FOR FAGE-NO₂

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂ + hv ---&gt; NO₂⁺⁺</td>
<td>Iσ_{NO₂}</td>
</tr>
<tr>
<td>NO₂⁺⁺ + hv ---&gt; NO₂ + 2hv</td>
<td>Iσ_{NO₂}</td>
</tr>
<tr>
<td>NO₂⁺⁺ + M ---&gt; NO₂⁺</td>
<td>3x10⁻¹⁰</td>
</tr>
<tr>
<td>NO₂⁺ ---&gt; NO₂ + hv⁺</td>
<td>1.6x10⁴</td>
</tr>
<tr>
<td>NO₂⁺ + M ---&gt; NO₂ + M</td>
<td>4x10⁻¹¹</td>
</tr>
<tr>
<td>NO₃ + hv ---&gt; NO₂ + O</td>
<td>Iσ_{NO₃}</td>
</tr>
</tbody>
</table>

Units are: 1st order, sec⁻¹, 2nd order, sec⁻¹ cm³.

I is the intensity of the laser beam normalized to a sine wave pulse (photons cm⁻² sec⁻¹), σ is the absorption cross-section (cm²), hv and hv⁺ are photons from the laser and from fluorescence, respectively. This mechanism (excluding NO₃ photolysis) was derived from the mechanism for NO₂ excitation and fluorescence developed by Donnelly and co-workers, 1979.
pressures (which will independently give greater sensitivity) and/or increasing the flow velocity to minimize double pulse problems.

BACKGROUND

The major source of background signal in these systems was the intense burst of scattered photons due to the laser pulse. The time-dependence of this background is related to the recovery time of the PMT and is possibly due to fluorescence of optical components (such as filters) in the cell. As the system is improved to reduce the intensity of the scattered signal (by reducing cell pressure and perhaps by finding better cell baffling), the background may be limited by other effects. These include fluorescence of species other than NO\textsubscript{2} (aerosols are the only known atmospheric constituents with absorption and fluorescence in this region), the dark current of the PMT and/or the efficiency of removal of NO\textsubscript{2} as a fluorescing species.

The signal-to-noise ratio (SNR) determines the ultimate sensitivity of an instrument. Increasing laser power is predicted to linearly increase fluorescence signal by equation 11. If the background also increases linearly with laser power,

\[
\text{SNR} = \frac{S}{(S + 2B)^a}
\]
the SNR should improve as the square root of the laser power. However, if saturation effects occur, the *improvement* in SNR with laser power will be smaller. Saturation decreases the linearity of the fluorescence response of the system.

Saturation effects in the FAGE2 and FAGE3 system were modeled with the simplified photochemical system shown in Table III. For FAGE2, these calculations indicate that at the highest laser power utilized (1.7W) the system would deviate from linearity by 7% relative to zero saturation. This result appears to be in contradiction to the experimental results shown in Figures 24 and 25 where the signal response was linear with laser power. The concentration of excited state was calculated for the laser powers used in those experiments in order to simulate the experimental results. The calculated slope (log laser power vs log signal) of the simulated results is 0.98 with a regression coefficient of 0.9995 compared to the slope of the experimental value of $1.01 \pm 0.02$. Comparing these results, it is clear that the experiment shown in Figures 24 and 25 is a necessary but not a sufficient test for saturation. In order to determine saturation levels experimentally, a greater range of laser powers must be utilized.

The calculations for FAGE3 indicate that at the average power used (1.2W), the response is deviating from linearity by $\sim 0.4\%$. If the laser power is increased by one order of magnitude, deviations rise to 3.3%. Increased laser power is desirable for increased sensitivity or decreased averaging time, but must be weighed against increased NO$_3$ interference which is also linear with laser power. Overall, the FAGE3 system is superior to FAGE2 for a number of reasons: 1.) it is less susceptible to NO$_3$ interference - due to lower pulse energy and lower NO$_3$ absorption at 511nm; 2.) predicted saturation
levels are lower and 3.) detection limit is somewhat better than FAGE2 (see table II) -
due largely to greater NO$_2$ absorption cross-section at 511nm.
CHAPTER VI

AMBIENT MEASUREMENTS AND URBAN NO\textsubscript{x} CHEMISTRY

INTRODUCTION

In an environment that contained only NO\textsubscript{x} and air (N\textsubscript{2} and O\textsubscript{2}) the primary reaction cycle of NO\textsubscript{x} in the presence of solar radiation would be:

\begin{align*}
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} & \text{R4} \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M} & \text{R5} \\
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 & \text{R6}
\end{align*}

Reactions of species containing nitrogen in oxidation states >4 (see Table IV) are important in the dark but will not contribute significantly in the presence of solar radiation due to the high rates of photodissociation of these species (see Table IV).

In a real or simulated atmosphere in which constituents such as hydrocarbons and water are present, the explicit chemistry of the system becomes complex. A complete set of rate expressions for NO, NO\textsubscript{2} and O\textsubscript{3} includes reactions with HO\textsubscript{x} (HO and HO\textsubscript{2}) and
TABLE IV

REFERENCE REACTION MECHANISM

|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 1 | RH | HO | --> | R | H₂O |
| 2 | O₁ | hv | --> | O₁(D) |
| 3 | O₁(D) | H₂O | --> | 2HO |
| 4 | NO₂ | hv | --> | NO | O |
| 5 | O | O₂ | M --> | O₃ | M |
| 6 | NO | O₃ | --> | NO₂ | O₂ |
| 7 | RO₂ | NO | --> | RO | NO₂ |
| 8 | HO₂ | NO | --> | HO | NO₂ |
| 9 | HO | NO₂ | M --> | HNO₃ | M |
| 10 | NO₂ | O₃ | --> | NO₃ | O₂ |
| 11 | NO₃ | NO | --> | 2NO₂ |
| 12 | NO₂ | NO₃ | M --> | N₂O₅ | M |
| 13 | N₂O₅ | hv | --> | NO₂ | NO₃ |
| 14 | NO₃ | hv | --> | NO | O₂ |
| 15 | NO₃ | hv | --> | NO₂ | O |
| 16 | R | O₂ | M --> | RO₂ | M |
| 17 | RO₂ | NO | --> | RONO₂ |
| 18 | RO₂ | NO₂ | --> | ROONO₂ |
| 19 | HO₂ | NO₂ | M --> | HNO₄ | M |
| 20 | HNO₄ | M | --> | HO₂ | NO₂ | M |
| 21 | HO | NO | M --> | HONO |
| 22 | HONO | hv | --> | HO | NO |
| 23 | H₂CO | hv | --> | 2HO₂ | CO |
| 24 | H₂CO | hv | --> | H₂ | CO |
| 25 | HO | CO | --> | HO₂ | CO₂ |
| 26 | O₃ | alkene | --> | products |
| 27 | O₃ | hv | --> | O | O₂ | M |
| 28 | O₃ | HO₂ | --> | HO | 2O₂ |
| 29 | CH₄ | HO | --> | CH₃O₂ | H₂O |
| 30 | CH₃O₂ | NO | --> | CH₃O | NO₂ |
| 31 | CH₃O | O₂ | --> | CH₃O | HO₂ |
hydrocarbons. The rate expressions below include a subset of some of these reactions (the steady-state approximation for O atoms has been made):

\[
d[\text{NO}_2]/dt = k_6[\text{NO}][\text{O}_3] + k_8[\text{NO}][\text{HO}_2] + k_7[\text{NO}][\text{RO}_2] + 2k_{11}[\text{NO}][\text{NO}_3] - k_{19}[\text{HO}_2][\text{NO}_2][\text{M}] + k_{20}[\text{HNO}_4][\text{M}] + J_{\text{NO}_2}[\text{NO}_3] - J_{\text{NO}_2}[\text{NO}_2] - k_{10}[\text{NO}_2][\text{O}_3] \tag{18}
\]

\[
d[\text{NO}]/dt = J_{\text{NO}_2}[\text{NO}_2] - k_6[\text{NO}][\text{O}_3] - k_8[\text{NO}][\text{HO}_2] - k_7[\text{NO}][\text{RO}_2] - k_{10}[\text{NO}][\text{NO}_3] + J_{\text{HONO}}[\text{HONO}] + J_{\text{NO}_2}[\text{NO}_3] \tag{19}
\]

\[
d[\text{O}_3]/dt = J_{\text{NO}_2}[\text{NO}_2] - k_6[\text{NO}][\text{O}_3] - k_{26}[\text{O}_3][\text{alkene}] - k_{10}[\text{O}_3][\text{NO}_2] + k_{28}[\text{HO}_2][\text{O}_3] \tag{20}
\]

Rate constants for reactions involving photolysis are written in terms of the species photolyzed, i.e. the rate constant for R4 is written as \(J_{\text{NO}_2}\). Despite the seemingly complex nature of the chemistry involving these species, it was recognized in early experimental and theoretical studies of photochemical smog in smog chambers that the primary reaction cycle for \(\text{O}_3\) and \(\text{NO}_x\) under many conditions is limited to R4-R6 [Leighton, 1961].

Inspection of the expressions 18,19 and 20 indicates that this observation can be explained if the rates of the reactions other than R4-R6 are comparatively small in magnitude. If this condition is met, setting any of the three equations, 18,19 or 20 to zero (steady-state for \(\text{NO}_2\), \(\text{NO}\) or \(\text{O}_3\)) would yield the following simple relationship:

\[
p = \frac{J_{\text{NO}_2}[\text{NO}_3]}{k_6[\text{O}_3][\text{NO}]} \tag{21}
\]
The right hand side of Equation 21 is known as the $O_3$-NO$_x$ photostationary state (PSS) expression. If the system is in steady-state and the contributions from reactions other that R4-R6 are exactly nil, then $p$ is exactly unity. It follows, that under steady-state conditions, the value of $p$ is a measure of the relative contributions of reactions other than R4-R6 to expressions 18,19 and 20. It is important to note that equation 21 can be derived from any of the expressions 18,19 or 20 but that not all of the reactions neglected are the same for each species. This has implications when considering the nature of the deviations of $p$ from unity. When $p$ is close to one, the relative magnitude of side reactions are small. Reversible reactions must be considered in terms of their net rate (forward-reverse) not their individual absolute rates. The net rate is the actual contribution of an equilibrium to the complete rate expression. For example, the rates of formation ($k19[HO_2][NO_2]$) and destruction ($k20[HNO_4]$) of peroxynitric acid ($HNO_4$) in expression 18 can be high but if their net reaction, net formation or destruction of NO$_2$ is small, $p$ will still be close to one. Since the quantities in equation 21 have been, for the most part, more easily measured than the concentrations of other compounds appearing in expressions 18,19 and 20, this simple relationship has been an important tool in testing our understanding of the role of nitrogen oxides and ozone formation in the troposphere.

PHOTOCHEMICAL MODEL PREDICTIONS

The reactions, R4-R6, complete a null reaction cycle. For a given $k_6$ and $J_{NO_2}$ the reactants NO, NO$_2$ and O$_3$ establish a photoequilibrium with no net loss or production of
NO\textsubscript{x} or O\textsubscript{3}. In this case the value of \( p \) would be unity. If, for example, other reactions besides R6 are important in oxidizing NO to NO\textsubscript{2}, such as the reactions:

\[
\begin{align*}
\text{RO}_2 + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{HO} + \text{NO}_2
\end{align*}
\]

(R7) (R8)

significant deviations from unity will result. Conceptually, any process that produces NO\textsubscript{2} without the destruction of O\textsubscript{3} potentially increases the ozone production rate since the primary process for producing ozone in the troposphere is through the photolysis of NO\textsubscript{2}. This results in a positive deviation (\( p > 1 \)) from the photostationary state. On the other hand, if reactions such as, O\textsubscript{3} + alkene \( \rightarrow \) products, are important in the destruction of ozone, a net destructive term for ozone would result. This would also result in positive deviation of the PSS.

In the real atmosphere, \( p \) is never exactly equal to one since the rates of the side reactions in expressions 18,19 and 20 are never zero. Measurable deviations of \( p \) from unity can provide information as to the concentrations of likely oxidants, such as HO\textsubscript{2} and RO\textsubscript{2}, present in the atmosphere. Uncertainties in the measurement of the quantities in equation 21 are a constraint on the level of deviation that can be accurately measured.

Regions in which the PSS is valid and invalid are clearly of interest in understanding the mechanisms of ozone formation. The chemistry of the atmosphere can be evaluated by computer-based kinetic modeling and direct measurement of the species of interest. These two techniques are intrinsically dependent on one another for validation.
and development. A computer simulation of a reaction set simulating the chemistry of the atmosphere can indicate the regions in which the PSS is expected to be close to one and the predicted magnitude of the deviations from unity.

By varying the initial NO$_x$ and hydrocarbon concentration (HC) the value of the PSS can be calculated for ranges of NO$_x$ and HC concentrations and NO$_x$/HC ratios (Figure 27). The calculations employed the ERTC reaction mechanism (ERTC) which was developed by ERT Corporation and the Environmental Protection Agency (EPA, 1987). This mechanism incorporates a condensed reaction mechanism for hydrocarbon oxidation with detailed NO$_x$ chemistry. The mechanism was integrated from sunrise until noon with a diurnal light intensity. The PSS values were calculated with the concentration values and light intensity reached at noon. Figure 27a shows the relationship of the calculated PSS to the initial HC and NO$_x$ concentrations. Figures 27b, 28a,b and 29a,b show the isopleths for O$_3$, NO, NO$_2$, HO$_2$ and RO$_2$ concentrations, respectively, for the same simulation.

The calculated PSS shown in Figure 27 is close to 1 in the upper left-hand portion of the graph. In this region, NO$_x$ concentrations are relatively high and HC concentrations are relatively low. As the NO$_x$ and HC initial concentrations are lowered from 0.1ppm to 0.01ppm for NO$_x$ and 0.25ppm to 0.025 ppm for HC, the PSS value increases. This can be understood in terms of the increasing competition between O$_3$ and other species in the oxidation of NO to NO$_2$. As the NO level decreases, the rates of reactions involving NO are decreased proportionally. However, the levels of oxidants such O$_3$, RO$_2$ and HO$_2$ vary at different rates with respect to NO. For example in this
Figure 27. ERTC isopleths of PSS and O_3.
Figure 28. ERTC isopleths of NO and NO₂.
Figure 29. ERTC isopleths of HO$_2$ and RO$_2$. 
case, the O₃ level changes from 37ppb to 100ppb while HO₂ changes from 1e6 to 2e8 molec/cc and RO₂ increases from 5e5 to 1e7 molec/cc. Summarizing, a factor of 10 decrease in both NOₓ and HC results in an increase of a factor of 2.7, 20 and 200 for O₃, RO₂ and HO₂ respectively, all measured at noon. Thus the rates of R7 and R8 contribute a greater fraction of the total oxidation rate of NOₓ without destroying O₃.

Ozone production depends on the rate of cycling between NO and NO₂ via peroxy radicals such as HO₂ and RO₂. In regions of highly reducing chemistry, i.e., high NOₓ or high HC, the steady-state ozone concentration will be lower (see Figure 27b). Hydrocarbons can be a net sink for ozone at high HC concentration since at low NOₓ levels the rate of reaction with RO₂ and HO₂ (leading to O₃ formation) can be lower than the direct destruction of O₃ by reactions such as R28. In addition, at high HC/NOₓ ratios, NOₓ can be sequestered in alkyl nitrate compounds further reducing available NOₓ.

The sources of deviation of the PSS from unity can be studied more carefully by analyzing the contributing rates during the course of a 1-day simulation with various initial concentrations of HC and NOₓ. These simulations were carried out here earlier with a somewhat different mechanism [Calvert and Stockwell, 1983] but were found to give results similar to those of the ERTC mechanism. The initial concentrations used in the simulations are given in Table V.

In these simulations the ratios \( J_{NO₂}/k₆ \) and \([NO][O₃]/[NO₂]\) are plotted versus time of day. When the value of \( p \) in equation 21 is unity these ratios are equal.

\[
J_{NO₂}/k₆ = [NO][O₃]/[NO₂]
\]  
(22)
### TABLE V

INITIAL CONDITIONS FOR PSS SIMULATIONS

Concentration, ppb for the case shown

<table>
<thead>
<tr>
<th>Species</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>25</td>
<td>2.5</td>
<td>.025</td>
<td>.0025</td>
</tr>
<tr>
<td>NO</td>
<td>75</td>
<td>7.5</td>
<td>.075</td>
<td>.0075</td>
</tr>
<tr>
<td>CO</td>
<td>100</td>
<td>200</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>ALKANE(C₃H₈)</td>
<td>1</td>
<td>10</td>
<td>1</td>
<td>.1</td>
</tr>
<tr>
<td>ALKENE(C₃H₆)</td>
<td>4</td>
<td>40</td>
<td>4</td>
<td>.4</td>
</tr>
<tr>
<td>O₃</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>CH₂O</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>CH₃CHO</td>
<td>.1</td>
<td>1</td>
<td>.1</td>
<td>.01</td>
</tr>
<tr>
<td>KETONE</td>
<td>.05</td>
<td>.5</td>
<td>.05</td>
<td>.005</td>
</tr>
<tr>
<td>SO₂</td>
<td>.6</td>
<td>6</td>
<td>.6</td>
<td>.06</td>
</tr>
<tr>
<td>CH₄</td>
<td>1400</td>
<td>1400</td>
<td>1400</td>
<td>1400</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.56E4</td>
<td>1.56E4</td>
<td>1.56E4</td>
<td>1.56E4</td>
</tr>
<tr>
<td>Calculated PSS value</td>
<td>1</td>
<td>1.4</td>
<td>1.5</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Figure 30 shows the effect of changing initial concentration of hydrocarbon and NO\textsubscript{x} on the right-hand side of equation 22. The deviations of the PSS can be studied in terms of the contributing rates to equation 18. For each case in Table V, the rates contributing to NO\textsubscript{2} (formation and destruction) were sorted in order of their magnitude. The largest 4 or 5 rates are plotted in Figure 31 for each case. Formation and dissociation rates of HNO\textsubscript{4} are small and their net rate is negligible. The net rate for NO\textsubscript{2} remains close to zero for all cases indicating that the steady-steady assumption is not in question.

Figure 31 demonstrates the importance of peroxy radicals in the deviations of the PSS. The relative importance of organic peroxy radicals increases with high HC concentration (case B). In addition the deviations in Figure 30 display a diurnal variation, with the highest deviation occurring at noon. Formation processes for HO\textsubscript{2} radicals are diurnally related since they are formed via the photolysis of formaldehyde and by the reaction of HO with CO and HC (see Table IV). Hydroxyl radical concentration is a strong function of light intensity. RO\textsubscript{2} radicals are formed via photolysis of aldehydes and the photooxidation of hydrocarbons.

Summarizing, these simulations combined with the results shown in Figure 27 provide some important predictions for the experimental measurement of the PSS in the real or chemically simulated atmosphere. From Figure 27, the PSS is expected to be close to 1 at high to moderate NO\textsubscript{x} levels and low to moderate HC levels. As the NO\textsubscript{x} decrease and/or HC levels increase, deviations from the PSS are expected. In addition, when deviations are present, these deviations are expected to have a diurnal variation (Figures 30 and 31).
Figure 30. Simulation of diurnal variation of PSS.
Figure 31. Rates contributing to deviation of PSS.
In order to test Equation 21 experimentally, simultaneous measurements of NO, NO$_2$ and O$_3$ concentrations must be made. Ideally, the photolysis rate of NO$_2$ should be measured on an absolute basis (chemical actinometry) but may be approximated, with limitations, based on solar irradiance calculations or by radiometric measurements (flat plate radiometers). Clearly, the accuracy with which NO, NO$_2$, O$_3$ and J$_{NO2}$ can be measured reflects directly on our ability to assess our understanding of atmospheric chemistry based on the PSS. An propagation of error analysis of equation 21 yields:

$$\sigma_{PSS/PSS} = (\sigma_{NO/NO^2}^2 + \sigma_{NO2/NO2^2}^2 + \sigma_{O_3/O_3^2}^2 + \sigma_{\kappa}^2 + \sigma_{J_{NO2/NO2^2}}^2)^{1/2}$$

This equation indicates that in order to make a measurement of the PSS with an error of less than 1%, the quantities in equation 21 must be measurable with an accuracy of less than 1%. If this condition is not met, a deviation of 1.01 will not be distinguishable from random error.

The first laboratory determinations of the PSS were made in a smog chamber with high levels of NO$_x$ (~250ppb) and HC (~.25 to 1ppm) [O’Brien, 1974]. The extent to which the PSS was valid was tested by varying the levels of HC. These experiments demonstrated that the PSS appeared to be valid with HC levels of about .25ppm but when HC was increased to 1ppm deviations from equation 22 were observed. These observations are qualitatively consistent with Figure 27 which shows that a level of 250ppb NO$_x$ and 250ppb HC the PSS is close to 1. With increasing HC to 1ppm, deviations are predicted and were observed. If the deviation is assumed to be due
primarily to RO₂, the magnitude of the deviations can be used to predict the actual level of RO₂ concentration:

\[ k8[RO₂] = J_{NO₂}[NO₂]/[NO] - k6[O₃] \]  

(23)

For the level of deviation measured in these experiments, an RO₂ concentration of \(~1\)ppb was calculated. This concentration of RO₂ is in rough agreement with the ERTC simulations. However, this agreement is probably fortuitous since the hydrocarbon mixture used in the actual experiment was not as complex as is present in the ERTC mechanism. These experiments were important in establishing the validity of the PSS at one NOₓ level and HC level and predicting the possible cause of the deviations as HC was increased.

The actual level of RO₂ present in the atmosphere is important in determining ozone production rates. Ambient measurements of the PSS in the urban and remote environment have been made by several workers. PSS measurements in the real atmosphere can be confounded by effects of transport of air masses, local emission sources, and interferences in instrumentation.

NOₓ instruments have had moderate to severe interferences in the NO₂ measurement mode [Fehsenfeld, 1988]. Generally, positive interferences were encountered resulting in measured NO₂ values that were higher than actually present. In NO-chemiluminescence instruments these interferences were due the reduction of other nitrogen oxides species such as PAN and HNO₃ to the detected NO molecule [Shetter et
al., 1983; Fehsenfeld, 1988]. The magnitude of this type of interference is larger at low NO\textsubscript{x} levels since the relative magnitude of the interferants to NO\textsubscript{x} can be quite high [Singh et al., 1985]. An apparently high value of NO\textsubscript{2} results in a calculated PSS value that is higher than 1. Using equation 23, a calculated value of RO\textsubscript{2} would be higher than actually present and would indicate, erroneously, that the ozone formation rate was higher that actually present. Note that the PSS is predicted to increase as NO\textsubscript{x} decreases, so that photochemical theory could be erroneously be "confirmed" by the presence of NO\textsubscript{2} artifacts.

Measurements made in urban environments are also susceptible to misleading effects of transport and mixing of local sources resulting in heterogeneity of sampled air parcels. Even if local equilibrium in a given air parcel is achieved, time averaging or, equivalently, spatial averaging results in calculating the PSS with average values of NO, NO\textsubscript{2} and O\textsubscript{3} contained in possibly several different air masses. This is not necessarily equivalent to the average value of the PSS of the air parcels encountered, which should be close to 1 if the PSS is obeyed locally in each parcel.

Theoretical studies of these effects have been undertaken with some experimental measurements confirming the results [Chock and Kumar, 1979; Janssen, 1986; Seinfeld, 1977; Bilger, 1978; Feigley, 1978]. These studies conclude that the mixing of fresh NO emissions into a background of O\textsubscript{3}-rich air results in a measured PSS value less than 1. Conversely, mixing of clean air (low NO and O\textsubscript{3}) with polluted air (high NO and O\textsubscript{3}) results in PSS values greater than 1. The extent of deviation is a function of the extent of mixing, heterogeneity and turbulence of the system.
When sources are nearby, the measured value of $p$ can deviate from unity as the chemistry of the system reestablishes equilibrium. The relaxation time of the equilibrium:

$$\text{NO}_2 \iff \text{NO} + \text{O}_3$$

can be determined to be:

$$\tau = \{(\text{[NO]}_e + \text{[O}_3)_e)k_6 + J_{\text{NO}_2}\}^{-1}$$

assuming that the perturbation is small. $\text{[NO]}_e$ and $\text{[O}_3)_e$ are the equilibrium concentrations. When $(\text{[NO]}_e + \text{[O}_3)_e)$ is $\sim 80$ ppb and $J_{\text{NO}_2}$ is about $0.5 \text{ min}^{-1}$ the relaxation time is about $22$ s for the perturbation to be reduced to $1/e$ of its original value. Thus if the transit time from the source of NO, NO$_2$ or O$_3$ is less than several times the relaxation time of the equilibrium, a deviation from $p$ will be measured.

PREVIOUS PSS MEASUREMENTS

Several workers have made ambient measurements of the PSS in both the urban and remote environments. Figure 32 shows measurements made in environments remote from urban areas. Figure 33 shows previous measurements of the PSS made in urban environments. Most of these measurements are expressed in terms of equation 21 or 22. In Figure 32a, the deviations are attributed to an oxidant $[OX]$, whose value is calculated as equivalent ozone via,
The diurnal variation of $k_2$ and the resulting values of the photostationary state number $n = k_1[NO_2]/k_2[O_3][NO]$. 

**Figure 32.** Previous urban air determinations of PSS.
Figure 33. Previous clean air determinations of PSS.
\[ [OX] = J_{NO_2}[NO_2]/k_6[NO] - [O_3] \]

This is similar in form to equation 23 except that the rate constant for the oxidation of NO by OX is assumed to be \( k_6 \) and OX is left as an unidentified oxidant.

Urban measurements clearly show the effect of inhomogeneity of sampled air parcels. Except for Figure 33a, the urban measurements are characterized by deviations that do not appear to be diurnally related. The fluctuations in the calculated PSS result in values less than and greater than one as predicted by the discussion above.

Measurements made under clean air conditions display a strong diurnal variation (Figure 32). Figure 32b shows data acquired with an instrument later demonstrated to have significant interferences [Ridley et al., 1988a] in the remote environment. This data is included to demonstrate the effect of known interferences on the PSS measurements. Figure 32a shows data acquired with an instrument that does not suffer from the same interferences encountered in Figure 32b. Deviations here are predominantly positive. Assuming the deviation is due to oxidation of NO by compounds other than \( \text{O}_3 \), the level of oxidant [OX] can be calculated. The authors calculate a value for [OX] that is higher than predicted for the conditions of their site. Clearly, the simultaneous determinations of oxidants, \( \text{HO}_2 \) and \( \text{RO}_2 \), and the PSS parameters, \( \text{NO}_x \), \( \text{NO}_2 \), \( \text{O}_3 \) and \( J_{\text{NO}_2} \) would be beneficial in understanding the true nature of the deviations encountered.

PSS MEASUREMENTS WITH FAGE3

Ambient measurements of the PSS were made from the rooftop of Science
Building II (SBII) at Portland State University. For these measurements an insulated, air-conditioned instrument enclosure was constructed on the south side of the rooftop. The Cu-vapor laser beam was directed to the enclosure through a pipe connecting the roof and the Laser Lab located on the 4th floor of SBII (Figure 34). One other pipe was used to feed gas supply lines, sample lines and power lines. Once in the enclosure, the two wavelength components of the laser beam were separated with a dichroic mirror. The 511nm and 578nm beams were directed into the FAGE-NO$_2$ and FAGE-HO$_x$ instruments, respectively.

The nitric oxide instrument was located in the Laser Lab to minimize the possibility of vacuum pump fumes affecting the measurements. Ozone was monitored by its absorption at 254nm with a Dasibi ozone analyzer. Environmental parameters such as wind speed, direction, temperature and pressure were monitored with a weather station (Heathkit, Model 4001). Relative ultra-violet light intensity was measured with a homemade device (UVMRD) consisting of a photodiode (MRD500) with a 300-400nm bandpass filter. All instruments were interfaced to and controlled by a microcomputer (Appendix C).

All measurements except NO were averaged for ~1 minute intervals and recorded. The design of the NO instrument introduced a ~40s dead time when switching between zero and measure modes. Consequently only one net measurement was calculated and recorded every 40s (instead of an average for that time) in order to decrease collection cycle time. NO$_2$ concentrations were calculated based on the calibration factor described in Chapter IV. Calibration for the nitric oxide instrument was determined by diluting a
Figure 34. Location of PSU monitoring site.
measured volume of pure NO with pure air into a large reaction vessel of known volume. The ozone instrument was not calibrated (due to instrument failure at the end of these experiments) but did not indicate any positive offset in the presence of zero air. Absolute calibration errors would result in an offset of the PSS from its true value but could not contribute time dependence to the calculated PSS (such as the diurnal variation predicted by the simulations described above). The effect of light intensity measurements on the PSS is discussed below.

In addition to calibration, all three concentrations were corrected for reaction during transit in the sample lines. Since $k_6$ is 26.8ppm$^{-1}$min$^{-1}$ (at 298K, 760 torr), the 1/e lifetime of NO in the sample line is ~40 seconds with 50ppb of O$_3$. The delays in the NO,NO$_2$ and O$_3$ sample lines were determined to be 4 sec, 4 sec and .6 sec, respectively. This loss is most significant when either NO or O$_3$ is low in concentration. The maximum correction term was ~10% when O$_3$ was about 50 times higher than NO. The rate constant for R6 was calculated using the recorded ambient temperature ($k_6=2.0\times10^{12}\text{EXP}(-1400/T)\text{cm}^3\text{sec}^{-1}$, DeMore et al., 1989).

Since actinometric measurements of $J_{NO2}$ were not made, the photolysis rate was estimated based on the UV measurements made by the UVMRD and the results of an irradiance model [Madronich, 1990]. Irradiance models are best suited for calculating photolysis rates with clear sky conditions. In the presence of cloud cover or aerosols it is difficult to quantify the attenuation and albedo characteristics. On the other hand, flat plate detectors, such as the UVMRD, respond correctly to overhead isotropic radiation produced by scattering due to aerosols but produce a non-linear response curve with
An error in the measurement of $J'_{\text{W2}}$ that has a time dependence (such as an incorrect response with respect to zenith angle) will result in an apparent deviation from the PSS that has a time dependent characteristic - unlike systematic errors in calibration. In order to correct for these effects, irradiance model calculations and UVMRD data were fit with an empirical equation with data from a day with clear sky conditions, July 13, 1990. With minimal ambiguity due to aerosol scatter, an empirical fit between the irradiance model and UVMRD should correct for the response of the direct solar beam on the UVMRD. When the best fit equation is applied to days where haze and cloud cover were present, the results seem reasonable between the hours of 10am and 4pm. However, the corrected intensities in the early morning and late afternoon hours seem anomalously high. On the other hand, UVMRD data does appear to have some additional features during these hours not apparent in the clear sky case of July 13th. It is difficult to ascertain whether or not the calculated intensities of the early morning and early afternoon hours (10H>Time>16H) are real effects of aerosol scatter or due to the inadequacy of the fitting equation in this region.

Complete data sets for three days, July 13, Sept 5 and Sept 21, 1990 (hereinafter referred to as J13, S5 and S21) are shown in Figures 35, 37 and 39. (Figures 36, 38 and 40 respresent these data sets with a 5 minute running average). The key to Figures 35, 37 and 39 is given in Table VI. The data in these figures, with one exception, are shown without any signal averaging in order to show the magnitude and frequency of fluctuations. Wind direction data are presented with a 5 minute running average in order
TABLE VI

KEY TO FIGURES 35, 37 AND 39

Figure 35: July 13, 1990 - clear and sunny all day
Figure 37: Sept 5, 1990 - morning haze, clearing in afternoon
Figure 39: Sept 21, 1990 - early morning haze

Graph A PSS
solid line - UVMRD empirical fit (normalized)
dashed line - irradiance model (normalized)
dotted line - PSS calculated with UVMRD fit

Graph B CONCENTRATION
solid line - NO, ppb
dashed line - NO₂, ppb
dotted line - O₃, ppb
open diamonds - UVMRD, normalized

Graph C ENVIRONMENTAL
solid line - Temperature ÷ 10, °C
dotted line - Wind Speed, miles/hr

Graph D ENVIRONMENTAL
solid line - North, South wind component
dotted line - East, West wind component
Figure 35. Complete data set for July 13, 1990.
Figure 36. Averaged data for July 13, 1990.
Figure 37. Complete data set for Sept 5, 1990.
Figure 38. Averaged data for Sept 5, 1990.
Figure 39. Complete data set for Sept 21, 1990.
Figure 40. Averaged data for Sept 21, 1990.
to emphasize trends in wind direction.

Nitric oxide sources in an urban environment derive primarily from high
temperature combustion products, such those emanating from auto exhaust. Consequently,
the NO measured at an urban site is a strong function of its proximity to traffic areas and
the direction of the wind transporting air parcels to the monitoring instrument.

The rooftop monitoring site at PSU is closely bounded to the west by a major
freeway (Figure 34). Air parcels coming from this direction are likely to contain fresh
exhaust emissions containing NO, NO₂ and hydrocarbons. This effect is vividly seen in
Figure 39 at -19H. At this time the wind direction shifts sharply from its generally
easterly trend to a westerly direction carrying along with it fresh emissions from the
freeway. Over one order of magnitude change in NO concentration is evident. The effect
of westerly transport to the monitoring site is evident in the other data sets as well. On
the other hand, the NO concentration appears to be largely independent of the north-south
component of the wind direction, reflecting similar source components in these directions.

Comparing graphs B and C in Figures 35, 37 and 39 the variation in NO
concentration appears related to fluctuation in wind speed, with large velocity fluctuations
resulting in a "noisier" NO signal. This behavior is predicted by the formulation of the
distribution of a pulse of emission after entering a flow, where velocity fluctuations have
a Gaussian probability distribution [Seinfeld, 1986]. The average standard deviations for
wind velocity in 9 minute periods are plotted versus the average relative standard
deviation in NO, NO₂ and O₃ in Figure 41. The lowest fluctuation in NO occurs with the
Figure 41. Fluctuations in ambient concentrations vs. fluctuations in wind velocity.
lowest wind fluctuation (S5). Instrument noise for NO is estimated at 2 ppb. The average fluctuations for NO₂ and O₃ appear less coupled to wind fluctuations consistent with source dominance by NO. NO₂ represents about 5% of the NOₓ produced in car exhaust [Seinfeld, 1986]. If this was the primary source of the observed NO₂, NO/NO₂ would be on the order of 20. However, the observed levels of NO₂ and NO in the data sets are similar. This indicates that the observed levels of NO₂ are the result of its production by the oxidation of NO present or the transport of NO₂ from other regions. Thus, car exhaust cannot be a significant direct source of NO₂ and therefore is not expected to exhibit the higher fluctuations seen in source driven NO levels.

Graphs A in Figure 35,37 and 39 show the calculated PSS using the ambient NO,NO₂ and O₃ values along with the UVMRD corrected light intensity. Since absolute values of J_{NO2} were not measured, the photolysis rates were scaled to give an approximately average PSS value of 1. The values used were consistent within 10% of the clear sky irradiance model calculations for this latitude (46°N) and time of year for each data set.

Figures 36,38 and 40 show averaged data of Graph A and B of Figures 25,37 and 39. Smoothing with a 5 minute running average reduces the higher frequency fluctuations so that the relationship between the PSS and the chemical quantities measured can be more easily seen. PSS is shown calculated with both the UVMRD fit and the irradiance model. Overall these data sets clearly show that despite daily changes in concentration of NO, NO₂ and O₃ of factors of 4-10 each, the PSS remains relatively constant to within ~50%. This is in itself strong confirmation of the primary importance of the NOₓ-O₃
photostationary state in controlling the relative concentrations of these species at these concentrations. In addition, these experiments also serve to demonstrate that the monitoring instruments, including NO$_2$-FAGE, are not subject to serious interferences or artifacts at these concentration levels.

However, large positive spikes and some negative spikes in the PSS are noted in all three data sets. Large positive spikes correlate with low NO values unaccompanied by concomitant changes in either NO$_2$ or O$_3$. These low NO values may be indicative of the transport of "cleaner" air into the vicinity. Deviations of this nature have been discussed as being possibly caused by sampling of clean air parcels with urban air. Conversely, negative spikes can be understood as due to sampling and averaging of air parcels containing fresh NO emissions with those of background air. These spikes are indicative of cases where the sampled averaged value of NO is higher than the average value of the PSS in the air samples encountered. In Figures 36, 38 and 40 note that negative spikes usually correspond to peaks in NO.

The wind speed characteristics, concentration fluctuations and constancy of the PSS for the S5 data indicate a greater homogeneity of the downtown Portland air mass for that date. These factors facilitate a computer simulation of the results with fewer ambiguities caused by rapid changes in concentration due to transport or emission. In order to simulate the results of S5 the measured NO concentration at 1 minute intervals were input into a numerical integration routine using the ERTC atmospheric reaction set. Between each 1 minute data point the NO concentration was interpolated to its next experimentally measured value. The values of [O$_3$] and [NO$_2$] were determined as the
result of the computer integration of the reaction set. Since the hydrocarbon concentration
was not measured, a sequence of initial hydrocarbon concentrations was tried. The
Department of Environmental Quality (DEQ) measured the HC concentration at a site
about 2 miles from the PSU monitoring site during the years 1982-1988 [DEQ, 1988].
These measurements suggest a value of ~200ppbC of HC. The results of these
simulations are shown in Figure 42 along with the results of the actual measurements.

The simulation utilizing 100ppb HC demonstrates an exceptionally good
correlation to the measured data of NO$_2$ and O$_3$. As an algebraic relationship, equation
22 does not require that NO$_2$ and O$_3$ be held at any particular values given the [NO], k$_6$
and J$_{NO2}$. Only the ratio of NO$_2$ to O$_3$ is constrained by equation 22 when the PSS is
valid. The simulations shown in Figure 42 demonstrate that the quantities measured are
not only consistent with the PSS being approximately valid but that the concentrations
measured are also consistent with the entire reaction mechanism of over 150 reactions
simulated.

The measurement of the PSS in the above downtown urban environment in which
its value is expected to be close to one can be thought of as a test of the instruments
making the measurements. Overall, the ambient measurements made of the PSS in
Portland confirm model predictions that the NO$_x$-O$_3$ photostationary state is obeyed at the
observed levels of NO$_x$ (<150ppb). This relationship is generally obeyed despite several-
fold changes in concentration of NO, NO$_2$ and O$_3$ during the course of a day. Thus these
first ambient studies utilizing the FAGE-NO$_3$ instrument indicate that this instrument is
capable of making meaningful ambient measurements at these concentration levels.
Figure 42. Computer simulation of Sept 5, 1990 measurements.
REFERENCES


Madronich, S., personal communication, 1990.


Sandholm, S.T, J.D. Bradshaw, K.S. Dorris, M.O. Rodgers and D.D. Davis, An airborne compatible photofragmentation two-photon laser-induced fluorescence instrument for measuring background tropospheric levels of NO, NO$_x$ and NO$_2$, J. Geophys. Res., 95, 10155-10161, 1990.


Details of SNR Calculation

Equation 1 is the expression for signal-to-noise ratio (SNR) based on Poisson photon counting statistics for an integrated signal with exponential decays for the signal and background with magnitudes $S_o, B_o$ and decay rates of $k_s$ and $k_b$, respectively. A constant background signal $d0$ is also included. To optimize SNR with respect to delay time ($t_g$) and gate width ($t_d$) the partial derivative of equation 1 was symbolically computed (SolverQ, University of Wisconsin) with respect to $t_g$ and $t_d$, equations 2 and 3, respectively.

$$
\text{SNR} = \frac{S_o/k_s (\text{EXP}(-k_s t_d) - \text{EXP}(-k_s (t_d + t_g)))}{(S_o/k_s (\text{EXP}(-k_s t_d) - \text{EXP}(-k_s (t_d + t_g))) + 2(t_g d0 + B_o/k_b (\text{EXP}(-t_g k_b) - \text{EXP}(-k_b (t_d + t_g))))^{0.5}} \quad (1)
$$

$$
\frac{d(\text{SNR})/d(t_g)}{d(\text{SNR})/d(t_d)} =
S_o/ (S_o/k_s \text{EXP}(-k_s t_d) - S_o/k_s \text{EXP}(-(k_s t_d + k_s t_g)) + 2B_o/k_b \text{EXP}(-t_g k_b) - 2B_o/k_b \text{EXP}(-(t_g k_b + k_s t_g) + 2d0 t_g)^{0.5}(\text{EXP}(-(k_s t_d + k_s t_g)) - S_o/k_s d0 \text{EXP}(-(k_s t_d)) + S_o/k_s d0 \text{EXP}(-(k_s t_d + k_s t_g))) - S_o/k_s B_o \text{EXP}(-(k_s t_d) \text{EXP}(-(t_d k_b + k_b t_g)) + S_o/k_s B_o \text{EXP}(-(k_s t_d + k_s t_g)) \text{EXP}(-(t_d k_b + k_b t_g)))) - 0.5S_o^{2/k_s} \text{EXP}(-(k_s t_d) \text{EXP}(-(k_s t_d + k_s t_g)) + 0.5S_o^{2/k_s} \text{EXP}(-(k_s t_d + k_s t_g))^2} \quad (2)
$$
\[
d(SNR)/d(t_d) = \frac{S_0/k_s}{(S_0/k_s(\exp(-k_s t_d) - \exp(-k_s(t_d + t_g)))+2(d_0 t_s + B_0 k_b (\exp(-t_d k_b) - \exp(-k_b(t_d + t_g)))))^0.5(-k_s \exp(-k_s t_d) + k_s \exp(-k_s(t_d + t_g))) - 0.5S_0/k_s (S_0/k_s(-k_s \exp(-k_s t_d) + k_s \exp(-k_s(t_d + t_g))) + 2B_0/k_b(-k_s \exp(-k_s t_d) + k_s \exp(-k_s(t_d + t_g))))(\exp(-k_s t_d) - \exp(-k_s(t_d + t_g)))};
\]

(3)

Solving simultaneously, with equations 2 and 3, the optimal values for \( t_d \) and \( t_g \) can be computed (SEQS, Provo, Utah) given values for \( k_s, k_b, S_0, B_0 \) and \( D \).
APPENDIX B

ELECTRONIC CIRCUIT
Summary of data flow of the QVT-Computer interface (circuit diagram on following page):

After each laser pulse fires, the QVT integrates signal from the photomultiplier tube (see Figure 11). Digital output of charge acquired appears at rear interface of QVT-pins A-L. When data is ready at the interface, SEL (pin S, QVT rear interface) goes low for 300ns. This signal is captured by the 74ALS244 buffer/line driver. The line driver then signals the two 74ALS374, D-Type Flip-flops to store the data. The SEL signal is also sent to the parallel port to initiate a parallel strobe of data in the computer from the flip-flop. This simple interface acquires data after each laser pulse and therefore must be used in conjunction with software interfaces that collect data at the necessary repetition rate. The circuit was tested extensively before and during actual field use.
APPENDIX C

COMPUTER PROGRAMS
APPENDIX C

2qvt.c - program to control data acquisition from LeCroy QVT:
only main program, qvt and stepper motor subroutines are printed

#include <stdio.h>
#include <conio.h>
#include <bios.h>
#include <time.h>
#include <graph.h>
#include <string.h>
#include <math.h>

void qvt( double ,unsigned long *,unsigned long *);
int fnckey(void);
void delay(unsigned);
void delaysec(unsigned);
void chemlum(float,float *,float *,float *);
float oz(void);
void initialize(void);
double pwrinO;
int initgraf(void);
void viewq (int,int,int,int);
int initgrafO;
void testkeyO;
void initmotoO;
void motomove(int,int,int);
void motobrake(int);
float rtime( void);
void clearqvtO;
void findpdt(double);

double shots,cycie;
float fs,coul,pdt,xtra=0;
FILE *fp1,*fp2;
time_t initime;
unsigned valvedelay;
double xw1,xw2,yw1,yw2,xwa,ywa;
unsigned vx1, vx2, vy1, vy2, xw, yw;
float px, py;

struct videoconfig screen;
double wx1, wy1;

main()
{
    unsigned long chargesum, q1, q2;
    double qvt1, qvt2, pwr = 0, a[3] = {0, 0, 0};
    int i, j, k, l;
    int dbas = 768;
    float no, no2, o3, realtime, pdtime;
    time_t nowtime;
    char buffer[100];
    int v[2] = {32, 0};

    initialize();
    initgraf();
    initmoto();
    motobrake(1);
    viewq(20, 90, 20, 90);
    _setcolor(5);
    windowq(xw1, xw2, yw1, yw2, xwa, ywa);
    realtime = realtime();
    delaysec(1);
    findpdt(shots);
    pdtime = realtime;
    for (i = 1; i < cycle; i++)
    {
        testkey();
        for (j = 1; j < 3; j++)
        {
            outp(dbas + 2, v[j - 1]);
            delaysec(valvedelay);
            qvt(shots, &q1, &q2);
            chargesum = q1;
            a[j - 1] = (chargesum - pdt * shots) / coul;
            chemlum(fs, &no, &no2, &o3);
            sprintf(buffer, "%4.1f
 %4.1f", pdt, (float)(chargesum / shots - pdt));
            _settextposition(24, 30);
            _outtext(buffer);
            sprintf(buffer, "%d", i);
            _settextposition(1, 2);
            _outtext(buffer);
_settextposition(1,30+j*13);
sprintf(buffer,"%1.4le",a[j-1]);
_outtext(buffer);
pwr=pwrin()*1000;
sprintf(buffer,"%4.1f",pwr);
_settextposition(1,7);
_outtext(buffer);
}
time(&nowtime);nowtime-=initime;
_setcolor(3);
sprintf(buffer, "%3.3f", realtime);
_settextposition(24,15);
_outtext(buffer);
a[2]=0;
if (a[0]+a[1]>0)
    a[2]=(a[0]-a[1])/sqrt(a[0]+a[1]); /* SNR */
sprintf(buffer,"%4.1le %2.11e",a[2],a[0]-a[1]);
_settextposition(24,55);
_outtext(buffer);
realtime=ftime();
if (realtime>(pdtime+.1))
{
    findpdt(shots);
    pdtime=realtime;
}
plotpointq(realtime,a[0]-a[1]);
fprintf(fp2,"%f %le %le 
",realtime,a[1],a[0]-a[1]);
fprintf(fp2,"%f %4.11f %f
",pdt,pwr,xtra);
fcloseall();
fp2=fopen("c:out.dat","at");
while(!kbhit());
getche();
endgraf();
}

void clearqvt()
{
    outp(0x312,6);delay(10000);
    outp(0x312,5);delay(10000);
}

void findpdt(double hits)
{
unsigned long q1, q2;
clearqvt();
motomove(1, 25, 0);
delaysec(2);
qvt(hits, &q1, &q2);
pdt=(float)(q1/hits);
motomove(1, 25, 1);

void qvt(double cyc, unsigned long *q1, unsigned long *q2)
{
    unsigned sum2, q1l=0, q1h=0, q2l=0, q2h=0;
    unsigned int cyc1, cyc2;
    double test, sxtn=65536.0;

    outp(0x313, 0x91); delay(10000); /* control word */
    outp(0x311, 0xff); outp(0x311, 0xdb); delay(10000);
    outp(0x311, 0xff); outp(0x311, 0xed); delay(50000);
    outp(0x312, 0xff); outp(0x312, 0xf); test=cyc/sxtn;
    cyc1=0;
    cyc2=cyc-65536*(int)test; /* cyc2 counter for cyc<=65535 */
    while(test>=1) /* cyc counter for cyc>=65536 */
    {
        cyc1++;
        cyc-=sxtn;
        test=cyc/sxtn;
    }

    asm \\
    { 
        mov dx, 312h ; initialize variables
        mov cx, 310h
        mov ax, 0ffh ; clear resets
        out dx, ax ; ****
        L1: in al, dx ; test portc
        test al, 8 ; test for data present at pc2
        jnz L1
        mov ax, 0bfh
        out dx, ax ; select qvt 1
        in al, dx ; input higher byte data pc0 & pc1
        and al, 3 ;
        mov ah, al ;
mov dx, cx
in al, dx ; input lower byte data pa0-pa7
add q1l, ax
adc q1h, 0
mov dx, 312h
mov ax, 7fh
out dx, ax ; reset qvt 1
mov ax, 0efh
out dx, ax ; select qvt 2
in al, dx ; input higher byte data pc0 & pc1
and al, 3 ;
mov ah, al ;
mov dx, cx
in al, dx ; input lower byte data pa0-pa7
add q2l, ax
adc q2h, 0
mov dx, 312h
mov ax, 0dfh
out dx, ax ; reset qvt 2
dec cyc2
jnz L1
add cyc1, 0
jz L2
dec cyc1
mov cyc2, 65536
jmp L1

L2:
}
*q1=q1l+q1h*65536;*q2=q2l+q2h*65536;
}

void initmoto()
{
int mco=748, mpc=744, j;
outp(mco, 192); /* motor control word */
outp(mpc, 5); /* enable motor board */
}

void motomove(int motor, int sts, int dir)
{
int i, z, mpa=736, mpb=740, s1, s0, mcw;
motor=(int)pow(2, motor);
dir=dir*motor*16;
s0=dir; s1=dir+motor;
mcw=-(motor&15)&15;
outp(mp, mcw);
for(i=1;i<=sts;i++)
{
        outp(mpa,s1);
        for(z=1;z<=300;z++){;}
        outp(mpa,s0);
        for(z=1;z<=300;z++){;}
    }

void motobrake(int motor)
{
    int mpb=740,mcw;
    motor=(int)pow(2,motor);
    mcw=-(motor&15)&15+240;
    outp(mpb,mcw);
}
/* envir.c program to acquire environmental parameters, only routines related
to data acquisition are shown */

#define PI 3.14159265359
#include <stdio.h>
#include <conio.h>
#include <bios.h>
#include <time.h>
#include <graph.h>
#include <string.h>
#include <math.h>

int fnckey(void);
void delay(unsigned);
void delaysec(unsigned);
float oz(void);
void initialize(void);
int initgraf(void);
void viewq(int, int, int, int);
void windowq(double, double, double, double, double, double);
void movetoq(double, double);
void linetoq(double, double);
void plotpointq(double, double);
void endgraf();
void testkey();
void weasm(void);
void weathin(float *, float *, float *, float *);
void dash8(float *, int);
void d8io(int);
float rtime(void);

extern unsigned short parma; /* wind direction */
extern unsigned short parmb; /* wind speed */
extern unsigned short parmc; /* temperature */
extern unsigned short parmd; /* pressure */
floa t fs, cou l, pd t, xtra = 0;
FILE *fp1, *fp2;
t ime_t initime;
unsigned savetime;

unsigned vx1q, vx2q, vy1q, vy2q, xwq, yhq;
flo a t py q, px q;
 struct videoconfig screen;
double wx1q, wy1q;

main ()
{
    int i, j, k, l;
    int dbas = 0x300;
    int p1bas = 0x308;
    int p2bas = 0x310;
    float no, no2, o3, noberta, nozero = 0, nosig = 0;
    float mrd, dew, od;
    float sno, sno2, so3, snob = 0, lsod = 0, lsnob = 0, lso3 = 0, rtl;
    double cwdir, swdir, cwdirsum = 0, sdirsum = 0;
    time_t nowtime;
    char buffer[100];
    int v[2] = {32, 0}, sig = 1, iostat = 0;
    float wdir, wvel, ambtemp, ambpres;
    float swvel, sambtemp, sambpres;
    float smrd, sdew, sod, jno2;
    float now, nowhr, ptime = 0, switch_nx = 0, realtime;
    float d8[] = {0, 0, 0, 0, 0, 0, 0, 0};
    float cnt;

    initialize();
    initgraf();
    rtl = realtime();
    vewq(20, 90, 20, 90);
    _setcolor(5);
    windowq(0, 28, 0, 5, 3, 1);
    i = 0;
    swdir = 0; cwdir = 0; sambpres = 0; sambtemp = 0;
    while (1kbbhit())
    {
        smrd = 0; sdew = 0; sod = 0; so3 = 0;
        time(&nowtime); nowtime -= initime;
        nowhr = (float)(nowtime / 3600.0);
        while ((float) nowtime < ptime + savetime)
        {
            testkey();
            i++;
            time(&nowtime); nowtime -= initime;
            nowhr = (float)(nowtime / 3600.0);
            dash8(d8, iostat);
        o3 = oz();
    }
weathin(&wdir,&wvel,&ambtemp,&ambpres);
realtime=rtime0;
if((float)nowtime>swtch_nx+40)
{
    if(sig==1)
        {nosig=d8[2]*2;iostat=128;d8io(iostat);
         sig=0;swtch_nx=(float)nowtime;
        }
    else
        {nozero=d8[2]*2;iostat=0;d8io(iostat);
         sig=1;swtch_nx=(float)nowtime;
        }
}
_sprintf(buffer,"%4.5f %4.5f %4.5f %4.5f \n"
 ,wdir,wvel,ambtemp,ambpres);
_settextposition(1,2);
_outtext(buffer);
sprintf(buffer,"%4.5f %u\n",rtime0,i);
_settextposition(24,15);
_outtext(buffer);
sprintf(buffer,"%3.2f %3.3f %3.3f %3.3f \n",d8[3],d8[4] ,d8[5]);
_settextposition(1,40);
_outtext(buffer);
sprintf(buffer,"%3.2f %3.2f %3.2f\n",nosig,nozero,nosig-nozero);
_settextposition(2,40);
_outtext(buffer);
if (d8[0]<=0) { d8[0]=-10;}
sprintf(buffer,"%2.2f %2.3f %3.3f %3.3f \n",d8[0],d8[1],d8[1]/d8[0],d8[1]+d8[0]);
_settextposition(3,40);
_outtext(buffer);
noberta=nosig-nozero;
cwdir+=cos((double)(wdir/360.0*2*PI));
swdir+=sin((double)(wdir/360.0*2*PI));
sono+=noberta;
sno+=d8[1];sno2+=d8[0];so3=so3+s03;
smd+=d8[3];sdew+=d8[4];sod+=d8[5];
swvel+=wvel;sembpres+=ambpres;sambtemp+=ambtemp;
cnt=(float)i;
}
ptime=(float)nowtime;
swdir/=cnt;cwdir/=cnt;swvel/=cnt;sambtemp/=cnt;sembpres/=cnt;
sdew/=cnt;smrd/=cnt;sod/=cnt;
snob/=cnt;so3/=cnt;
sno/=cnt;sno2/=cnt;
/*file printing*/
fprintf(fp2,"%f %2.4f %2.4f %3.4f %3.2f %3.1f %3.f\n", rtime(),sdew,smrd,so3,swvel,swdir,cwdir,sambpres,sambtemp,snob);
fcloseall();
fp2=fopen("c:out.dat","at");
/*plot routine*/
plotpointq(realtime,smrd);
so3/=10;
movetoq(rtl,ls03);linetoq(realtime,so3);ls03=so3;
sambtemp/=10;
plotpointq(realtime,sambtemp);
snob/=2;
movetoq(rtl,lsnob);linetoq(realtime,snob);lsnob=snob;
rtl=realtime;
i=0;swdir=0;swvel=0;sambpres=0;sambtemp=0;snob=0;
}
endgraf0;
}
float oz(void)
{
    int pbas=0x310,03a,03b;
    float o3;
    outp(pbas+3,0x92);
    do
    {
        o3a=inp(pbas);o3b=inp(pbas+1);
    }while((o3b&31)>9);
    o3=(int)(o3a/16)*10+o3a%16+(int)(o3b/16)*1000+o3b%16*100;
    return o3;
}
void dash8(float *d8,int iostat)
{
    int dbas=0x300,ch,chandio;
    for (ch=0;ch<8;ch++)
    {
        iostat=iostat&255;
        chandio=iostat&ch;
        outp(dbas+2,chandio);
        outp(dbas+1,0);
    }
while(inp(dbas+2)>=128)
{
  d8[ch]=inp(dbas)/16.0+inp(dbas+1)*16.0;
  d8[ch]=d8[ch]*1D/4096.5;
}

void d8io(int state)
{
  int dbas=768;
  outp(dbas+2,state);
}

void weathin(float *wdir,float *wvel,float *ambtemp,float *ambpres)
{
  float direct[16]={0,22.5,67.5,45,157.5,125,90,112.5,337.5,
                     315,270,292.5,180,202.5,247.5,225};
  outp(0x30b,0xbe);
  weasm();
  *wdir=360-direct[parma];
  *wvel=parmb;
  *ambtemp=parmc;
  *ambpres=parmd/100.;
}

void delay(unsigned a)
{
  unsigned i;
  for(i=1;i<a;i++)
  {
  
  }
}

float rtime(void)
{
  char buffer[9];
  unsigned hr,min,sec;
  long l;
  float time;
  _strtime(buffer);
  sscanf(buffer,"%u:%u:%u",&hr,&min,&sec);
  time=(float)hr+(float)min/60+(float)sec/3600;
  return (time);
}

void delaysec(unsigned a)
{ 
    time_t time1, time2;
    unsigned diff;
    time(&time1);
    do 
    { 
        time(&time2);
        diff = time2 - time1;
    } while (diff < a);
}