

GAS CHROMATOGRAPHIC DETERMINATION OF
CARBON DIOXIDE, CARBON MONOXIDE, AND
NITRIC OXIDE IN DIESEL EXHAUST

by

Charles Watson Jordan, Jr.

Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE
in
Mechanical Engineering

APPROVED:

H. P. Marshall, Chairman

W. C. Thomas

C. E. Trent

H. M. McNair

March, 1974

Blacksburg, Virginia

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to his major professor, Prof. Harold P. Marshall, for suggesting the subject of this thesis, and for his advice and assistance throughout the investigation. Appreciation is also expressed to Dr. C. E. Trent, Dr. W. C. Thomas, and Dr. H. M. McNair, who, as members of the author's committee, offered their helpful criticisms and assistance.

A special acknowledgement is extended to the author's wife, , for her encouragement and typing.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS.....	ii
LIST OF FIGURES.....	iv
LIST OF TABLES	vi
I. INTRODUCTION.....	1
Thesis Objective.....	5
II. LITERATURE REVIEW.....	6
Significance of Carbon Dioxide, Carbon Monoxide, and Nitric Oxide.....	6
Gas Chromatography.....	9
Diesel Engine Exhaust Gas Analysis.....	19
Water Injection as a Means of Reducing Oxides of Nitrogen.....	28
III. EXPERIMENTAL INVESTIGATION.....	33
Description of Equipment and Apparatus.....	33
Experimental Procedure.....	42
IV. PRESENTATION AND DISCUSSION OF RESULTS.....	54
Calibration.....	54
Engine Tests.....	64
V. CONCLUSIONS AND RECOMMENDATIONS.....	93
VI. REFERENCES.....	96
VII. VITA.....	99

LIST OF FIGURES

	Page
1. Simple Gas Chromatography System.....	11
2. Chromatogram.....	13
3. Exhaust Gas Sampling System.....	35
4. Schematic of Fisher-Hamilton Gas Partitioner and Recorder.....	39
5. Calibration Apparatus.....	40
6. Water Injection System.....	41
7. Calibration Curve For Water Injection System.....	52
8. Carbon Dioxide: Concentration = 470 ppm, Attenuation = 1	56
9. Carbon Monoxide: Concentration = 376 ppm, Attenuation = 1	59
10. Nitric Oxide: Concentration = 470 ppm, Attenuation = 1	60
11. Preliminary Calibration Curves for CO ₂ , CO, NO	61
12. Chromatogram Showing Elution Sequence of CO ₂ , CO, and NO.....	63
13. Fuel Consumption At 1400 RPM	65
14. Calibration Curves For Group I, Tests 1-5	68
15. Chromatogram of Diesel Exhaust Obtained After 3-Hour Heat Treatment of Molecular Sieve Column (Group I, Test 1).....	69
16. Calibration Curves For Group I, Tests 6-10	72
17. Chromatogram Of Diesel Exhaust Obtained After 3-Hour Heat Treatment Of Molecular Sieve Column And Recalibration Of Gas Chromatograph (Group I, Test 6).....	74
18. Calibration Curves For Group II	76

19.	Chromatogram Of Diesel Exhaust Obtained After 4-Hour Heat Treatment Of Molecular Sieve Column (Group II, Test 1).....	78
20.	Chromatogram Of Diesel Exhaust Obtained When New Fuel Was Used (Group II, Test 2).....	79
21.	Chromatogram Of Diesel Exhaust Obtained During Water Injection Test (Group II, Test 7).....	81
22.	Carbon Dioxide Concentration Vs. Fuel/Air Ratio.....	83
23.	Carbon Dioxide Concentration Vs. Brake Mean Effective Pressure.....	84
24.	Carbon Monoxide Concentration Vs. Fuel/Air Ratio....	85
25.	Carbon Monoxide Concentration Vs. Brake Mean Effective Pressure.....	86
26.	Relative Retention Times For Nitric Oxide, Carbon Monoxide, And Methane.....	88
27.	Nitric Oxide Concentration Vs. Fuel/Air Ratio.....	89
28.	Nitric Oxide Concentration Vs. Brake Mean Effective Pressure.....	90
29.	Effect Of Water Injection On Nitric Oxide Concentration.....	92

LIST OF TABLES

	Page
1. Engine Specifications	34
2. Calibration Data for CO ₂ , CO, and NO	62
3. Engine Data. Group I, Tests 1-5.....	67
4. Engine Data. Group I, Tests 6-10.....	71
5. Engine Data. Group II, Tests 1-5.....	75
6. Engine Data. Group II, Tests 6-8 (Water Injection Tests).....	80

I. INTRODUCTION

In recent years, the conventional internal combustion engine, as found in automotive vehicles of all types, has come under close scrutiny by various federal and state agencies because it is believed to be a major contributor to atmospheric air pollution. Consequently, stringent controls have been proposed for certain exhaust products (unburned hydrocarbons, carbon monoxide, and oxides of nitrogen), whereby the amounts of these substances which may be exhausted into the atmosphere by any given vehicle are limited by law. It is still uncertain whether or not the degree of stringency found in present regulations is actually necessary to achieve the desired air quality; however, it is apparent that as the number of motor vehicles in use continues to rise, the fate of the internal combustion engine will become increasingly more dependent upon its ability to adapt to the standards mandated by society.

Specifically, the number of vehicles powered by compression ignition (diesel) engines has increased significantly during recent years, and this trend is expected to continue into the foreseeable future. In addition to its inherently good brake specific fuel consumption and unmatched durability, the diesel engine has demonstrated that it is a relatively low emitter of harmful exhaust products (1). However, as the diesel engine population

continues to increase, its contribution to the overall air pollution problem will become more significant. For this reason it is of paramount importance that those design parameters which are most critical insofar as harmful vehicle emissions are concerned be identified so that appropriate corrective action can be taken where necessary. Moreover, it is desirable that any increase in the number of diesel-powered vehicles will not be accompanied by a corresponding reduction in atmospheric air quality.

The desire to learn more about diesel exhaust emissions, and thus place the automotive diesel engine in proper perspective as far as its contribution to air pollution is concerned, has resulted in the publication of numerous studies related to this subject. A review of this literature reveals that previous investigators have used a wide variety of exhaust gas sampling and analysis (experimental measurement) techniques; however, in general, they have all arrived at essentially the same conclusion: under normal operating conditions the levels of unburned hydrocarbons and carbon monoxide produced in diesel engines are negligibly small, and oxides of nitrogen appear to be present in amounts which are approximately equal to those usually found in comparable gasoline engines.

Some of these investigators have used methods of analysis which are unjustifiably complex. In the literature review which follows, cases will be noted where two or more

totally different techniques have been utilized on the same engine for analyzing different exhaust gas components. There are also examples of certain substances being selectively removed from exhaust gas samples and stored for future analysis. Although such actions may be essential to the particular method employed, it is doubtful that they enhance the accuracy of the experiments. On the contrary, it seems reasonable to expect more error arising from the uncertainty of whether or not the component in question has undergone compositional change in the time period between sampling and analysis.

In light of all this, it seems quite natural to wonder if there may be some experimental analysis technique which is relatively quick and simple, gives good accuracy and reproducibility, and can simultaneously analyze all of the components of interest in a given exhaust sample. Such a method would have obvious advantages in exhaust gas studies. In considering the above characteristics, a suitable technique which comes to mind is gas chromatography. In addition to those traits already mentioned, gas chromatography has perhaps the greatest degree of flexibility of any analytical method. It also enables the experimenter to perform qualitative, as well as quantitative, analyses. This is not to suggest that the technique is without fault; however, the advantages appear to be far more significant than the disadvantages.

Gas chromatography has been used almost exclusively in exhaust gas studies to determine the types and amounts of unburned hydrocarbons present in exhaust samples. However, reports of its use in the analysis of other exhaust components are rare. This investigation will examine some of the aspects of gas chromatography relative to its use in the analysis of carbon dioxide, carbon monoxide, and nitric oxide in diesel exhaust. The nitric oxide is of particular interest in this study, because the author is unaware of any method described herein having been used previously in the analysis of this compound in engine exhaust. For this reason, the work is believed to be unique.

The final decision to use gas chromatography in this investigation of diesel exhaust gas composition was based on careful consideration of several factors. First of all, the method should utilize existing equipment and facilities wherever possible in order to keep costs at a minimum and avoid unnecessary delays. Secondly, the method must be compatible with the type of engine and gases to be studied. Also, the instrumentation should not be adversely affected by engine heat and vibration, or by any product of combustion. Finally, duplication of procedures used in previous investigations should be avoided.

Thesis Objective

This investigation was undertaken to determine the feasibility of using gas chromatography for the qualitative and quantitative analysis of gaseous compounds, other than unburned hydrocarbons, known to be present in diesel exhaust. Specifically, it was desired to use this method in determining the amounts of carbon dioxide, carbon monoxide, and nitric oxide present during various modes of engine operation. The problem included the selection and preparation of appropriate chromatographic columns, calibration of the gas chromatograph using known concentrations of the three gases to be analyzed, and, finally, the actual analysis of exhaust gas samples taken from a diesel engine.

Several secondary experiments were also designed; however, their performance was contingent on the development of the aforementioned analytical technique. Among these experiments were studies of the effects of two different fuels on levels of carbon dioxide, carbon monoxide, and nitric oxide in diesel exhaust, and the effect of sampling probe composition on nitric oxide levels. Also, an experiment using the injection of water into the intake air stream as a means of reducing the concentration of nitric oxide was planned.

II. LITERATURE REVIEW

In order to achieve a more thorough understanding of all aspects of this investigation, background information from several different areas was required. Consequently, this section will be divided into four parts, each treating a distinct topic.

Significance of Carbon Dioxide, Carbon Monoxide, and Nitric Oxide

In discussing exhaust emissions produced by the diesel engine (or any other internal combustion engine for that matter) it is often convenient to categorize exhaust constituents as products of complete combustion, products of incomplete combustion, or products originating from the intake air. Carbon dioxide (CO_2), carbon monoxide (CO), and nitric oxide (NO) fall respectively into these three categories. Therefore, this investigation may be viewed as an experimental analysis of three gaseous compounds, each representing a different aspect of the combustion process.

Each of these three compounds can be harmful to human beings if the latter are exposed continuously to high enough concentrations. According to Elliott and Davis (2), the maximum allowable concentrations for continuous exposure are 0.5% by volume for CO_2 , 0.01% by volume for CO, and 0.0025% by volume for oxides of nitrogen. Since the oxides of

nitrogen figure includes several compounds, the maximum allowable continuous exposure concentration for NO is probably somewhat lower than that indicated. It is apparent from these figures that CO₂ can be tolerated at much higher levels than the other two compounds; moreover CO and NO are known to be toxic substances. Federal air quality standards proposed by the Environmental Protection Agency in 1971 (3) recommend 9.0 parts per million of CO as the maximum advisable level for eight hours of continuous exposure. Corresponding figures for CO₂ and NO are not given.

Although CO₂ is much less harmful to humans than CO and NO, the fact that it is a primary product of combustion indicates that significant quantities are being emitted into the atmosphere. Obert (4) suggests that this may be cause for alarm. According to him, global carbon dioxide levels have been increasing steadily for the past fifty years, and the ultimate effect this will have on life forms is unknown. It is not uncommon for CO₂ to represent more than 10% by volume of the total exhaust products in internal combustion engines.

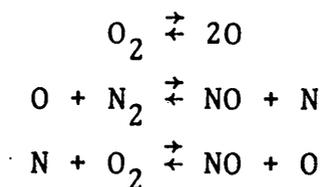
As mentioned previously, CO is a product of incomplete combustion. This means that its formation is due to a deficiency of oxygen during the combustion process. Also, since CO is readily absorbed in the bloodstream in place of O₂, it is highly poisonous. Typical amounts of CO present in diesel exhaust range from about 0.01% to 0.1% by volume.

Nitric oxide is one of several oxides of nitrogen, and is the principle one found in the exhaust of internal combustion engines. Like CO, it is readily absorbed in the bloodstream and can cause oxygen deficiency. However, NO levels in the atmosphere are so low that this is not considered to be a major problem. The most objectionable features usually associated with NO are its ability to slowly oxidize and form the more toxic NO₂, and its active participation in the photochemical smog formation process. Caplan (5) lists thirteen chemical reactions believed to describe the formation of photochemical smog, and NO appears explicitly in six of these. Although NO is indeed an active ingredient in this process, Caplan hastens to point out that a reduction in NO concentration does not necessarily mean less smog.

The formation of nitric oxide is a process which is not completely understood. The high temperatures associated with combustion cause normally inert nitrogen to react with oxygen and form NO. Temperatures in excess of 1200°C cause the reaction to proceed rapidly. The amount of NO actually produced is believed to depend on the peak combustion temperature, the length of time the gases remain at this temperature, and the amount of excess oxygen present during combustion (6). If the NO were allowed to cool very slowly, it would gradually dissociate back into N₂ and O₂. However, the rapid cooling which is characteristic of the combustion

process in internal combustion engines causes NO levels to be frozen at or near peak flame temperature values.

Several models have been proposed to describe the formation of NO. The one which seems to have gained the most widespread acceptance is the Zeldovich chain reaction mechanism. Patterson and Henein (3) represent this with three chemical equations:



According to this model, the NO forming reactions are initiated by the high temperature dissociation of molecular oxygen into the atomic form of the species.

The amount of NO emitted by a diesel engine depends on many factors, such as whether the engine is naturally aspirated or turbocharged, and whether direct injection or indirect injection are utilized. In general, the exhaust of a properly operating diesel will contain approximately 2000 or less parts per million NO.

Gas Chromatography

Gas chromatography is a technique which is used extensively in analytical chemistry for the qualitative and quantitative identification of unknown gaseous compounds.

The instrument used for this analysis is called a gas chromatograph. The principle of operation is that the various components of a gaseous mixture can be physically separated from each other by passing the mixture through a specific, chemically active substance. Molecular interaction occurs and the molecules of some compounds are retained more tenaciously than those of others, thus enabling separation to be achieved. The components are then eluted in sequence and identified.

A simple gas chromatography system is shown schematically in Fig. 1. It consists of five basic components: carrier gas, sample introduction ports, column, detector, and recorder. The carrier gas is allowed to flow continuously through the system, with a pressure regulator valve assuring steady flow. At some point in time, a gaseous sample is introduced into the moving carrier gas stream and is swept along to the column. Once inside the column, the selective retardation process previously described occurs, and the sample mixture is separated into its various components. These separated components exit the column in a certain sequence and pass through the detector, which indicates the presence of each by initiating an electrical signal. This is received by the recorder and a permanent record made. A strip chart recorder is generally used so that as each component is eluted from the column the deflection of the pen causes a distinct peak to appear as a

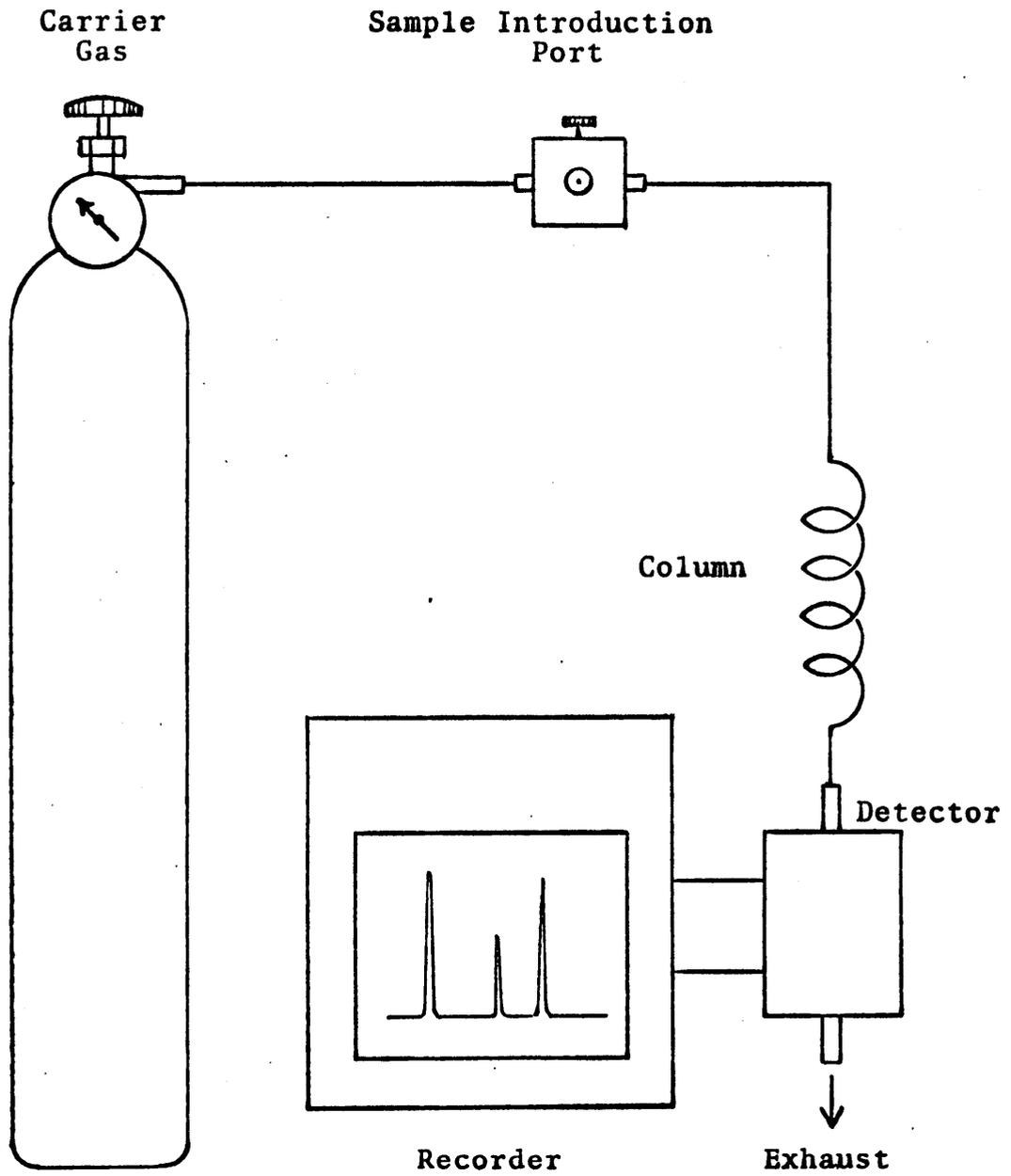


Figure 1. Simple Gas Chromatography System

function of time. This recorder output is called a chromatogram.

The time from sample introduction to component elution is unique for each compound in a given column under the same operating conditions, and thus it can be used to identify an unknown substance. This time is called the retention time. The retention time for each compound is measured along the abscissa of the chromatogram from the point of sample injection to the point corresponding to the peak maximum.

A chromatogram derived from a sample of atmospheric air is shown in Fig. 2. The first peak is a composite, or unresolved, air peak. The second peak is O_2 and the third is N_2 . The retention times are measured from the instant of sample introduction (indicated by the vertical arrow at lower left) and, as shown, are 1.4 min, 2.6 min, and 3.0 min for the three peaks which appear. Thus, if a subsequent mixture containing unknown compounds were analyzed in this chromatograph under the same operating conditions, and a peak maximum appeared at 2.6 min, one would be correct in assuming that it was oxygen.

Quantitative information can also be obtained from the chromatogram. The response magnitude is directly proportional to the amount of a compound which passes through the detector. The peak height or area can therefore be used to estimate the quantity of a substance present,

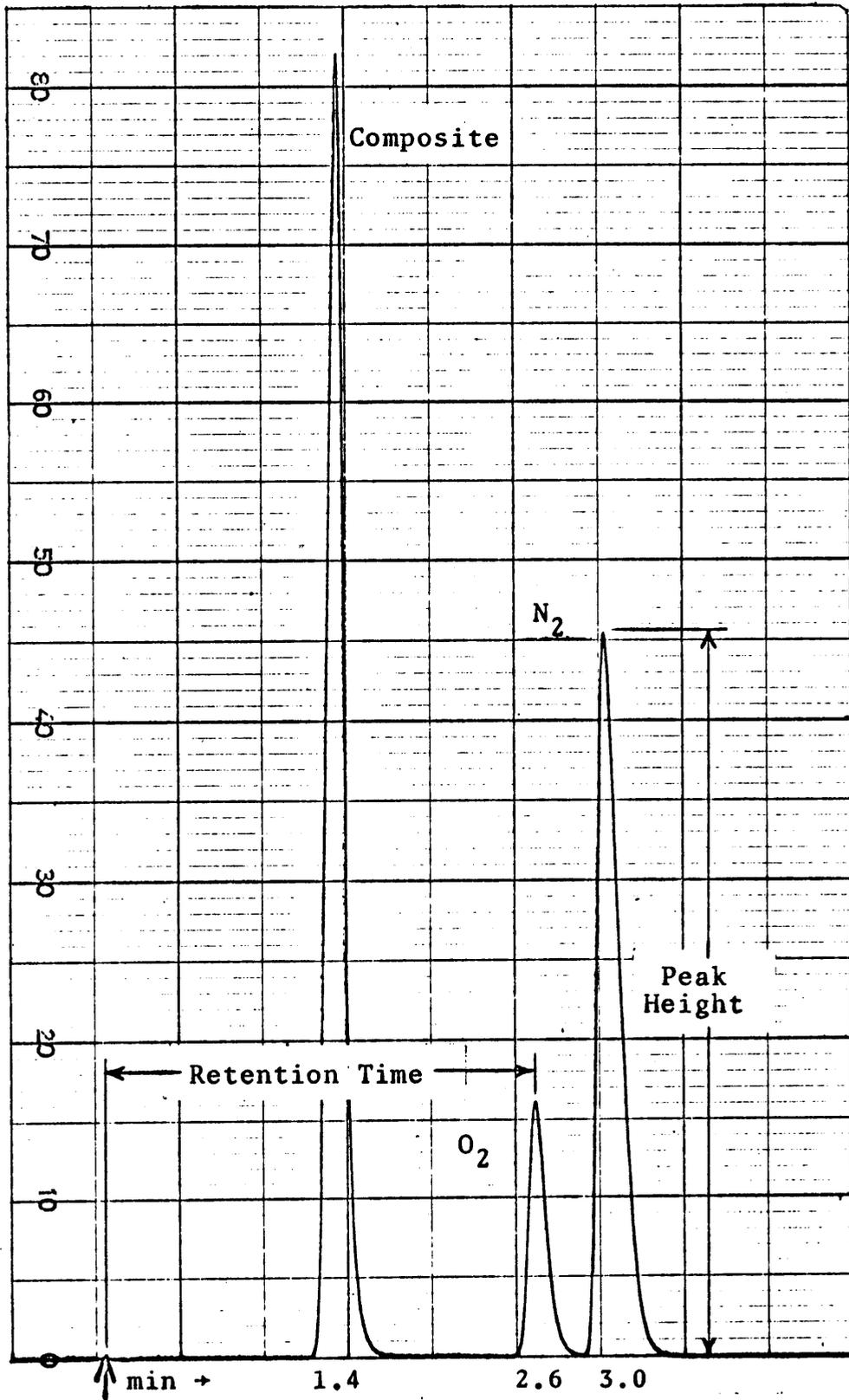


Figure 2. Chromatogram

provided known concentrations of that same substance have been analyzed previously and calibration curves plotted.

One aspect of gas chromatography which required special attention in this investigation was column selection and preparation. The chromatograph to be used was equipped with two columns in series, one of which was packed with molecular sieve, a substance which is supposedly suitable for the separation of many inorganic compounds. However, preliminary trials indicated that the separation of low concentrations of NO on untreated molecular sieve was somewhat less than satisfactory. So it was apparent that additional information concerning the nature of molecular sieves, as well as other adsorbents which might possibly be used, was needed.

When a chromatographic column is packed with an active solid which is capable of selectively adsorbing gases passing over it, the technique is referred to as gas-solid chromatography. Several materials have been used successfully to this end. Among the more commonly used of these are alumina, silica gel, activated charcoal, and molecular sieves. These adsorbents appear to be especially suitable for the separation of the more permanent gases.

Janák was one of the early investigators who made extensive use of gas-solid chromatography. He reports the utilization of charcoal for the separation of such gases as nitric oxide, nitrous oxide, carbon monoxide, and krypton.

He also found that silica gel worked quite well for the separation of some hydrocarbons (7). Also, using carbon dioxide for carrier gas, he found that sodium zeolites effected good separations of paraffins and paraffin impurities in olefinic mixtures (8).

A review of the literature dealing with adsorbents reveals that the particular properties of molecular sieves make them quite suitable for the separation of carbon monoxide and nitric oxide. Molecular sieves are synthetic zeolites whose crystal structure is characterized by silicon-oxygen and aluminum-oxygen tetrahedra containing exchangeable ions such as sodium, potassium, or calcium. Whereas most crystal structures extend uniformly in all directions, molecular sieves are honeycombed with a network of relatively large cavities which are filled with water during formation of the crystal. If these cavities are dehydrated, they will readily adsorb other molecules. They are connected by a series of small apertures through which only certain size molecules can pass. These properties make them suitable for the separation of certain gases.

Breck and Smith (9), who did work in the development of synthetic zeolites in 1948, fabricated several sieves which were capable of performing useful separations. They also found that molecules as much as 0.5 angstrom unit larger in diameter than the free diameter of the apertures could easily pass through the crystal. However, molecules

one angstrom larger were unable to enter. Breck and Smith attributed this peculiar behavior to a combination of the pulsation of non-rigid crystal atoms and the kinetic energy of incoming molecules.

As stated previously, the active pores in molecular sieve will readily adsorb other molecules. This may or may not be a favorable characteristic in gas chromatography, depending upon which gases are being separated for analysis. For example, water molecules are retained more tenaciously than any other molecules, and if they are allowed to fill the cavities, the usefulness of the molecular sieve as a means of gas separation will be temporarily lost. Molecular sieve also has an affinity for carbon dioxide molecules. Therefore if a molecular sieve column is exposed to substantial quantities of either of these two compounds, a heat treatment may be necessary to effect evacuation of the active cavities and thus restore the sieve to its original state. The need for this becomes apparent when the resolution between adjacent peaks begins to decrease, indicating that effective separation is failing to occur.

Molecular sieve behaves somewhat differently when it is exposed to nitric oxide. Before the column can be used to successfully separate small amounts of nitric oxide, it must first be saturated with the latter substance. This process apparently neutralizes overactive adsorption sites in the cavities and enables the small amounts of NO in

subsequent samples to pass on through the apertures. Otherwise, these small amounts of NO will be permanently retained in the column, and this is not desirable if one is trying to analyze the NO. The saturation treatment has no adverse effects on peak resolution.

Trowell (10) was the first researcher to report a gas chromatographic technique for the simultaneous determination of nitric oxide and nitrogen dioxide. In addition to these two compounds, he was also able to analyze carbon dioxide, carbon monoxide, oxygen, nitrogen, nitrous oxide, and some light hydrocarbons. His technique utilized three columns in series and dual detectors. The first column was cooled to -76°C and separated nitrogen dioxide and water vapor from the other gases. Columns 2 and 3 were maintained at 25°C . Oxygen, nitrogen, nitric oxide, and carbon monoxide were separated in column 3, which was packed with 13X molecular sieve (11 angstrom apertures). Trowell activated this column by heating at 250°C for five minutes while purging with helium flowing at approximately 200 cc per minute. He does not mention any nitric oxide treatment. He does note, however, that overactivation resulted in extreme tailing of the nitric oxide peak during analysis.

A more recent gas chromatographic technique for the determination of nitric oxide is presented by Dietz (11). His apparatus included a molecular sieve 5A (4 angstrom apertures) column and a thermal conductivity detector. The

activation procedure for the column was rather involved. It was first heated at 300°C for twenty hours under vacuum to remove H₂O, then purged with pressurized helium at the same temperature. Next it was saturated with NO at 300°C and at 20°C. After again flushing with helium, O₂ was introduced to convert the adsorbed NO into NO₂. This was done at 25°C and at 100°C. Dietz reports good resolution of peaks with absolutely no tailing of the NO peak. He attributes the elimination of this tailing to the conversion of adsorbed NO at certain sites in the sieve to permanently bound NO₂. Dietz also noted that NO and CH₄ peaks were virtually indistinguishable because their retention times were nearly identical.

The application of gas chromatography to exhaust gas analysis has been confined mainly to the identification of unburned hydrocarbons. Gas-liquid chromatography is generally used in these investigations. In gas-liquid chromatography, the column is either packed with a granulated, inert solid substance which has a liquid phase film adsorbed on the surface, or else it is of very small inside diameter like a capillary, and the liquid film adheres to its inner surface. The liquid phase acts as a solvent, and the interaction of its molecules with those of a gaseous sample causes separation to occur. The large selection of solvents available enhances the flexibility of this technique to a degree which makes it superior to other methods

insofar as the analysis of individual hydrocarbons is concerned.

One of the earlier investigations of exhaust gases using gas-liquid chromatography was conducted by Hurn, et al. (12). Their analysis excluded hydrocarbons above C_9 , and they reported problems in the identification of C_6 and higher compounds. The removal of CO_2 , H_2O , and N_2 from the samples was necessary prior to their introduction into the two-column chromatograph.

Papa (13) was somewhat more successful. He used a two-column chromatograph and flame ionization detector to identify C_1 through C_{12} hydrocarbons in automobile exhaust. More than 200 hydrocarbons of all classes were detected.

Dimitriades, et al. (14) utilized gas-liquid chromatography to analyze hydrogen, unburned hydrocarbons, and oxygenated hydrocarbon derivatives in vehicular exhaust. C_1 through C_{12} hydrocarbons in the exhaust from gasoline engines were separated and identified, as well as C_1 through C_{22} hydrocarbons in diesel exhaust. Dimitriades also noted the need for a chromatographic system capable of separating H_2 , O_2 , CO , CO_2 , NO , and NO_2 .

Diesel Engine Exhaust Gas Analysis

An important consideration in the analysis of diesel engine exhaust gases is the type of sampling technique to be

used. It should be kept as simple as practicable to avoid possible compositional changes prior to actual analysis, and, at the same time, it must be fully compatible with the analytical method employed. If probes are utilized, they must be completely inert with respect to all products of combustion. The Society of Automotive Engineers (15) recommends the use of stainless steel probes when analyzing CO_2 , CO, and NO_x (oxides of nitrogen) in diesel exhaust. However, England, et al. (16) reported considerable decomposition of NO when using stainless steel probes in the analysis of flue gases from a furnace. They attributed this to the catalytic action of metallic oxides originating from compounds in the stainless steel at high temperatures. The exhaust gas temperature in their experiments was approximately 2500°F. Subsequent tests using quartz probes showed increases in detected NO levels of as much as 200%.

Many investigations have been undertaken to determine the exhaust characteristics of both automotive and non-automotive type diesels. Obviously, all of these cannot be discussed in detail in this paper. There are, however, certain studies which are either believed to be representative of a particular analytical technique, or whose results are presented in a manner which is convenient for future comparison. Brief summaries of these, including engine types, exhaust analysis procedures, and significant results will be presented below, with emphasis on CO_2 , CO and NO.

An early investigation of diesel exhaust gas was conducted by Holtz and Elliott (17) in 1940. Exhaust gas composition was determined for two four-cylinder, four-stroke cycle, naturally-aspirated diesels of different displacement and combustion chamber configuration. Carbon dioxide, carbon monoxide, oxygen, hydrogen, and methane were analyzed in either an Orsat apparatus or a Haldane apparatus. Also, carbon monoxide and oxides of nitrogen in some samples were determined by unspecified special methods. The emphasis in these tests was on establishing the relationship between exhaust component levels and fuel-air ratios; therefore, engine speeds were kept nearly constant while loads and fuel-air ratios were changed.

Carbon dioxide levels increased approximately linearly with fuel-air ratios up to about 0.06 pounds of fuel per pound of air, at which point they began to level off and then decreased. The maximum of 13.7% CO₂ by volume was achieved at the stoichiometric ratio of 0.0679 lb per lb.

Carbon monoxide concentrations were always less than 0.12% as long as the engines were run at fuel-air ratios which conformed to the manufacturers' specifications; however, levels rose sharply when richer ratios were used. Also, there were considerable differences in the amounts of carbon monoxide measured in each engine.

The oxides of nitrogen were reported as equivalent NO₂, which, the authors acknowledged, included NO. Maximum

concentrations occurred at fuel-air ratios between 0.025 and 0.045 and in general were less than 500 ppm (parts per million). Some variation with speed as well as engine design were noted. For example, at the same speed of 1400 rpm, the maximum amounts of NO_x produced by the two engines were 340 ppm and 450 ppm.

Elliott and Davis (2) conducted similar tests on two engines identical to those used by Holtz and Elliott, and a third which was considerably larger than the other two, and had a different type of combustion chamber. In general, there was good correlation between their results and those of the previous investigation, as one might expect. The larger engine, which was naturally aspirated, produced the highest carbon monoxide concentrations at fuel-air ratios greater than 0.02 lb per lb. Concentrations rose sharply beyond a ratio of about 0.045, reaching the 1% level at a ratio slightly below stoichiometric. Elliott and Davis also observed that engine speed had a negligible effect on carbon monoxide concentrations.

The concentration of oxides of nitrogen reached a maximum at intermediate fuel-air ratios. The highest concentration observed was about 1300 ppm.

An investigation which attempted to relate various modes of diesel engine operation to oxides of nitrogen formation has been reported by McConnell (18). His study entailed the use of three fundamentally different diesel

engines--a two-stroke cycle engine, a four-stroke cycle, direct-injection engine, and a four-stroke cycle, indirect-injection engine. Oxides of nitrogen levels were determined in accordance with A.S.T.M. Method D1608-58T, the "Standard Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenol-Disulfonic Acid Procedure)". With this method all oxides of nitrogen except nitrous oxide (N_2O) are reported as equivalent NO_2 .

McConnell found that NO_x concentrations decreased steadily and predictably at all speeds when the injection timing was retarded. In the case of the four-stroke, direct injection engine operating at 1500 rpm, NO_x levels ranged from nearly 2800 ppm down to about 600 ppm. Much lower concentrations were present in the exhaust of the indirect injection engine.

The effects of engine speed were also studied, using fixed injection timing. The direct injection engine produced NO_x amounts which increased with rpm to a maximum of about 2700 ppm at 1500 rpm, and then decreased rapidly at higher speeds.

The engines were run at 1500 rpm and the fuel delivery rate was varied to determine what effects air-fuel ratio had. The direct injection engine showed a nearly linear increase in NO_x from 1100 ppm to 2500 ppm when 30% to 65% of the air available for combustion was actually used. The NO_x peaked at slightly more than 2500 ppm, and then

decreased rapidly.

Additional tests included intake air throttling, which had very little effect on NO_x concentration, and secondary injection, which caused a significant decrease. Also, the effects of turbocharging were evaluated. When high fuel delivery rates were used, the turbocharged, direct injection engine produced much higher NO_x concentrations than did the same engine when it was normally aspirated. McConnell states that in general, turbocharging increases the absolute quantity of NO_x emitted, while the concentration may increase or remain the same.

Yumlu and Carey (19) limited their research to four-stroke, direct-injection diesels. Three engines were tested: one turbocharged and two naturally aspirated. Stainless steel probes conveyed samples from the exhaust pipe to the analysis apparatus. CO_2 , CO , O_2 , and N_2 were analyzed using gas chromatography and a thermal conductivity detector. Oxides of nitrogen were converted to NO_2 and measured with a spectrophotometer using a modified Saltzman technique.

Like Elliott and Davis, Yumlu and Carey concluded that engine speed had little or no effect on carbon monoxide levels. In general, these levels were much less than 1% when the fuel-air ratio was kept below about 0.035 lb per lb, which was the beginning of the overload range. The effect of brake mean effective pressure on carbon monoxide

concentrations was also studied. In the turbocharged engine, CO levels increased gradually with b.m.e.p., while in the naturally aspirated engines, a sharp increase was observed when the b.m.e.p. exceeded 90 psi.

NO_x concentrations decreased slightly with speed in the two naturally aspirated engines, and increased rapidly in all engines as the fuel-air ratio was increased. Also, the turbocharged engine appeared to produce less NO_x than the other engines at a given b.m.e.p. In most cases NO_x concentrations remained below 1600 ppm.

The experiments of Abthoff and Luther (20) were conducted primarily to study the effects of various modes of engine operation on the levels of oxides of nitrogen found in diesel exhaust. However, other constituents were also analyzed. They used three water-cooled, four-stroke, four-cylinder engines and three air-cooled, four-stroke, single-cylinder engines. Exhaust gas samples were cooled and dried prior to analysis. CO and CO₂ amounts were determined using infrared absorption. Oxides of nitrogen were measured as NO₂ using a Beckman NO₂ spectrophotometer. Arrangements were made for the oxidation of NO so that it would be completely converted into NO₂ when the analysis occurred.

The results compiled by Abthoff and Luther correlate well with those of previous investigators. In their tests, each engine was operated between 1000 and 3000 rpm and over a range of mean effective pressures with 6 Kg/cm² being the

upper limit in most cases. Load appeared to have a significant effect on NO_x levels, though this effect was not the same for all engines. In one case, NO_x concentrations ranging from 100 ppm to 2500 ppm were recorded over the entire m.e.p. range. Such a wide variation was not typical, however. Maximum NO_x values generally appeared between three-fourths of full load and full load. Combustion chamber shape and injector design also seemed to influence the amount of NO_x produced.

At low loads, CO concentrations were generally much less than 1000 ppm. However, at full load they increased sharply to a maximum of about 3000 ppm, or 0.3% by volume.

Marshall and Flemming (21) considered fuel characteristics, as well as engine operating variables, in their research work. The engines used in this investigation included two four-stroke, naturally-aspirated diesels, one four-stroke, turbocharged diesel, and one two-stroke, air-scavenged diesel. All engines utilized direct injection. CO_2 , CO, and NO were measured by nondispersive infrared analysis in accordance with S.A.E. Recommended Practice (15).

The fuel characteristics study revealed that CO levels increased with the specific gravity of the fuel being burned. The authors attributed this to the fact that using higher density fuels was tantamount to increasing the fuel-air ratio. When the engines were operated at their rated speeds, CO concentrations were very low (less than 300 ppm),

and fairly constant up to a fuel-air ratio of about 0.035 lb per lb, beyond which CO increased rapidly.

The engine variables study was an investigation of the effects of various internal and external engine parameters on pollutant formation. The internal parameters included injection timing, the retardation of which was observed to decrease NO_x concentrations, and various nozzle characteristics, whose modification had no beneficial effects. The authors concluded from these tests that an engine tuned for optimal performance would have the best exhaust emission characteristics, with the exception of NO_x .

External engine parameters included intake air density, temperature, and composition. Changing the density of the intake air was accomplished by throttling. This resulted in slight increases in both NO_x and CO concentrations. NO_x also appeared to increase approximately 2% for each 10°F rise in intake air temperature between 50°F and 260°F. Intake air composition was altered by water injection, which will be discussed in the next section, and exhaust gas recirculation. The cooling and recirculation of 10% of the exhaust gases led to a 25% reduction in NO_x levels with practically no adverse effects on power output or fuel economy. Marshall and Flemming also concluded that NO_x decreases almost linearly with oxygen concentration for any given mode of operation. NO_x concentrations in all tests were generally less than 2500 ppm.

The Federal Register (22) specifies the maximum amounts of certain pollutants which may be emitted by new diesel-powered vehicles in the 1975 model year, as well as the test procedure to be used in certifying these vehicles. Hydrocarbons will be limited to 0.41 grams per vehicle mile, carbon monoxide to 3.4 grams per vehicle mile, and oxides of nitrogen to 3.1 grams per vehicle mile. The test procedure involves operating the vehicle through a prescribed cycle which includes accelerations, decelerations, and cruising. All of the exhaust emitted during this cycle is collected in sample bags, diluted with air, and subsequently analyzed. Carbon dioxide and carbon monoxide concentrations are determined by nondispersive infrared analysis. Chemiluminescent analysis is used to measure the oxides of nitrogen concentrations. In using this method NO_2 must first be converted into NO .

The foregoing survey gives some indication of the wide variety of techniques available for the analysis of diesel exhaust. However, all appear to give quite similar results. This would seem to imply that no one method is inherently more accurate than the others in measuring a given compound.

Water Injection as a Means of
Reducing Oxides of Nitrogen

Several investigators have used the injection of water

into the intake air stream as a means of reducing oxides of nitrogen emissions in internal combustion engines. The theory is that the addition of an inert substance in the combustion chamber will effectively reduce peak flame temperatures and thus NO_x amounts. The inert substance can be a gas phase diluent, as in exhaust gas recirculation, or a noncombustible liquid such as water. One advantage of using a liquid phase diluent is that it has a negligible effect on the volumetric efficiency of the engine. Marshall and Flemming (21) state three main ways in which water acts to reduce NO_x levels. First, vaporization lowers the intake air temperature and compression temperatures. Secondly, the dilution of intake air with water lowers the oxygen concentration during combustion. Finally, the inherently high heat capacity of water is responsible for a decrease in peak flame temperature. Other investigators, such as Robison (23), have reported that nitric oxide levels decrease with increasing humidity of the intake air. Synopses of several investigations in which water injection has been utilized as a means of reducing NO_x will be presented below.

Nicholls, et al. (24) investigated the effectiveness of water injection as a means of reducing oxides of nitrogen emissions from a single-cylinder, C.F.R., gasoline engine. NO_x concentrations were determined by an ultraviolet light absorption technique. Nozzles made from flame-drawn, glass capillary tubing were used to inject a continuous stream of

highly filtered, distilled water into the induction pipe at predetermined rates. The technique proved to be effective in reducing NO_x concentrations, with a reduction of as much as 90% being reported for a water-fuel mass ratio of 1.0. The authors also noted a slight increase in brake mean effective pressure, and a slight decrease in brake specific fuel consumption at low water-fuel ratios.

Using the engines and exhaust gas analysis techniques described in the previous section, Abthoff (20) conducted several experiments which were designed to improve diesel engine exhaust characteristics. Among these was water injection into the intake air stream. In general NO_x reductions of approximately 60% occurred at a water-fuel ratio of 0.8. There were also slight increases in CO as the amount of water injected was increased.

Valdmanis and Wulfhorst (25) used water-fuel emulsions and water induction in separate tests on a single-cylinder, direct-injection diesel engine. CO_2 , CO, and NO were measured using infrared analyzers in accordance with S.A.E. Recommended Practice. Tests conducted with the engine operating at optimum injection timing and constant fuel-air ratio showed that as the water content increased, NO_x levels increased with emulsified fuels, and decreased when the water was inducted with the intake air. No significant trends were noted for CO with either water addition method. Water-fuel emulsions also caused a slight decrease in

b.m.e.p.

Torpey, et al. (26) conducted a series of experiments related to diesel engine exhaust emissions. Their single-cylinder research engines were equipped with both direct and indirect fuel injection. NO and CO were determined in infrared gas analyzers. Their tests included studies of the effects of water injection, exhaust gas recirculation, and variation in combustion chamber configuration on exhaust emissions. They also investigated the effects of speed, load, and injection timing. Water was injected into the intake manifold of the indirect injection engine, using a pressure-control valve and calibrated jets to achieve the desired flows. NO_x was reduced by 60% when a water-fuel volume ratio of 2.0:1 was used.

Zeilinger (27) injected water-fuel emulsions into a six-cylinder, water-cooled, four-stroke cycle, gasoline engine using the engine's mechanical fuel injection system. Exhaust gas samples were analyzed with an infrared absorption spectrometer. Zeilinger realized a reduction in NO to 55% of the original value when a mixture of 28% water by volume was used, and at this level there was no loss in fuel economy or b.m.e.p. Greater NO reductions could be achieved at the expense of these parameters. Maximum, uncontrolled NO concentrations were in excess of 3000 ppm; an emulsion containing 30% water lowered this maximum to about 1500 ppm.

The experimental work of Marshall and Flemming (21) has

been introduced previously. Water was injected into the intake air stream of the direct injection, turbocharged diesel engine. NO_x decreased nearly linearly as water content was increased. A 50% reduction in NO_x was observed when water composed 6% by mass of the intake air.

III. EXPERIMENTAL INVESTIGATION

Description of Equipment and Apparatus

The engine used in this study was a Cummins four-stroke cycle, direct injection, turbocharged diesel. Additional specifications are given in Table 1. The engine was mounted on steel supports and connected to an electric dynamometer which could be operated in either a speed control mode or a torque control mode. The moment arm on the dynamometer was 1.854 ft long. Thermocouples were provided on the engine for monitoring the temperatures of the jacket water, cooling water in and out, lubricating oil, intake air, and exhaust manifold. The unfiltered intake air passed through a 3-inch bell mouth orifice in the intake stack, and the pressure drop at this point, indicated by a U-tube manometer, was used to calculate air flow. Fuel consumption was determined utilizing a balance on which a weight and a beaker of fuel were placed. A mercury switch on the balance started and stopped a timer which measured the time required to burn a one pound mass of fuel.

Figure 3 shows the exhaust gas sampling system. A 1/4 in. OD probe, fabricated from type 304 stainless steel, was inserted in the exhaust pipe at a point 5½ ft downstream from the exhaust manifold. The overall length of the stainless steel line was 23.2 in., and its wall thickness was 0.035 in. A needle valve was utilized to control exhaust

Table 1. Engine Specifications

Manufacturer	Cummins
Model	JT-6-B
Type	Turbocharged Diesel
Number of Cylinders	6
Cylinder Bore, in.	4.125
Cylinder Stroke, in.	5
Piston Displacement, cu in.	401
Maximum Horsepower	175
Rated Speed, RPM	2500
Maximum Torque, lb-ft	407
RPM @ Maximum Torque	1750

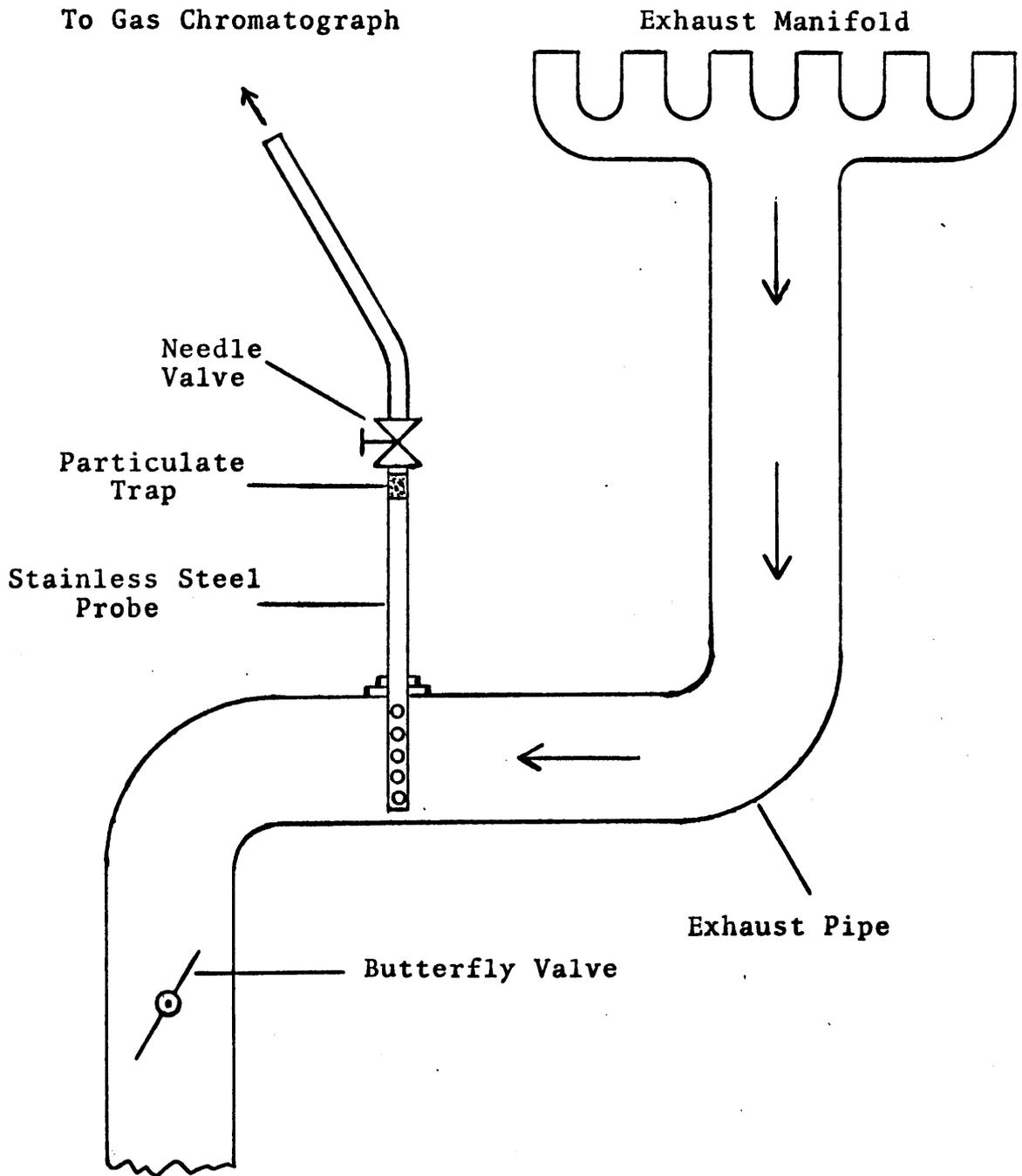


Figure 3. Exhaust Gas Sampling System

gas flow to the gas sampling valve in the chromatograph. Filtration of exhaust gases to remove particulates such as soot was accomplished with a glass wool trap located upstream from the needle valve. The probe itself was perforated with 34 holes, each being 5/64 in. in diameter, to assure that samples representative of the entire cross section of the exhaust pipe were analyzed. A glass probe of similar configuration was also used in one experiment. A butterfly valve located downstream from the probe created a slight back-pressure, and thus caused samples to flow to the chromatograph when the needle valve was opened.

Carbon dioxide, carbon monoxide, and nitric oxide were analyzed with a Fisher-Hamilton Model 29 Gas Partitioner. This chromatograph incorporated two columns in series, each of which eluted into separate thermal conductivity cells equipped with tungsten filaments. The first column, which was made of aluminum tubing 6 ft long and 1/4 in. in diameter, was packed with 30% DEHS (Di-2-ethylhexylsebacate)* adsorbed on 60-80 mesh Chromosorb P. CO₂ was separated from other compounds in this column. The second column, also made of aluminum, was 6½ ft long and 3/16 in. in diameter. This column was packed with 40-60 mesh molecular sieve 13X and separated O₂, N₂, NO, and CO. A stainless steel column 39.4 in. long and 1/4 in. in diameter which was packed with 30-60 mesh molecular sieve 5A, was used briefly as a second

*A liquid phase solvent

column; however, its performance was inferior, as will be seen later. Column temperatures were ambient, and the thermal conductivity cell temperature stabilized at approximately 70°C.

An attenuation control was provided so that a wide range of sensitivities could be selected. Also, controls for balancing the Wheatstone bridge circuit used with the thermal conductivity detectors were provided. Cell current and carrier gas flow rate could also be regulated.

The carrier gas used in this investigation was commercially available helium. The relatively high thermal conductivity of this gas makes it ideal for use with the aforementioned detectors. The carrier gas flow rate was determined with a soap bubble flowmeter.

Gas samples can be introduced into this chromatograph by two methods. The simplest way is to use a gas-tight syringe to inject the sample directly into the carrier gas stream through a rubber septum. However, inaccuracies stemming from human error become more apparent as the sensitivity of the instrument is increased. The best method is to use a gas sampling valve equipped with a constant volume sample loop. This assures the best possible accuracy and consistency by eliminating the possibility of human error. The Fisher-Hamilton chromatograph had such a device incorporating a 2.5 ml sample loop. The sampling valve method was used exclusively in this investigation.

Following their introduction into the chromatograph, gas samples passed through a drying tube to remove water vapor. Drierite was used as a drying agent.

A strip chart recorder was used to obtain a permanent record of all analytical data. The chart speed was variable and was set at 1 in./min during all experiments. The Fisher-Hamilton Gas Partitioner and the recorder appear schematically in Fig. 4.

Before the chromatograph could be used to analyze diesel exhaust, it first had to be calibrated with known concentrations of CO_2 , CO, and NO. The procedure used for this will be described in the next section. The calibration apparatus is shown in Fig. 5. A glass bottle of 1063 cc capacity and a small vial containing mercury were the major components of this system. Both were affixed to a ring stand. The bottle had a two-position petcock valve at one end and a one-position petcock valve at the other. A septum attached to the side of the bottle provided a means for the introduction by syringe of small volumes of sample gas.

As stated previously, one experiment was designed to study the effect of water injection on NO levels. The system used for this is depicted in Fig. 6. The steel tank was fitted with a water inlet line, a compressed air inlet line, and a water outlet line which extended to the bottom of the tank. The spray nozzle was fabricated from a section of 1/4 in. stainless steel which was plugged at one end and

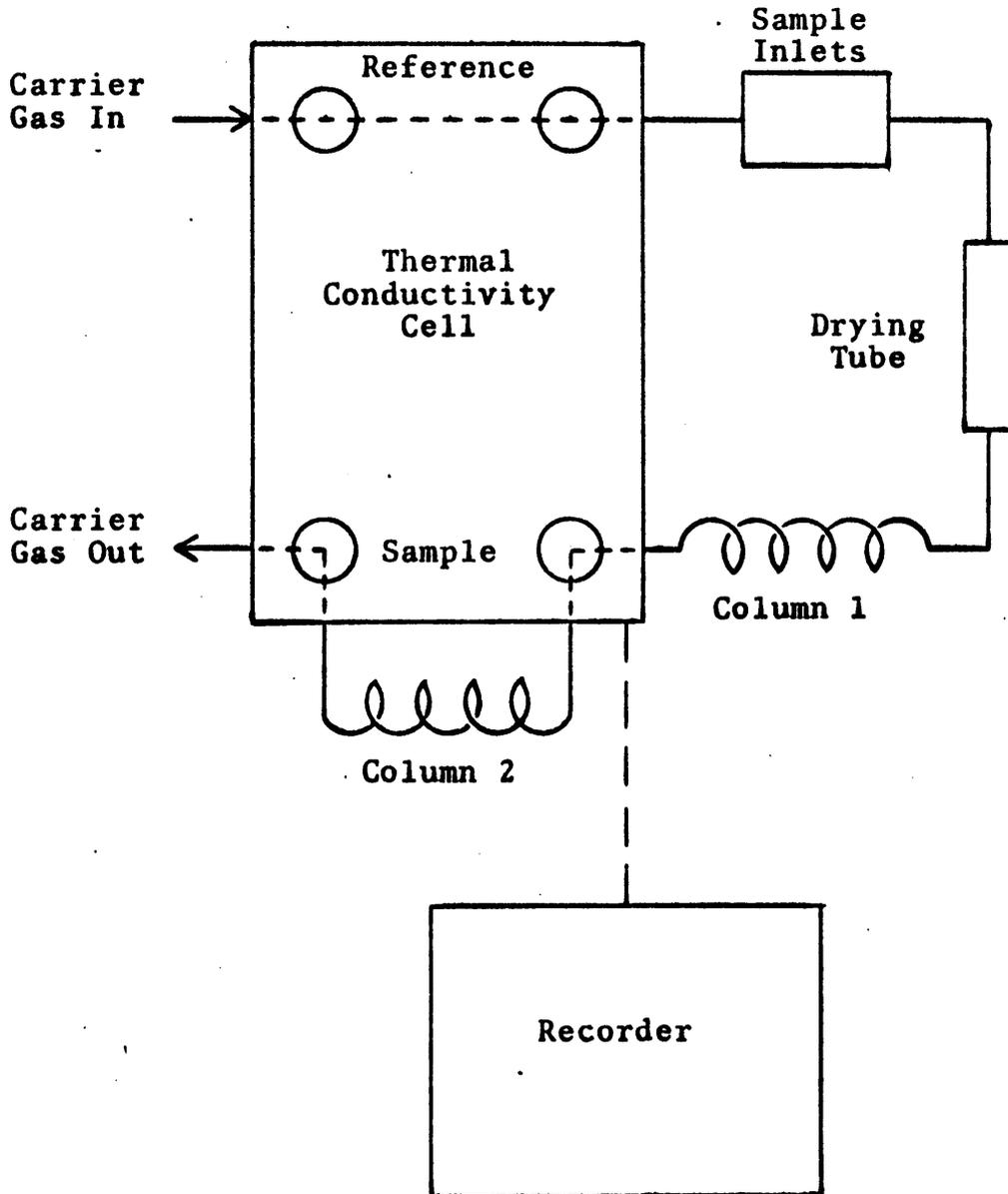


Figure 4. Schematic of Fisher-Hamilton Gas Partitioner and Recorder

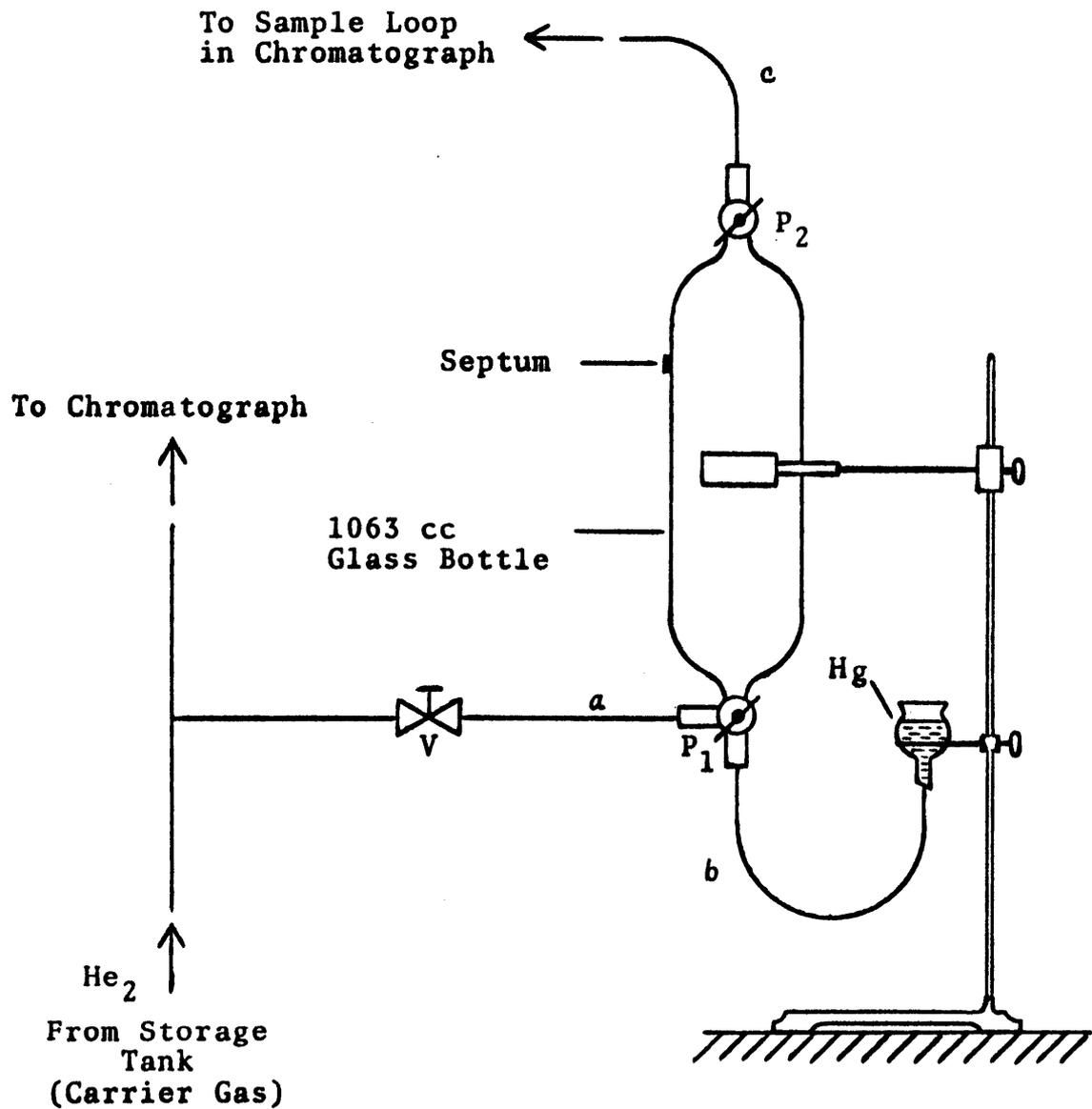


Figure 5. Calibration Apparatus

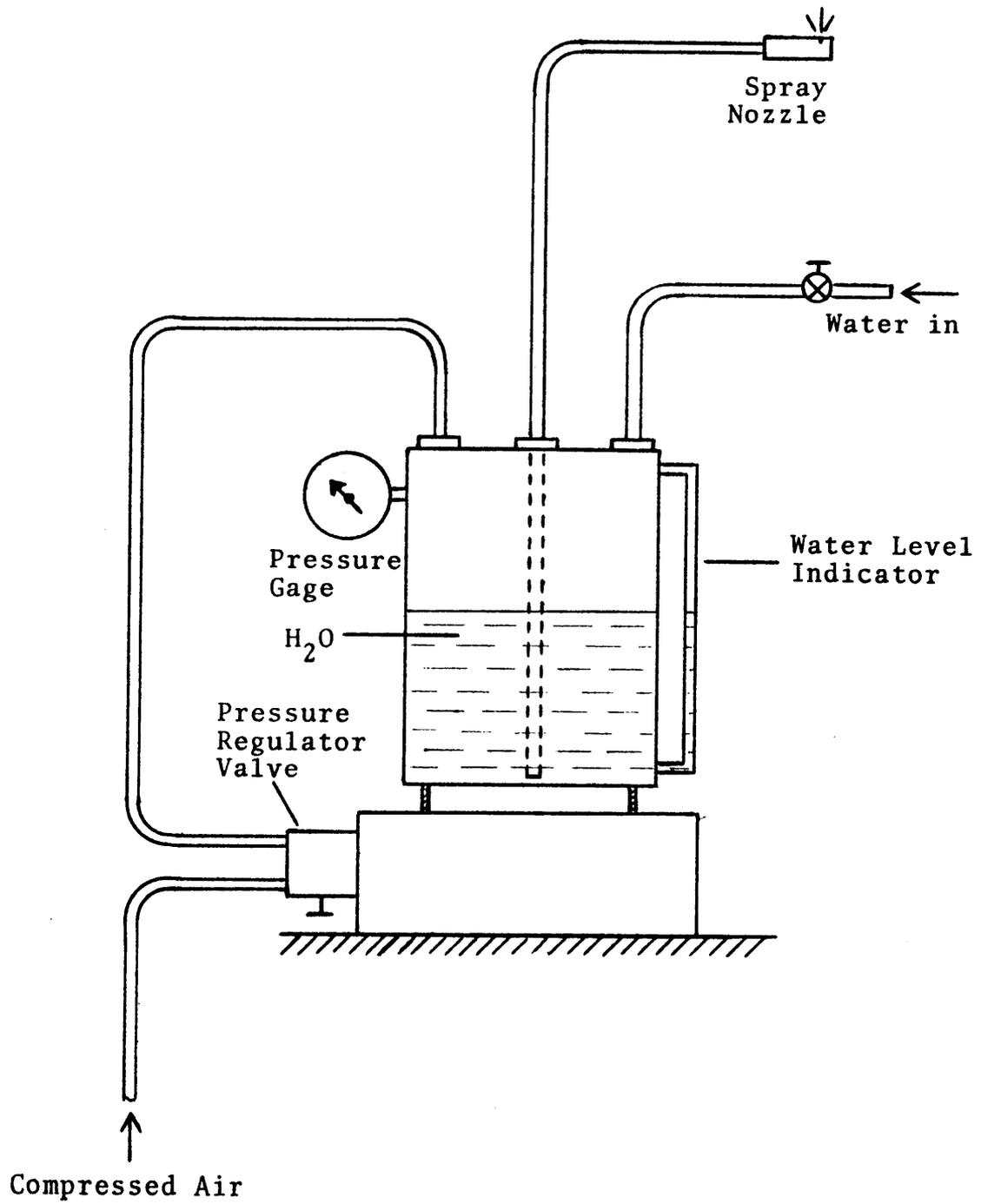


Figure 6. Water Injection System

had a 0.037-inch-diameter orifice drilled in the side near that end. Unfiltered cold water from a water main was fed into the tank and subsequently injected into the intake air stream of the diesel engine. Compressed air was allowed to enter the tank through a pressure regulator valve which limited the maximum overpressure to 30 psig.

Experimental Procedure

Preparation of Molecular Sieve Column

The 3/16 in. column was straightened and emptied of old molecular sieve, and then purged with compressed air. New 40-60 mesh molecular sieve 13X was prepared by pulverizing commercially available cylindrical pellets and passing the granulated material through the appropriate sieving apparatus several times to assure that only grains of proper size were retained. One end of the straightened column was plugged with glass wool, and the new molecular sieve was slowly poured in at the other end, using a small funnel. Uniform packing was achieved by lightly tapping the plugged end on the floor, and rapping on the sides of the column with a metal spoon. When the column was full, the open end was plugged with glass wool. The column was then wound into a coil so that its 6½ ft length could be accommodated in the compact space available in the chromatograph.

When molecular sieve is handled in atmospheric air, it readily adsorbs moisture, and its ability to separate gaseous

compounds is greatly impaired. For this reason a heat treatment was necessary to reactivate the column. The initial heat treatment consisted of placing the column in a preheated, thermostatically-controlled oven, maintained at 300°C, for three hours. Helium flowed continuously through the column at a rate of approximately 20 ml/min.

A similar treatment was used to reactivate the column after ten diesel exhaust gas samples had been analyzed. In this case the heating time was extended to four hours. This improved resolution slightly and increased retention times.

Several trials using low concentrations of NO (less than 500 ppm) revealed that the NO was being adsorbed in the column, rather than separated and eluted. As mentioned previously, this was believed to be due to the presence of overactive sites in the molecular sieve where NO molecules became permanently bound. The column was therefore connected to a lecture bottle of NO and purged with approximately 100 cc of that substance at room temperature. This procedure effectively neutralized the overactive sites in the molecular sieve and enabled it to successfully separate small quantities of NO. The column was then returned to the chromatograph.

An attempt was also made to activate a 1/4 in. stainless steel column which had been prepacked with 30-60 mesh molecular sieve 5A. It was thought that much better resolution could be attained using this column. First it was heat

treated at 300°C for three hours while helium flowed slowly through it. Efforts to make it separate small amounts of NO proved totally unsuccessful; several purges with pure NO apparently failed to saturate the molecular sieve to the point where the overactive sites were effectively neutralized. The result was that this column could not be satisfactorily activated using the same techniques which had been used on the 13X column. Perhaps a treatment such as that used by Dietz (11) would have been more successful. Additionally, it was felt that the excessive retention times obtained with this column would be a handicap when analyzing exhaust gases.

Calibration

The heater in the chromatograph was switched on and the system was allowed to stabilize overnight, or for a least six hours. The carrier gas (helium) pressure was set at 25 psig. When flow through the system was established (indicated by the soap bubble flowmeter), the thermal conductivity cell current was switched on. Cell current was maintained at 200 milliamperes during all experiments. The carrier gas flow rate was adjusted for 40 ml/min; this value was used throughout the investigation. The recorder was switched on and zeroed by setting the attenuation control on the chromatograph at the "Short" position.

The actual calibration procedure entailed mixing known concentrations of the compounds to be analyzed (CO₂, CO, and

NO) in a suitable container, introducing a predetermined amount of this mixture into the chromatograph for analysis, and then recording the response. Peak heights were used for all quantitative determinations in this investigation. When peak heights for several concentrations were known, a calibration curve could be plotted for each compound. This procedure is outlined by McNair and Bonelli (28). Calibration chromatograms also provided retention time data which could be used in subsequent identifications.

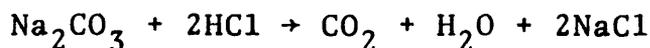
Sample mixtures of known concentration were produced with the apparatus shown in Fig. 5. P_1 and P_2 were set so that when needle valve V was opened, helium would flow through line a into the bottle and then out through line c into the sample loop in the chromatograph. In this manner, helium was used to purge the glass bottle of air and other gaseous residuals. Experience has shown that a purge volume at least five times the volume of the container being purged is required to adequately remove any undesirable compounds which may be present. With this in mind, the helium was bled off at rates in excess of 150 ml/min for at least 50 min. This proved to be successful, as no traces of CO_2 , CO, or NO were detectable.

When the bottle was purged with a sufficient amount of helium, valves V and P_1 were closed. After the helium in the bottle had stabilized at atmospheric pressure, P_2 was also closed. Thus, the bottle was in effect a sealed container

which held 1063 cc of helium at atmospheric pressure. Next, small quantities of sample gas at atmospheric pressure were injected into the bottle through the rubber septum with a 1 ml gas-tight syringe. The concentration was calculated using the known volumes. For example, if 1 cc of NO were injected into the bottle, then the concentration would be 1 part NO in 1064 parts of mixture, or about 940 parts per million.

The CO and NO were contained in lecture bottles. Small amounts were allowed to bleed out into rubber hoses and stabilize at atmospheric pressure, at which time the syringe was inserted into the hose and the desired quantity withdrawn.

Carbon dioxide was generated by the reaction of sodium carbonate with diluted hydrochloric acid. The chemical equation for this reaction is:



A chilled glass container was used so that any water vapor formed would condense on the walls. The dry CO₂ left the container through a small-orifice glass tube and then passed into a rubber hose, where samples could be taken with the syringe.

Initially, CO₂, CO, and NO were prepared and analyzed separately to ascertain the linearity of their respective calibration curves, and to identify retention times. After

it was established that the curves were indeed linear, the three compounds were mixed and analyzed together.

In order to be certain that a homogeneous mixture existed in the 1063 cc glass bottle, it was necessary to allow at least twenty minutes for gaseous diffusion to occur. Actually, the gases probably adequately diffused in much less time than this; however, to be on the safe side, twenty minutes was set as a minimum.

Sample mixtures were introduced into the chromatograph for analysis by means of the 2.5 ml sample loop. Again referring to Fig. 5, P_2 was opened and P_1 was set so that line *b* was unobstructed. Then, by moving the small vial up the ring stand and reclamping it, mercury was caused to flow through line *b* and into the bottle, displacing a certain volume of sample gas out the other end through the sample loop. Predetermined marks on the ring stand stem enabled the vial to be raised to a position which assured adequate purging of the sample loop with the mixture. When the gas in the sample loop had reached equilibrium at atmospheric pressure, the gas sampling valve was activated and the 2.5 ml sample in the loop was swept away by the flowing carrier gas.

The components in the sample mixture were physically separated as they moved through the columns. As each compound was eluted from a column and passed across the filament in the thermal conductivity cell, a distinct peak

appeared on the recorder. The heights of the appropriate peaks were measured (chart units were used), and these were plotted as functions of concentration.

The procedure for mixing and analyzing samples was repeated for several different concentrations until enough data was obtained to plot accurate calibration curves. Calibration curves and representative chromatograms appear in Section IV. It was necessary to calibrate the chromatograph prior to tests of diesel exhaust and as close as practicable to the actual times of those tests in order to preclude the possibility of operating conditions changing between the time of calibration and the time of exhaust gas analysis.

Analysis of Diesel Exhaust

In most cases the chromatograph was ready to operate because previous calibration tests had recently been completed. The calibration apparatus was disconnected from the sample loop and the exhaust gas sampling probe was connected in its place. A heat shield, which had been fabricated from fiberglass insulation, was inserted between the diesel engine and the chromatograph to protect the latter from engine heat.

Commercially available Number 2 fuel oil was used in all tests. Although two different fuels were utilized, both were assumed to meet or exceed the specifications of ASTM

Standard D396-73. The possibility of nitrogen compounds in the fuel reacting to form NO during the combustion process, as suggested by Pinkerton (29), was acknowledged; however, it was felt that overall NO amounts arising from this source would be relatively insignificant in comparison to levels produced by the dissociation and reaction (during combustion) of oxygen and nitrogen from the intake air. Therefore, no corrections were made, and the NO concentrations reported were gross amounts, irrespective of the origin of the reactants.

The dynamometer was operated in the speed control mode. Preliminary tests had shown that maximum NO concentrations occurred when the engine speed approximated 1400 rpm; therefore, it was decided to conduct all tests at this speed so maximum NO responses would be obtained on the chromatograms. The engine was allowed to warm for at least thirty minutes before any data was taken.

Different loads were placed on the engine while it ran at 1400 rpm. The diesel was allowed to operate at a given load until the exhaust manifold temperature had stabilized, and then the actual analysis of exhaust gases was made. When manifold temperature stabilization was indicated by the pyrometer, the valve on the exhaust gas sampling probe was opened (see Fig. 3) and exhaust flowed into the sample loop. To assure adequate purging, the flow of exhaust gas was allowed to continue at a moderate rate for one minute. Then

the needle valve was closed, and immediately thereafter the gas sampling valve was actuated. While the sample was being analyzed another load was placed on the engine so that by the time one exhaust analysis test had been completed, operating conditions were correct for testing the next sample. The analysis time for each test generally ranged from five to six minutes.

Altogether, eighteen diesel exhaust analyses were made. After the molecular sieve column had undergone the three-hour heat treatment and NO purge, and the chromatograph was calibrated, five tests were made at 1400 rpm and loads ranging from 90 lb to 197 lb. The chromatograph was then recalibrated and five more similar runs were made.

The molecular sieve column was then removed and heat-treated for four hours, after which it was purged with NO and returned to the chromatograph, and that instrument was again calibrated. During this time the valve timing and injection timing on the engine were reset to the manufacturer's specifications in an effort to reduce moderate load CO levels, which the previous tests had shown to be relatively high.

Subsequent tests included one run at 1400 rpm and maximum load, using fuel which had been in storage for several years. Three runs were also made using a quantity of recently procured commercial fuel. One test was at maximum load, and the other two were at intermediate loads. The

stainless steel probe was used in all cases. No differences in exhaust emission characteristics were detected with the two fuels.

Next, a glass probe was connected between the diesel exhaust pipe and the chromatograph. One test was made at 1400 rpm and maximum load to determine if probe composition had any effect on NO levels. Apparently it did not, for there was no significant change in the amount of NO indicated on the chromatogram.

The last phase of the diesel exhaust gas test routine was concerned with analyzing the effectiveness of water injection into the intake air stream as a means of reducing NO concentrations. The system shown in Fig. 6 was calibrated by measuring the water mass flow rates obtained with various tank overpressures. This data was then used to plot the calibration curve shown in Fig. 7. When the calibration had been completed, the spray nozzle was inserted in the intake air line which extended from the turbocharger to the intake manifold of the diesel engine. It was placed at a point 17.0 in. upstream from the manifold, and the nozzle orifice faced upstream toward the turbocharger.

The engine was operated at 1400 rpm and maximum load. A mercury-filled U-tube manometer indicated the pressure of the intake air at the point where water was to be injected. The calibration curve was then used to determine the tank overpressure which would be necessary to obtain the desired

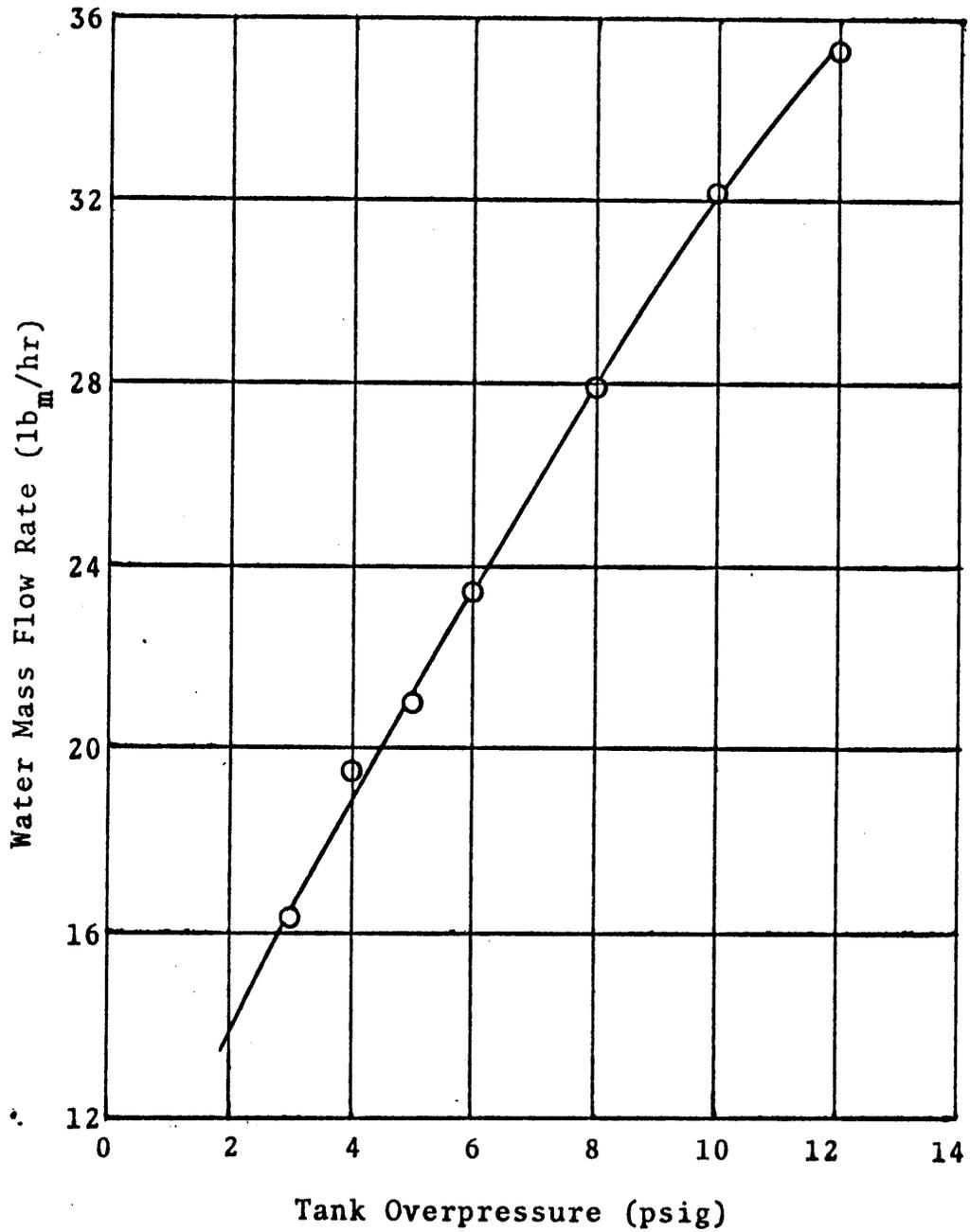


Figure 7. Calibration Curve For Water Injection System

water mass flow rate. Three water/fuel mass ratios were utilized: 0.5 lb H₂O/lb fuel, 1.0 lb H₂O/lb fuel, and 0 lb H₂O/lb fuel (no water). The stainless steel probe conveyed exhaust samples from the exhaust pipe to the chromatograph.

A problem encountered during the water injection tests was the leaking of liquid water around the intake manifold gasket. This was alleviated by tightening the bolts which fastened the manifold to the cylinder head.

The chromatograph required close attention during all exhaust gas tests. The large variation between CO₂, NO, and CO concentrations necessitated using three different sensitivities during most tests. Typically, CO₂ was analyzed using an attenuation of "256" (minimum sensitivity). Then, after the O₂ and N₂ had eluted, the attenuation was switched to "1" (maximum sensitivity) for the analysis of NO. Immediately after the NO peak appeared, an intermediate sensitivity was selected so that the CO peak would be on scale. In some cases the drastic change in attenuation between peaks caused baseline instability. These effects can be seen in the chromatograms which appear in the next section.

IV. PRESENTATION AND DISCUSSION OF RESULTS

For the sake of clarity, this section is divided into two parts. The first part contains the results of the preliminary chromatograph calibration tests as well as an interpretation of these results. Chromatograms and calibration curves are presented. The second part deals with exhaust gas analysis results. Calibration curves which were constructed immediately prior to engine tests (i.e., those calibration curves which are directly applicable to a given set of engine tests) are also included in this part. Additionally, significant results from these tests are tabulated and plotted.

Calibration

As indicated previously, CO₂, CO, and NO samples were analyzed separately in the initial calibration tests. This was done to establish retention times of the compounds, and thus the sequence of elution, and also to affirm the linearity of calibration curves. More than fifty separate tests were run during this phase of the investigation in order to obtain sufficient data to warrant the conclusion that the thermal conductivity cell produced linear responses for all three compounds. In addition to providing valuable information about the nature of the calibration curves, this phase of the investigation led to the development of several useful

techniques. The most notable of these were the calibration sample preparation and the analysis procedure, and the successful reactivation technique used on the molecular sieve column.

Figures 8, 9, and 10 are chromatograms selected from the initial calibration tests to illustrate the elution sequence of CO_2 , CO, and NO respectively. In each of the chromatograms, the instant of sample introduction into the chromatograph is indicated by a small vertical arrow in the lower left corner. Time is measured along the abscissa; the scale is 1 in. = 1 min. The absolute peak height is found by multiplying the observed peak height by the attenuation.

A typical CO_2 peak appears in Fig. 8. The hump immediately after sample introduction is caused by a pressure surge. When the gas sampling valve is actuated, the carrier gas flow is momentarily interrupted and, consequently, the rate of heat transfer from the filaments in the thermal conductivity cell to the surrounding gas decreases. The temperature of the filaments rises, causing their electrical resistance to increase, and the Wheatstone bridge circuit becomes unbalanced. This produces a drastic shift in baseline position. As the carrier gas flow rate returns to normal, the baseline gradually settles down to its original position. This phenomenon is only observed when very high sensitivities are utilized. The heights of peaks which appear on the pressure surge hump (i.e., CO_2) are determined by

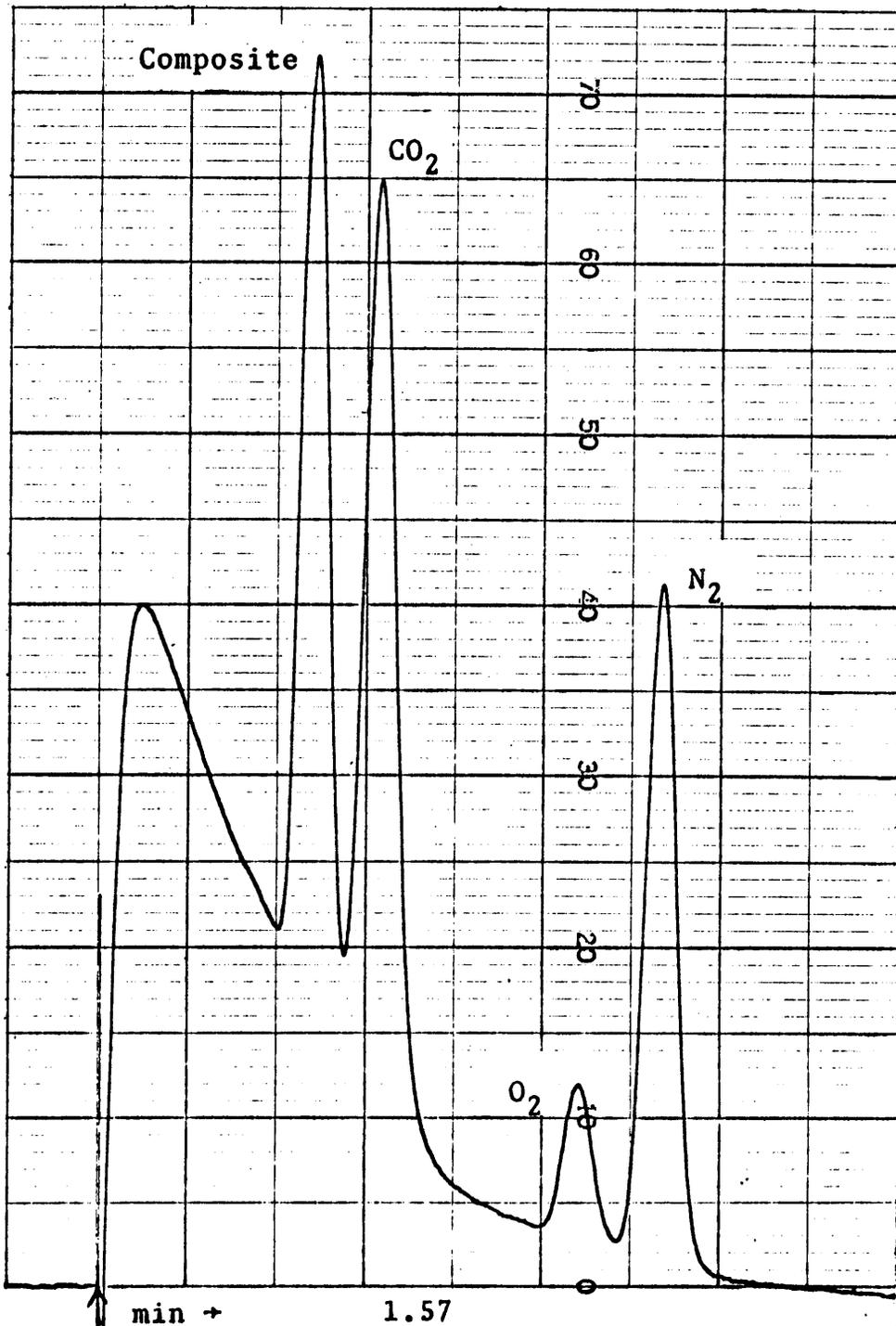


Figure 8. Carbon Dioxide: Concentration = 470 ppm, Attenuation = 1.

first connecting the baseline with the aid of a French curve, and then measuring the vertical distance from the peak maximum to this constructed line.

A total of four peaks appear in Fig. 8. In the order of their appearance, they are the composite peak, CO_2 , O_2 , and N_2 . CO_2 is separated from other gases in the first column. The other gases (in this case air) elute together and appear as the composite peak. All compounds then pass into the second column, where the CO_2 is adsorbed. The gases which formerly comprised the composite peak are further separated. In this particular case, the separation yields O_2 and N_2 .

The presence of air peaks in these chromatograms indicates that air apparently entered the system at some point. One explanation is that the 1063 cc glass bottle in which samples were mixed was not adequately purged with helium. This does not seem likely though, for in one case the bottle was purged for sixteen hours and the same results were obtained. Therefore, it is more probable that a very small quantity of air entered the system when the syringe was pushed through the rubber septum on the bottle, or when the gas sampling valve was actuated. In any case, it was determined that air peaks did not adversely affect the accuracy of the experiments, because recorder response was proportional to the actual amount of a compound present in the sample loop.

In general the foregoing comments also apply to Figures

9 and 10. Figure 9 shows the composite peak, followed by O_2 , N_2 , and CO. Here the composite peak represents air and CO. If CO_2 had been present, it would have been eluted immediately after the composite peak, as in Fig. 8. The composite peak is followed by O_2 , N_2 , and NO in Fig. 10. Tailing of the NO peak is evident here; this chromatogram was made before the treatment technique for the molecular sieve column had been fully developed.

The calibration curves plotted in Fig. 11 were constructed from data obtained during the course of these preliminary calibration tests (see Table 2). The absolute peak heights of each compound are plotted as functions of concentration. These curves clearly show that the response of the detector is linear in the concentration range considered. In subsequent experiments where CO_2 concentrations substantially beyond this range were frequently encountered, the response was also assumed to be linear, and the calibration curves were extrapolated accordingly.

Subsequent calibration tests were conducted by mixing predetermined quantities of CO_2 , CO, and NO together in the glass bottle. The elution sequence obtained when using this method is shown in Fig. 12. This technique reduced the time required for calibration significantly.

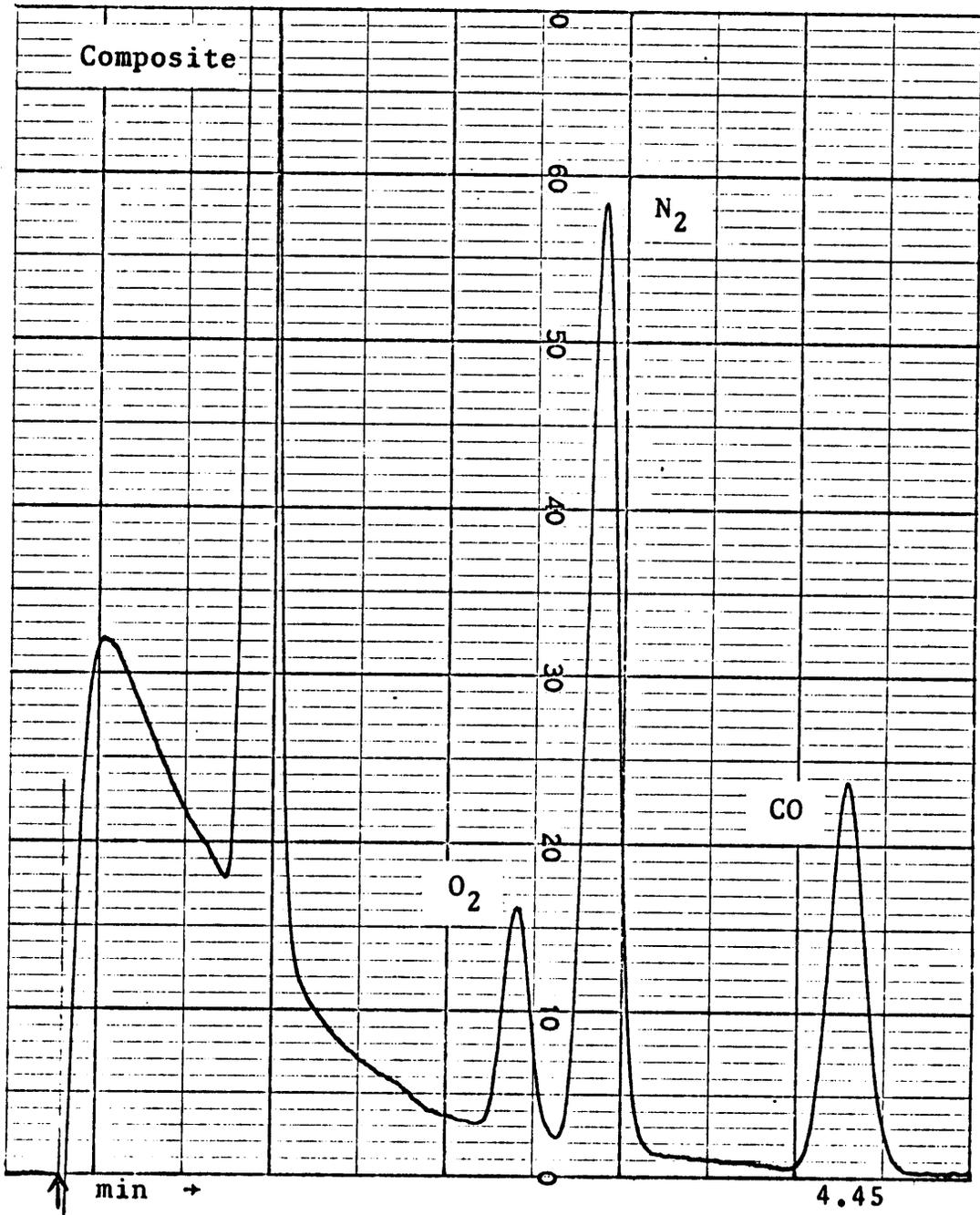


Figure 9. Carbon Monoxide: Concentration = 376 ppm, Attenuation = 1.

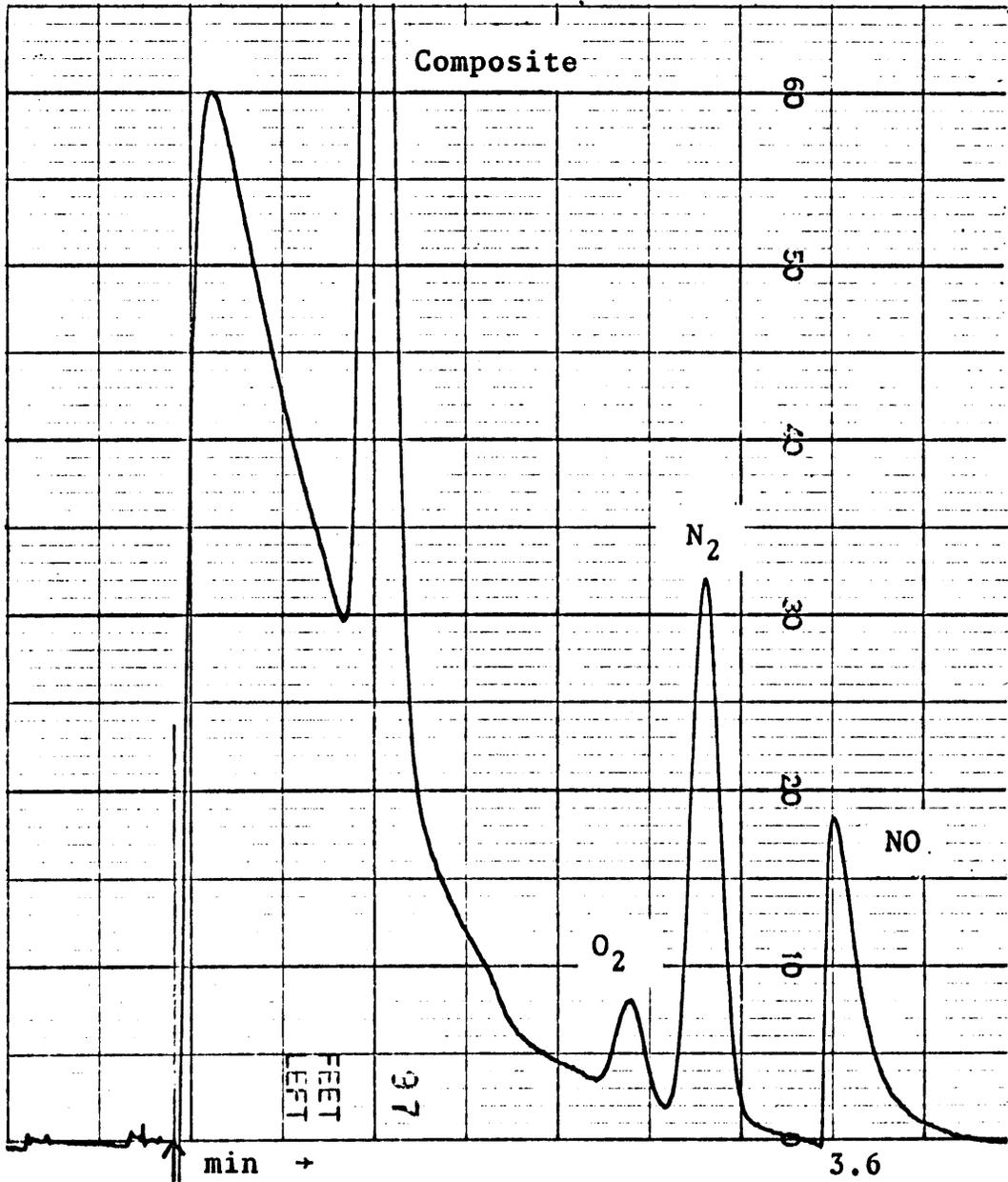


Figure 10. Nitric Oxide: Concentration = 470 ppm,
Attenuation = 1.

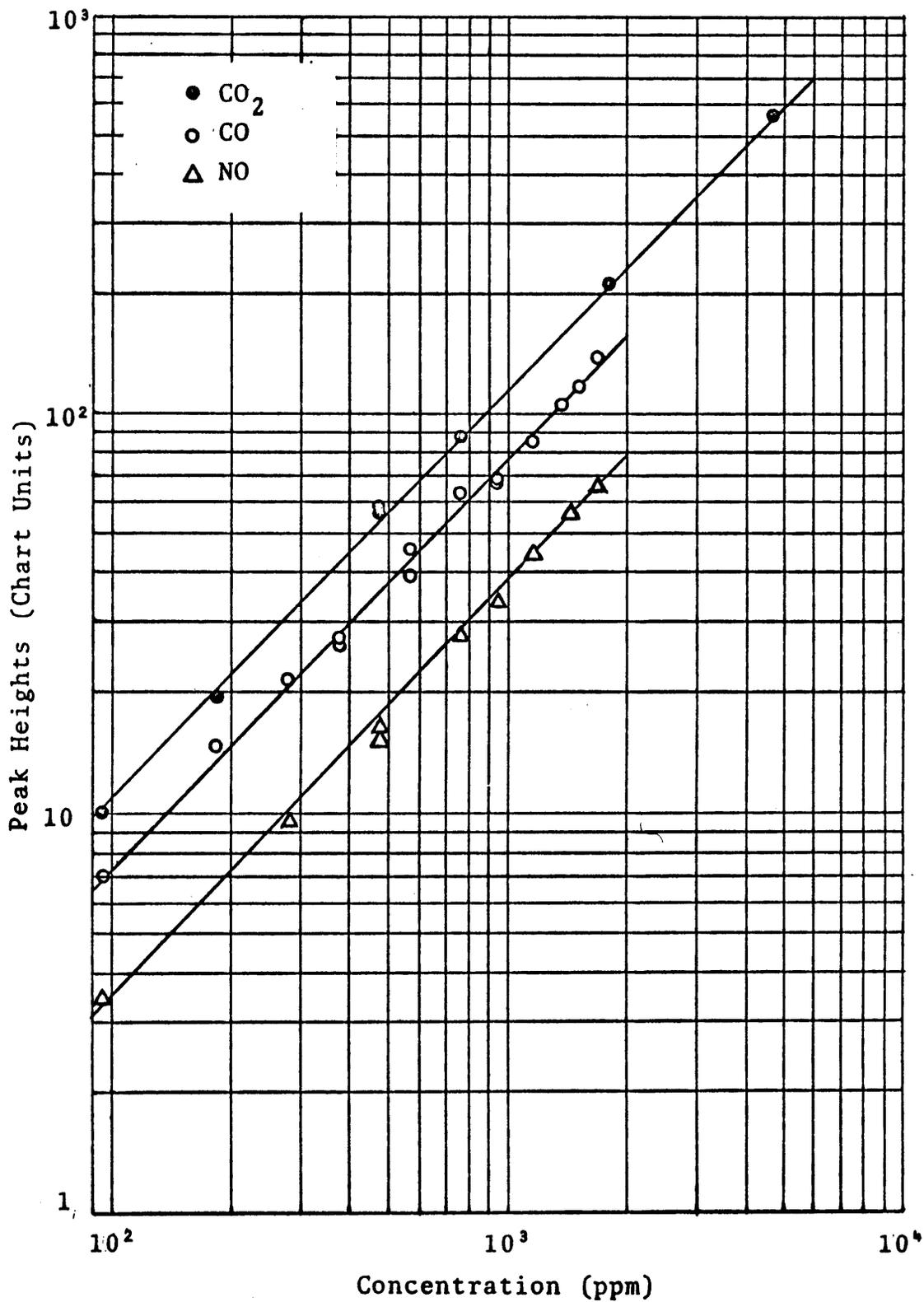


Figure 11. Preliminary Calibration Curves for CO_2 , CO , NO .

Table 2. Calibration Data for CO₂, CO, and NO

Compound	Concentration (ppm)	Chromatograph Attenuation	Observed Peak Height (Chart Units)	Absolute Peak Height (Chart Units)
CO ₂	94	1	10	10
	188	1	19.5	19.5
	470	2	28	56
	470	1	54	54
	752	2	43.5	87
	1880	4	51	204
	4700	8	68.5	548
CO	94	1	7	7
	188	1	14.6	14.6
	282	1	20.5	20.5
	376	1	23.5	23.5
	376	1	25	25
	564	1	39	39
	564	1	46	46
	752	1	62	62
	940	1	68	68
	940	1	66.5	66.5
	1128	2	42	84
	1320	2	53.4	106.8
	1504	2	61.7	123.4
1692	4	34.5	138	
NO	94	1	3.5	3.5
	282	1	9.5	9.5
	470	2	8	16
	470	1	18.5	18.5
	752	1	29	29
	940	1	32.5	32.5
	1128	1	44.5	44.5
	1410	1	55	55
	1692	1	63.5	63.5

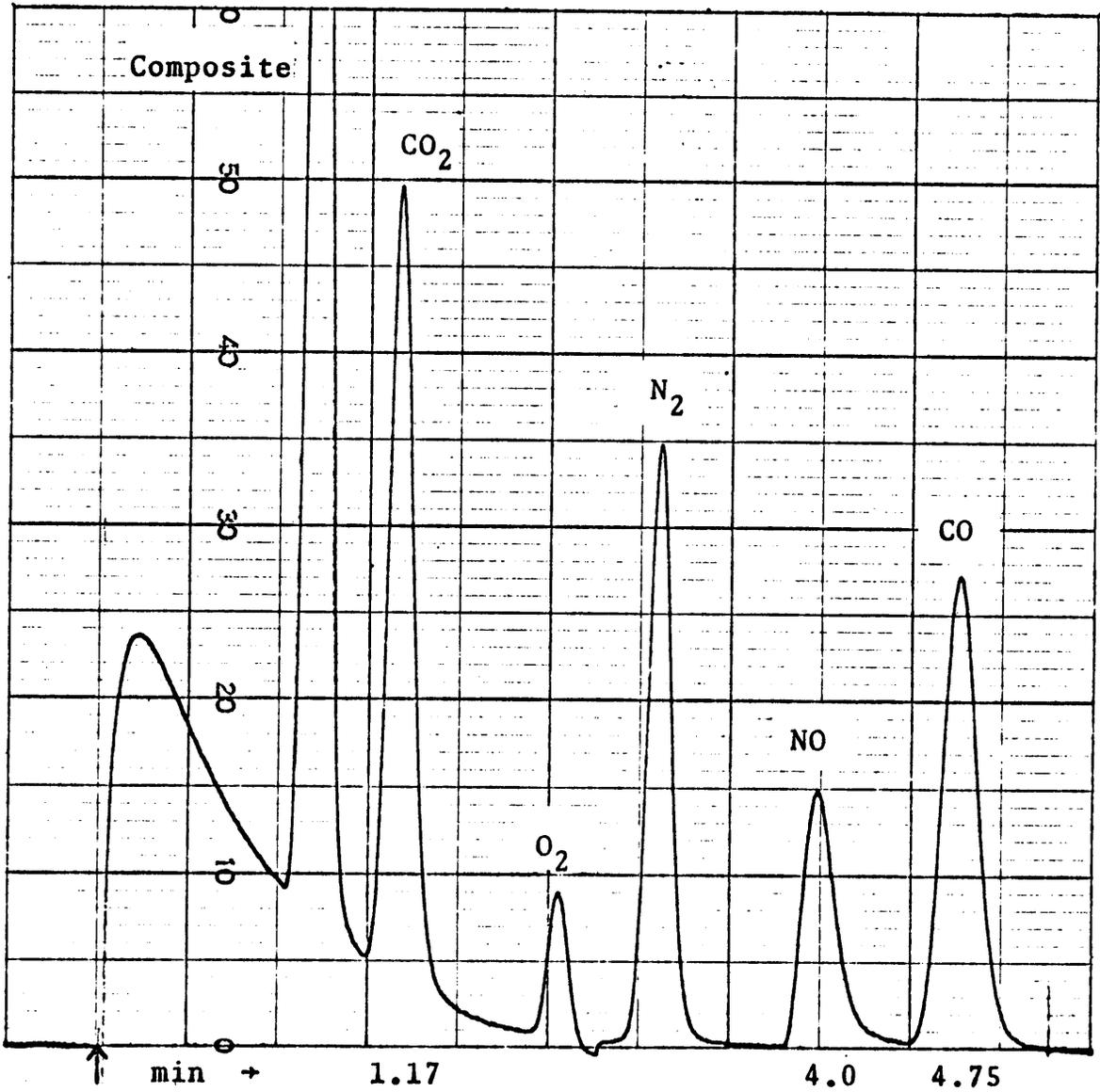


Figure 12. Chromatogram Showing Elution Sequence of CO₂, CO, and NO. Concentration = 940 ppm For Each Compound, Attenuation = 2.

Engine Tests

The eighteen engine exhaust gas tests are divided into two groups. Group I is composed of ten tests made after the molecular sieve column had undergone a 3-hour heat treatment and NO purge. The chromatograph was recalibrated after the first five tests had been completed. Group II contains the results of tests made after the molecular sieve column was heat treated for four hours and purged with NO. Water injection tests are included in this group. The data will be introduced by group in the following sequence: (1) table listing engine operating conditions and significant results from the tests, (2) calibration curves used for a set of tests, (3) representative exhaust gas chromatograms.

Fuel/air ratios for all tests were calculated from data obtained during actual engine operation. The time required to burn 1 lb of fuel was measured at five different loads and the curve shown in Fig. 13 was plotted. The fuel flow rate at a given load could then be readily obtained from this curve. Air flow was calculated using an equation from Obert (4):

$$\dot{m}_{\text{air}} = \frac{1.62 C_a P_1 d^2}{\sqrt{T_1}} \sqrt{\left(\frac{P_2}{P_1}\right)^{1.43} - \left(\frac{P_2}{P_1}\right)^{1.71}} \quad \frac{\text{lb}_m}{\text{sec}}$$

C_a = discharge coefficient (assumed to be 0.97)

P_1 = inlet air pressure (psia)

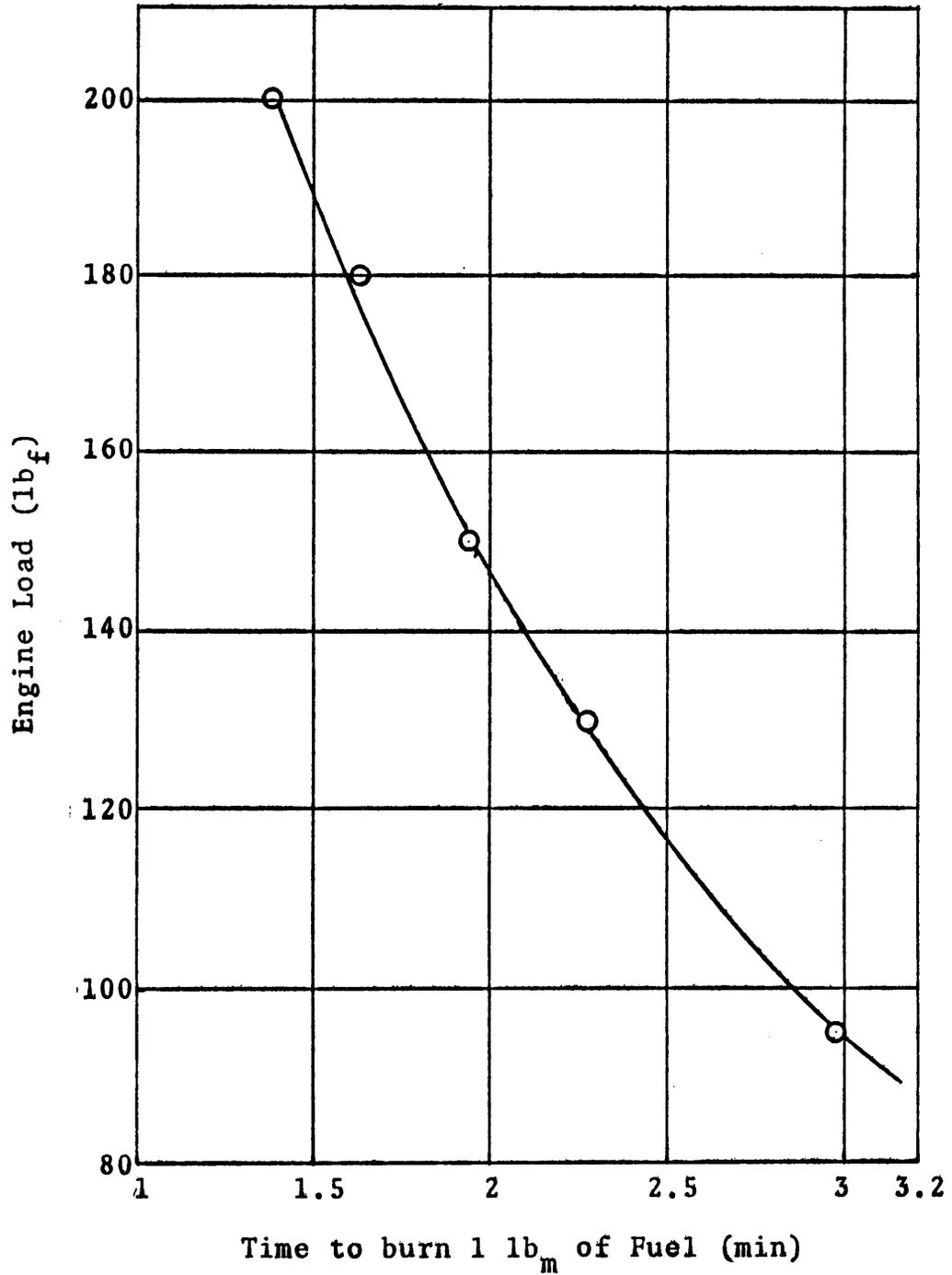


Figure 13. Fuel Consumption At 1400 RPM.

P_2 = throat pressure (psia)

d = diameter of throat (in.)

T_1 = inlet air temperature ($^{\circ}$ R)

The term "throat" refers to the restriction in the intake air stack. P_2 was measured with a water-filled, inclined U-tube manometer. The fuel/air ratio was obtained by dividing the fuel flow rate by the air flow rate.

The data shown in Table 3 summarizes the operating conditions and exhaust gas analysis results for Tests 1-5 of Group I. Blank spaces in this table (as well as those tables which follow) indicate that inconclusive data was obtained. In most cases this was due to an oversensitive attenuation selection which caused certain CO peaks to go off scale.

After the molecular seive column had been heat treated for three hours and purged with NO, it was returned to the chromatograph, and that instrument was calibrated shortly before Tests 1-5 were run. The calibration curves obtained at this time are shown in Fig. 14. These curves were used solely for the analysis of data acquired during Tests 1-5 of Group I.

Figure 15 shows the chromatogram obtained from Test 1. This chromatogram is representative of the entire set of tests, which were run at 1400 rpm and loads ranging from 90 lb to 197 lb. The truncation of the CO peak illustrates the previously discussed problem of oversensitivity.

Table 3. Engine Data. Group I, Tests 1-5.

Test	1	2	3	4	5		
RPM	1400	1400	1400	1400	1400		
Load, lb _f	185	197	135	90	90		
BHP	91.4	97.4	66.7	44.5	44.5		
BMEP, psi	129	137.4	94.1	62.7	62.7		
Inlet Air Temp., °F	75	76	76	76	76		
Relative Humidity, %	51	51	51	51	51		
Atm. Pressure, in. Hg	28.2	28.2	28.2	28.2	28.2		
Fuel Flow Rate, lb/hr	38.7	42.25	27.77	19.23	19.23		
Air Flow Rate, lb/hr	620	620	620	620	620		
Fuel/Air Ratio, lb/lb	0.0624	0.068	0.045	0.031	0.031		
Exhaust Sampling Probe	SS*	SS	SS	SS	SS		
Exhaust Temp., °F	1180	1200	940	750	750		
Exhaust Analysis Data	CO ₂	Attenuation	256	256	256	256	256
		Response	43	49.6	36	26	26.5
		% by volume	11.4	13.2	9.55	6.9	7.03
	CO	Attenuation	1	64	1	1	1
		Response		26.5	90	25	26
		% by volume		2.07	0.11	0.0305	0.032
	NO	Attenuation	1	1	1	1	1
		Response	8	7.5	3	1	1
		ppm	137	128	51	17	17

*Stainless Steel

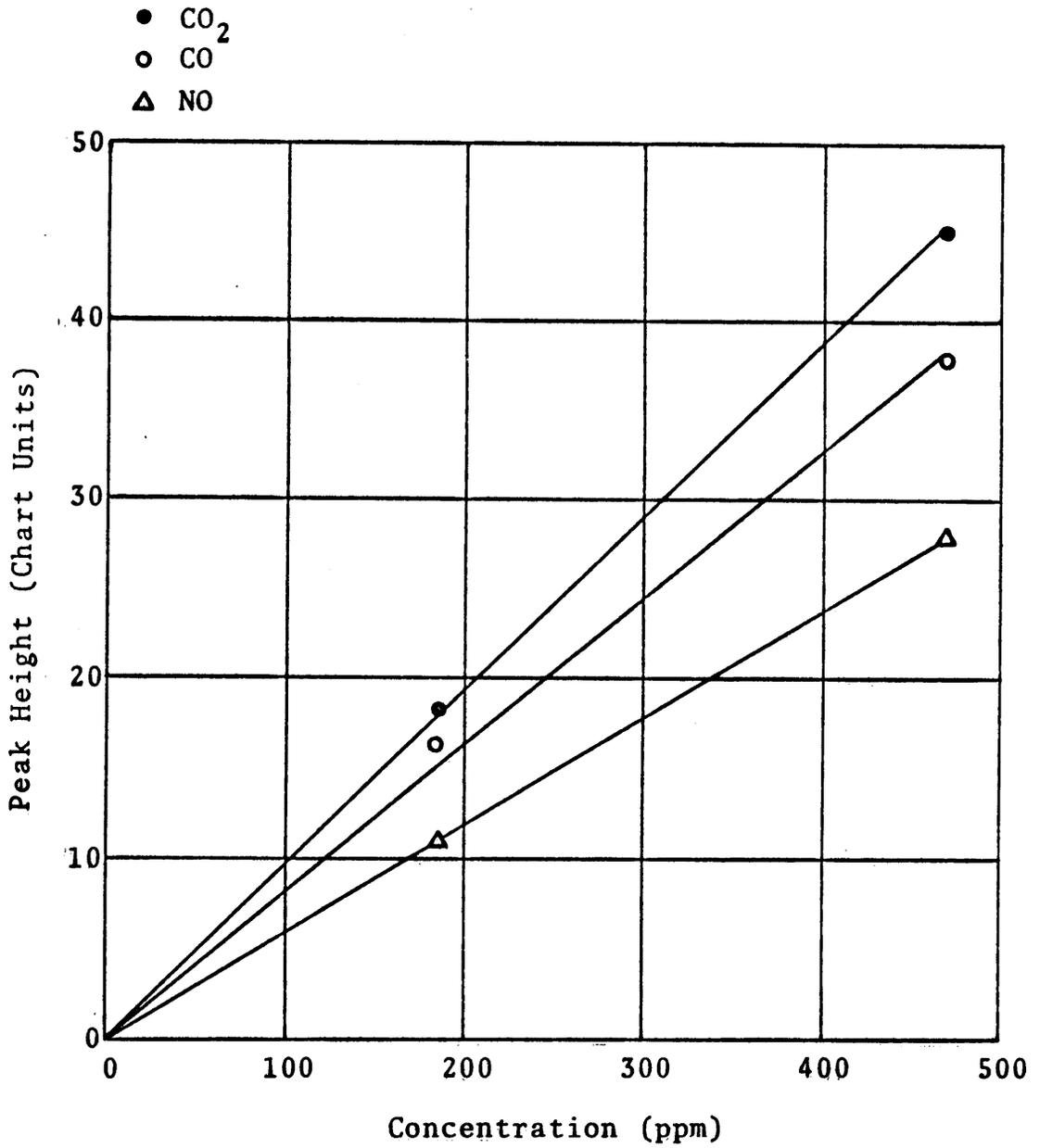


Figure 14. Calibration Curves For Group I, Tests 1-5.

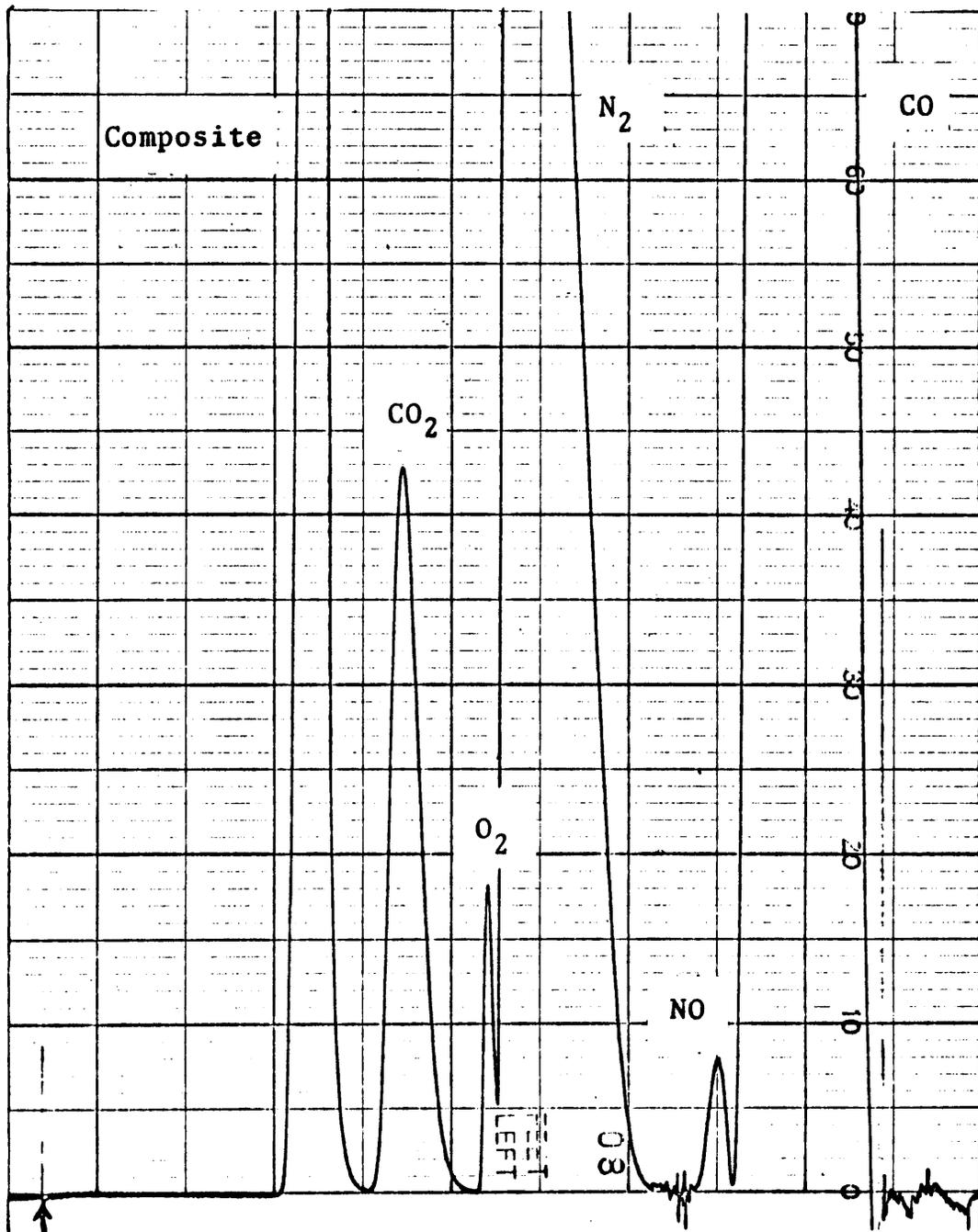


Figure 15. Chromatogram Of Diesel Exhaust Obtained After 3-Hour Heat Treatment Of Molecular Sieve Column (Group I, Test 1). Attenuation: CO₂ 256, NO 1, CO 1.

The wide range of concentrations encountered for the various compounds necessitated changing the chromatograph attenuation in the middle of each analysis. Evidence of this procedure appears in Fig. 15 in the form of baseline instability between the N_2 and NO peaks. CO_2 , O_2 , and N_2 were recorded at minimum sensitivity (attenuation = 256). Then the chromatograph was switched to maximum sensitivity (attenuation = 1) so that the relatively low levels of NO could be detected. In most cases an intermediate sensitivity had to be selected immediately after the NO peak so that CO would appear on scale. Subsequent tests showed that an attenuation of 32 should have been used for the CO peak in Fig. 15.

Referring again to Table 3, one notes that CO_2 , CO, and NO levels all show a definite trend of decreasing as the engine load decreases. CO appears to be most sensitive to load, as its concentration changes by entire orders of magnitude.

Tests 6-10 of Group I were conducted at a later date. The results of these tests are summarized in Table 4. Recalibration of the chromatograph prior to these tests provided data for the curves shown in Fig. 16. A comparison of this figure with Fig. 14 clearly shows why it is necessary to calibrate the instrument each time it is used. The fact that the slopes of the curves differ between the two figures indicate that column operating conditions have changed.

Table 4. Engine Data. Group I, Tests 6-10.

Test	6	7	8	9	10		
RPM	1400	1400	1400	1400	1400		
Load, lb _f	198	175	150	125	100		
BHP	97.9	86.5	74.1	61.8	49.4		
BMEP, psi	138	122	104.6	87.2	69.7		
Inlet Air Temp., °F	75	75	75	75	75		
Relative Humidity, %	58	58	58	58	58		
Atm. Pressure, in. Hg	28.1	28.1	28.1	28.1	28.1		
Fuel Flow Rate, lb/hr	42.55	36.14	30.93	25.64	21.13		
Air Flow Rate, lb/hr	620	620	620	620	620		
Fuel/Air Ratio, lb/lb	0.069	0.058	0.05	0.041	0.034		
Exhaust Sampling Probe	SS	SS	SS	SS	SS		
Exhaust Temp., °F	1205	1175	1025	900	790		
Exhaust Analysis Data	CO ₂	Attenuation	256	256	256	256	256
		Response	51	49	43	37	31
		% by volume	11.9	11.4	10.0	8.61	7.21
	CO	Attenuation	32	16	1	4	1
		Response	65	20		17	32
		% by volume	2.31	0.355		0.076	0.036
	NO	Attenuation	1	1	1	1	1
		Response	8			2.5	1.5
		ppm	170			53	32

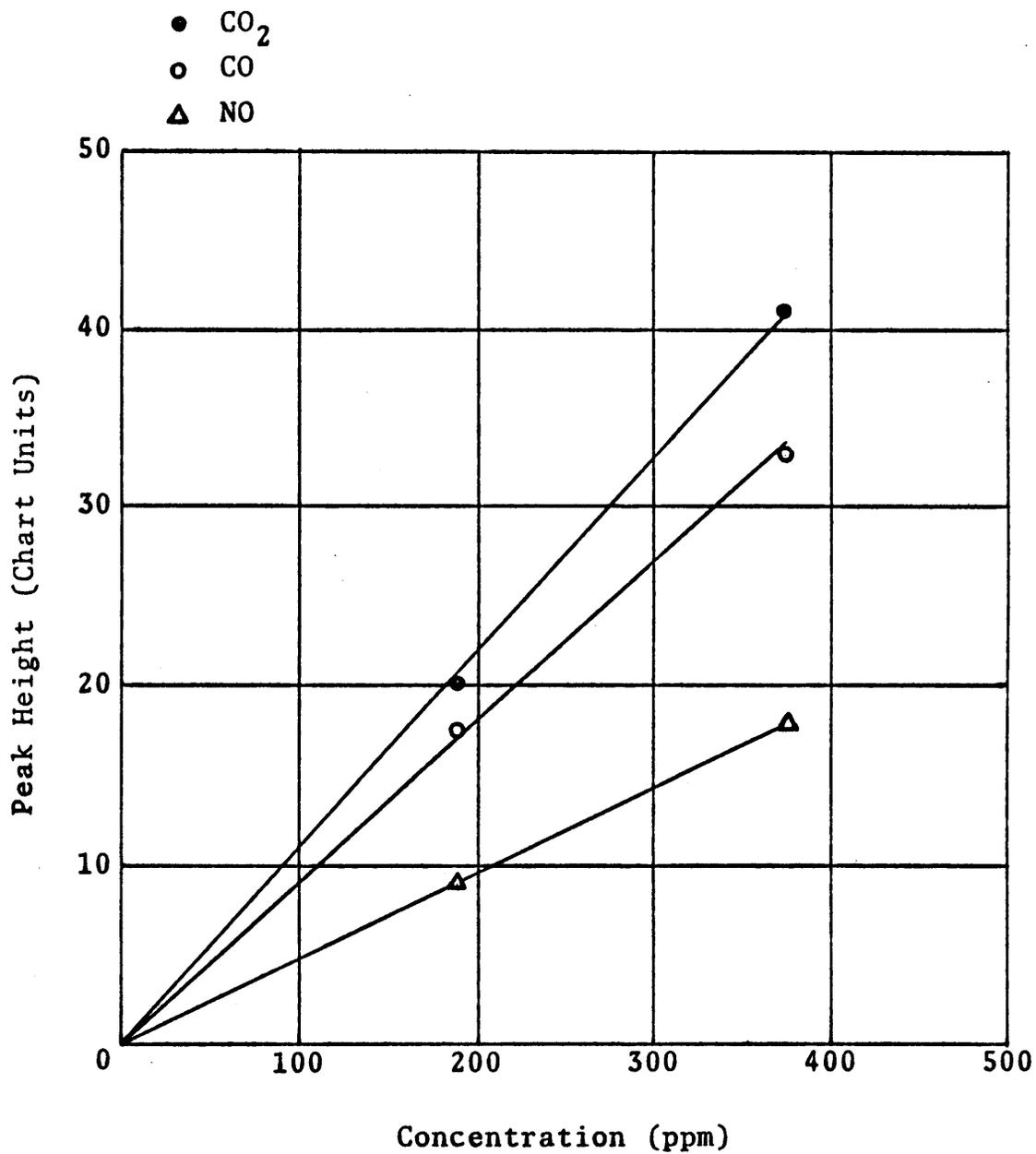


Figure 16. Calibration Curves For Group I, Tests 6-10..

Tests 6-10 of Group I were all run at 1400 rpm and at loads ranging from 100 lb to 198 lb. The results in Table 4 confirm the trend noted previously (i.e., CO₂, CO, and NO increase as the load increases).

Figure 17 shows a typical chromatogram taken from this set of tests. An important characteristic of this chromatogram is the relatively poor separation of the NO peaks from the CO peak. The resolution of these two peaks was so poor in tests 7 and 8 that it was impossible to obtain conclusive data for NO. The decreasing resolution was probably caused by contamination of the molecular sieve column by CO₂.

The peak resolution problem was solved by heat treating the molecular sieve column for four hours and then purging with NO. All Group II data was obtained after this treatment and subsequent chromatograph calibration.

The results of the first five tests from Group II are summarized in Table 5. The calibration curves used for all Group II analyses appear in Fig. 18. Tests 1 and 2 were both run at 1400 rpm and maximum load, but different fuels were used. Old fuel, which had been in storage for several years, was used in Test 1, while a newer fuel was used in Test 2. Although the physical properties of these fuels were not determined, it appears that the newer fuel may have had a slightly lower specific gravity than the old. This conclusion is based on the decrease in maximum obtainable power at 1400 rpm, and the slight reduction in CO concentration.

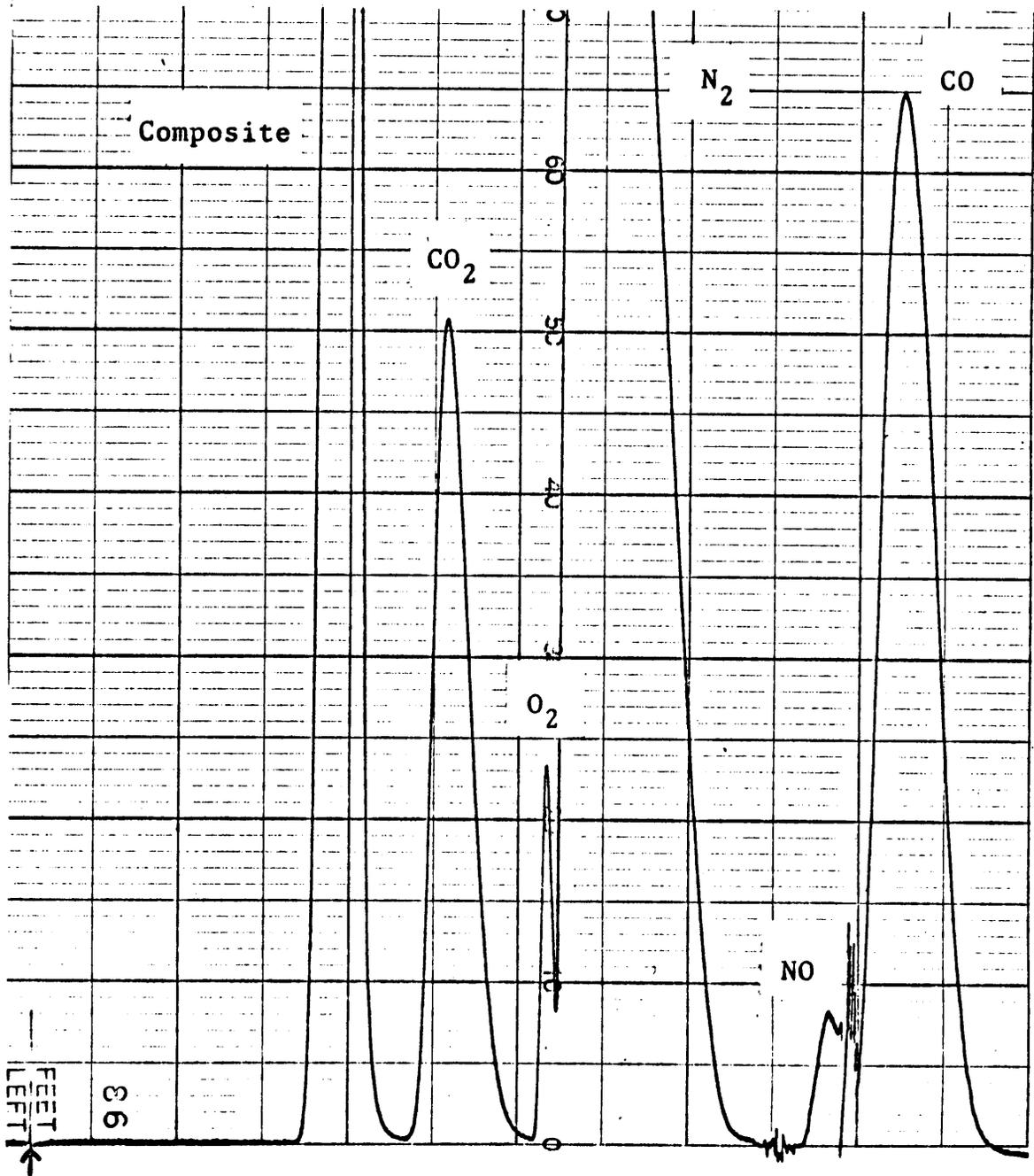


Figure 17. Chromatogram Of Diesel Exhaust Obtained After 3-Hour Heat Treatment Of Molecular Sieve Column And Recalibration Of Gas Chromatograph (Group I, Test 6). Attenuation: CO_2 256, NO 1, CO 32.

Table 5. Engine Data. Group II, Tests 1-5.

Test	1	2*	3*	4*	5		
RPM	1400	1400	1400	1400	1400		
Load, lb _f	193	190	175	150	189		
BHP	95.4	93.9	86.5	74.1	93.4		
BMEP, psi	134.6	132.5	122	104.6	131.8		
Inlet Air Temp., °F	77	78	78	78	80		
Relative Humidity, %	37	37	37	37	37		
Atm. Pressure, in. Hg	27.92	27.92	27.92	27.92	27.92		
Fuel Flow Rate, lb/hr	40.8	40.0	36.14	30.93	39.73		
Air Flow Rate, lb/hr	592	592	592	592	592		
Fuel/Air Ratio, lb/lb	0.069	0.068	0.061	0.052	0.067		
Exhaust Sampling Probe	SS	SS	SS	SS	Glass		
Exhaust Temp., °F	805	1160	1090	1000	1160		
Exhaust Analysis Data	CO ₂	Attenuation	256	256	256	256	256
		Response	48	49	47	41	50
		% by volume	11.6	11.8	11.3	9.87	12.03
	CO	Attenuation	32	32	8	2	32
		Response	42	29	41	68.5	36
		% by volume	2.34	1.61	0.57	0.238	2.00
	NO	Attenuation	1	1	1	1	1
		Response	12	12	9	6	11
		ppm	353	353	265	176	324

*New fuel used.

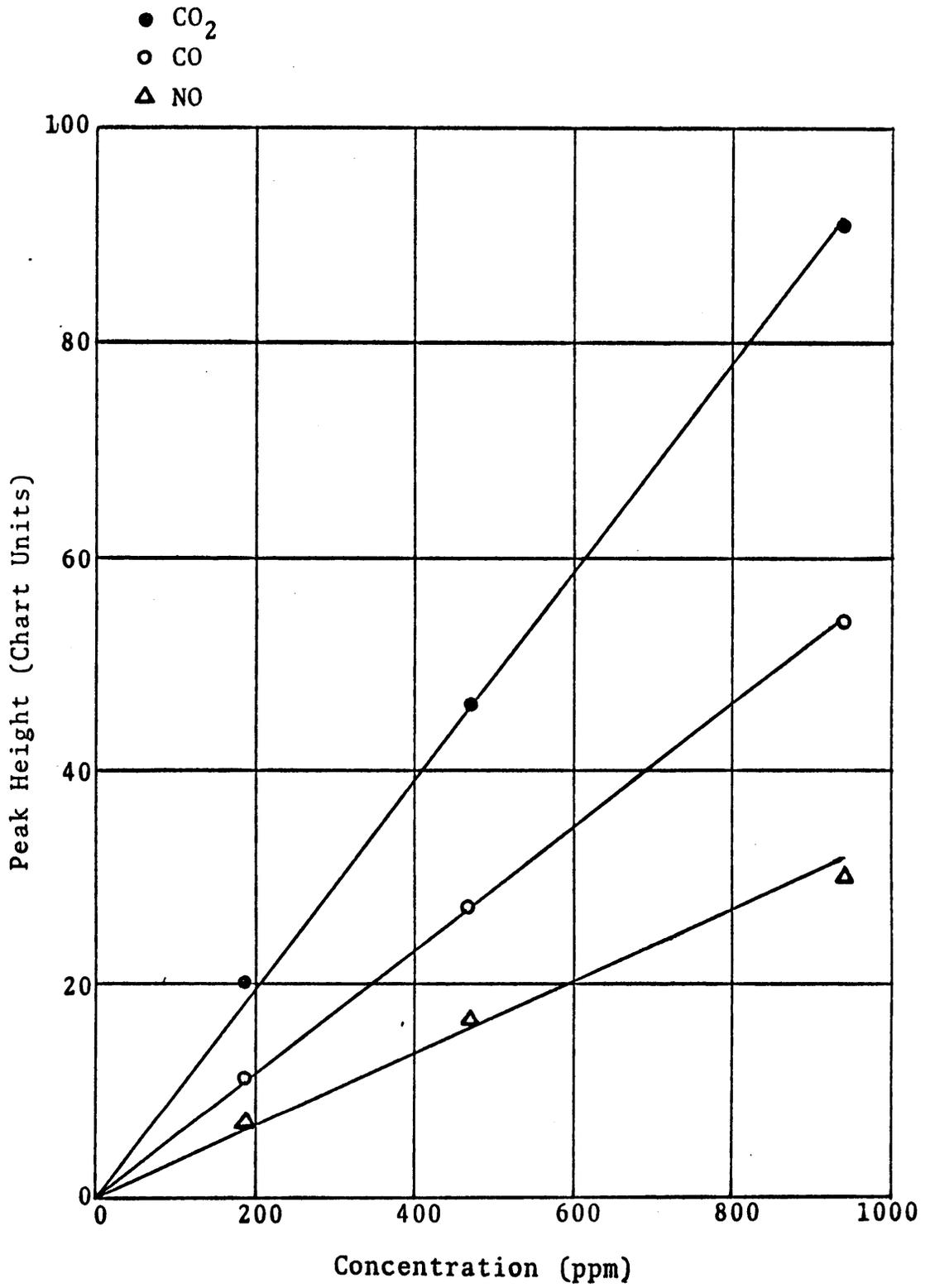


Figure 18. Calibration Curves For Group II.

The reader will recall that Marshall and Flemming (21) found CO levels increased with the specific gravity of the fuel being burned. The chromatograms obtained during Tests 1 and 2 appear in Fig. 19 and Fig. 20 respectively. CO₂ and NO levels remained virtually unchanged when the newer fuel was used.

The stainless steel probe was used for all tests except Test 5. A glass probe was used for this test in an effort to determine if probe composition had any effect on NO concentrations in the exhaust. A very slight reduction in NO occurred when the glass probe was used; however, it was felt to be insignificant.

Tests 6-8 of Group II were the water injection tests. Water/fuel mass ratios ranging from 0 lb/lb to 0.75 lb/lb were used and the results shown in Table 6 were obtained. The 0.75 water/fuel ratio was used in Test 7, and NO levels decreased by 15%. The chromatogram from this test is shown in Fig. 21. At lower water/fuel ratios the NO levels remained constant. Increasing the water/fuel ratio would probably effect further reductions in NO, as reported by previous investigators. A slight reduction in brake mean effective pressure was also noted in Test 7. All water injection tests were conducted at 1400 rpm and maximum load.

All of the chromatograms obtained from Group II tests showed excellent resolution of the NO and CO peaks. This indicates that the 4-hour heat treatment of the molecular

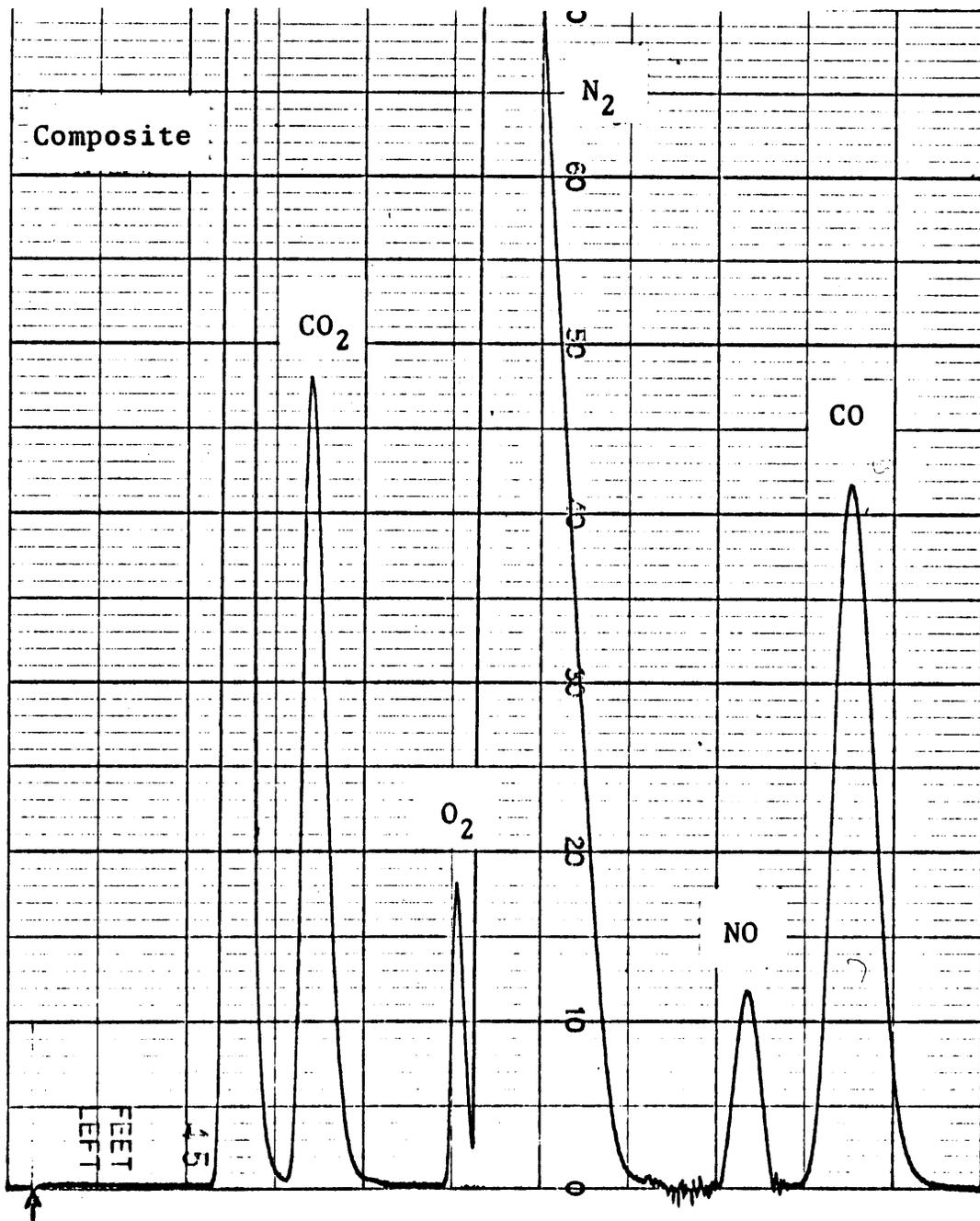


Figure 19. Chromatogram Of Diesel Exhaust Obtained After 4-Hour Heat Treatment Of Molecular Sieve Column (Group II, Test 1). Attenuation: CO₂ 256, NO 1, CO 32.

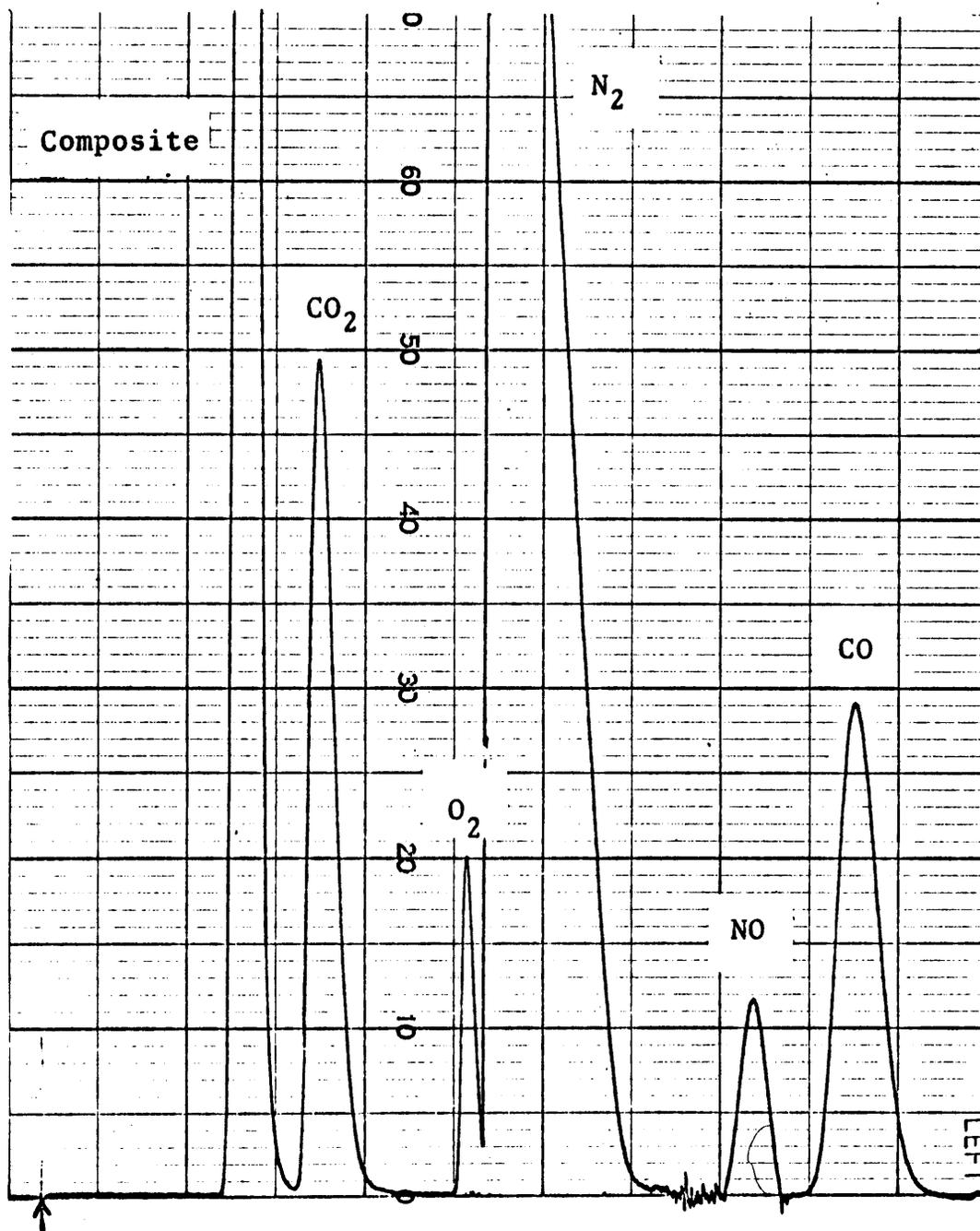


Figure 20. Chromatogram of Diesel Exhaust Obtained When New Fuel Was Used (Group II, Test 2). Attenuation: CO_2 256, NO 1, CO 32.

Table 6. Engine Data. Group II,
Tests 6-8 (Water Injection Tests).

Test	6	7	8		
RPM	1400	1400	1400		
Load, lb _f	189	186	189		
BHP	93.4	91.9	93.4		
BMEP, psi	131.8	129.7	131.8		
Inlet Air Temp., °F	79	79	79		
Relative Humidity, %	37	37	37		
Atm. Pressure, in. Hg	27.92	27.92	27.92		
Fuel Flow Rate, lb/hr	39.73	38.96	39.73		
Air Flow Rate, lb/hr	592	592	592		
Fuel/Air Ratio, lb/lb	0.067	0.066	0.067		
Exhaust Sampling Probe	SS	SS	SS		
Exhaust Temp., °F	1150	1100	1170		
Water/Fuel Mass Ratio, lb/lb	0.38	0.75	0		
Exhaust Analysis Data	CO ₂	Attenuation	256	256	256
		Response	49.6	50	50.4
		% by volume	11.9	12.03	12.1
	CO	Attenuation	32	32	32
		Response	46	51	48
		% by volume	2.56	2.84	2.67
	NO	Attenuation	1	1	1
		Response	10	8.5	10
		ppm	294	250	294

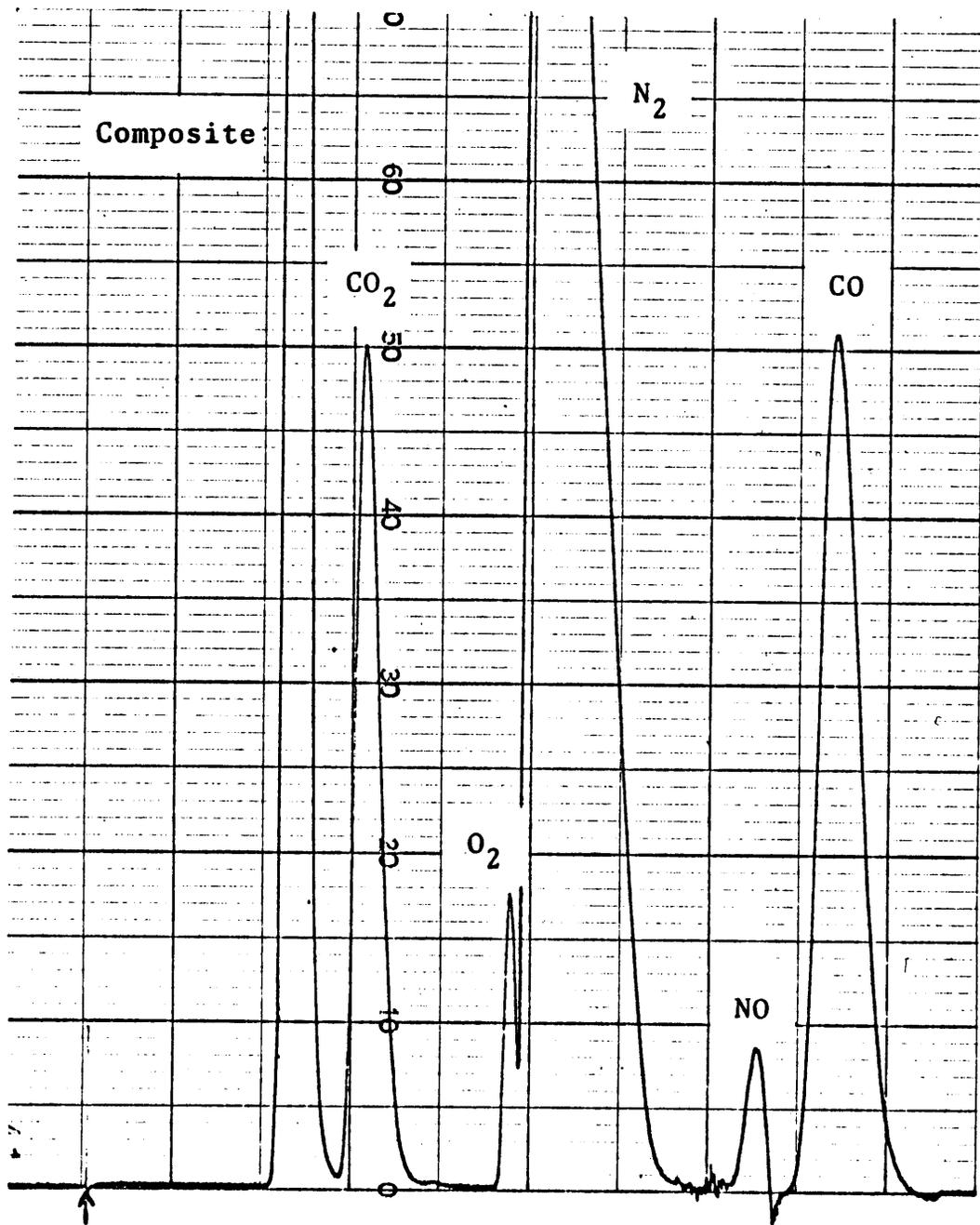


Figure 21. Chromatogram Of Diesel Exhaust Obtained During Water Injection Test (Group II, Test 7). Water/Fuel Mass Ratio = 0.75. Attenuation: CO_2 256, NO 1, CO 32.

sieve column was apparently more effective than the 3-hour heat treatment.

Graphical representations of the data compiled in Tables 3, 4, 5, and 6 are presented in Fig. 22-Fig. 29. CO_2 , CO, and NO concentrations are plotted as functions of fuel/air ratio and brake mean effective pressure. The results of the water injection tests are also plotted.

Figures 22 and 23 show carbon dioxide concentration as a function of fuel/air ratio and brake mean effective pressure respectively. CO_2 levels increase approximately linearly with fuel/air ratio and b.m.e.p., and reach a maximum of slightly over 12% by volume in the vicinity of the stoichiometric fuel/air ratio of 0.068. There appears to be little difference between Group I data and Group II data (including the water injection tests), as all points lie very close to the curves. These results are generally in good agreement with the results of other investigators, notably Holtz and Elliott (17), and Elliott and Davis (2). These investigators reported that CO_2 increased linearly with fuel/air ratio and peaked at over 13% at the stoichiometric ratio.

Carbon monoxide concentration is plotted as a function of fuel/air ratio and b.m.e.p. in Fig. 24 and Fig. 25 respectively. CO shows a tendency to increase sharply with fuel/air ratio and b.m.e.p. over the load range which was used in this study. Again there is good agreement between

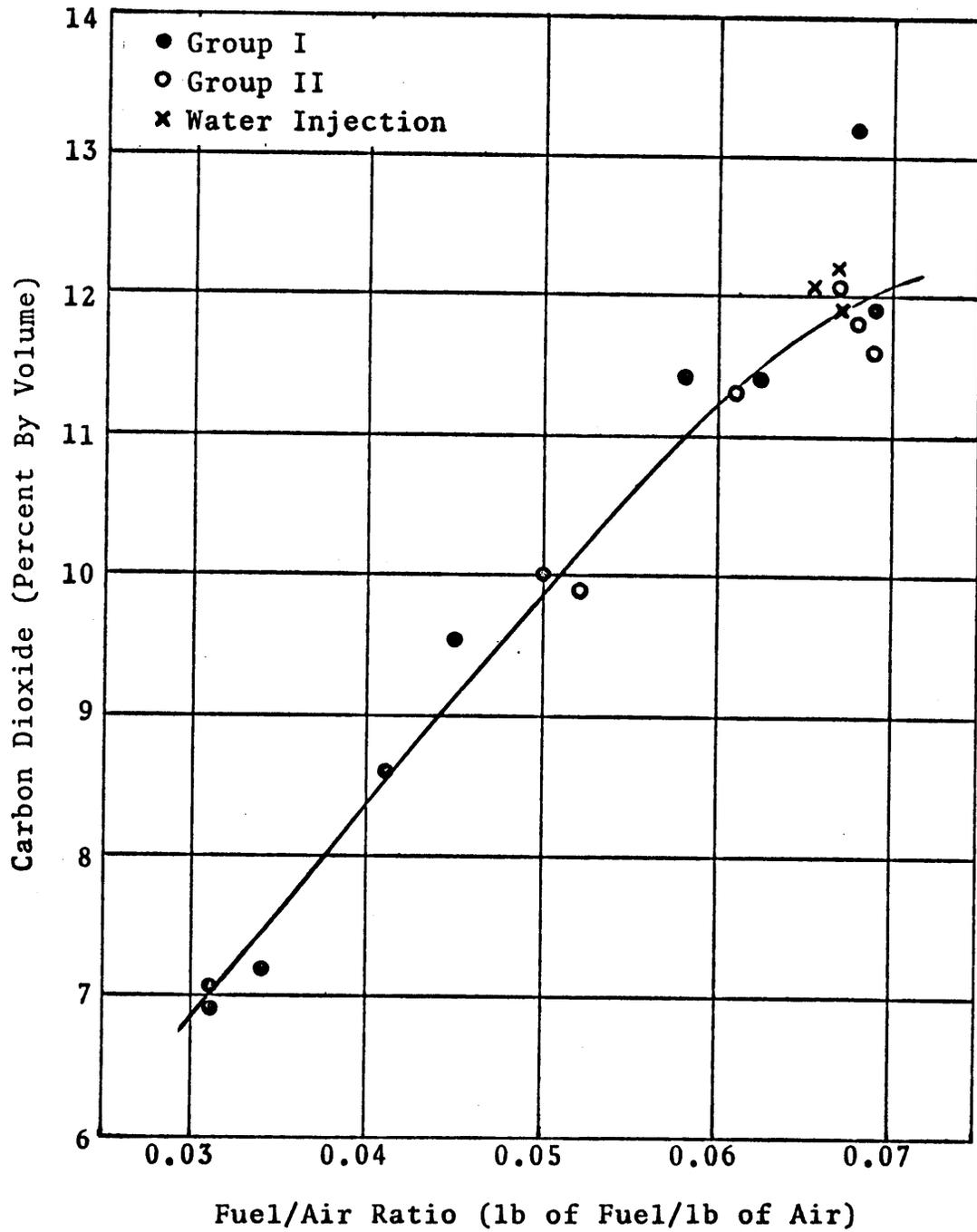


Figure 22. Carbon Dioxide Concentration Vs. Fuel/Air Ratio.

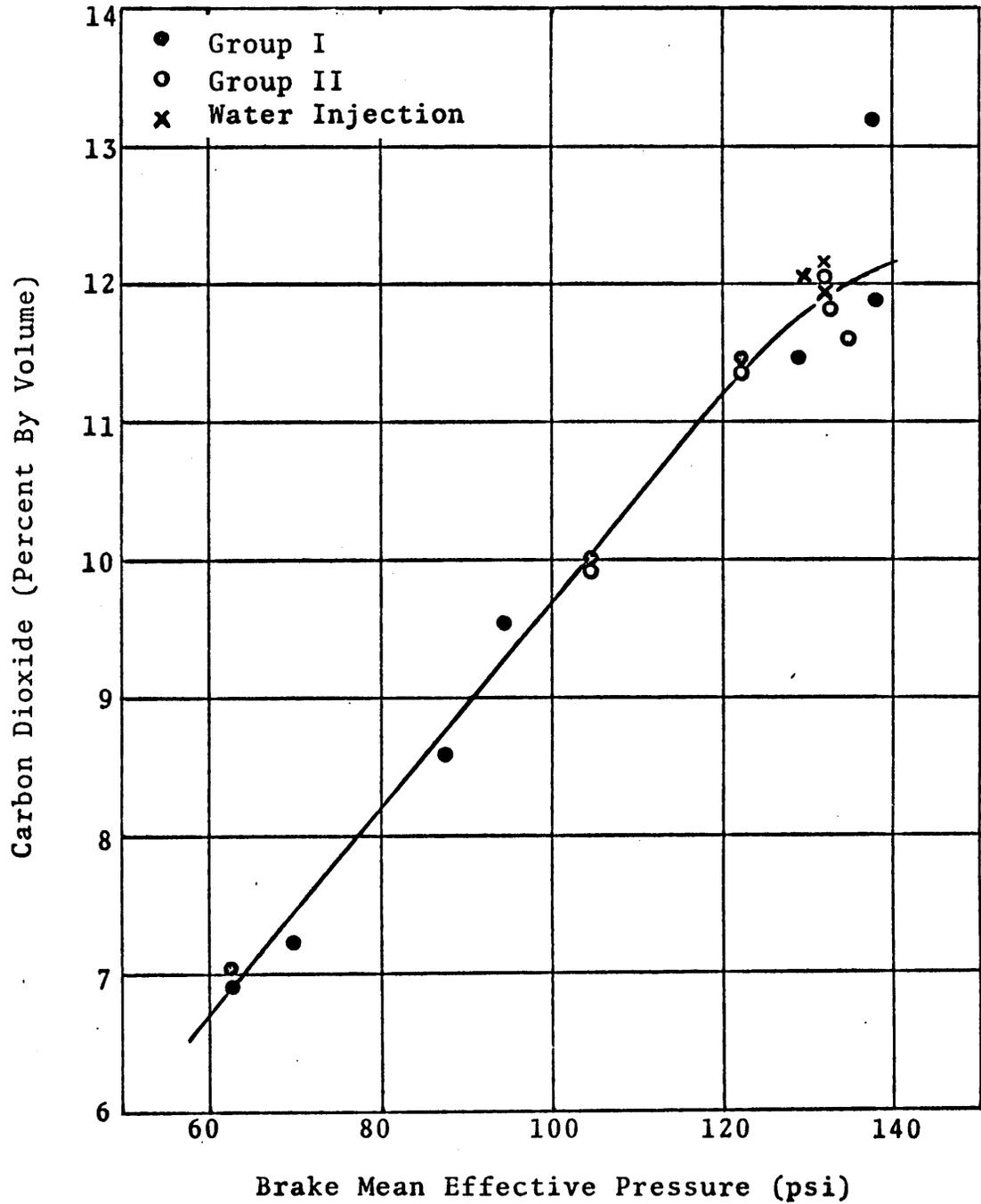


Figure 23. Carbon Dioxide Concentration Vs. Brake Mean Effective Pressure.

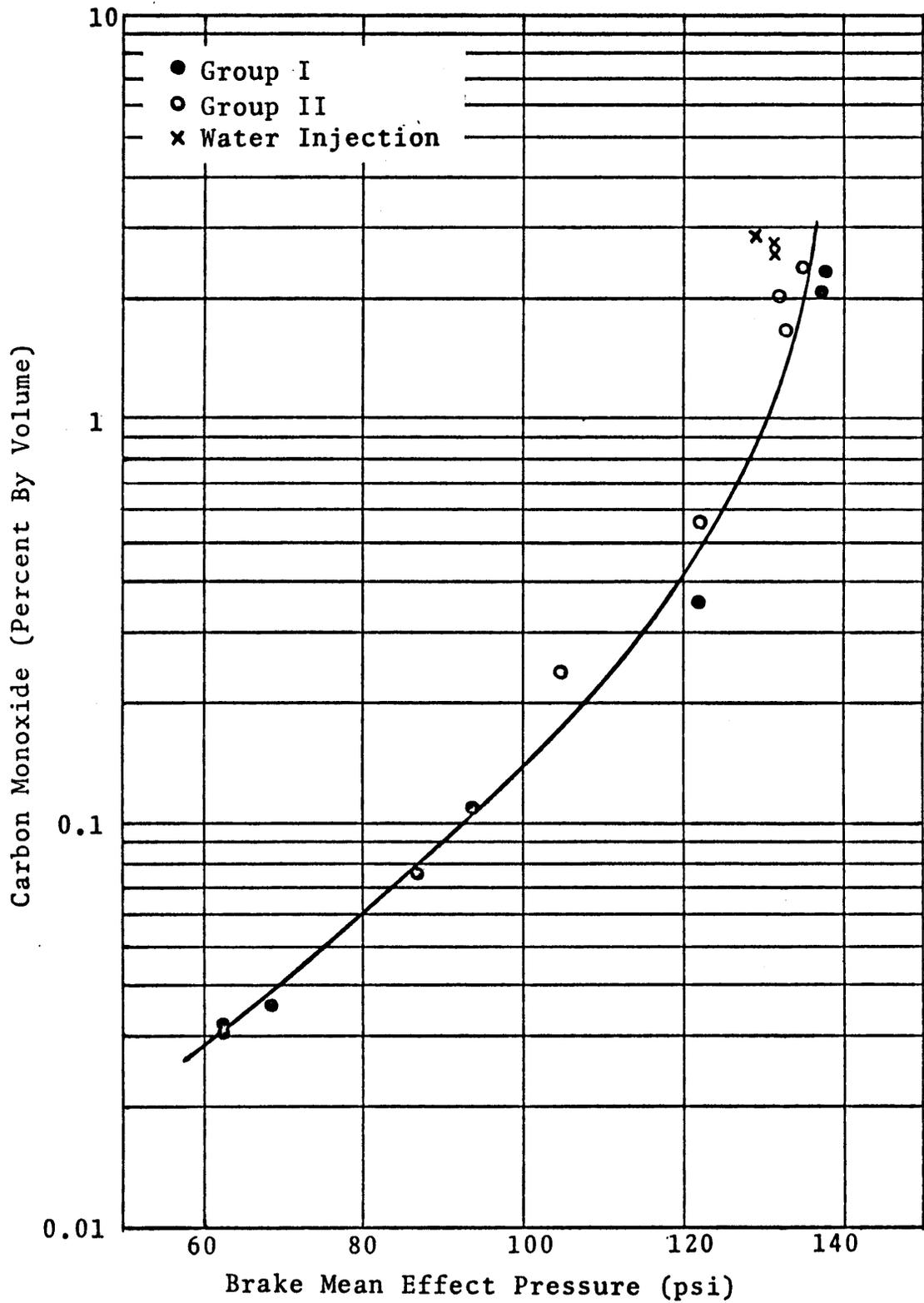
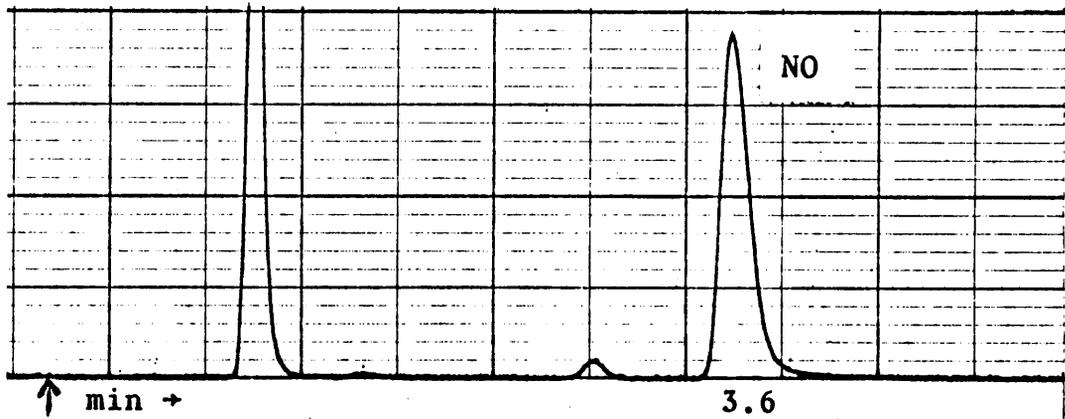


Figure 25. Carbon Monoxide Concentration Vs. Brake Mean Effective Pressure.

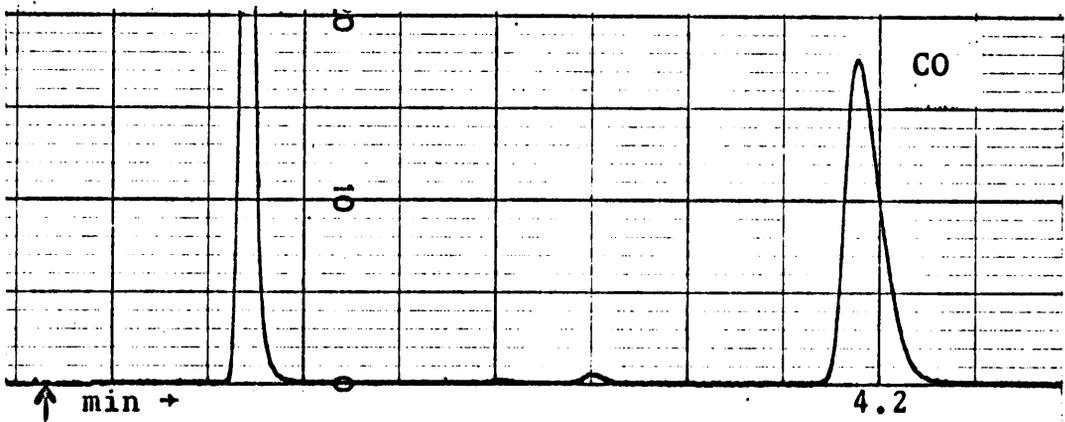
Group I and Group II data; however, water injection tests yielded slightly higher CO levels. This was probably caused by the decrease in oxygen available for combustion which accompanied water injection.

At fuel/air ratios in the stoichiometric region, CO levels greater than 2% were encountered. This is not consistent with the results obtained by other investigators. Elliott and Davis (2) reported CO concentrations of slightly more than 1% in this region for one of their diesels; in most cases, however, other investigators have reported concentrations below the 1% level. One explanation for this apparent discrepancy is the appearance of methane (CH_4) at relatively high fuel/air ratios. Diesel exhaust generally contains very low concentrations of CH_4 at fuel/air ratios less than about 0.05; however, above this the concentrations tend to become more significant. The possible effect this has on CO responses can be seen in Fig. 26, which shows the relative retention times for NO, CO, and CH_4 . The similarity in retention times for CO and CH_4 make the two compounds indistinguishable in a mixture. Therefore, it is possible that the "CO" peaks observed at fuel/air ratios near stoichiometric are actually produced by mixtures of CO and CH_4 .

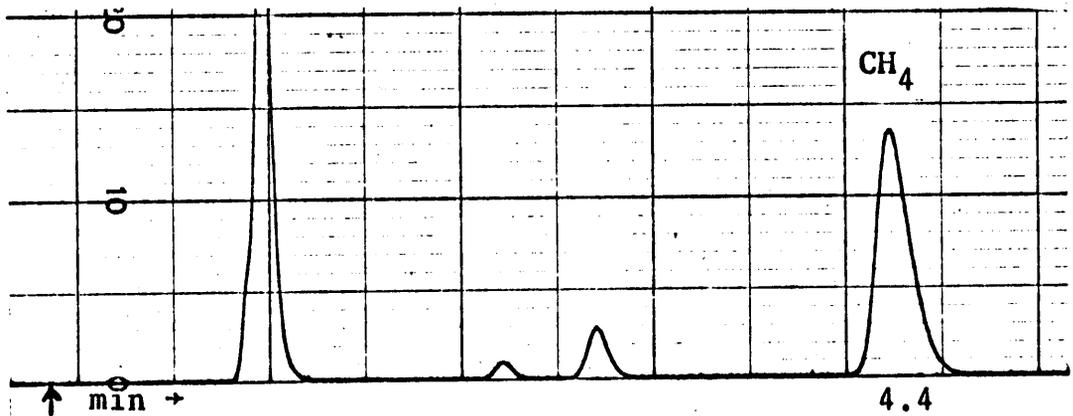
Nitric oxide concentration is shown as a function of fuel/air ratio in Fig. 27, and as a function of b.m.e.p. in Fig. 28. The most significant feature of these curves is



(a)



(b)



(c)

Figure 26. Relative Retention Times For (a) Nitric Oxide, (b) Carbon Monoxide, and (c) Methane. 0.2 ml syringe injection for each compound, attenuation = 128.

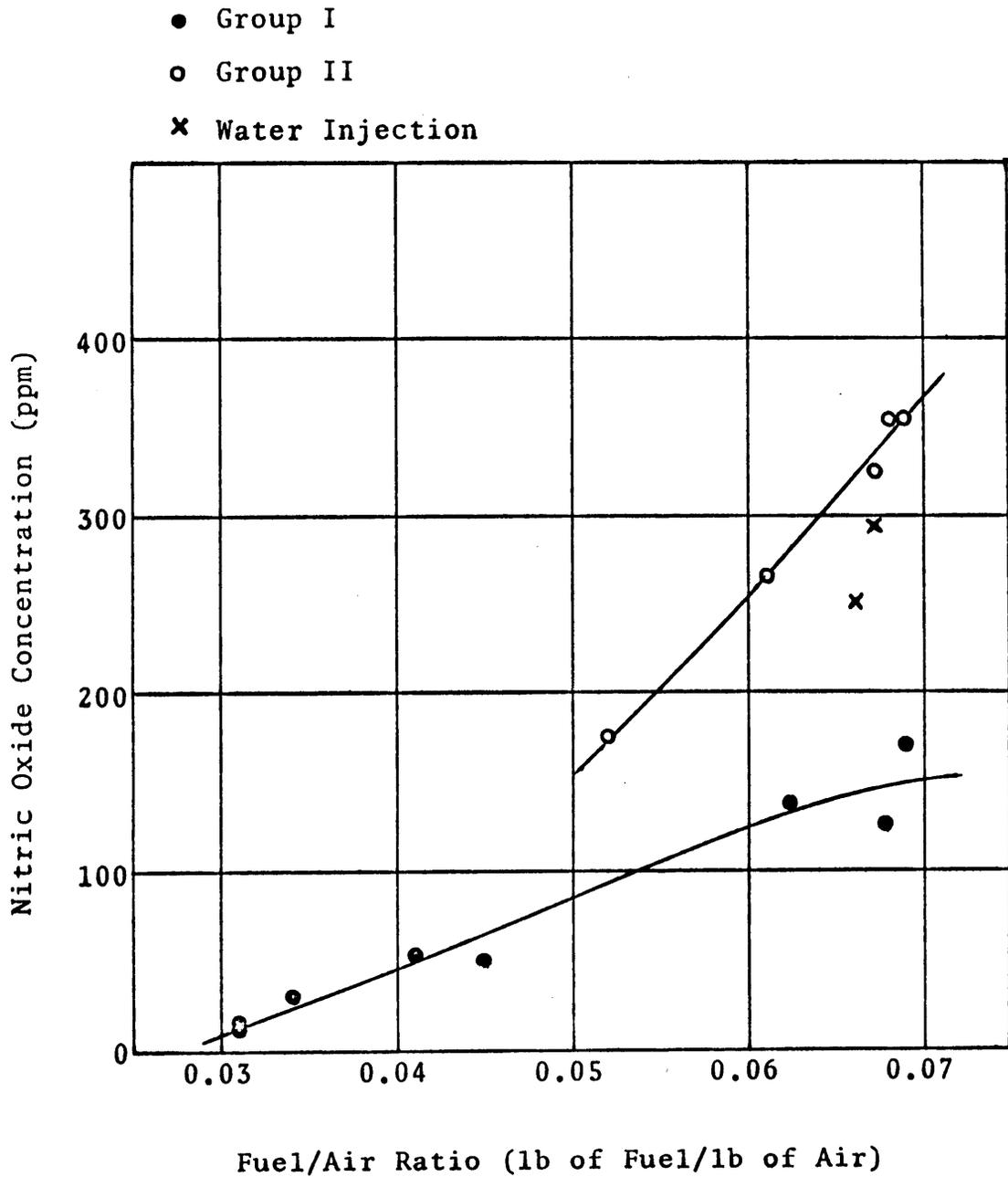


Figure 27. Nitric Oxide Concentration Vs. Fuel/Air Ratio.

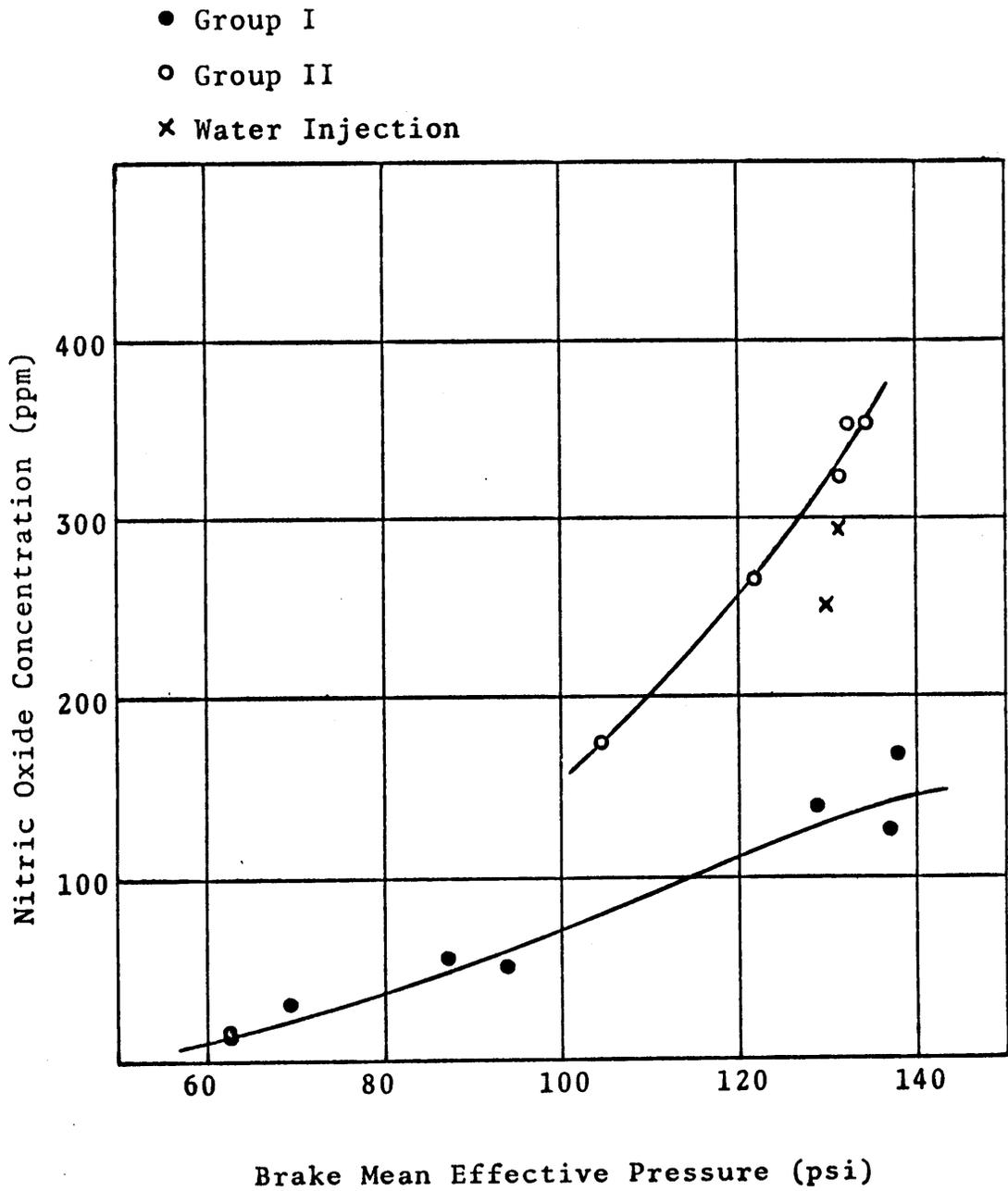


Figure 28. Nitric Oxide Concentration Vs. Brake Mean Effective Pressure

the difference between NO concentrations in Group I and in Group II. The maximum NO level observed in Group I was 170 ppm, while in Group II, 353 ppm appeared. Maximum levels were at or near the stoichiometric fuel/air ratio. Also, NO concentrations in Group II increased more sharply with fuel/air ratio and b.m.e.p. than did those in Group I.

Two explanations are submitted as possible reasons for the difference between Group I data and Group II data. First, the engine was retuned to manufacturer's specifications between the Group I tests and the Group II tests. Retuning modifications may have caused peak flame temperatures to be somewhat higher when the Group II tests were conducted. Secondly, Group I tests were run at higher relative humidities than Group II. Investigators such as Robison (23) have reported that oxides of nitrogen concentrations decrease as the relative humidity of the intake air increases.

Figure 29 shows the effect of water injection on nitric oxide concentration. The greatest reduction in NO (15%) occurred when a water/fuel mass ratio of 0.75 was used. One would expect even greater reductions if more water were added. However, since this engine emits relatively low amounts of NO in comparison to some of the engines studied by other investigators, it is doubtful that the reductions in excess of 50%, which have been reported in some cases, would occur.

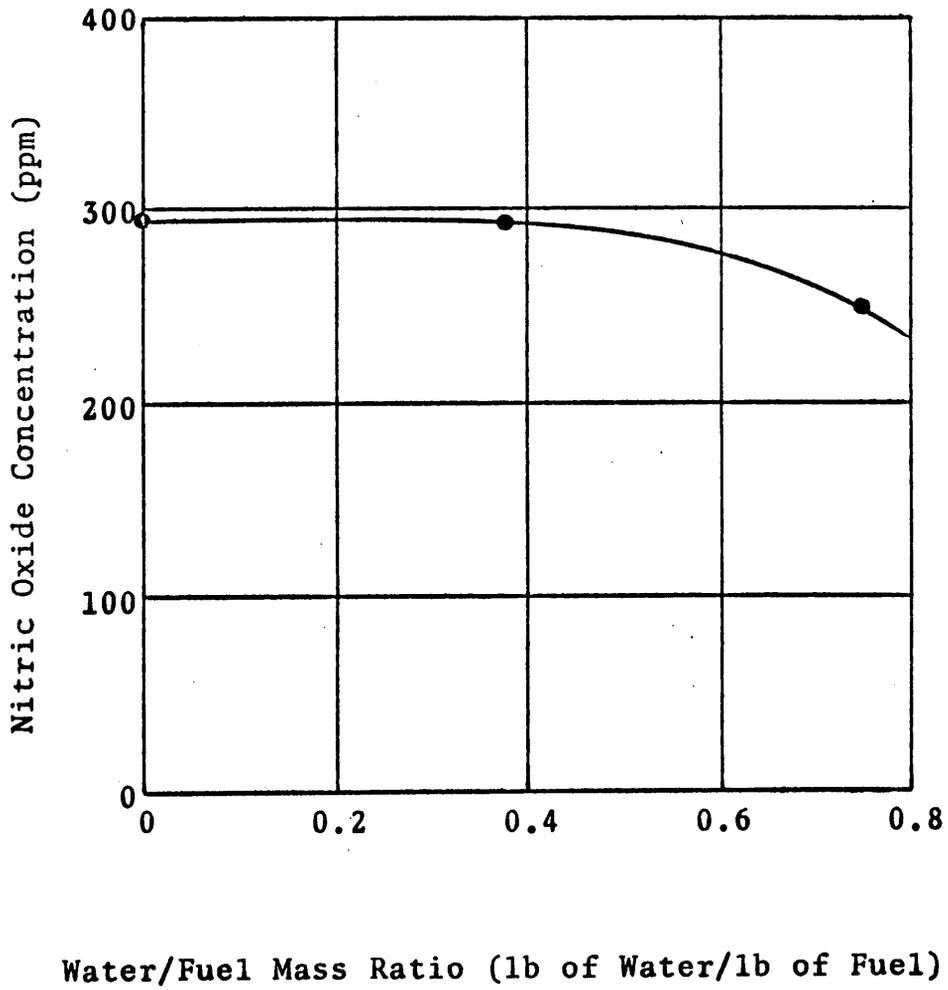


Figure 29. Effect of Water Injection On Nitric Oxide Concentration

V. CONCLUSIONS AND RECOMMENDATIONS

As stated in the Introduction, one of the main objectives of this investigation was to determine the feasibility of using gas chromatography for the qualitative and quantitative analysis of carbon dioxide, carbon monoxide, and nitric oxide in diesel exhaust. The results obtained clearly indicate that this method of analysis is indeed effective. The high degree of flexibility, wide range of sensitivity, and good accuracy and reproducibility make gas chromatography superior to many other analysis techniques. Its simplicity and relatively low initial cost add to its advantages over other methods. Based on the results of this investigation, one must conclude that gas chromatography is a viable and practical method to use in the analysis of CO₂, CO, and NO in diesel exhaust.

In spite of the many advantages of gas chromatography, certain shortcomings were also noted during the course of this investigation. First, analysis is only possible during steady state engine operation. Each sample analyzed is representative of the average exhaust gas composition at a fixed load and speed. Therefore, exhaust gas composition during variable speed and load modes, such as acceleration and deceleration, cannot be accurately determined. Secondly, the 13X molecular sieve column used would not separate CH₄ from CO. This may have caused problems in accurately

analyzing CO, particularly in the vicinity of the stoichiometric fuel/air ratio. One recommendation in connection with this would be to determine which column parameter(s) should be altered so that CO and CH₄ would be effectively separated. A longer column might be a good starting point.

Several conclusions were also drawn regarding the exhaust emission characteristics of the Cummins JT-6-B diesel engine. These are listed below.

1. CO₂, CO, and NO all increase with fuel/air ratio and b.m.e.p. in the load range considered. CO shows a greater dependence on load than the other two compounds.
2. CO₂ concentrations correlate well with concentrations reported by other investigators studying different engines.
3. CO levels appear to be slightly higher than expected.
4. NO concentrations are relatively low for a diesel engine.
5. The stainless steel probe has no adverse effects on NO concentration.
6. Water injection reduced NO by a small amount; however, it is felt that greater reductions can be achieved by using higher water/fuel ratios.

One recommendation concerned with NO analysis is submitted. The effects of intake air relative humidity should

be thoroughly investigated and established before an analysis of NO in engine exhaust is undertaken.

VI. REFERENCES

1. Schmidt, Robert C., Al W. Carey, and Roy Kamo. "Exhaust Characteristics of the Automotive Diesel." S.A.E. Transactions, 75, paper 660550, 1967. 7p.
2. Elliott, Martin A. and Rogers F. Davis. "Composition of Diesel Exhaust Gas." S.A.E. Quarterly Transactions, 4, 3, 330-346, July 1950.
3. Patterson, Donald J. and N. A. Henein. Emissions From Combustion Engines and Their Control. Ann Arbor Science Publishers, Inc., Ann Arbor, Mich., 1972. pp. 12, 134.
4. Obert, Edward F. Internal Combustion Engines. International Textbook Company, Scranton, Pa., 3rd ed., 1968. pp. 366, 386.
5. Caplan, John D. "Spotting the Chemical Culprits in Smog Formation." S.A.E. Journal, 73, 12, 62-65, December 1965.
6. Stoker, H. Stephen and Spencer L. Seager. Environmental Chemistry: Air and Water Pollution. Scott, Foresman, and Company, Glenview, Ill., 1972. p. 26.
7. Janák, J. "The Concept of the Chromatographic Spectrum of Gases and Volatile Materials." Vapour Phase Chromatography 1956, D. H. Butterworth, London, 1956. pp. 235-246.
8. Janák, J. "Vapour Phase Chromatography on Zeolites." Vapour Phase Chromatography 1956, D. H. Butterworth, London, 1956. pp. 247-255.
9. Breck, D. W. and J. V. Smith. "Molecular Sieves." Scientific American, 200, 1, 85-94, January 1959.
10. Trowell, J. M. "Gas Chromatographic Separation of Oxides of Nitrogen." Analytical Chemistry, 37, 9, 1152-1154, August 1965.
11. Dietz, Russell N. "Gas Chromatographic Determination of Nitric Oxide on Treated Molecular Sieve." Analytical Chemistry, 40, 10, 1576-1578, August 1968.

12. Hurn, R. W., K. J. Hughes, and J. O. Chase. "Application of Gas Chromatography to Analysis of Exhaust Gas." Published in S.A.E. Technical Progress Series, Vol. 6, Vehicle Emissions, Society of Automotive Engineers, Inc., New York, 1964. pp. 94-101.
13. Papa, Louis J. "Gas Chromatography--Measuring Exhaust Hydrocarbons Down to Parts Per Billion." S.A.E. Transactions, 76, paper 670494, 1967. 9p.
14. Dimitriadis, Basil, C. F. Ellis, and D. E. Seizinger. "Gas Chromatographic Analysis of Vehicular Exhaust Emissions." Advances in Chromatography, Vol. 8, Marcel Dekker, Inc., New York, 1969. pp. 327-362.
15. S.A.E. Recommended Practice. "Measurement of Carbon Dioxide, Carbon Monoxide, and Oxides of Nitrogen in Diesel Exhaust--SAE J 177." S.A.E. Handbook, Society of Automotive Engineers, Inc., New York, 1971, pp. 806-811.
16. England, Christopher, John Houseman, and D. P. Teixeira. "Sampling Nitric Oxide From Combustion Gases." Combustion and Flame, 20, 3, 439-442, June 1973.
17. Holtz, John C. and M. A. Elliott. "The Significance of Diesel-Exhaust-Gas Analysis." Transactions of the A.S.M.E., 63, 2. 97-102, February 1941.
18. McConnell, G. "Oxides of Nitrogen in Diesel Engine Exhaust Gas: Their Formation and Control." Proceedings of the Institution of Mechanical Engineers, 178, pt. 1, 38, 1001-1014, 1963-1964.
19. Yumlu, V. S. and A. W. Carey. "Exhaust Emission Characteristics of Four-Stroke, Direct Injection, Compression Ignition Engines." S.A.E. paper 680420 presented at Mid-Year Meeting, Detroit, Mich., May 1968. 5p.
20. Abthoff, J. and H. Luther. "Die Messung der Stickoxid-Emission von Dieselmotoren und ihre Beeinflussung durch Massnahmen am Motor." Automobil Technische Zeitschrift, 71, 4, 124-130, April 1969.
21. Marshall, W. F. and R. D. Flemming. "Diesel Emissions as Related to Engine Variables and Fuel Characteristics!" S.A.E. paper 710836 presented at National Combined Fuels and Lubricants, Powerplant and Truck Meetings, St. Louis, Mo., October 1971, 7p.

22. "Control of Air Pollution from New Motor Vehicles and New Motor Vehicle Engines--Light Duty Trucks and Diesel-Powered Vehicles." Federal Register, 38, 151, pt. III, August 1973.
23. Robison, J. A. "Humidity Effects on Engine Nitric Oxide Emissions at Steady State Conditions." S.A.E. Transactions, 79, paper 700467, 1970. 9p.
24. Nicholls, J. E., I. A. El-Messiri, and H. K. Newhall. "Inlet Manifold Water Injection for Control of Nitrogen Oxides - Theory and Experiment." S.A.E. Transactions, 78, paper 690018, 1969. 10p.
25. Valdmanis, E. and D. E. Wulfhorst. "The Effects of Emulsified Fuels and Water Induction on Diesel Combustion." S.A.E. paper 700736 presented at Combined National Farm, Construction and Industrial Machinery and Powerplant Meetings, Milwaukee, Wis., September 1970, 10p.
26. Torpey, P. M., M. J. Whitehead, and M. Wright. "Experiments in the Control of Diesel Emissions." Air Pollution Control in Transport Engines, The Institution of Mechanical Engineers, London, 1972. pp. 21-33.
27. Zeilinger, K. "Influence of Water Injection on Nitric Oxide Formation in Petrol Engines." Air Pollution Control in Transport Engines, The Institution of Mechanical Engineers, London, 1972. pp. 7-13.
28. McNair, H. M. and E. J. Bonelli. Basic Gas Chromatography. Consolidated Printers, Berkeley, Calif., 5th ed., 1969. p. 149.
29. Pinkerton, R. D. "Physical and Chemical Characteristics of Diesel Fuel Oils." Diesel Fuel Oils: Production, Characteristics, and Combustion, A.S.M.E., New York, 1948. p. 33.

**The vita has been removed from
the scanned document**

GAS CHROMATOGRAPHIC DETERMINATION OF
CARBON DIOXIDE, CARBON MONOXIDE, AND
NITRIC OXIDE IN DIESEL EXHAUST

by

Charles Watson Jordan, Jr.

(ABSTRACT)

A method using gas chromatography for the analysis of carbon dioxide, carbon monoxide, and nitric oxide in diesel exhaust was developed. A gas chromatograph containing a liquid phase column in series with a molecular sieve column, each of which eluted into thermal conductivity detectors, was utilized. Activation of the molecular sieve column was achieved by heat-treating and purging with nitric oxide. The chromatograph was calibrated by introducing sample mixtures of known concentration and measuring the responses.

The exhaust gases of a diesel engine were analyzed while the engine operated at constant speed and load. Engine speed was kept at 1400 rpm while several different loads were applied. The results of these tests indicated that carbon dioxide, carbon monoxide, and nitric oxide concentrations all increased with load in the load range studied. Carbon monoxide exhibited a greater dependence on load than did the other compounds.

Additionally, water was injected into the intake air stream to study its effect on nitric oxide concentration. Nitric oxide levels were reduced by 15% when a water/fuel mass ratio of 0.75 lb/lb was used.