CALIFORNIA STATE UNIVERSITY, NORTH RIDGE

DEVELOPMENT OF A LABORATORY EXPERIMENT
IN INVOLVING THE MEASUREMENT OF NITRIC
OXIDE EMISSIONS

A graduate project submitted in partial satisfaction
of the requirements for the degree of Master of
Science in

Engineering

by

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June, 1974
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ABBREVIATIONS AND SYMBOLS

A/F  Air/fuel mass ratio
ASTM  American Society for Testing and Materials
BTDC  Before top dead center
$c_v$  Specific heat at constant volume
CFR  Coordinating Fuel Research
CR  Compression ratio
P  Absolute pressure
ppm  parts per million
psig  pounds per square inch, gage
$Q_c$  Heat of combustion, units like BTU/ pound mass
SCFH  Standard cubic feet per hour
T  Absolute temperature
TDC  Top dead center
V  Volume
$\gamma$  Gamma, the ratio of specific heats
ABSTRACT

DEVELOPMENT OF A LABORATORY EXPERIMENT

INVOLVING THE MEASUREMENT OF NITRIC
OXIDE EMISSIONS

by

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Master of Science in Engineering

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A Beckman non-dispersive infrared nitric oxide analyzer and a Teledyne oxygen analyzer are incorporated into a movable sampling system which includes a water vapor removal system. Instrument operating characteristics are reported. A laboratory experiment involving the measurement of nitric oxide emissions from a CFR single cylinder spark ignited internal combustion engine is presented. A description of the nitric oxide formation process and the effects of various engine operating parameters on nitric oxide emissions is included.
I Introduction

This report describes the development of a laboratory experiment involving the measurement of nitric oxide emissions from an internal combustion engine using instruments recently acquired by the University. The instruments, a Beckman non-dispersive infrared nitric oxide analyzer and a Teledyne oxygen analyzer, were installed into a sampling system. The characteristics of the instruments, sampling system and the CFR engine are described and a laboratory procedure for obtaining data is presented. The nitric oxide formation process and the effects of engine parameters on nitric oxide concentration are also discussed.

II Instrument Characteristics

A. General System Description

A flow diagram of the sampling and measurement system is shown in Figure 1. The sample or calibration (span) gases are patched into the system through one of two quick disconnects. The sample gases pass through two glass condensers to remove water vapor, and through a U-shaped tube filled with Drierite to further remove any moisture. Water vapor in the sample gas will interfere with the operation of the instruments. The sample is then pumped into the
**FIGURE 1**

**SCHEMATIC OF SAMPLING SYSTEM**
oxygen and nitric oxide (NO) analyzers, (these will be referred to respectively as the "O2 analyzer" and the "Beckman" throughout this report) and vented to the atmosphere. Adequate ventilation should be provided.

A vent valve downstream of the Beckman allows trapping CO2 gas in the system, which is required to preserve the fuel cell used in the O2 analyzer. A pressure gauge is provided to assure excessive pressure is not trapped in the system. (The fuel cell container in the O2 analyzer assembles with a friction O-ring fit; high pressure can cause it to separate with possible damage to the instrument). The pressure should not exceed 15 psig.

Zero and span gasses are required to calibrate the Beckman. These gases are patched into the system using a teflon lined flexible steel hose. The gases bypass the Drierite and condensing systems and enter directly into the O2 analyzer. (1) A flowmeter and

(1) The coarseness of the pressure regulator adjustments can result in a pressure buildup in the condensing system causing the rubber stoppers to pop off. Equivalent NO readings with and without the vapor removal system indicate no water vapor is present in the calibration gases now being used.
needle valve located in the O₂ analyzer provide flow control for both sample and calibration gases. The O₂ analyzer requires only air for calibration.

Due to the corrosive nature of NO, stainless steel, glass and teflon were used whenever possible in assembling the sampling system. The major exception is the rubber stoppers in the condensing towers, however the rubber area exposed to the gas is small. The instruments, including the calibration gases, are mounted in a movable cart. The only external requirement is 115 ac electrical power.

B. Beckman Nitric Oxide Analyzer
1. Operating Principles
The instrument, a non-dispersive infrared NO analyzer, consists of an electronic package containing the output meter, and an analyzer section through which the sample gas is passed. Figure 2 presents a functional diagram of the analyzer section. A continuous stream of the gas to be analyzed passes through the sample cell. A reference cell contains a gas which has minimal infrared energy absorption in the wavelengths characteristic of NO (5 to 5.5 microns). The detector is filled with NO at subatmospheric
Figure 2 - Diagram of Beckman Non-Dispersive Infrared Nitric Oxide Analyzer
pressure and is divided by a diaphragm. A beam of infrared light is passed through the reference and sample cells. The following steps describe the transformation of the infrared beam energy into an electrical signal.

a) In the sample cell part of the energy of the infrared beam is absorbed by the nitric oxide in the sample gas. In the reference cell, absorption is negligible, and the infrared beam loses no energy.

b) The beams pass through windows into the compartmented detector, however the gas in the reference cell side is heated more because the energy in the reference beam is greater.

c) The higher temperature on the reference side of the detector causes a higher pressure than on sample side.

d) The higher pressure deflects the diaphragm which divides the detector.

e) The diaphragm and the adjacent stationary metal button constitute a two plate variable capacitor. Deflection of the diaphragm away from the button decreases the capacitance.

The chopper alternately blocks and passes the infrared beams, resulting in a pulsating deflector. This
oscillating capacitance is processed into an electrical signal and resulting deflection of the output meter. A non-linear calibration curve relates the meter deflection to NO concentration.

2. **Instrument Calibration**

The instrument requires one hour to warm up before any calibration should be attempted. The calibration will be valid for only a short time if accomplished before full warm-up.

The initial start-up of the instrument required tuning the oscillator. This may again be required if the reading in the tune mode after full warm-up varies more than a few percent full scale of the previous readings. Frequent recording of the tune mode reading on a card attached to the instrument cart provides the required history. The oscillator adjustment is internally located in the analyzer section, and the instructions for the adjustment are found in the operating manual, reference 1. In two months of frequent usage, only one adjustment to the oscillator was required.

An initial adjustment of the bias setting was also
required. With the gain control set at zero and the zero adjust knob at midrange (500 on the dial), the meter should read zero. The bias adjustment, a trimming potentiometer internal to the electronic section of the instrument, is adjusted to give a zero reading. No adjustment has been required since the initial setting.

The instrument must be calibrated after each warm-up and sometimes during use. Nitrogen gas is used to set the instrument zero. Range 1 (0-2000 ppm) is set using the 1864 ppm NO span gas supplied from a bottle on the cart. With the gas passing through the instrument, the gain control is adjusted to give a meter reading of 95. This is determined from the calibration curves of NO concentration versus meter reading provided with the instrument. Copies are attached to each operating manual and to the cart.

Range 2 (0-500 ppm) is set with the 464 ppm span gas passing through the instrument. The meter is set at 93½ by adjusting the range 2 trimming potentiometer internal to the electronic section. Care must be used as this adjustment is located right next to the bias adjustment. If a change in the zero setting is required after initial calibration, the gain must
also be reset because the zero setting has an effect on the gain setting. The gain, however, has no effect on the zero. Particles may collect on the detector window resulting in an insufficient range of zero adjustment. A shutter located at the bottom of the sample cell can be adjusted to restore the necessary adjustment range. The operating manual provides detailed instructions.

Operating experience has shown that the instrument needs to be calibrated every time it is warmed up. Drift of two to three percent full scale has been encountered during continuous operation, therefore calibration every one to two hours is recommended.

Our configuration of the instrument is designed for measuring a maximum of 2000 ppm NO. To use the instrument to measure higher concentrations such as those in automobile exhausts, an additional calibration curve is required. Concentrations in the CFR engine can exceed 3000 ppm. Unfortunately the relation of the meter deflection to concentration is not linear and cannot be extrapolated from the existing curves. Reference 2 presents a calibration curve for 0-2000 and 0-4000 ppm NO for a prototype Beckman non-disper-
sive infrared analyzer. Comparison of the 0-2000 ppm curve to the one in the operating manual shows the curves are the same shape and are within one percent full scale of each other. Based on this, the 0-4000 ppm calibration curve of reference 2 was used for all measurements of concentrations greater than 2000 ppm NO. This calibration curve is presented in Figure 8.

3. **Speed of Response**

The speed of response of the instrument system, including all the equipment from the flex hose to the analyzers, is defined as the time from zero to a designated percent of the full scale meter deflection. Table I shows the speed of response at different sample flow rates using the span gases.

<table>
<thead>
<tr>
<th>Flow rate (SCFH)</th>
<th>95% Response time, seconds</th>
<th>99% Response time, seconds</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>28</td>
<td>110</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>47</td>
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<tr>
<td>3</td>
<td>11</td>
<td>22</td>
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<td>4</td>
<td>9</td>
<td>16</td>
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<td>5</td>
<td>8</td>
<td>13</td>
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From the data a recommended flowrate of 3 SCFH was chosen. This flowrate provides adequate response
time while keeping any pressure buildup in the sample cell to a minimum.

The speed of response to a change in operating conditions (and thus NO concentration) of the CFR engine gives much different results. Times up to five minutes may be required to obtain a stable reading after a change in engine conditions such as air/fuel ratio (A/F) or spark advance. This occurs because the combustion gas temperature may vary with changing engine conditions until all of the engine temperatures and flows reach equilibrium.

4. Interferences
Interferences occur when a molecule absorbs infrared energy at similar wavelengths as NO. Reference 2 shows that for a development model of the Beckman NO analyzer, water, CO, and CO₂ are the primary interference gases. Using a method of removing these components and NO and NO₂ from an internal combustion engine exhaust, the reference shows that the combined effect of all other components in the exhaust was no more than 60 ppm equivalent NO. Reference 2 shows water vapor to have the most significant interference effect. Three percent water yielded a 262 ppm NO equivalent reading.
The zero and span gases were examined for water content by comparing meter deflections bypassed and passed through the Drierite and condensing towers. The meter deflections were identical, indicating no water is present in the calibration gases, and validating the method of bypassing the vapor removal system during instrument calibration.

Air, CO, and CO₂ were passed through the Beckman to determine their interference effects. Table II presents the results.

<table>
<thead>
<tr>
<th>Component</th>
<th>Instrument equivalent response -- ppm NO</th>
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<tr>
<td>99+% CO₂</td>
<td>30</td>
</tr>
<tr>
<td>99+% CO₂*</td>
<td>30</td>
</tr>
<tr>
<td>99+% CO₂*</td>
<td>20</td>
</tr>
<tr>
<td>Air (80°F room)</td>
<td>155</td>
</tr>
<tr>
<td>Air*</td>
<td>20</td>
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*through Drierite and condensing towers

Table II shows the interference effects to be small compared to total NO in a typical engine exhaust. Reference 2 indicates the relation of interference effect to concentration of CO and CO₂ is very non-linear and that the interference effect is relatively independent of concentration above about ten percent.
Thus the effects of CO and CO$_2$ could be significant under circumstances such as extremely low $A/F$ ratios in automobile exhaust or in flue gases from powerplants.

C. Oxygen Analyzer

1. Operating Principles

A Teledyne Analytical Instruments Model 326A oxygen analyzer is installed in series with the Beckman NO analyzer. The O$_2$ analyzer utilizes a fuel cell to measure the concentration of oxygen in the sample gas. The fuel cell consumes oxygen from the sample gas and generates a proportionate current which results in a meter deflection. The instrument responds only to oxygen and thus has no interfering components and requires no zero gas. The instrument is calibrated by passing air through the fuel cell and adjusting the gain to give a meter reading of 20.9, the percent by volume of oxygen in air.

2. Instrument Characteristics

The analyzer requires infrequent calibration, however if the instrument has not been in regular use, calibration is recommended. The fuel cell should be installed at least 15 minutes before calibration.
The instruction manual, reference 8, indicates the analyzer will respond to 90% of the actual oxygen concentration in 60 seconds. Experience with the instrument indicates three to five minutes are required for the reading to stabilize.

The analyzer output is not affected by sample gas components other than oxygen. It is installed downstream of the sample conditioning system to remove any water or particulates which could damage the fuel cell.

3. A-3 Fuel Cell

The A-3 fuel cell which is currently being used in the instrument requires special storage facilities. The A-3 cell is used in applications where the carbon dioxide concentration is above one percent. The cell must not be allowed to experience a carbon dioxide free environment, such as air, for more than four hours. If the instrument is going to be out of service only for short periods, the system should be filled with CO₂ gas from the bottle on the cart. This is done by passing the CO₂ through the system and then shutting the vent and flowmeter valves.

The pressure inside the fuel cell holder should not
exceed 15 psig, as the holder may blow apart. If the instrument is to be out of service for longer periods of time (greater than one day), the cell should be removed from its container. In doing this it is necessary to install the shorting clip on the cell, put the cell in its storage bottle, flush the cell thoroughly with CO₂ gas, and securely install the storage bottle lid. The CO₂ gas, being heavier than air, will stay in the bottle while the lid is installed.

4. Use of the Oxygen Analyzer

The analyzer is useful in determining the amount of excess oxygen in the flue gases. Emission concentrations are often standardized to a fixed percent of oxygen in the exhaust. In the analysis of internal combustion engine exhaust, the analyzer can be used to determine the approximate point at which stoichiometry is reached. As the A/F ratio is increased past the stoichiometric ratio, the amount of oxygen in the exhaust will increase. In practice the oxygen increase occurs at slightly richer than stoichiometric due to the incomplete combustion in the cylinder. Figure 3 shows the relation of oxygen to A/F ratio setting for the CFR engine.
Figure 3 - Effect of Air/Fuel Ratio on Oxygen in the Exhaust of the CFR Engine
III NO Formation in Internal Combustion Engines

Nitric oxide (NO) is a colorless, odorless gas formed by the following reaction.

$$N_2 + O_2 \rightleftharpoons 2NO$$  \hspace{1cm} (1)

The equilibrium constant for this reaction is (ref. 3)

$$k = 1.37 \times 10^{-5} \text{ at } 2500^\circ K \text{ (4040^\circ F)}$$

$$k = 2.85 \times 10^{-17} \text{ at } 298.16^\circ K \text{ (77^\circ F)}$$

indicating that considerable quantities of NO can be expected to form at high temperatures, but little NO will be formed at ambient temperatures. When rapid cooling occurs, such as in the expansion stroke of a piston engine, there is insufficient time for the reverse reaction to proceed to equilibrium, resulting in significant quantities of NO remaining in the exhaust.

The mechanism of equation (1) predicts concentrations much lower than those measured in internal combustion engines. The following reaction, attributed to Zeldovich (ref. 7), considers atomic oxygen to initiate the reaction.

$$O_2 \rightleftharpoons 2O$$

$$O + N_2 \rightleftharpoons NO + N$$  \hspace{1cm} (2)

$$N + O_2 \rightleftharpoons NO + O$$
In combustion processes oxygen atoms are formed as chain carrying species. This reaction gives a better correlation to the actual measured data.

NO formation is favored by a combination of high temperature and excess oxygen. Thus conditions which increase temperature in the presence of oxygen result in increased NO concentrations. Increased compression ratio and increased spark advance are examples of this. Increasing the residence time at these conditions also increases NO formation.

In the presence of oxygen, NO will convert to nitrogen dioxide as follows.

\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \]  \hspace{1cm} (3)

The reaction rate varies as the square of the NO concentration. The rate constants permit significant formation of NO\(_2\) only at concentrations of NO greater than 100 ppm (ref.4). Experiments have shown that the concentration of NO\(_2\) in internal combustion engines is usually less than .5 percent of the total oxides of nitrogen (NO + NO\(_2\)). As the exhaust exits into the atmosphere, about 10 percent of the NO will convert to NO\(_2\) before the concentration is
significantly diluted. At concentrations less than one ppm, little NO reacts to NO₂. In the atmosphere NO, NO₂, and hydrocarbons react in the presence of sunlight to form photochemical smog.

IV CFR Engine
A. General Description
The CFR engine (CFR stands for Coordinating Fuel Research) was designed for determining the octane ratings of motor fuels. It is a single cylinder, variable compression, four stroke engine. A synchronous motor is used to start the engine and then is used to absorb its load and control its speed to 900 rpm. The spark advance is adjustable and is indicated on a strobe at the base of the engine. Three fuel bowls have adjustable height for varying the air/fuel ratio. The air inlet temperature and the air/fuel mixture temperature are controlled by heaters and are adjustable. The coolant temperature is automatically controlled at 210 F. A knockmeter is provided to determine the extent of engine knock.

The compression ratio of the engine is adjustable from 4 to 10:1 by raising and lowering the cylinder
head. The compression ratio was initially calibrated by using an automotive type compression gauge following the instructions of the ASTM operating manual, reference 5. The large, accurate gauge provided with the engine did not have a check valve in the sensing line, therefore was not usable due to the rapid pressure oscillations. The initial setting was checked using a plug gauge to assure adequate piston-valve clearance.

A micrometer was mounted to the engine to determine the head position at other than the calibration position. The head position is related to the compression ratio by a table in the ASTM manual, reference 5. The micrometer provided with the engine was missing. The replacement micrometer reads in the opposite direction as the original, i.e., a decrease in head height (increase in compression ratio) gives an increase in micrometer reading. The original micrometer indicated a decrease.

In order to relate the micrometer reading to the micrometer-compression ratio table in the manual, the micrometer reading in the table must be subtracted from one.
The exact air/fuel ratio of the engine cannot be determined from instrumentation currently available. Each fuel bowl, which is adjustable in height, has
a window with a scale to indicate the relative height. Varying the fuel bowl height changes the air/fuel ratio. Comparing the measured data from the CFR engine to data given in reference 6, it is seen that CFR fuel heights of .8 to 2.2 encompass an air/fuel ratio range of about 12:1 to 20:1. The oxygen data of Figure 3 indicate stoichiometry (≈14.5:1) occurs at a fuel bowl height of about 1.5. Thus the fuel bowl range covers all A/F ratios of interest. The data have all been plotted against the fuel bowl height.

One important maintenance is required when using the CFR engine: oil from a squirt can should be applied to both ends of the rocker arms and to the rocker arm shaft. This should be done every few hours of operation.

B. Effect of Operating Conditions on NO Emissions

1. Air/Fuel Ratio

The stoichiometric air/fuel ratio may be found by calculating the moles of oxygen required for the complete combustion of the fuel. This ratio is about 14.5:1 for automotive gasolines. In general an increase in the combustion temperature results
in an increase in the amount of NO formed. The maximum cycle temperature occurs at a slightly rich air/fuel ratio (ref.7), however in this case the maximum NO formation occurs at a lower cycle temperature corresponding to a slightly fuel lean ratio. The addition of extra oxygen causes an increase in the NO reaction that offsets the effect of the decreasing combustion temperature. At very rich mixture ratios little NO is produced due to the lack of oxygen and the lower combustion temperature associated with the incomplete combustion of the fuel. At very lean mixtures, the excess air dilutes the combustion gases causing lower combustion temperatures and low NO emissions.

All the measured data taken from the CFR engine have been plotted as NO concentration versus air/fuel ratio, since the air/fuel ratio has the predominant effect on NO emissions.

2. Compression Ratio

The compression ratio is defined as the volume of the cylinder at the beginning of the compression stroke (V_{BDC}) divided by the volume of the cylinder at the top of the compression stroke (V_{TDC}). Referring to Figure 4, a diagram of the idealized
Figure 4 - Idealized Otto Cycle

Figure 5 - Idealized Otto Cycle with Spark Advance
Otto cycle, the piston is at bottom dead center (BDC) at point 1. From point 1 to point 2 the air/fuel mixture is isentropically compressed. At point 2 a pressure increase at constant volume occurs as the mixture is ignited. Points 3 to 4 represent the expansion stroke of the piston, with the exhaust valve opening at point 4.

To evaluate the effect of compression ratio on the peak cycle temperature, and thus the NO concentration, we need only consider the isentropic compression of the mixture from points 1 to 2 because the combustion process occurs at constant volume and is therefore independent of compression ratio. The equation representing the isentropic compression is

\[ \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad (5) \]

where \( \frac{V_1}{V_2} = \frac{V_{BDC}}{V_{TDC}} = CR \)

and we have assumed constant specific heats and a perfect gas. The mixture consists mostly of air for which the ratio of specific heats \( \gamma \) is 1.4. Thus \( T_2 \) is proportional to the 1.4 power of the compression ratio.

\[ T_2 = T_1(CR)^{1.4} \quad (6) \]
The maximum cycle temperature occurs at point 3 and is given by

\[ T_3 = \frac{Q_c}{c_V(1+A/F)} + T_2 \]  

(7)

Thus we see \( T_3 \) is increased only by the effect of compression ratio. This increase in peak combustion temperature results in increased NO formation.

Figure 6 shows the NO concentration plotted against air/fuel ratio for various compression ratios. As compression ratio is increased, the amount of nitric oxide formed increases, but at a smaller rate proportional to the combustion temperature \( T_3 \). The effect of the compression ratio on NO formation is less at fuel rich mixture ratios.

3. Ignition Timing

In order to have a smooth pressure buildup, spark ignition should occur before the piston reaches TDC. Figure 5 shows an idealized Otto cycle which includes partial combustion (a to b) representing the spark advance. It is shown in Appendix I that the peak temperature \( T_3' \) is increased due to the spark advance. This results in increased NO formation, as the data in Figure 7 indicate. The effect of spark timing is most pronounced at lean mixture ratios.
Speed = 900
Spark = TDC

CR
• 6.00
• 7.88
• 8.76

Figure 6 - Effect of Compression Ratio on Nitric Oxide Concentration
Figure 7 - Effect of Spark Advance on Nitric Oxide Concentration
4. Other Parameters

Increased engine speed increases the flame speed due to increased turbulence and reduces the heat losses per cycle, which tends to increase the combustion temperature. If the spark timing is held constant, the increased speed results in more of the combustion occurring during the expansion stroke. This is especially pronounced at lean mixture ratios where the flame speed is the slowest. For rich mixture ratios the effect of the reduced heat transfer at higher speeds predominates. Therefore at rich mixture ratios an increase in engine speed increases NO formation. At lean mixture ratios, more of the combustion occurs during the expansion stroke, and this effect predominates and results in lower peak temperatures and NO formation.

Increased coolant temperature reduces the heat transfer, increasing combustion temperature and NO formation. An increase in intake manifold vacuum decreases the engine load and peak temperature, decreasing NO formation. Increased humidity decreases the combustion temperature and NO formation.
C. Laboratory Experiment

An experiment for use in a junior year engineering laboratory course was developed using the exhaust analyzers and the CFR engine. The purpose of the experiment is to investigate the effect of engine parameters on NO emissions. The parameters to be investigated are spark advance and compression ratio as a function of air/fuel ratio.

The adjustable head height allows the compression ratio to be varied within the range of 4 to 10:1, however to avoid severe engine knocking, the compression ratio should not exceed 8.9 if much leaner than stoichiometric air/fuel ratios are to be investigated (premium fuel and spark at TDC).

The spark is adjustable to plus or minus 30 degrees from TDC. To avoid knocking, a low compression ratio of 6.0:1 is used with the spark being varied from TDC to 15 degrees BTDC. This gives a large enough variation in the NO emissions to clearly show the effect of spark advance.

The lab procedure is presented in Appendix II. The actual time required for preparation and taking the
data is about 6 hours, not including the hour required to warm up the Beckman. It is suggested that the Beckman be turned on the day before to avoid unnecessary delay.

The sample gas is exhausted from the instruments into the room atmosphere. The small flowrate (3 SCFH) results in adequate dilution of the exhaust gases in the air. In addition the position of the cart puts the vent line directly under the room fan. Thus venting the sample gas into the room is not dangerous. If the instrument system is to be used in a small, poorly ventilated area, caution should be used.

Typical data obtained using this procedure are shown in Figures 6 and 7.

V. Conclusions
1. Both instruments performed properly in the sampling system.
2. Measurements using the sampling system showed similar trends to data in the literature.
3. The instruments and sampling system can be effectively used in an undergraduate laboratory course.
4. A laboratory experiment and procedure were devel-
5. The Beckman analyzer requires frequent calibration. An instructor familiar with the internal adjustments of the instrument should be present during its use.

6. The sampling system is adaptable to measuring NO emissions from other sources. The Pontiac V-8 and the small gas turbine are examples.
Figure 8 - Beckman Calibration Curves
REFERENCES


APPENDIX I

To determine if the peak cycle temperature, $T_3'$, of the Otto cycle with spark advance is greater than, less than, or equal to the peak cycle temperature, $T_3$, for the cycle without spark advance, consider the idealized pressure-volume diagram below.

Let $x$ = the fraction of combustion occurring before the piston reaches TDC, i.e. $a$ to $b$.

Then $1-x$ = the fraction of combustion occurring between $2'$ and $3'$.

The following relationships describe the various temperatures.

I 1 to a (isentropic compression)  
$T_a = T_1 \left( \frac{V_1}{V_a} \right)^{\gamma-1}$

II a to b (combustion)  
$T_b = T_a + \frac{x Q_c}{C_V (1 + A/F)}$

III b to $2'$ (isentropic compression)  
$T_{2'} = T_b \left( \frac{V_2}{V_a} \right)^{\gamma-1}$

IV $2'$ to $3'$ (combustion)  
$T_{3'} = T_{2'} + \frac{(1-x) Q_c}{C_V (1 + A/F)}$
Combining III and IV,
\[ T_3' = T_b \left( \frac{V_b'}{V_2'} \right)^{\gamma-1} + \frac{(1-x)Q_c}{C_V(1+A|F)} \]
Substituting for \( T_b \),
\[ T_3' = \left( T_a + \frac{xQ_c}{C_v(1+A|F)} \right) \left( \frac{V_b}{V_2'} \right)^{\gamma-1} + \frac{(1-x)Q_c}{C_v(1+A|F)} \]
Substituting for \( T_a \),
\[ T_3' = T_1 \left( \frac{V_1}{V_a} \right)^{\gamma-1} + \frac{xQ_c}{C_v(1+A|F)} \left( \frac{V_b}{V_2'} \right)^{\gamma-1} + \frac{(1-x)Q_c}{C_v(1+A|F)} \]

but \( \frac{V_1}{V_a} \frac{V_b}{V_2'} = \frac{V_1}{V_2'} = CR \)

\[ T_3' = T_1(CR)^{\gamma-1} + \left( \frac{V_b}{V_2'} \right)^{\gamma-1} \frac{xQ_c}{C_v(1+A|F)} + \frac{(1-x)Q_c}{C_v(1+A|F)} \]

From the analysis of the effect of compression ratio on \( T_3 \), we saw that
\[ T_3 = T_1(CR)^{\gamma-1} + \frac{Q_c}{C_v(1+A|F)} \]

and therefore
\[ T_3' = T_1(CR)^{\gamma-1} + \frac{Q_c}{C_v(1+A|F)} + \frac{Q_c}{C_v(1+A|F)} \left[ \chi \left( \frac{V_b}{V_2'} \right)^{\gamma-1} + (1-x) \right] \]
\[ T_3' = T_3 + \frac{xQ_c}{C_v(1+A|F)} \left[ \left( \frac{V_b}{V_2'} \right)^{\gamma-1} - 1 \right] \]

and
\[ \frac{xQ_c}{C_v(1+A|F)} \left[ \left( \frac{V_b}{V_2'} \right)^{\gamma-1} - 1 \right] \]

is the difference in the peak cycle temperature due to the spark advance.
From the P-V diagram, \( \frac{V_b}{V_2'} > 1 \)

Since \( \gamma - 1 \) is also a positive quantity,

\[
\left( \frac{V_b}{V_2'} \right)^{\gamma - 1} > 1
\]

and thus \( \frac{V_b}{V_2'} - 1 \) is positive.

Therefore, \( T_3' = T_3 + \) a positive quantity,

giving \( T_3' > T_3 \)

Thus spark advance increases peak combustion temperature. The increased temperature results in a higher NO concentration present in the exhaust.
APPENDIX II

Lab Procedure

Purpose: Obtain data of nitric oxide concentration (ppm) versus air/fuel ratio for three compression ratios and three spark advances.

Material required: Emissions measuring cart, Operating manuals for the Beckman, O₂ analyzer, and CFR engine, Squirt can of motor oil, A-3 fuel cell for the O₂ analyzer, 3/8 inch open end wrench

Procedure:

1. Turn the Beckman power switch to the TUNE mode and allow the instrument to warm up for at least one hour. This should be done prior to the lab period.

2. CFR Engine Preparation
   a. Turn on the room fan and the under floor exhaust fan.
   b. Position the fuel selector valve between any two of the inscribed numbers. This is the off position.
   c. Fill all three fuel bowls with premium grade motor fuel.
   d. Adjust the fuel bowl to be used for engine warm-up to .7 on the sight glass.
e. Check to see that oil is visible in the viewing window at the base of the engine. The level should be visible but no more than one half full. Add oil as required.
f. Check to see that cooling water is visible in the cooling water sight tube. The level will be below the "level hot" mark until the engine is fully warmed up.
g. Turn on the engine cooling water.
h. Turn on the circuit breaker.
i. Push the start switch to "on" and hold until the engine is running.
j. Turn the ignition switch to "on".
k. Turn the fuel selector valve to the warm-up fuel bowl.
l. Ignition can be recognized by a muffled popping sound in the exhaust. If ignition does not occur, raise the fuel bowl to richen the mixture.
m. Check to see there is at least 20 psig oil pressure.
n. Apply oil from the squirt can to both ends of the rocker arms and to the rocker arm shaft.
o. Turn the temperature controller switch to "on".
p. Turn the inlet heater and mixture heater
switches to "on".

q. Adjust the inlet heater to 1.2 amperes.

r. Adjust the mixture heater to 6.4 amperes.

s. Turn the oil heater switch to "medium".

t. Allow the engine to warm up until the water temperature is 210°F and the inlet and mixture temperatures have stabilized at about 100°F and 300°F respectively.

3. Installation of the A-3 Fuel Cell

a. Obtain access to the inside of the O₂ analyzer.

b. Pull the fuel cell holder out of its retaining sleeve by twisting it towards you.

c. Remove the cap.

d. Remove the fuel cell from its storage bottle and remove the shorting clip.

e. Install the fuel cell, contact end first, into the holder.

f. Screw on the cap and install the holder into its sleeve.

4. Fill the cooling water bucket with enough water to just cover the pump; then fill to the top with ice cubes.

5. O₂ Analyzer Calibration

a. Insert the flex hose into the "Bypass Drierite" quick disconnect (QD).
b. Plug in the air pump.

c. Calibrate the instrument following the procedure in paragraph 3.5 of the operating manual.

d. Unplug the air pump.

6. Beckman Calibration

a. Allow one hour for warm-up.

b. With the power switch in the TUNE mode, check to see that the meter reading is within a few divisions of the last value recorded on the card.

c. If so, record the meter reading on the card; if not, contact the instructor as an oscillator adjustment per paragraphs 5.1.5 to 5.1.9 of the operating manual is required.

d. Calibrate the instrument following paragraph 5.2.2 of the operating manual. Note:

-- Calibration gases are patched into the "Bypass Drierite" QD.

-- If a bias adjustment as described in paragraph 5.2.2 of the manual is required, contact the instructor.

-- While calibrating RANGE 1 (0-2000 ppm), also determine the gain setting required to give a meter reading of 63. Use this
gain setting and the 0-4000 ppm calibration curve when the NO concentration exceeds 2000 ppm.

-- The RANGE 2 calibration adjustment is located internal to the electronics section.

-- If there is insufficient adjustment available to set the instrument zero, contact the instructor as a shutter adjustment is required.

7. Obtaining Data

a. Assure that the CFR engine is fully warmed up.

b. Install the flex hose in the "Through Drierite" QD.

c. Plug in the air and water pumps.

d. Adjust the flow to 3 SCFH.

e. Insert the other end of the flex hose into the QD located in the CFR engine exhaust line.

f. Switch the fuel selector valve to a full fuel bowl.

g. Adjust the fuel bowl height to .8.

h. Adjust the compression ratio to the desired value using the table in the ASTM manual.

The actual micrometer reading is equal to 1 minus the micrometer reading in Table 35.
pages 112-113 of the manual. Do not lower the head to an indicated engine micrometer reading greater than .800.

1. Adjust the spark advance to the desired value. Be sure the linkage which connects the head to the distributor is loose at the distributor.

j. Take data after readings on both the Beckman and the \( O_2 \) analyzer have fully stabilized.

k. Vary the fuel bowl height over a range of .8 to 2.2.

l. Do not operate at conditions which result in severe knock.

m. Repeat the procedure obtaining data at three compression ratios with constant spark advance and three spark advances with constant compression ratio. Below is a table of suggested values.

<table>
<thead>
<tr>
<th>Air/fuel ratio</th>
<th>CR</th>
<th>Spark advance</th>
</tr>
</thead>
<tbody>
<tr>
<td>.8 to 2.2</td>
<td>6.0</td>
<td>0 TDC</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>0 TDC</td>
</tr>
<tr>
<td></td>
<td>8.7</td>
<td>0 TDC</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>7 BTDC</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>15 BTDC</td>
</tr>
</tbody>
</table>

8. Shutting Down the Equipment

a. Turn the fuel selector valve to an intermediate
position, and turn off the ignition.

b. Let the engine motor for one minute, then push the switch to "stop".

c. Turn off all the heater switches and the circuit breaker.

d. Unplug both pumps.

e. Blow nitrogen through the flex hose to remove any water which may have condensed. Then recheck the calibration of the Beckman.

f. Flush the system with nitrogen to remove any NO; it is very corrosive.

g. Remove the fuel cell from the O₂ analyzer, install the shorting clip, and place it in the storage bottle.

h. Flush the bottle with CO₂ gas from the cart and securely install the bottle lid.

i. Turn off the Beckman and O₂ analyzer.

j. Turn off the cooling water to the CFR engine.

k. Rotate the engine flywheel to TDC of the compression stroke.

l. Turn off the room and under floor fans.

**Possible Questions**

1. Plot the NO concentration versus air fuel ratio (i.e. fuel bowl setting) for the various compres-
sion ratios and spark advances.

2. Why do the higher compression ratios yield higher NO concentrations? (Hint: Consider the compression stroke as an isentropic compression of a perfect gas and show that the increased compression ratio gives increased temperature).

3. We know in general that as combustion temperature increases, so does the NO concentration. Explain why the NO concentration is small at extremely low and high air/fuel ratios.

4. Using the O₂ data estimate at which air/fuel ratio (i.e. fuel bowl setting) stoichiometry occurs.