THE UNIVERSITY OF MICHIGAN
COLLEGE OF ENGINEERING
Department of Mechanical Engineering

Final Report

TWO-STROKE GASOLINE ENGINE EXHAUST EMISSIONS

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I. INTRODUCTION

In the research program of the past year, we have significantly amplified the scope of the previous year's study of the exhaust emissions from the two-stroke, spark-ignition, outboard engine. Major emphasis has been placed on development of instrumentation and test techniques for evaluating gaseous emissions, particularly unburned hydrocarbons. In addition, a program to evaluate the influence of the underwater exhaust on water quality and marine life has been initiated.

The findings of this research activity to date have provided answers to a number of our stated objectives, but have also generated new areas of question and therefore provided redirection to some of our effort.

It is becoming increasingly apparent that environmental pollution in all its myriad forms is destined to be a major issue of the coming decade. Environmental pollution was recently labeled by President Richard M. Nixon as one of the four most significant domestic problems facing the United States. People from every segment of our society, the politician, the scientist, and the man on the street, are beginning to express their view on the subject and their disdain of those who ignore the problem. Unfortunately much of the information that is circulating and receiving so much public attention is not based on sound and objective scientific fact, but rather on a very pedestrian view of the situation.

A major effort has been initiated, and is being rapidly expanded in areas related to air and water quality standards, the contribution of the various pollution sources to environmental problems, and control of those sources. Government and industry alike are active in these programs, with the government emphasizing air and water quality standards and the industry, control of emissions. Both groups are investigating totally new systems in areas such as highway transportation and power generation which in the future could replace the current "high pollution" systems.

The automotive industry is extremely active. More than one thousand people are working on the four-cycle internal combustion engine exhaust emissions problem at General Motors alone, and significant advances have been made. The fully emission controlled vehicle of 1970 shows approximately a 70% carbon monoxide and hydrocarbon emission reduction over a pre-control car.

California in its "Pure Air Act" (AB 357) has defined the allowable automotive emissions from 1970 to 1974 expressed in grams/mile as

	Year			
	1970	1971	1972	1974
Hydrocarbons	2.2	2.2	1.5	1.5
CO	23.0	23.0	23.0	23.0
NO_x	--	4.0	3.0	1.3

and is suggesting that the 1975+ requirements will be even more stringent. To satisfy these standards the manufacturers will be producing essentially a zero pollution vehicle at the end of the decade. Certainly a formidable task lies ahead for the design engineer. However, a number of prototype vehicles are in operation that demonstrate the technical feasibility of achieving this goal. One new and very interesting standard that will be appearing in 1975 is the requirement for exhaust particulate control which almost certainly means that lead, anti-knock compounds will disappear from all motor fuels. Both General Motors and Ford have recognized this and have directed that all future engine development be done with nonleaded gasoline. This development is certainly good news for the two-stroke engine industry because of the deposit ignition problem.

In terms of pollution from transportation systems, the government has placed major emphasis on the automobile. However, if the automobile meets the projected 1975 standards, the significance of the automobile as a pollution source will decrease considerably on a relative basis. Both the Department of Transportation (DOT), and Department of Health, Education, and Welfare (HEW), recognize this and are beginning to look closely at all applications of the internal combustion engine. Recent communication with personnel at the Motor Vehicle Research and Development Division of NAPCA* has verified this fact. An investigation is to be made of all internal combustion engine applications to determine quantitatively the influence of each class of engine on atmospheric pollution. Included in this undertaking is a test program to evaluate the specific pollution contribution of a number of engine powered devices including the outboard engine. In fact, during the past year Olson Laboratories of Detroit, Michigan, under contract to the Public Health Service, has performed a number of tests on both two- and four-cycle motorcycles. The final report has been released and a copy sent to M. Boerma of OMC Marine Engineering.

The emphasis of the government and the concern of the citizenry with environmental pollution problems amplify the need to more fully understand the basic

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*NAPCA: National Air Pollution Control Administration.

emission processes of the two-stroke outboard engine. Preparation must be made for the day when the emission performance of the two-stroke engine will become a public issue and therefore achieve major importance as a design variable. It is strongly urged that this preparation include:

- Research on alternative power plants.
- Identification of boat driving cycles.
- Determination of the influence of the exhaust products on the air and water ecological systems.
- Research on pollutant measurement systems.
- Investigation of the basic nature of the emission formation processes.
- Development of conventional powerplants with lower emissions.
- Evaluation of the total economic impact of varying degrees of emission control.
- Evaluation of the current and proposed future outboard engine contribution to the total pollution problem.

Certainly the tasks suggested in the foregoing statements will place a major burden on every facet of the outboard industry, the decision-maker as well as the design engineer. It is imperative for the health of the industry as well as for the well being of the consumer that representatives of industry and government reach agreements and make decisions for future control based on truly objective evaluation and understanding of the total problem.

Summary

In the study of the past year we have continued our first-order evaluation of two-stroke engine pollutants but have placed emphasis on the development of systems for measuring these pollutants.

We have successfuly measured the following exhaust constituents from the 100 hp Johnson engine installed on our test stand.

- Unburned hydrocarbons with both the NDIR and FID techniques
- Carbon monoxide (CO)

- Nitric oxide (NO)
- Carbon dioxide (CO_2)
- Oxygen (O_2)

The results of this testing demonstrate that, of the major pollutants in the exhaust, (1) the unburned hydrocarbons are extremely high because of scavenging losses of fuel/air mixture, and at light load, misfiring, (2) CO is moderately high (approximately 6%) because of the rich mixture ratios used and (3) NO is low (100-600 ppm) because of the relatively low peak cycle temperatures caused by rich mixture ratios and significant exhaust dilution of the charge.

Work on the misfiring measurement system has also continued and good qualitative data has been taken with both the single ion-gap and photomultiplier techniques. At low speed and light load, misfiring and poor combustion are a major cause of unburned exhaust hydrocarbons and may contribute as much to the total problem as the "through scavenged" mixture. At higher speeds and loads, combustion appeared to be very good. These results also demonstrated the extreme sensitivity of the light load combustion quality to fuel-air ratio. With effective light load mixture ratio control and therefore decreased misfiring, the hydrocarbon emissions may be sharply reduced. It must be observed, however, that the mass emissions in this operating range are not significant because of the low indicated horsepower and therefore low air and fuel consumption. We have also instrumented one cylinder of the test engine with a multiple (3) ion gap arrangement which should provide a much better picture of the total combustion process. It will be possible to statistically relate the degree of flame propagation to partial combustion as a source of hydrocarbon emissions. Data acquisition circuitry is still being prepared for this system.

A significant effort has been directed to the development of emission test instrumentation for OMC Marine Engineering. Our early hydrocarbon emission work was performed using a conventional Beckman Model IR-315 Nondispersive Infrared (NDIR) Analyzer modified to accept the high concentration hydrocarbons in the two-stroke engine exhaust. In a succeeding study a more complete measurement of the total exhaust hydrocarbons was made using a Beckman 109A Flame Ionization Detector (FID). An improved hydrocarbon measurement system, a heated FID that permits sampling and analysis of the high boiling point hydrocarbons in addition to those measured with the unheated FID, is the latest instrument being used. This unit, a Beckman Model 106 EX heated FID analyzer, was purchased for Outboard Marine and is currently operational. By the time this report is published the system will have been delivered to Marine Engineering in Waukegan, Illinois.

A series of small fresh water marine ecological systems have been constructed in a test cell in the Automotive Laboratory. Water, through which the exhaust from a 1-1/2 hp Johnson engine has passed, is delivered in controlled concentrations (varying from tank to tank) to the aquariums. A common small fish, the

"Fathead minnow," was selected as the test subject. Their reproductive proficiency will be measured and hopefully correlated with the concentration of the water that was exposed to the engine exhaust. The effects of both leaded and non-leaded gasoline on the fish life is also being observed.

We have had significant problems with a common fish fungus which has infected many of the test subjects. Initially mortality was high but now appears to have stabilized. Aluminum nesting sites have been constructed and placed in the aquariums.

It is still too early to determine if the engine exhaust has any effect on the fish. However, there was no correlation between the early die-off and the exhaust concentration.

Another important investigation is concerned with the analysis of pollutants in water exposed to the two-stroke engine exhaust. Among the water soluble components being analyzed are:

- Organic combustion products
- Heavy metals (lead)
- Phosphates
- Halides

In the initial studies exhaust gas has been bubbled at a controlled rate through distilled water. Samples of this water were then analyzed in the Sanitary Engineering Laboratory at The University of Michigan.

A more complete discussion of the fish study and water analysis investigation will be included in a supplement to this report.

II. TEST EQUIPMENT

An important thrust of this year's project was the development of instrumentation techniques for measuring two-cycle engine exhaust constituents and for determining the internal engine sources of unburned hydrocarbons. In this section the following instrumentation will be discussed:

- Heated flame ionization detector
- Unheated flame ionization detector
- Nondispersive infrared analyzer
- Ionization probe and photomultiplier misfiring transducers

Preliminary data and peripheral studies concerning the use of the instrumentation will also be discussed in this section.

A. Heated Flame Ionization Detector

A major portion of the past year's effort was to have been devoted to developing the Beckman Model 106EX Flame Ionoization Detector (FID) as a tool to measure the hydrocarbons in the two-stroke engine exhaust. This heated FID, which was designed primarily for diesel engine hydrocarbon studies, was selected instead of a more conventional unheated model because it has the capability of measuring the heavier hydrocarbons which are quenched or trapped in the plumbing of the unheated analyzer. The presence of large quantities of the heavier fuel and smaller amounts of lubricating oil-type hydrocarbons in the exhaust gas cast doubt on the value of the unheated FID.

The instrument was ordered at the inception of this year's contract but unfortunately was not delivered until October. We have since added the necessary peripheral equipment and have performed preliminary tests to determine

1. Oxygen interference and
2. Optimum sampling temperature.

The FID in its present configuration is shown in Figures 1 and 2.

The oven which maintains the sample at the proper temperature during filtration (for removal of particulates in the sample) and during analysis in the

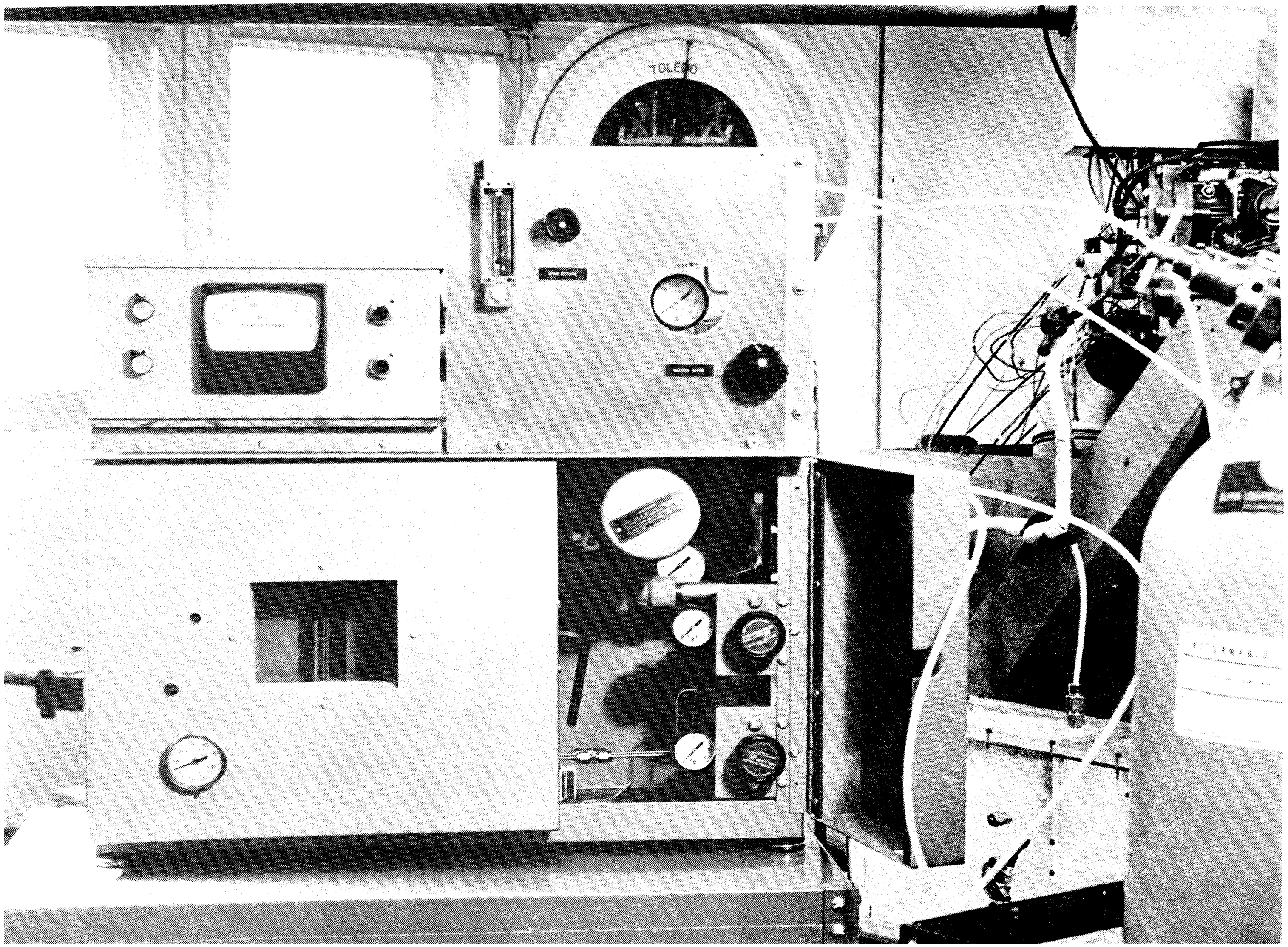

Figure 1. Beckman Model 106 EX heated flame ionization detector—front view.

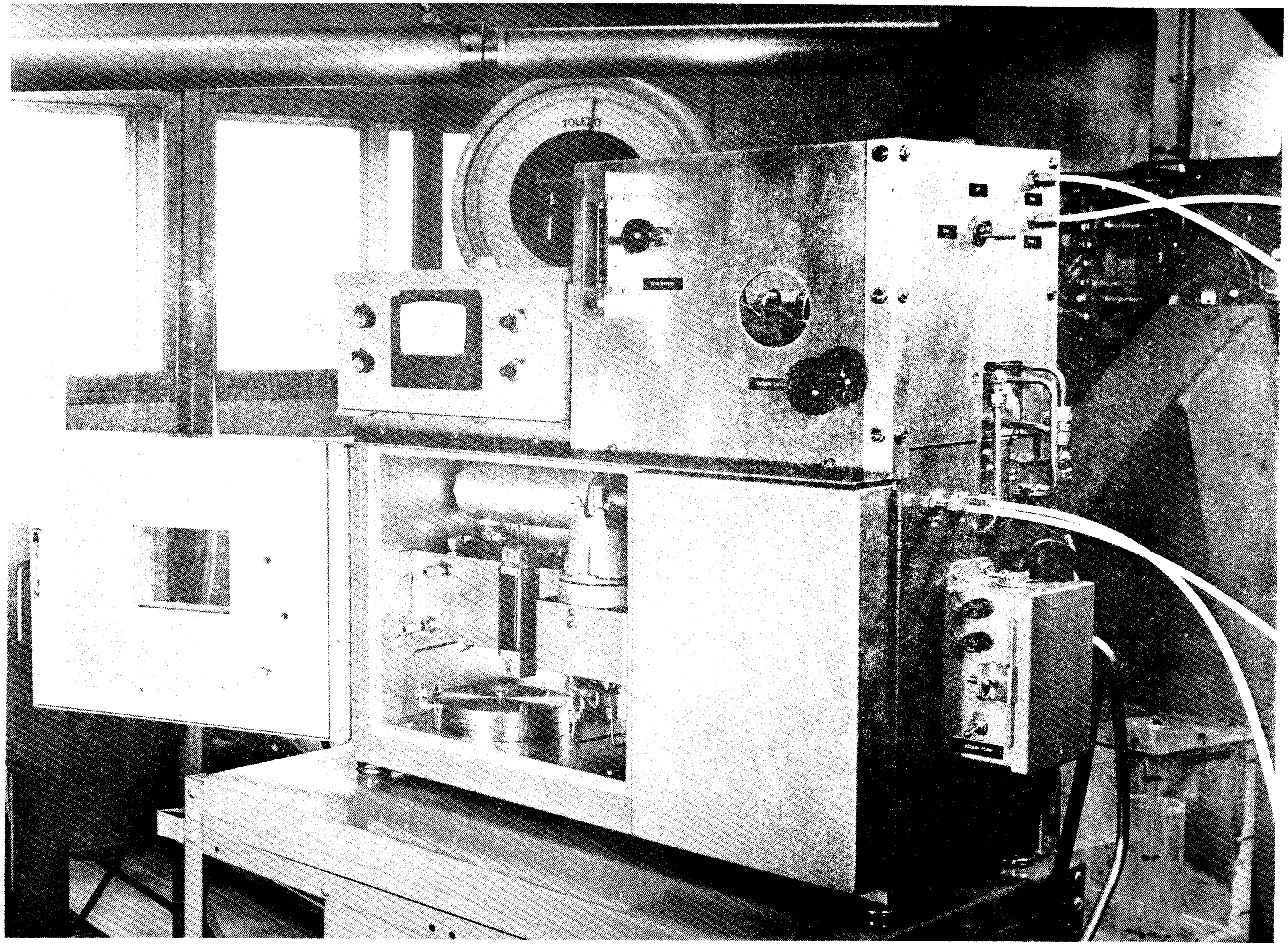

Figure 2. Beckman Model 106 EX heated flame ionization detector—front quartering view.

ionization flame is on the left side of the instrument. To the right of the oven section are located the controls for the ionization burner fuel and air supply and the control for shop air which is required to circulate hot air through the oven chamber.

NOTE: During operation this circulating air must always be turned on to prevent overheating of the heater circuit.

The electronic controls for the detector are located on top of the oven section. An aluminum panel was added to the instrument as a mounting platform for the required peripheral equipment. The total system is located on a mobile cart.

The heated FID utilizes vacuum to draw the sample into the ionization flame. This is achieved by lowering the pressure at the exit of the burner below atmospheric pressure with a diaphragm pump. Because the sample line is operated at a vacuum the instrument is susceptible to leakage at the various fittings which can cause dilution of the sample and therefore low hydrocarbon readings. Care must be exercised when disassembling and assembling the FID to minimize this possibility. A leakage check can be readily made by releasing propane from a soldering torch or span gas bottle into the oven. A nonzero meter reading while operating on the zero gas position indicates a leak.

A schematic of the flow system is shown in Figure 3. The parts of the system operated at a vacuum are illustrated by the heavy dashed lines ------. A detailed description of the theory of operation and operating instructions are included in the manual furnished with the instrument.

We made several significant changes in the original Beckman operating procedure when it was found to be erroneous. In fact, several weeks were lost trying to initiate a flame in the detector with little success. We thoroughly checked both the electronic and flow circuitry before we realized that the factory instructions were incorrect.

Either hydrogen or a hydrogen-nitrogen mixture can be used as the burner fuel and hydrocarbon free air as the fuel oxidizer. Span gases over an appropriate range are required for calibration. Because the instrument is quite linear only two calibration gases are required (7000 ppm and 16,000 ppm propane which are equivalent to approximately 3600 and 8300 ppm n-hexane, respectively, were used in our analytical work and appear to bracket the normal range of two-stroke exhaust hydrocarbons). Room air is used as the calibration "zero gas" even though it has some background hydrocarbon content. This background is totally insignificant compared to the hydrocarbon concentration in the engine exhaust.

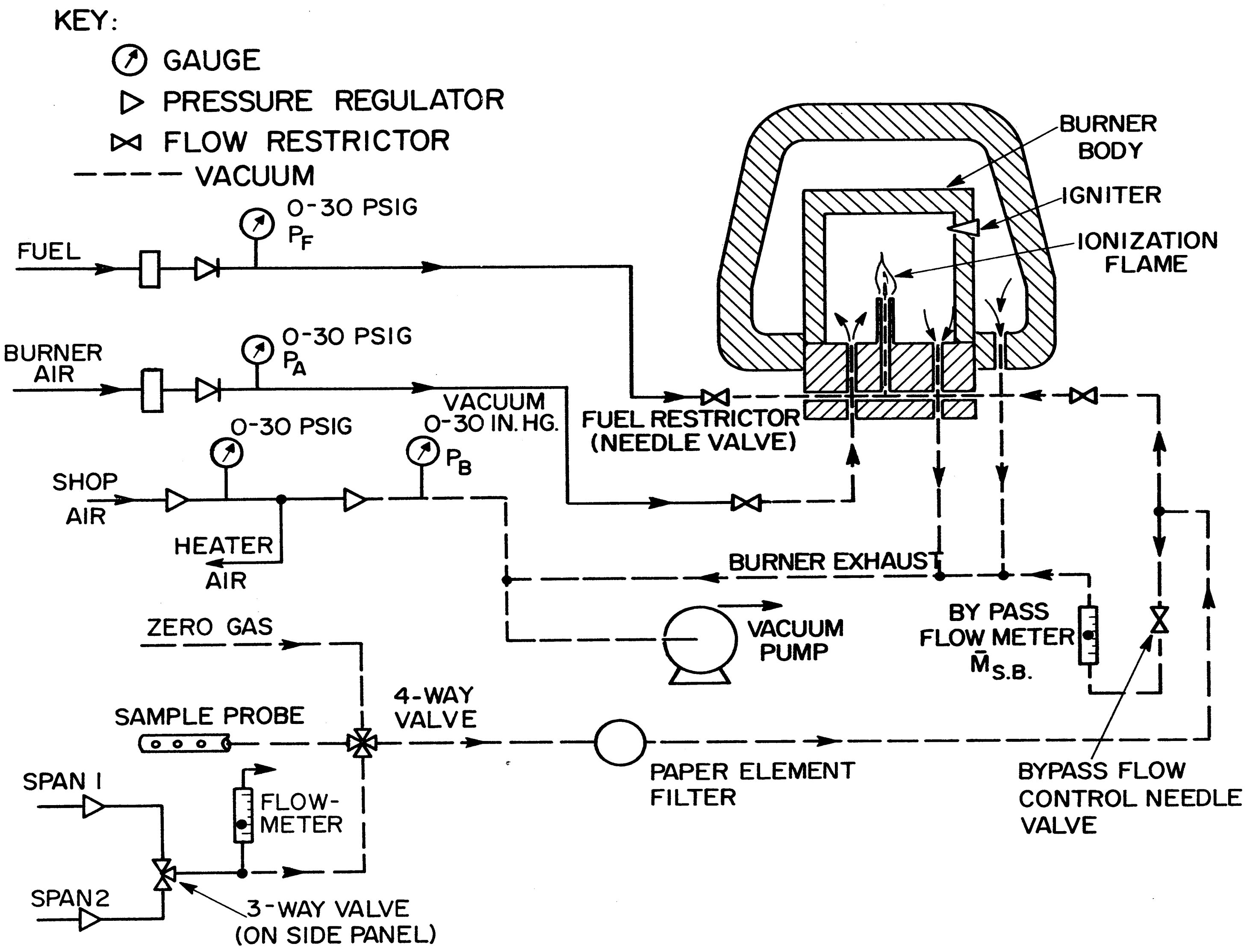

Figure 3. Schematic of the Beckman 106 EX flow circuitry.

1. OXYGEN INTERFERENCE STUDY

It has been shown by several investigators (1,2) that oxygen in the exhaust sample can cause an error or interference in the FID measurement of unburned hydrocarbon concentration. This oxygen interference, while not clearly understood, may be caused by several factors including:

1. Oxygen may change the sample viscosity and therefore change the regulated flow through the restrictor to the ionizing flame. This would affect the response significantly.

2. Oxygen added with the sample certainly affects the diffusion flame characteristics and may change the degree of ionization of the organic carbon atoms.

It is likely that a combination of both factors causes the observed interference. Since this interference is a result of a complex phenomena, it is not amenable to application of analytically derived correction factors but rather these factors must be determined experimentally for each FID model.

The hydrocarbon response and oxygen interference of the FID is strongly a function of two important flow parameters of the instrument itself, the hydrogen/diluent ratio (H/D) and the air/hydrogen ratio (A/H). A range of these has been investigated in an attempt to determine those values which give a minimum oxygen interference. It was not feasible to determine the flow of the sample, fuel and air as a rate per unit time but rather to use the pressure (psig) upstream of the fuel and air control restrictors, the sample bypass flowrate, (liters/min) and the vacuum (in. Hg) applied to the burner system as a measure of the relative flow rates. These readings are keyed to the schematic diagram of Figure 3. Since the maximum expected hydrocarbon concentration from the outboard is quite high, approximately 13,000 ppm n-hexane under complete misfiring conditions, the sensitivity of the FID must necessarily be low and therefore only a limited range of fuel, air and sample flow rates can be used.

In the test to quantitatively determine the oxygen-hydrocarbon interference three different gas mixtures were used. Each had very nearly the same hydrocarbon concentrations (7000 ppm propane) but differing concentrations of oxygen (3.0, 7.7, and 19.9% O_2). The response with each of these reference gases was compared to a standard span gas (propane in nitrogen) containing no oxygen.

Preliminary data has been obtained and shows that the interference with the hydrocarbon measurement is not significant. These data are plotted in Figure 4.

The minimum interference observed was obtained with the following instrument settings which are recommended for future testing.

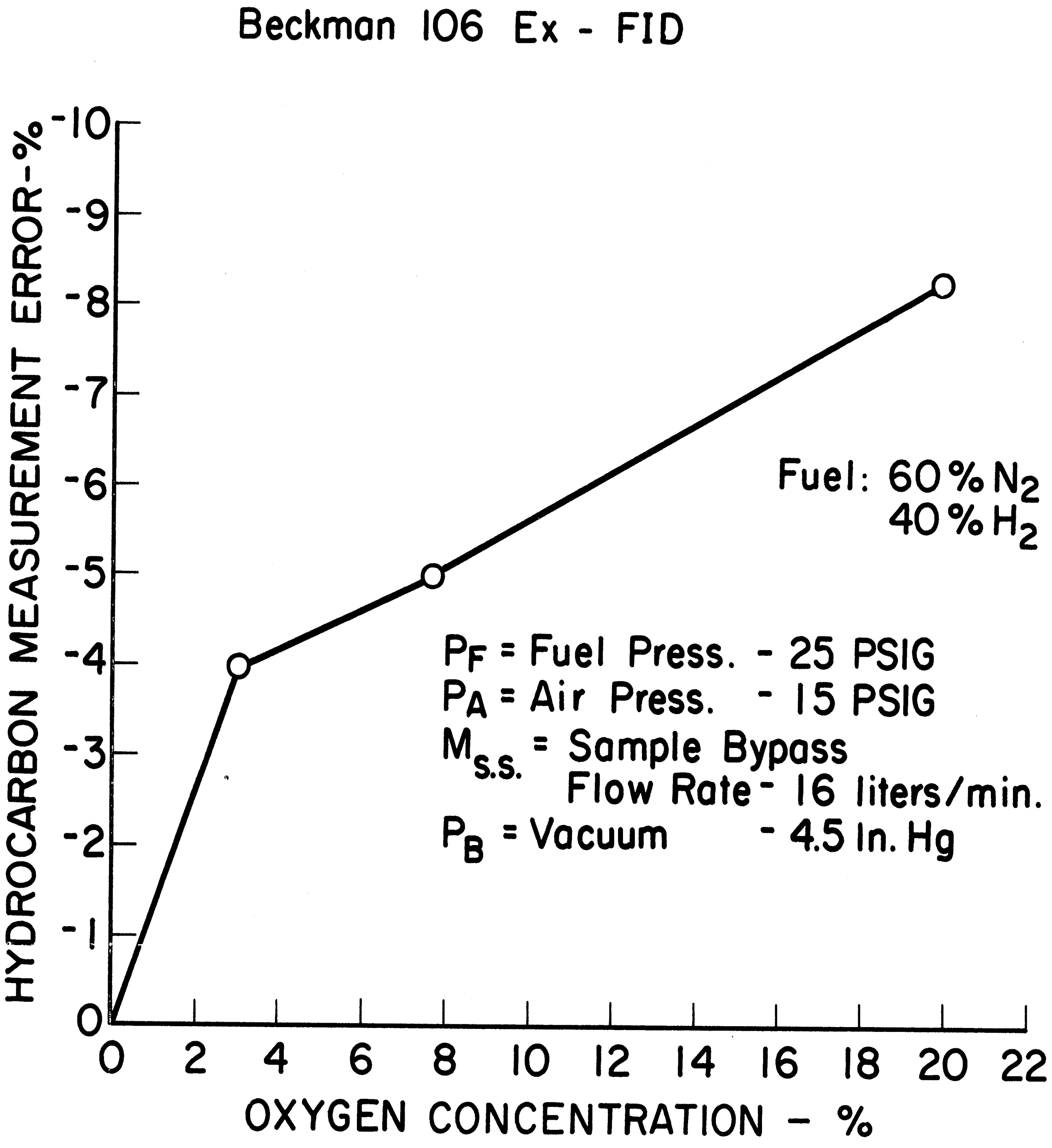

Figure 4. Effect of sample oxygen concentration on the measured hydrocarbon concentration in the Beckman 106 EX FID-O_2 interference test.

P_F = Fuel Pressure = 25 psig

P_A = Air Pressure = 15 psig

$M_{S.B.}$ = Sample Bypass Flow Rate = 16 liters/min

P_B = System Back Pressure (Vacuum) = 4.5 in. Hg

If the exhaust oxygen concentration is measured, it is quite easy to obtain the correction factor for hydrocarbon concentration from the appropriate curve. Since the outboard engine trapping efficiency is about 30% for most operating conditions, the oxygen percentage in the exhaust is approximately .35x21% $\simeq$ 7%. At this exhaust oxygen concentration level, the error in the FID is about -5.5%, i.e., the FID will indicate about 5.5% fewer organic carbon atoms than are actually present in the sample. If the FID indicates 3500 ppm n-hexane with 7% exhaust oxygen the true total hydrocarbon concentration is more nearly 3700 ppm n-hexane. This error is relatively small and may not be significant, since slight changes in the engine operating conditions from test to test often result in greater variationsthan 5%. One point must be made concerning this correction. The interference tests were conducted with reference gases consisting of N_2, O_2, and only a single hydrocarbon component, propane, whereas the engine exhaust consists of a complex array of gases including several hundred different hydrocarbons. Therefore the interference correction may not be exact for the exhaust sample but in lieu of a better technique this correction must suffice.

2. OPTIMUM SAMPLING TEMPERATURE

It was believed that with the two-stroke gasoline engine as in the diesel engine (3) there is an optimum sample line temperature which would minimize the "hang-up" of heavier hydrocarbons on the walls of the sample line but which would not result in excessive oxygenation of the exhaust hydrocarbons. A simple test was performed to determine this temperature. The engine was operated at a steady operating condition and the temperature of the sample system was varied from 150° to 300°F; the latter temperature being that of the FID oven.

The data based on limited testing are presented in Figure 5 and show that for the range tested the sample temperature has only a small effect on the measured hydrocarbons concentration up to 300°F. Beyond this temperature some oxygenation of the hydrocarbons may be occuring and therefore reduces the measured hydrocarbon concentration. The trend observed below 300°F was expected since the hydrocarbons which condense in the sample line would probably be associated primarily with the lubricating oil and since the fuel/oil ratio is about 50:1, even a moderate change in the percentage of oil entering the FID would not cause a significant change in the measured concentration. The gasoline is probably not being retained in the sample system to any great extent. This is

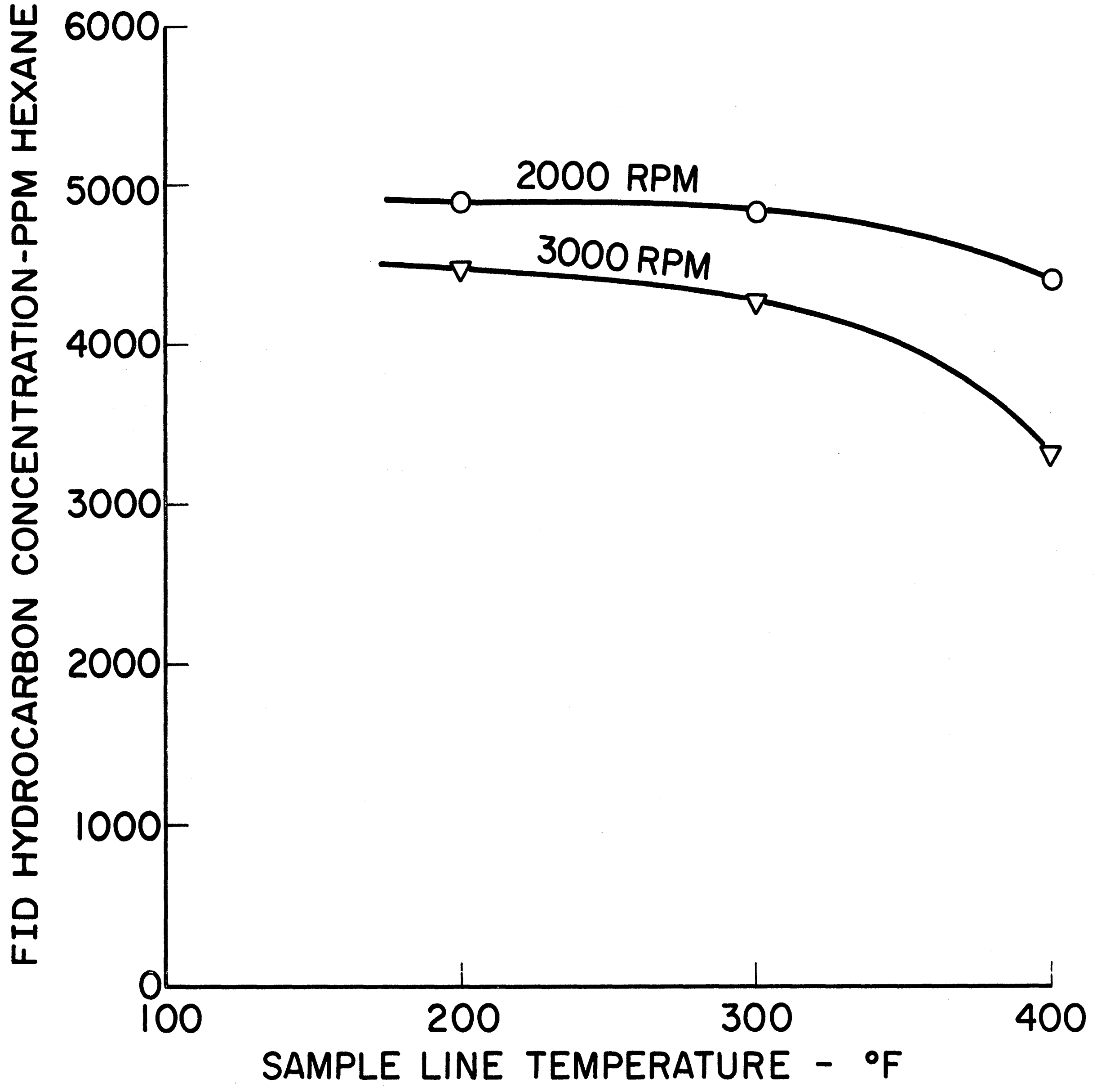

Figure 5. Effect of sample temperature on the measured hydrocarbon concentration—Beckman 106 EX FID.

supported by typical equilibrium air distillation (EAD) test data* for gasoline which shows that, except for a very small residue, vaporization should be nearly complete at the lowest tested sample line temperature of 200°F. Additional tests must be conducted to verify the results presented here.

Even though the residue remaining in the sample line is small it can accumulate with time and, perhaps then, influence FID operation. To prevent any problem with the residue it is suggested that the sample line be regularly back-flushed with nitrogen and periodically purged with a good solvent such as methanol.

The minimum allowable sample line temperature is determined by the saturation temperature of the water in the combustion products. For the maximum condition of complete burning of a stoichiometric mixture furnished to the engine, the mole fraction of water vapor in the combustion products is approximately .14.

If the sample line total pressure is 14.7 lbf/in.^{2}, the partial pressure due to the water vapor is .14 x 14.7 = 2.07 lb/in.^{2}, which is the saturation pressure of steam at approximately 127°F. Therefore if the sample line is maintained at 130°F or higher no condensation should occur.

The optimum sampling temperature is therefore really a range of temperatures from 150°-300°F. Further tests should be conducted to verify this conclusion.

B. Unheated Flame Ionization Detector

Much of our hydrocarbon emission work this year was conducted with the unheated Beckman Model 109A Flame Ionization Detector shown in the photograph of Figure 6, and schematically in Figure 7. This particular instrument is regularly used by automotive emission investigators and will be used in the future for Federal hydrocarbon emission testing. It is similar to the heated FID but uses a positive pressure to force the sample through the detector rather than draw the sample in with a vacuum. The sample, fuel, and air flow rates are controlled by capillary columns rather than restrictor valves as used in the heated FID.

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*The equivalent air/fuel ratio or perhaps it is better to use exhaust gas/fuel ratio in the exhaust of the two-stroke engine is much greater than the carbureted air/fuel ratio because most of the fuel has been burned. Assuming a trapping efficiency of 67%, no misfiring and a carburetor air/fuel ratio of 10:1, the exhaust gas/fuel ratio is about 30:1. Therefore, vaporization should be complete at temperatures significantly below 150°F.

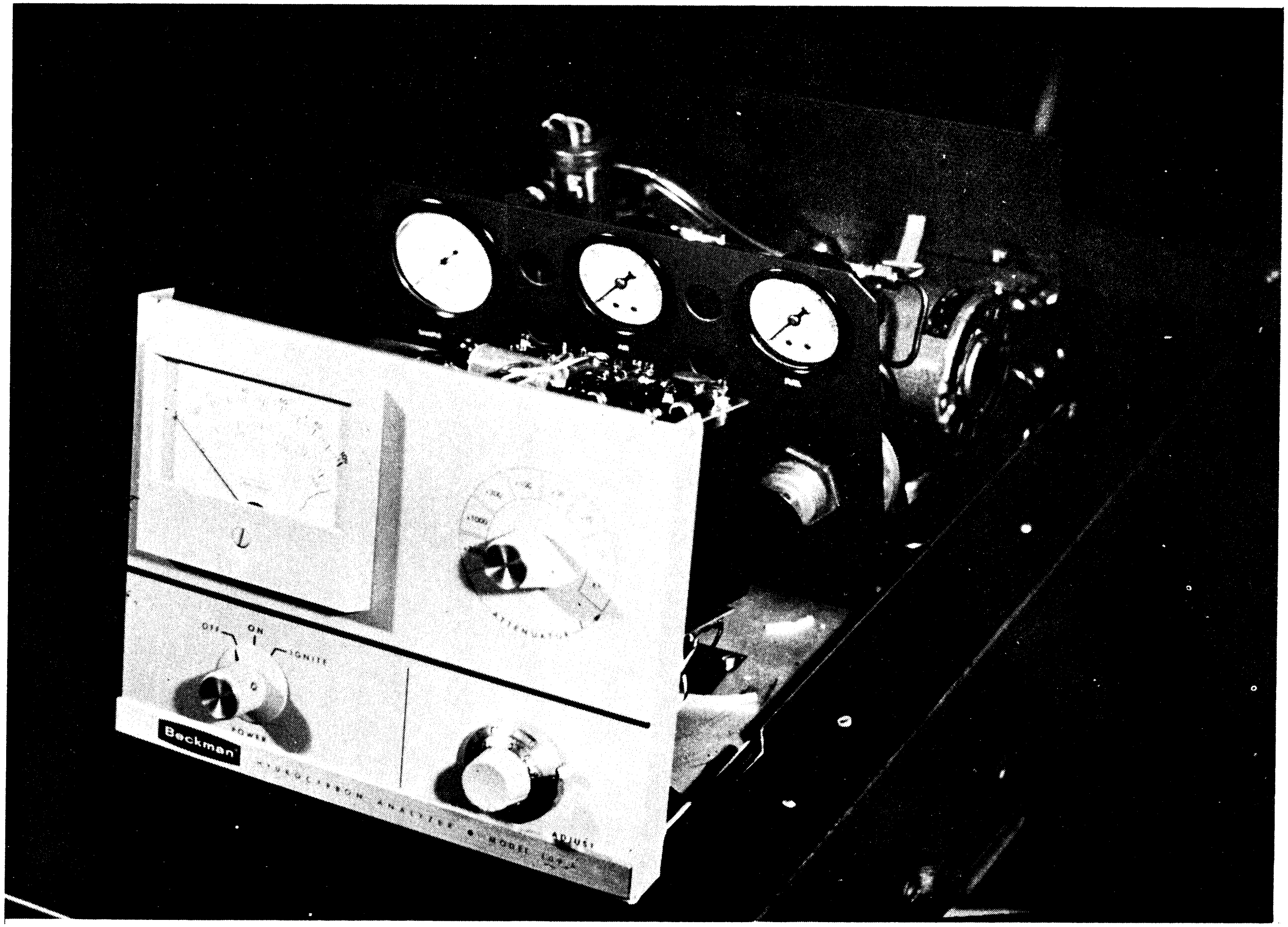

Figure 6. Beckman 109 A unheated flame ionization detector.

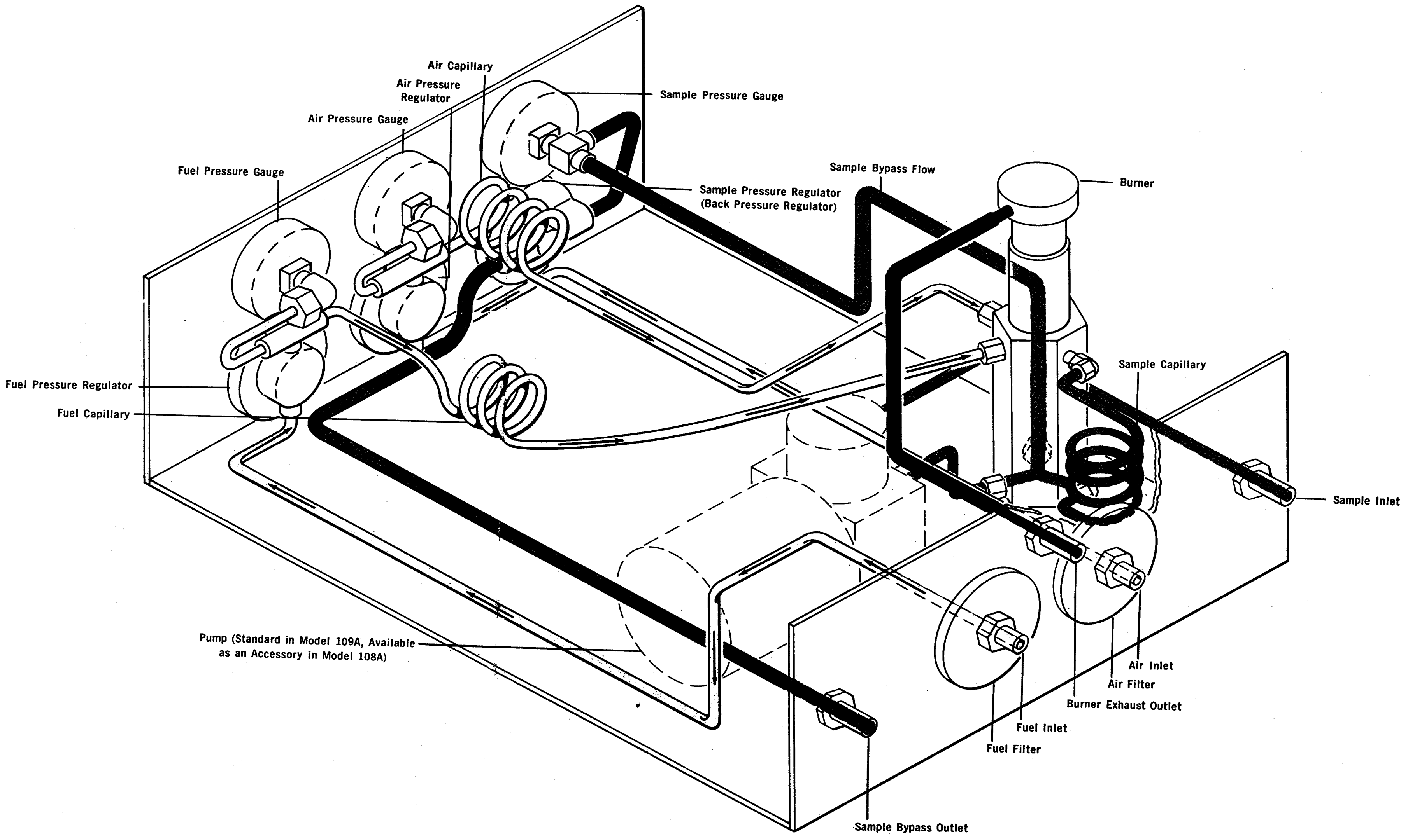

Figure 7. Schematic of the Beckman 109 A FID flow circuitry.

1. OXYGEN INTERFERENCE

The oxygen interference on the measured hydrocarbon concentration was studied extensively in the unheated FID. Unfortunately it is necessary to examine every model of FID instrument to determine the oxygen interference because no two behave in exactly the same manner. This is certainly the case of the unheated and heated Beckman units which are quite dissimilar and therefore oxygen interference data from the heated FID is not applicable.

As stated earlier for the heated FID, oxygen interference in a given instrument will vary as a function of the hydrogen/air ratio (H/A) and hydrogen diluent ratio (H/D). Fortunately the unheated FID uses a pressure flow control system and the relative flow of fuel, air and sample are controlled completely by three precision pressure regulators. The results of the oxygen interference test are shown in Figure 8 for a H/D ratio of .621 and H/A ratio of .0856 which were the settings used in all unheated FID hydrocarbon testing. It was found that this interference could be reduced slightly by decreasing the air flow to the burner. Unfortunately this was not discovered until we had completed our engine testing. The error, however, is small.

The data shows that the greater the oxygen concentration in the sample, the greater is the interference. A positive hydrocarbon correction is indicated because the interference was negative. The correction factor is applied in the following manner:

$$HC_{\text{corrected}} = \frac{HC_{\text{uncorrected}}}{1 - \%\ \text{Error}}$$

At most moderate and high speed operating conditions the outboard engine has approximately 7% oxygen in the exhaust. Thus the approximate error in FID measured hydrocarbon concentration is -7%. It is interesting and believed to be somewhat of a coincidence that the heated and unheated FID oxygen interferences were approximately the same.

2. RELATIVE RESPONSE OF THE NDIR AND FID HYDROCARBON ANALYZERS

Since hydrocarbon emission data is commonly reported for both the Non-Dispersive Infrared (NDIR) and Flame Ionization (FID) Analyzers, it is appropriate to compare their relative response to outboard exhaust hydrocarbons. It has been found (1,4) that the ratio of FID/NDIR data for the average four-stroke engine is approximately 2:1 but can vary from about 1.8:1 to 5:1 depending on the engine test condition and fuel used. Since there are major anomalies in the charging and combustion processes of the two-stroke engine, it was expected that the FID/NDIR hydrocarbon ratio would be significantly different.

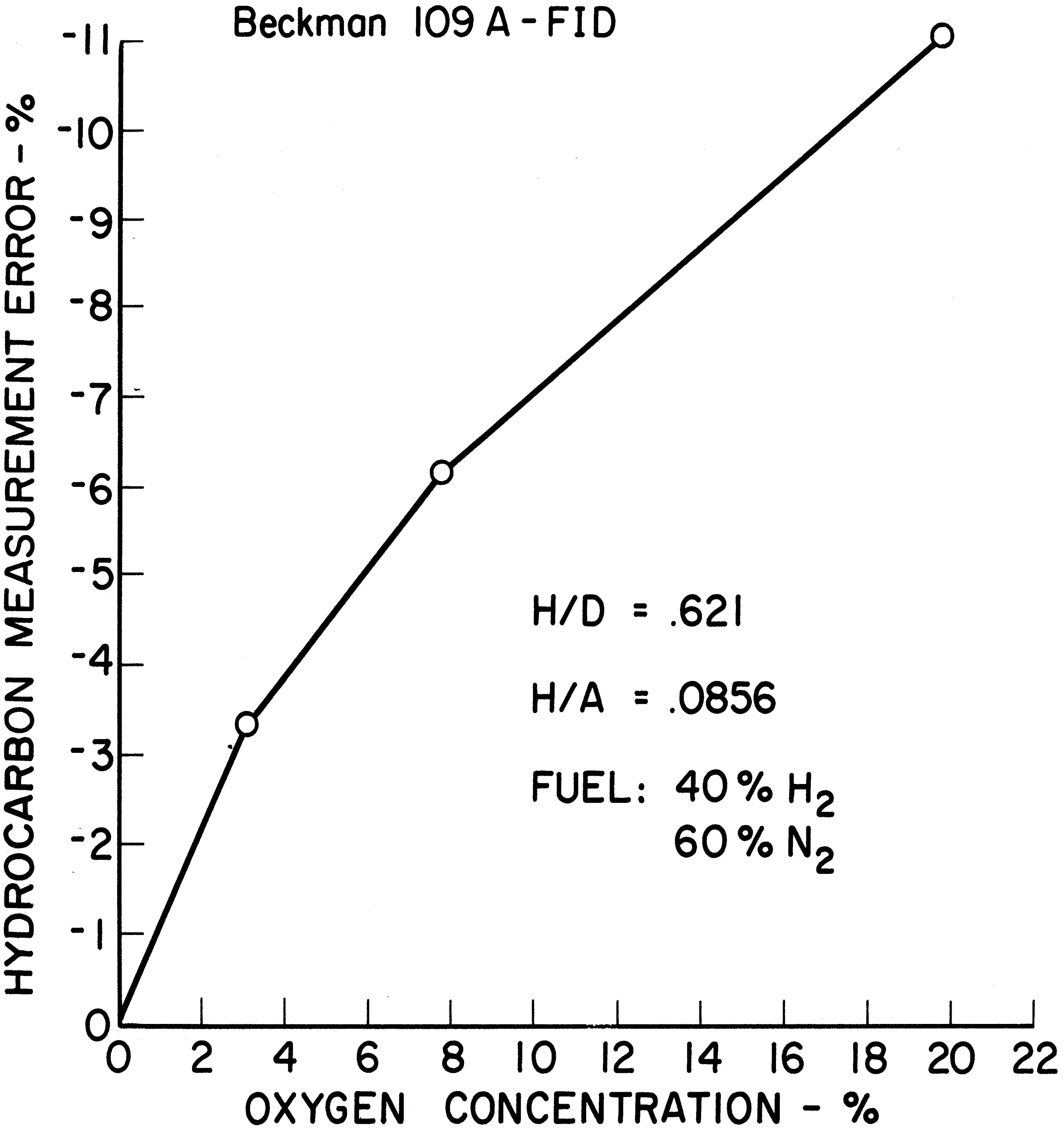

Figure 8. Effect of sample oxygen concentration on the measured hydrocarbon concentration in the Beckman 109 A FID-O_2 interference test.

General Comments on Hydrocarbon Sensitivity

NDIR: The NDIR analyzer is sensitized to a single component, n-hexane (C_6H_{14}) which is supposedly representative of the average unburned hydrocarbon molecule in the engine exhaust. But, since the exhaust hydrocarbons actually consist of over 200 different hydrocarbon species one must look at the response of the n-hexane detector to the various species before an accurate prediction of total exhaust hydrocarbon content can be made. Unfortunately, only the infrared absorbtion spectrum of the paraffinic compounds, except methane, compares favorably with n-hexane. Thus, the analyzer will respond to only the paraffinic carbon atoms on close to a one-to-one basis. The response of the NDIR to the exhaust olefins, diolefins, and aromatics is quite low. The average relative response of the NDIR to a few of the most important exhaust hydrocarbons is shown in Table I. Because several sample cell lengths are commonly used in the NDIR analyzer (a greater length cell is used to increase the sensitivity) the relative response is stated for three typical lengths. In our two-stroke engine work we have used the least sensitive, 2-1/2 in. cell.

TABLE I

HYDROCARBON RELATIVE RESPONSE OF THE NONDISPERSIVE INFRARED ANALYZER

Compounds	Average Relative Responses on Carbon Basis		
	2-1/2 in. Sample Cell	5-1/4 in. Sample Cell	13-1/2 in. Sample Cell
Paraffins			
Methane	29	30	30
Ethane	100	100	100
Propane	102	103	103
n-Butane	101	101	101
i-Butane	105	106	106
i-Pentane	99	99	99
n-Pentane	105	104	104
n-Hexane	100	100	100
n-Heptane	97	97	97
Olefins			
Ethylene	9	9	9
Propylene	30	31	31
1-Butene	---	53	---
1-Pentene	---	57	---
1-Hexene	---	61	---
Acetylenes			
Acetylene	1	1	1
Methylacetylene	16	16	16
Ethylacetylene	33	32	32
Aromatics			
Benzene	2	2	2
Toluene	12	13	13

No relative response is stated for the oxygenated hydrocarbons (aldehydes, ketones, etc.) because these components are removed from the sample in the condensate trap before entering the analyzer. This is likewise true in the FID system.

FID: The FID analyzer responds well to a broad range of hydrocarbons. In fact, with only a few exceptions, it responds almost linearly to the number of organic carbon atoms in the exhaust hydrocarbon molecules. The acetylenes, however, are an exception to the rule. Table II shows the relative response of the FID to the most important exhaust hydrocarbons for two hydrogen-diluent (H/D) ratios in the analyzer. The H/D ratio is the ratio of the FID fuel flow rate (by volume) to the sample flow rate. In our studies we have used an H/D ratio of approximately .6.

TABLE II

RELATIVE HYDROCARBON RESPONSE OF THE BECKMAN FLAME-IONIZATION ANALYZER

Compounds	H/D 0.6	H/D 4.0
Paraffins		
Methane	119	105
Ethane	106	102
Propane	104	103
n-Butane	104	103
i-Pentane	102	101
n-Pentane	103	102
n-Hexane	100	100
n-Heptane	100	100
Olefins		
Ethylene	105	104
Propylene	105	104
Acetylenes		
Acetylene	156	97
Methylacetylene	120	97
Ethylacetylene	123	98
Aeromatics		
Benzene	103	109
Toluene	103	109

Test Results

Both FID and NDIR hydrocarbon emission data were taken at the same time from each of the exhaust ports at 1000, 2000, 3000, and 4000 rpm, at the boat-load test conditions. "Standard" regular gasoline was used as the fuel, and the engine was set to factory specifications for all tests. The NDIR hydrocarbon concentration from cylinder 4 did not, however, agree with the early baseline measurements and suggests that the operating conditions in that cylinder were different from those of the earlier tests. A fouled sparkplug or other factor which could result in increased misfiring may have caused this. The NDIR data from cylinder 3 at 1000 rpm was also found to be outside of the expected range. This also may be related to random engine misfiring.

As expected, the FID measured concentrations were greater than the NDIR data. But the ratio of FID/NDIR hydrocarbons did not approach the 2/1 or greater ratio usually found in four-stroke gasoline engines. The ratio of FID/NDIR emissions is tabulated in Table III for each cylinder at each of the test conditions. Consistently the FID/NDIR ratio is within 10% of 1.3:1.

TABLE III*

RELATIVE RESPONSE OF THE FID AND NDIR ANALYZERS TO TWO-STROKE ENGINE EXHAUST HYDROCARBONS—REGULAR GASOLINE

Boat Load Test Condition, rpm	FID/NIDR Ratio Port No. 1	2	3	4
1000	1.36	1.25	1.35	1.39
2000	1.35	1.34	1.27	1.35
3000	1.33	1.28	1.32	1.30
4000	1.23	1.22	1.25	1.21

*Uncorrected for oxygen in the exhaust.

The chief reason for this difference is that the two-stroke exhaust hydrocarbons consist principally of fuel-type molecules which have a high paraffinic content. However, this measured ratio is slightly less than the true ratio if we correct for negative oxygen interferences in the measured FID hydrocarbon concentration.

C. Nondispersive Infrared Analyzer (NDIR)

The CO, CO_2, and NO data were obtained with Beckman Model IR315 NDIR analyzers which are the same as the NDIR hydrocarbon analyzer but with their individual detectors sensitized to the component of interest. A more detailed description of the NDIR type analyzer is included in last year's progress report. All of the analyzers are shown in Figure 9 installed in the specially constructed mobile cart which was designed and constructed following current automotive industry and government practice. Special care was taken in the NO analyzer to insure that a dry sample was delivered to the sample cell of the analyzer. This was achieved by ducting the sample through a high quality desiccant.

D. Engine Misfiring Instrumentation

An important extension of the past year's effort was the continued development of instrumentation to measure misfiring and/or the completeness of combustion in a given engine cylinder. The ultimate objective of this study is the quantification of "poor quality" combustion as a source of exhaust hydrocarbon emissions. Also, it should be possible to determine more accurately the trapping efficiency using this misfiring data and the measured exhaust oxygen concentration.

The relationships for determination of the trapping efficiency, Γ, and the distribution of the hydrocarbon emissions between the several internal engine sources was included in last year's report and is repeated in the following paragraph.

Let

x = percentage of atmospheric O_2 in the exhaust (% of 100%),
q = misfiring frequency,
Γ = engine trapping efficiency,
ppm NC = hydrocarbon concentration measured in the supplied mixture, 100% misfiring, no combustion,
ppm Com = hydrocarbon concentration in only the combustion products,
ppm = measured exhaust hydrocarbon concentration.

The trapping efficiency, Γ, is given by

$$\Gamma = \frac{100 - x}{100\,(1-q)}$$

$1-\Gamma$ = proportion of mixture lost during the scavenging process.

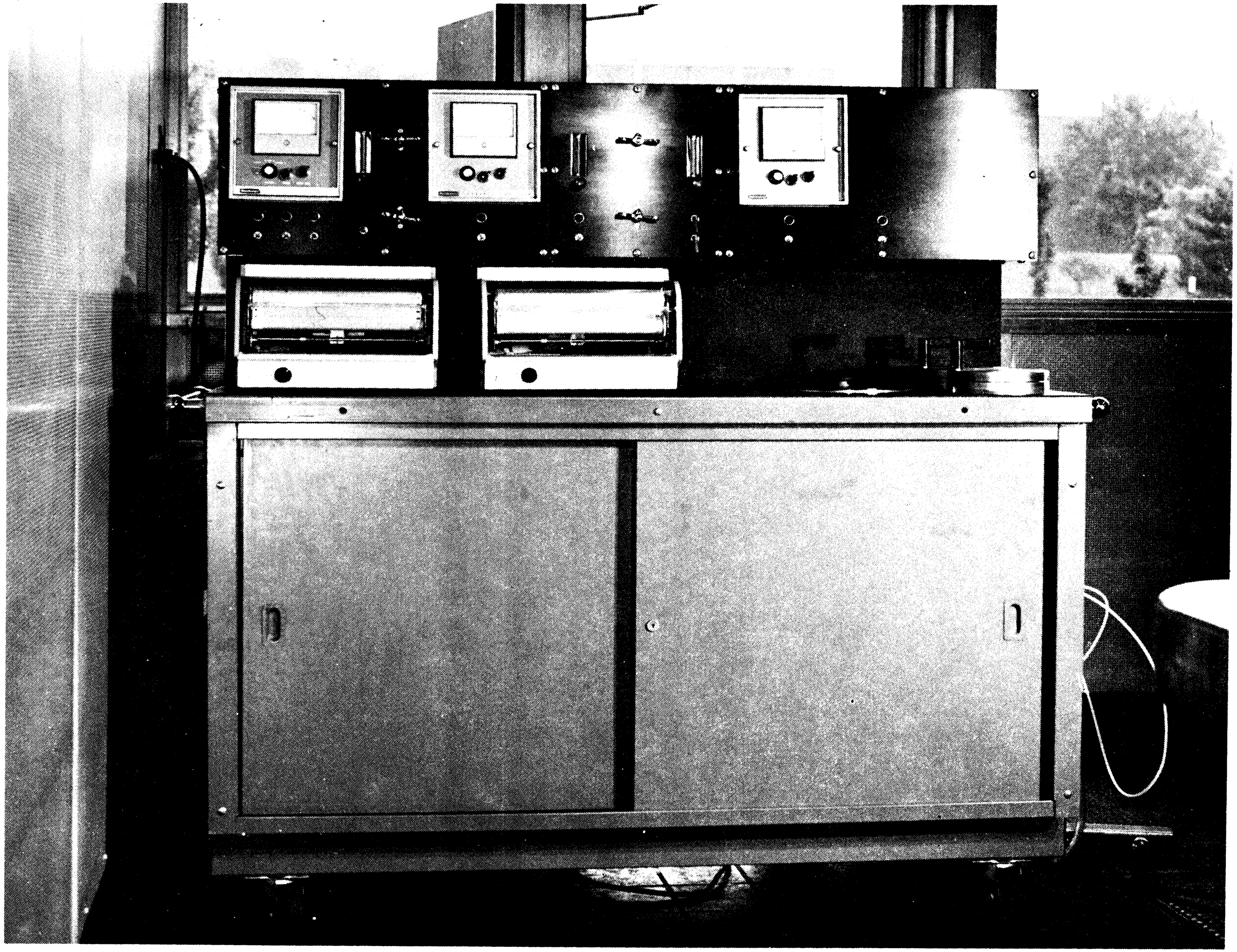

Figure 9. Emission analysis system for CO, CO_2, hydrocarbons and NO—instruments are Beckman IR 315 analyzers.

With this information the following can be determined:

Percentage of hydrocarbon emissions

due to the unburned mixture $= x \cdot \text{ppm NC/ppm}$
due to the scavenging losses $= (1-\Gamma) \cdot \text{ppm NC/ppm}$
due to the misfiring $= x - (1-\Gamma) \cdot \text{ppm NC/ppm}$
due to combustion $= (1 - x) \cdot \text{ppm Com/ppm}$

A number of potential techniques have been explored to measure misfiring, but only two have proved to be of significant value, the ionization probe and the photomultiplier.

1. IONIZATION PROBE

The first of these, the ionization probe or ion-gap (5,6), operates on the principle that the high temperatures of combustion cause significant ionization. An air gap formed by a pair of electrodes is located in the combustion chamber, and a voltage potential is placed across the "gap." As the flame front moves through the "gap," the gases ionize, decreasing the gap resistance and causing a current to flow in an external circuit. The ionization is sensed by measuring the voltage drop across a load resistance in the external circuit. A voltage pulse is an indication of at least some burning in the combustion chamber. The ionization probe circuitry and associated equipment is illustrated schematically in Figure 10. The "Buege Counter" in this figure is an electronic counter with an adjustable "count voltage" threshold. When the voltage pulse across the load resistor exceeds this threshold level the counter triggers and indicates a firing cycle. Another counter (not shown) is used to measure the number of engine revolutions. The difference between the engine revolutions N and the number of "fired" cycles, N_F, is the number of "misfired" cycles, N_{MF}. The misfiring frequency, q, is readily obtained by application of the following equation.

$$q = \frac{N - N_F}{N} = \frac{N_{MF}}{N}$$

Two different ion-gap arrangements are currently being used. In the first the probe is installed in a special holder in the cylinder head. The location of the probe in the cylinder head is shown in the photograph of Figure 11. The gap, itself, is formed at the tip of an insert which is shown schematically with the holder in Figure 12. One deficiency of this particular arrangement is that the ion-gap is located very close to the spark-plug and will be triggered by even a small diameter flame kernel. Therefore, a flame, which only partially traverses the chamber, will to the ionization probe appear as a complete firing cycle. A partial combustion cycle might contribute almost as much to the hydrocarbon emissions as a total misfire. To alleviate this deficiency a second cylinder head was prepared which employed three separate ion-gaps.

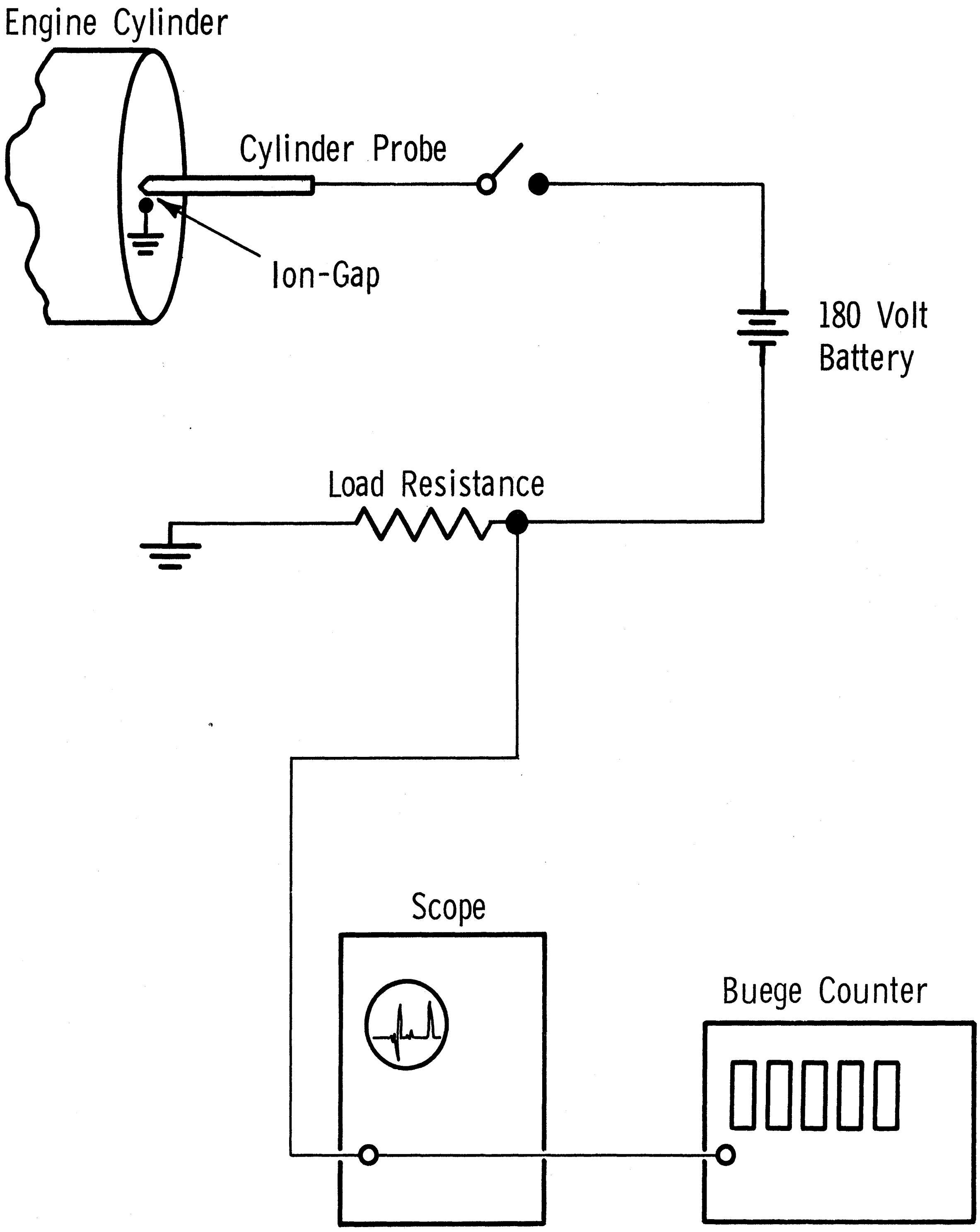

Figure 10. Schematic diagram of the ionization probe misfiring measurement system.

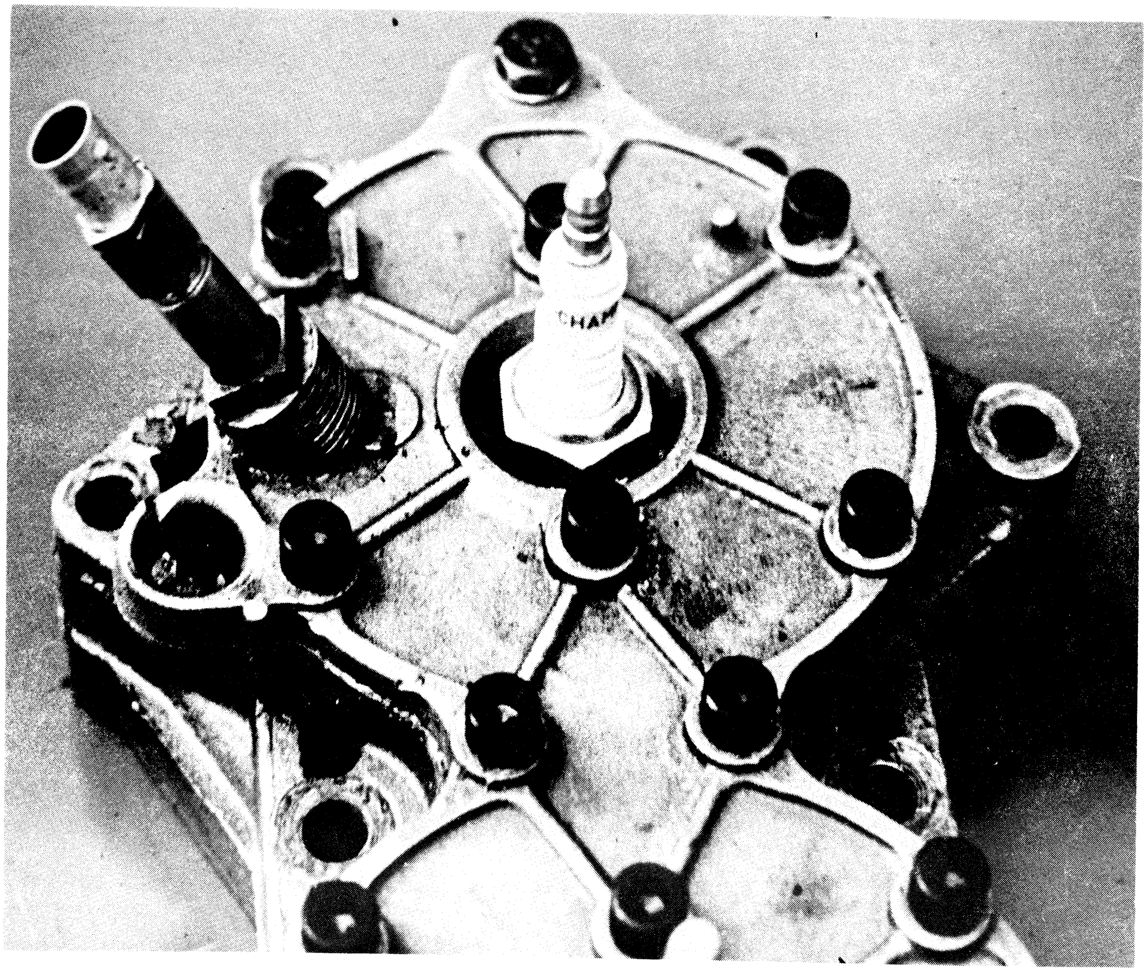

Figure 11. Single ionization probe installed in the cylinder head.

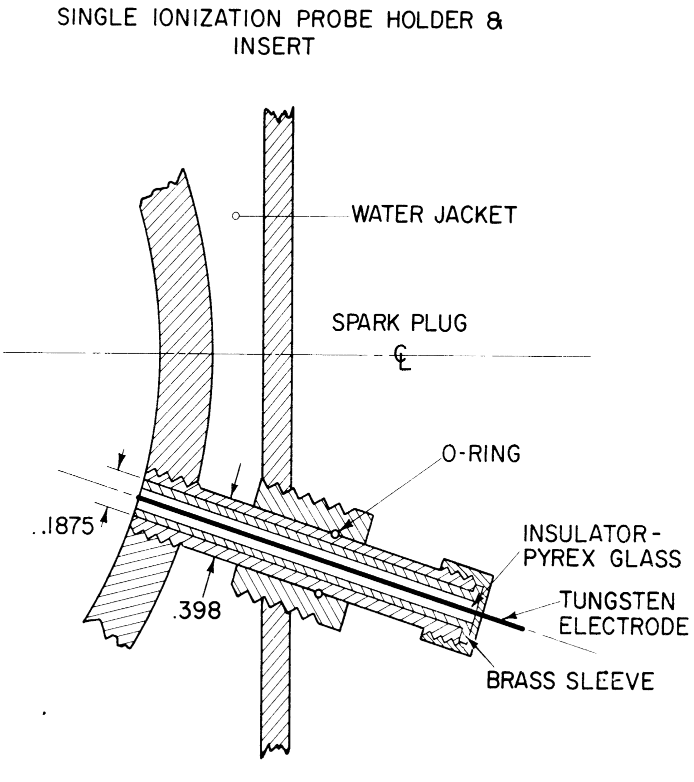

Figure 12. Schematic diagram of the single ionization probe and its holder.

The cylinder head with the three ion-gaps installed is shown in Figures 13 and 14. By using a number of ionization probes located along a radius of the combustion chamber (measured from the ignition source), it was hoped that not only could the appearance or nonappearance of a flame be detected but that reasonable quantification of the degree of flame propagation could be made. The data can be presented statistically to show the frequency of the flame occurring at each of the three ion-gaps. This information combined with knowledge of the hydrocarbon concentration in the unburned gases should lead to a much improved prediction of misfiring and incomplete combustion as a source of hydrocarbon emissions.

Very small No. VR-2 Champion spark plugs, which were originally designed for use in model airplane engines, were used as ion-gaps. Preliminary results using these small spark plugs have been very satisfactory. The ceramic insulator is effective and prevents the resistance breakdown between the electrodes commonly observed with other configurations after moderate use.

2. PHOTOMULTIPLIER

The second technique which we have used employs the light sensing properties of a photomultiplier tube (7,8) to detect the combustion generated light in the engine cylinder. A quartz window probe to permit viewing the flame was installed in the cylinder head through the same fixture that was used to hold the single ion-gap in place. The photomultiplier tube was then placed adjacent to the outside end of the window. We had hoped to place the phototube some distance from the engine, and duct the light with fiber-optics to the phototube, but found that the combination of the light transmitting characteristics of the quartz window and the fiber-optic device together with the wavelength response of the photomultiplier caused excessive attenuation of the signal.

The phototube in its container is shown adjacent to the quartz window in Figure 15 and the schematic of the system is shown in Figure 16. The electronic counter which was employed in the ion-gap study is also used in the light emission study to detect combustion. A special power supply which was built in our electronics shop was required for the photomultiplier tube.

The photomultiplier system suffers from the same deficiency as the single ionization probe because it can detect only the appearance or nonappearance of the flame. However, it may be possible to relate the quantity of light emitted, as measured by the voltage output of the photomultiplier tube, to the degree of combustion measured with the multiple ion-gap system.

The photomultiplier system has an important advantage if it can be developed to provide quantitative data. It is very sensitive to light and generates a high voltage output from even a weak flame. This contributes to a high signal/noise ratio and minimizes problems with capacitor-discharge ignition system noise.

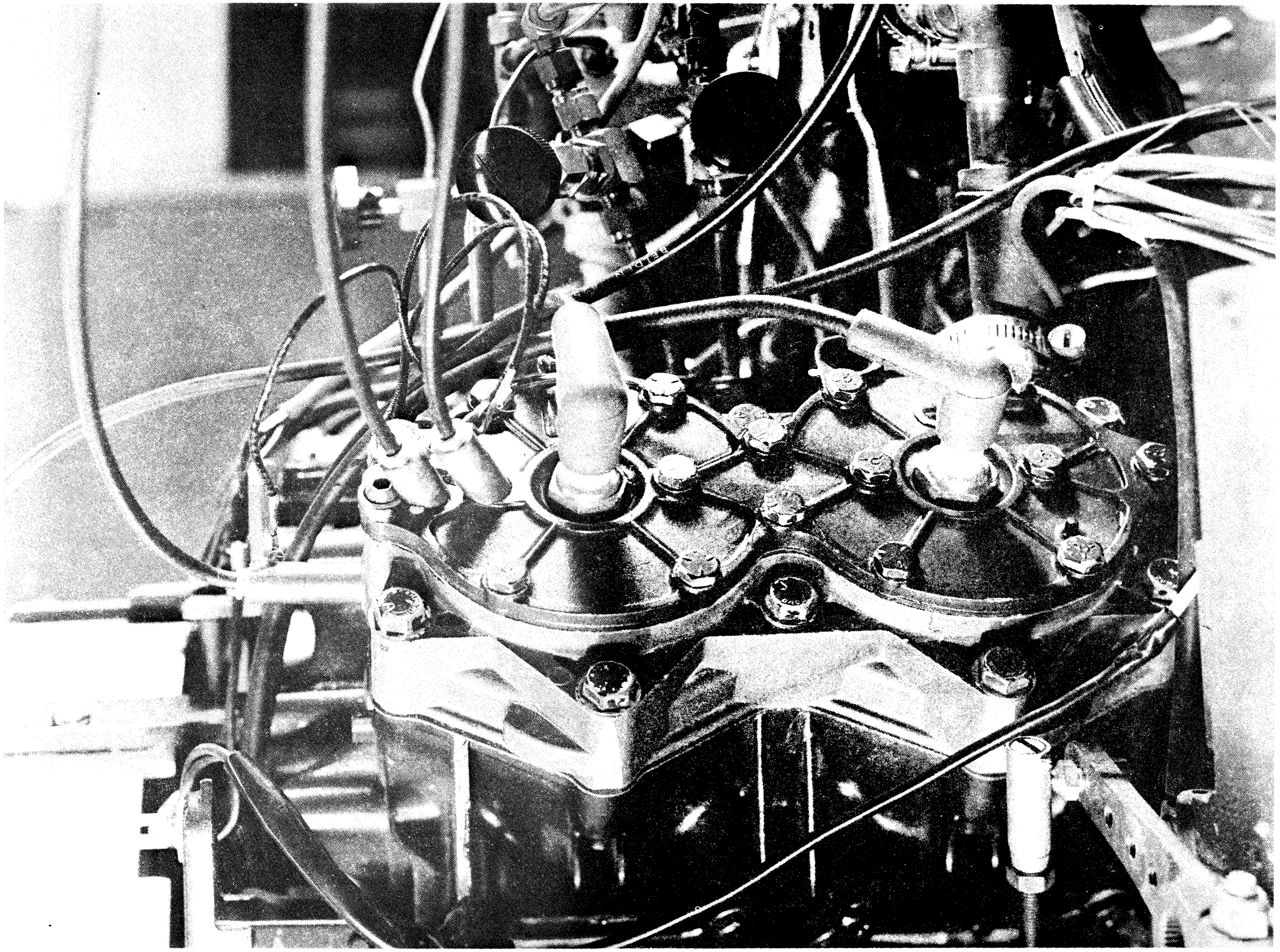

Figure 13. Multiple ionization probes installed in the engine cylinder head viewed from outside of the engine.

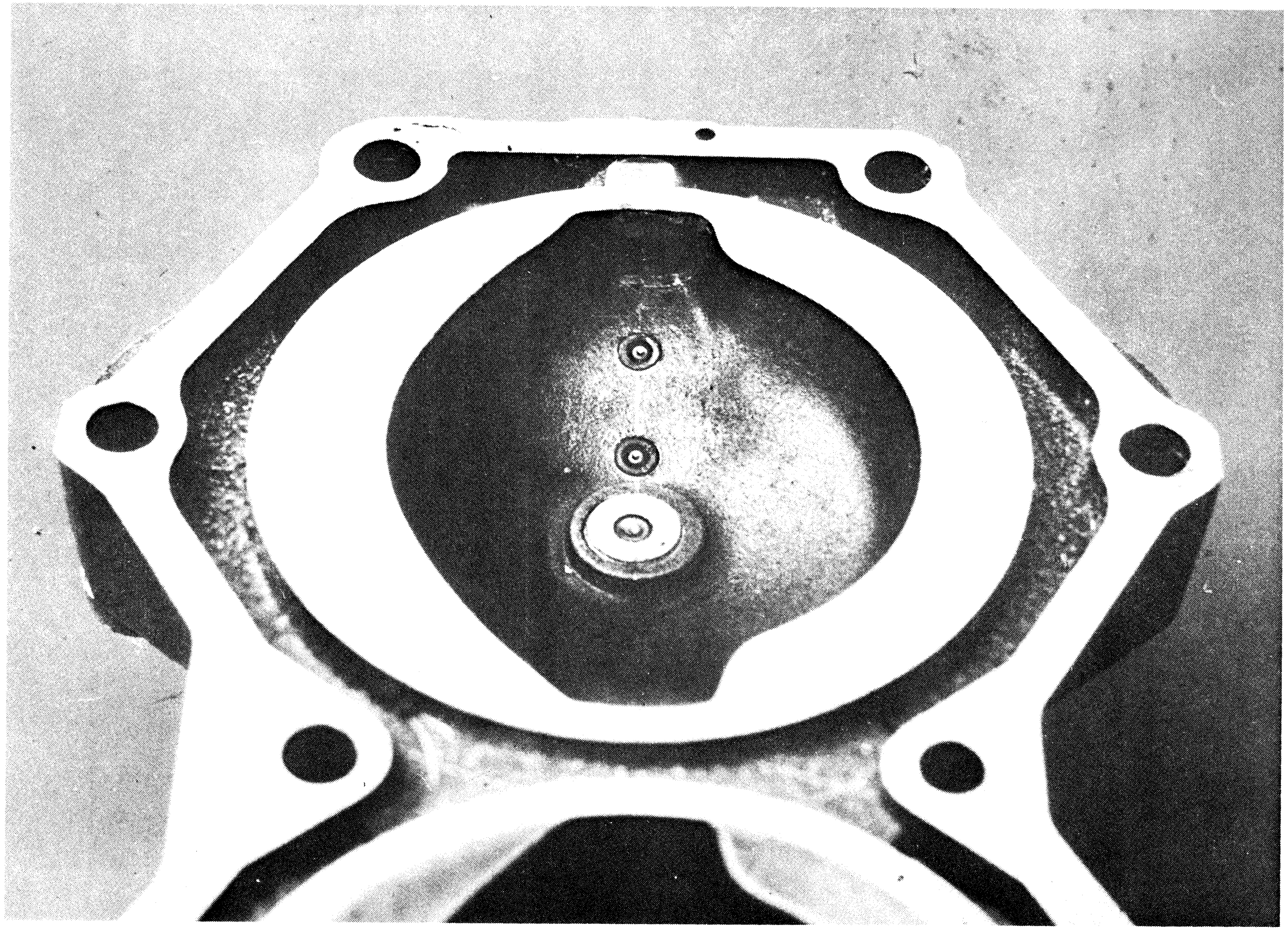

Figure 14. Multiple ionization probes installed in the engine cylinder head viewed from the combustion chamber.

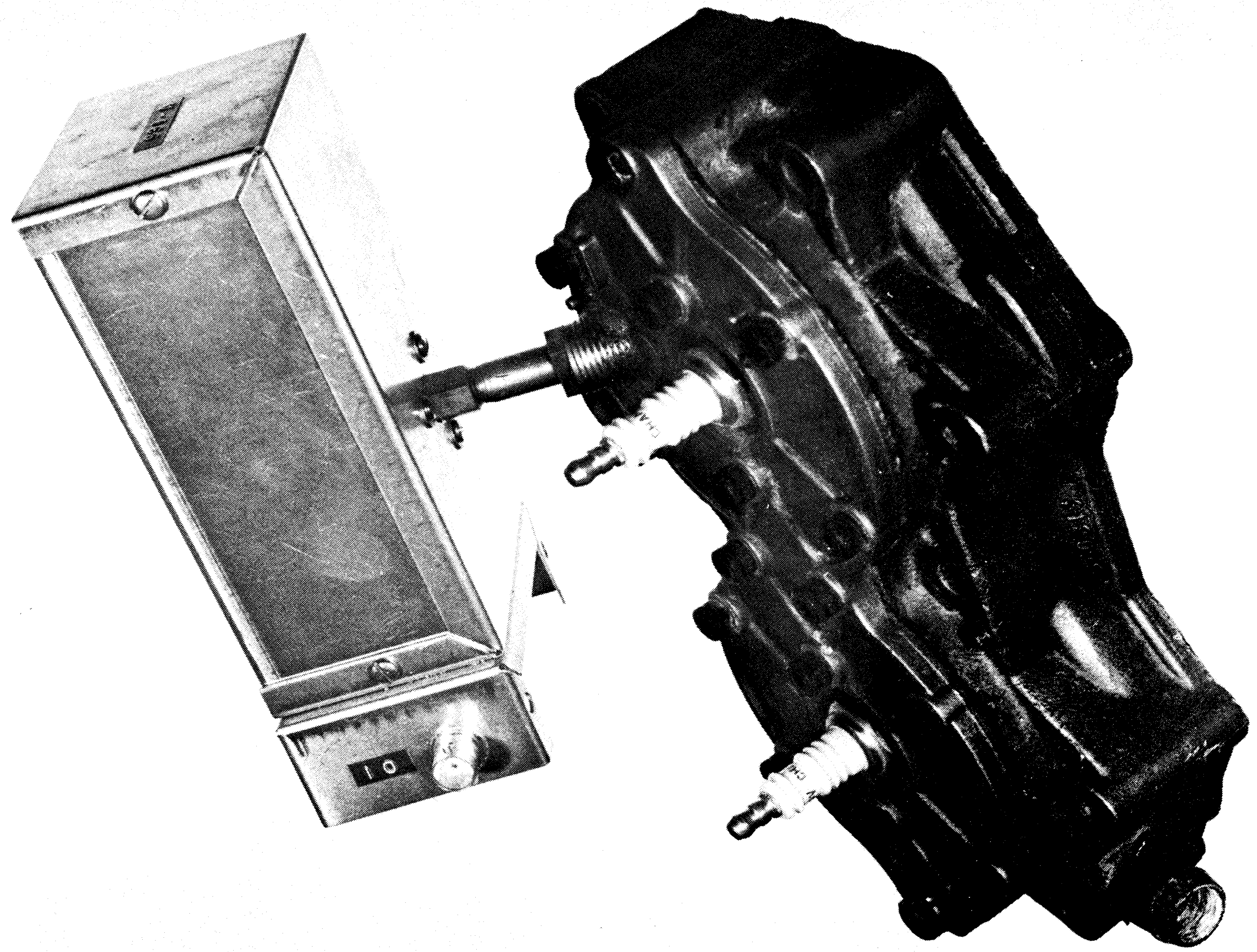

Figure 15. Photomultiplier tube in holder mounted in proximity to combustion chamber viewing window.

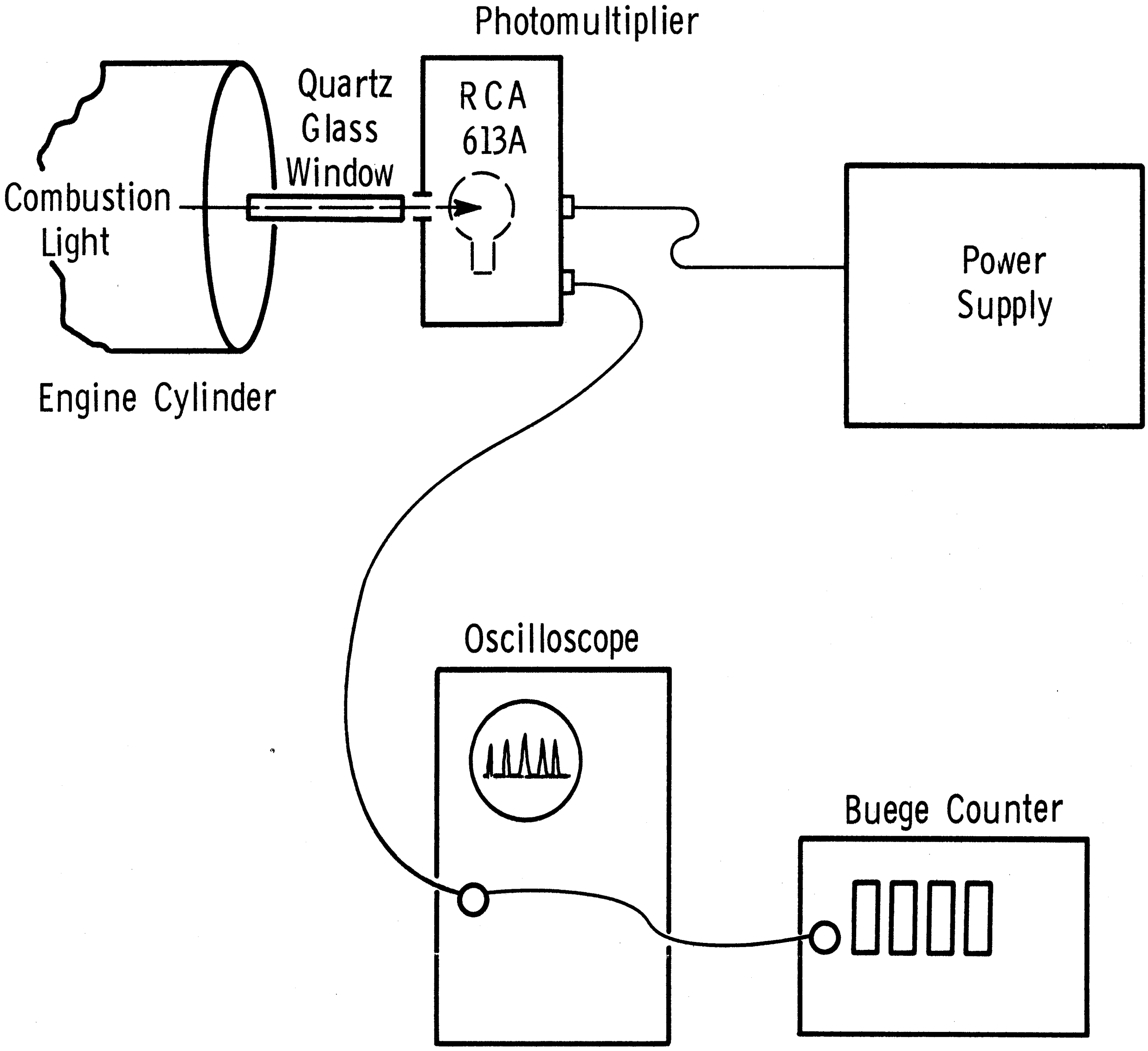

Figure 16. Schematic diagram of the photomultiplier tube misfire measurement system.

3. PRELIMINARY TEST RESULTS

Ionization Probe

With the single ion-gap system preliminary results showed that, as expected, the misfiring and poor combustion is a major problem only at low speed and light loads. At higher speeds (3000 + rpm) the incidence of misfiring was very low and indicates that the exhaust hydrocarbons in this region are almost completely a result of "through scavenging."

Sample data from cylinder 2 at 1000 rpm, boat-load, is presented in the oscilloscope photographs of Figures 17 and 18. Note the varying magnitude of the voltage response in Figure 17. This indicates a varying degree of ionization in the ion-gap and most probably is indicative of widely varying combustion quality. A flame front appears to have passed the ion-gap on almost every cycle but in some cases may not have traveled much further as shown by the low peaks. It is therefore not possible to quantitatively correlate this data with misfiring.

The expanded trace from a single cycle is shown in Figure 18 and illustrates one deficiency of the early circuit design. Occasionally, a secondary pulse occurs due to reionization of the gap, caused, perhaps, by a secondary flame front. This secondary pulse may cause a double count on the "Buege" electronic counter if the valley between the two voltages peaks is slightly below the counter threshold setting. Consequently, a new circuit has been designed to alleviate this problem. It utilizes a "Schmidt trigger" which causes a voltage step at the desired threshold level. The circuit is reset by a voltage pulse obtained from a magnetic pickup mounted near the engine flywheel. The final trace appears as a square wave with no secondary pulse if firing occurs, otherwise there is no response. Sample data obtained at 1000 rpm is shown in Figure 19.

At higher speeds the voltage output of the ion-gap circuit is much greater because of higher flame temperatures and is also more repetitive which is indicative of much more uniform combustion and decreased misfiring. Typical data at 3000 rpm is shown in Figure 20.

We have not yet obtained a full range of data with the multiple ion-gap system since several pieces of electronic circuitry have not been completed.

Photomultiplier

Typical 1000 rpm data for the photomultiplier is illustrated in Figures 21 and 22. The photomultiplier response from a moderate number of cycles is shown in the first photograph and illustrates the wide variation that occurs in the combustion generated light which is indicative of a varying degree of the completeness of combustion. No total misfires are shown. The data bears strong resemblance to the ion-gap data at 1000 rpm and reinforces the conclusion that the combustion process is quite nonrepetitive as to the degree of completeness.

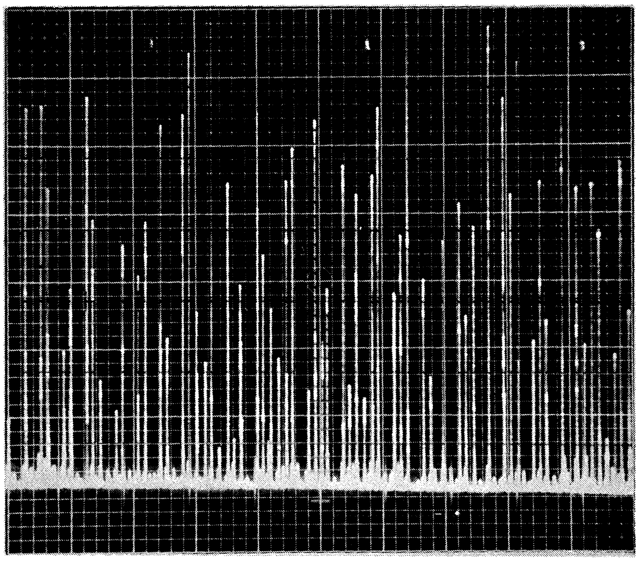

Figure 17. Sample misfiring data with the single ionization probe—1000 rpm, boat load.

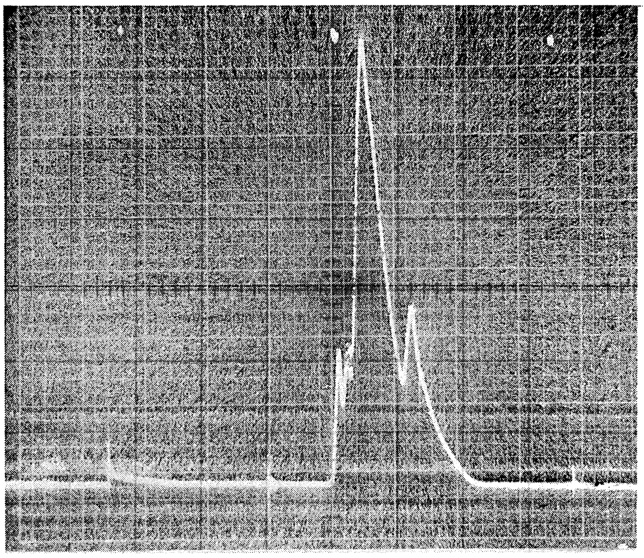

Figure 18. Sample misfiring data with the single ionization probe—1000 rpm, one engine cycle.

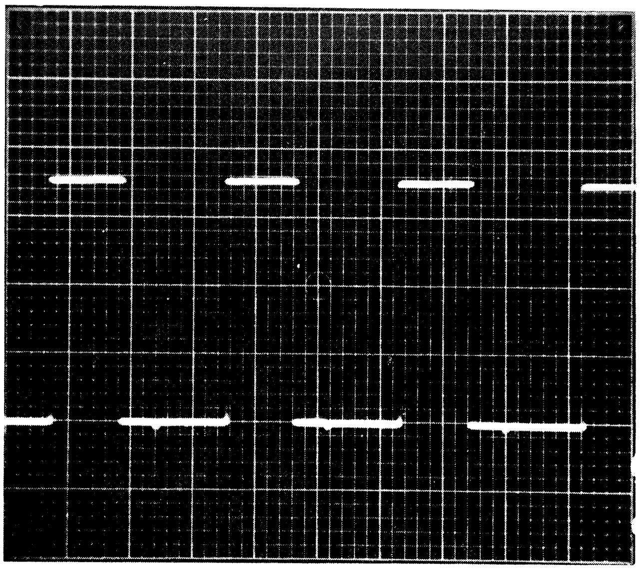

Figure 19. Sample square-wave conditioned ionization probe misfiring data.

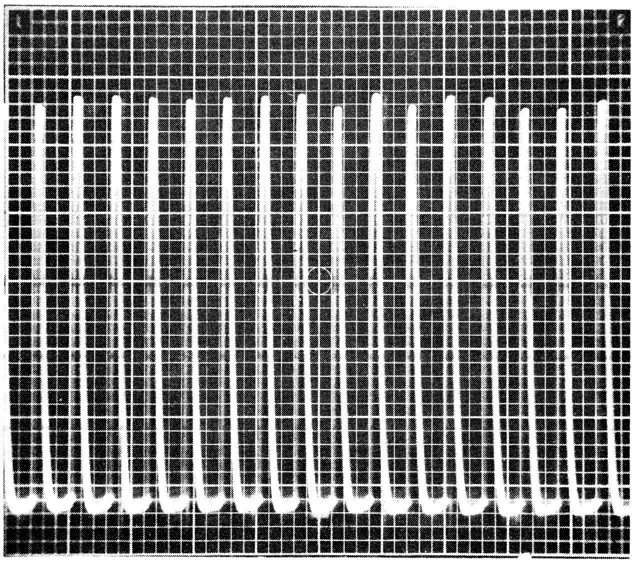

Figure 20. Sample misfiring data with the single ionization probe—3000 rpm, boat load.

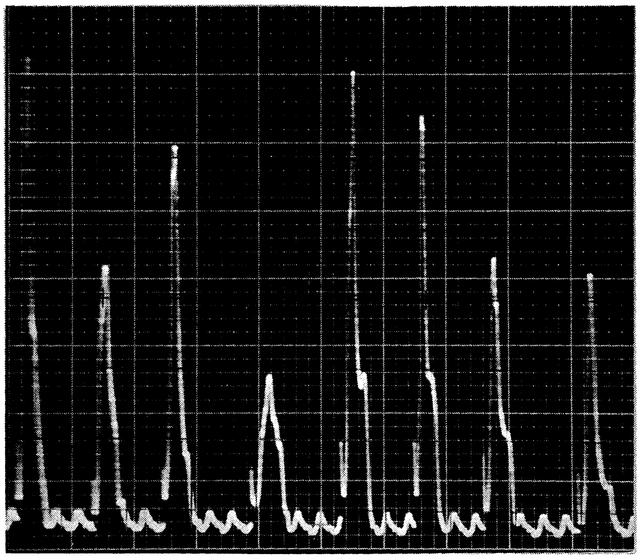

Figure 21. Sample misfiring data using the photomultiplier tube—1000 rpm, boat load.

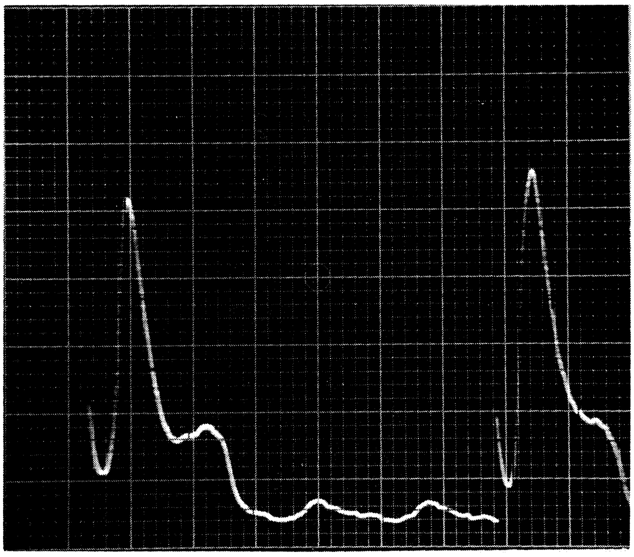

Figure 22. Sample misfiring data using the photomultiplier tube—3000 rpm, boat load.

The data from two engine cycles shown in Figure 22 illustrates several factors. First of all, the initial voltage spike is caused by the ignition-spark light. The counter threshold must be set above this value to prevent counting the spark as a firing cycle. Secondly, a secondary voltage pulse occurs in a similar manner to the ion-gap data. This is caused by a secondary flame or some perturbation of the primary flame. This extra pulse may also cause a double count for a given cycle and necessitates the use of a circuit similar to the step circuit prepared for the ion-gap system.

Unfortunately the development of these misfiring transducers has been relatively slow. The significant noise associated with the C-D ignition system and the erratic output signal have been the principal sources of difficulty.

III. RESULTS AND ANALYSIS

In this section of the report the results of an extensive exhaust gas analysis study are reported and discussed. Also the comparative hydrocarbon emission results of operating the engine on two fuels of widely varying composition are discussed. From this study, inference is made as to the internal engine sources of hydrocarbon emissions.

A. Total Emission from the Two-Stroke Engine

Last year our experimental effort was concentrated on the unburned hydrocarbon emissions from the two-stroke outboard engine because they were considered to be the most severe problem relative to the four-stroke engine. In this year's study several other important exhaust constituents were quantitatively investigated to determine their typical exhaust gas concentration and to place them in the proper perspective with respect to each other. The exhaust components measured in this study were:

- Carbon monoxide (CO)
- Nitric oxide (NO)
- Carbon dioxide (CO_2)
- Unburned hydrocarbons (NDIR and FID)

Carbon dioxide was included in this list, not because it is considered a pollutant, but because its measured concentration can be useful in providing further knowledge of the combustion process. An increase in the CO_2 concentration may be an indication of one of three things:

(1) The fuel/air ratio is decreasing (rich→stoichiometric);

(2) the trapping efficiency is increasing; and

(3) the misfiring frequency is decreasing.

Also if the exhaust CO and O_2 concentration are known it may be possible to predict the combustion fuel/air ratio in the following manner: From the O_2 measurement it is possible to predict the engine trapping efficiency, Γ, if misfiring is not significant. This factor may be considered as the proportion of the total exhaust gas which results from the combustion process, the remainder resulting from the "through scavenging" of unburned charge. It should be possible to determine the CO_2 and CO concentration in the combustion products as

$$CO_{combustion} \cong \frac{CO_{measured}}{\Gamma}$$

$$CO_{2\,combustion} \cong \frac{CO_{2\,measured}}{\Gamma}$$

With this data, charts such as developed by D'Alleva and Lovell (9) or the Eltinge (10) can be used to determine the combustion fuel/air ratio. An example of this type of chart is shown in Figure 23 for a fuel with a hydrogen/carbon ratio of 2.13. Note that the foregoing technique is not valid for lean mixture ratios but, since they are rarely used in the two-stroke engine, this is of little consequence. If misfiring or poor combustion is significant, this technique may still be used although Γ now represents only the trapped and totally burned mixture.

The following example illustrates the potential of this technique.

Example:

The exhaust composition from port 2 at 3000 rpm, boat-load was found to consist of:

$$CO_2 = 9.2\%$$

$$CO = 3.8\%$$

$$O_2 = .28 \times 21\% = 5.9\%$$

$$\Gamma = 1 - .28 = .72$$

Therefore the "combustion products" concentration of CO_2 and CO are:

$$CO_{2\,comb.} = \frac{9.2}{.72} = 12.8\%$$

$$CO_{comb.} = \frac{3.8}{.72} = 5.3\%$$

Assuming that the test fuel has a H/C ratio of 2.13 we obtain from the chart in Figure 23:

$$A/F \cong 13.0/1$$

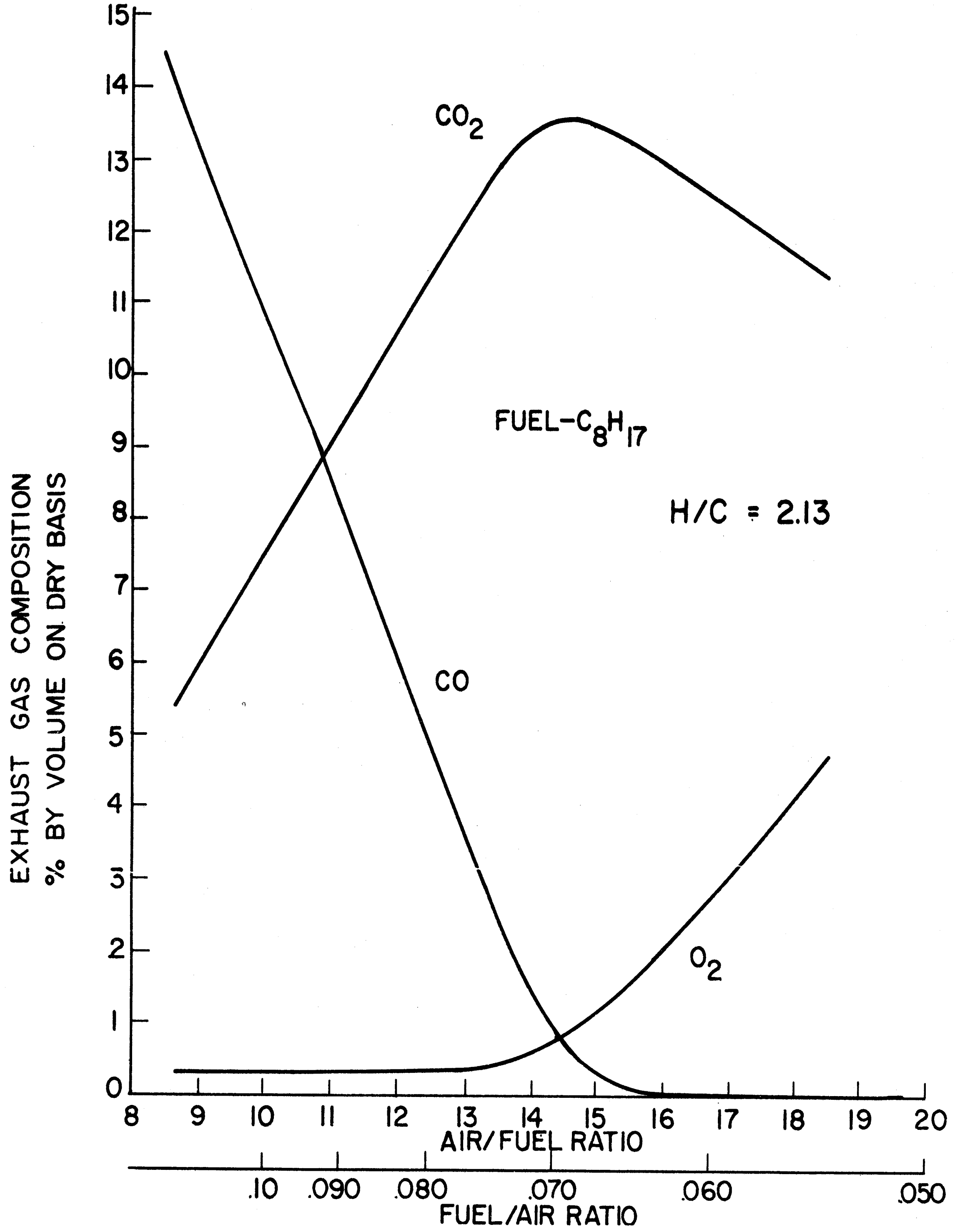

Figure 23. Exhaust gas composition as a function of air/fuel ratio for a hydrocarbon fuel with a hydrogen/carbon ratio of 2.13.

1. CARBON MONOXIDE AND CARBON DIOXIDE

Carbon monoxide has been recognized as a major pollutant for many years. Physiologically it destroys the ability of the blood to deliver life-supporting oxygen to the body cells. Even before a lethal concentration is attained, significant degradation of the body processes occur.

Current legislation restricts the allowable CO effluent from the automobile to 23 grams/mile (≈1.5%) based on the standard California Cycle. Future standards promise to be even more restrictive.

The formation of carbon monoxide is principally associated with the use of rich mixture ratios and/or poor mixing of the fuel/air mixture and therefore poor combustion quality. Generally, the leaner the fuel/air ratio the lower the exhaust CO concentration. Under steady-state operating conditions with a stoichiometric fuel/air ratio, the average automotive engine emits less than 1% CO.

The results of the CO, CO_2 investigation are shown in Figures 24-28 for the four individual cylinders and from the exhaust pipe at the boat-load test conditions. As a point of interest the NDIR hydrocarbon data are also plotted in these figures.

The data from cylinders 1 and 3 were quite similar. As would be expected from the hydrocarbon data, the CO decreases with increasing speed. In other words, the CO decreases with an increase in combustion efficiency and/or a decrease in fuel/air ratio. The low-speed CO emissions are high compared to those from a 1969 automotive engine but at higher speeds the CO level is comparable.

The CO emissions from ports 2 and 4 were similar to each other but were significantly different from the data of ports 1 and 3. At the 2000 rpm boat-load the CO emissions were the highest, approximately 8%. At 1000 rpm the CO concentration from all four cylinders was similar but from cylinders 2 and 4 the CO increased before eventually decreasing at the 3000 and 4000 rpm test conditions. Considering together the CO and CO_2 emissions from exhaust ports 2 and 4 at 1000 and 2000 rpm and comparing them with the emissions from ports 1 and 3 suggests that cylinders 1 and 3 are misfiring less or are being scavenged more efficiently. At the 3000 and 4000 rpm test conditions the CO concentration is greater and CO_2 concentration less than from cylinders 2 and 4 and suggests that cylinders 2 and 4 are receiving a substantially richer mixtures than cylinder 1 and 3.

The exhaust pipe CO, CO_2 and hydrocarbon emissions shown in Figure 28 are essentially the average of the individual cylinder emissions. There is some oxidation of the unburned hydrocarbons but only limited additional oxidation of CO.

The hydrocarbon data plotted in these figures are similar to the data reported for the baseline testing in last year's program. The only appreciable

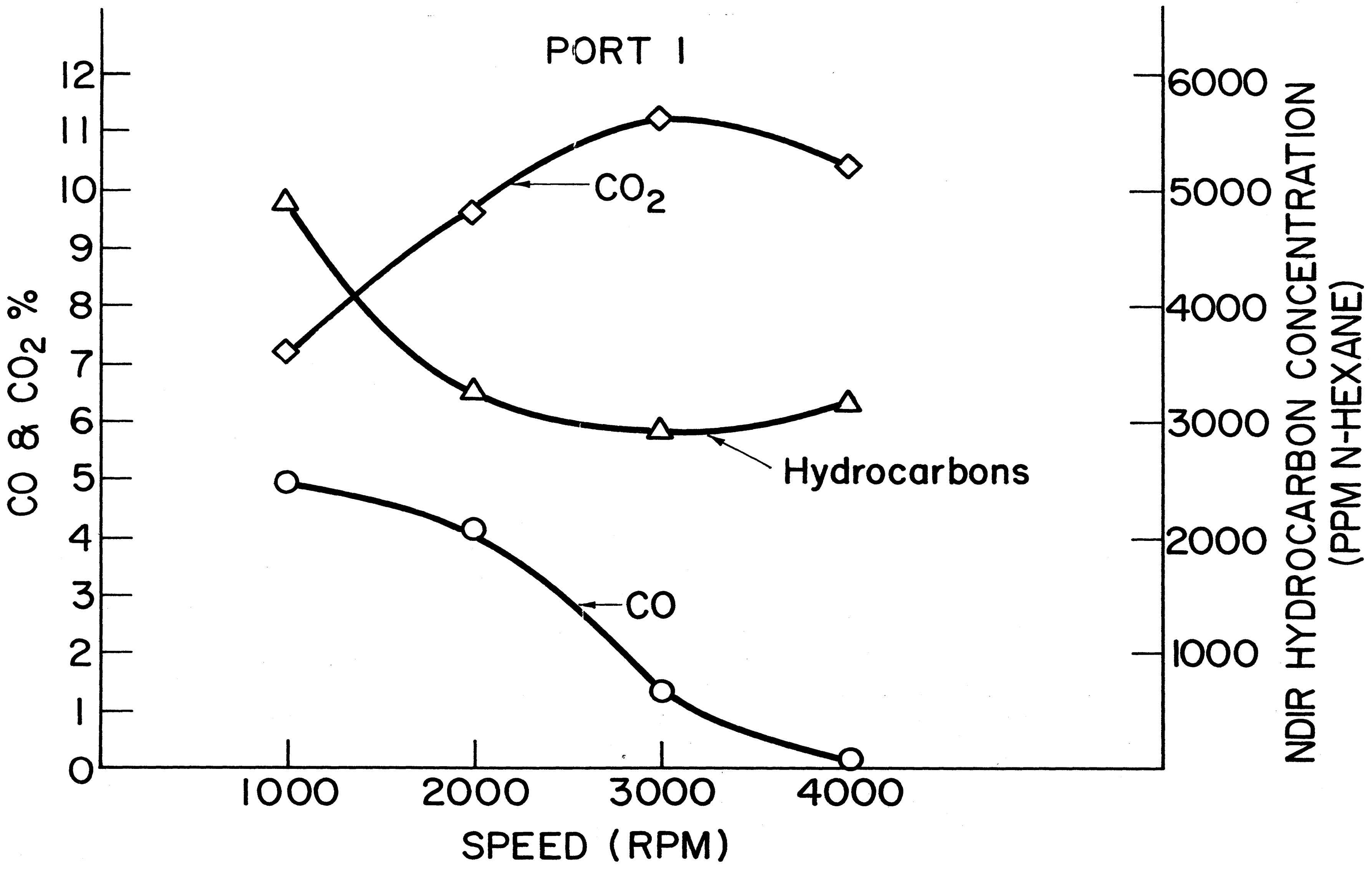

Figure 24. Hydrocarbon (NDIR), CO, and CO_2 exhaust emissions from cylinder 1 at the boat load test conditions.

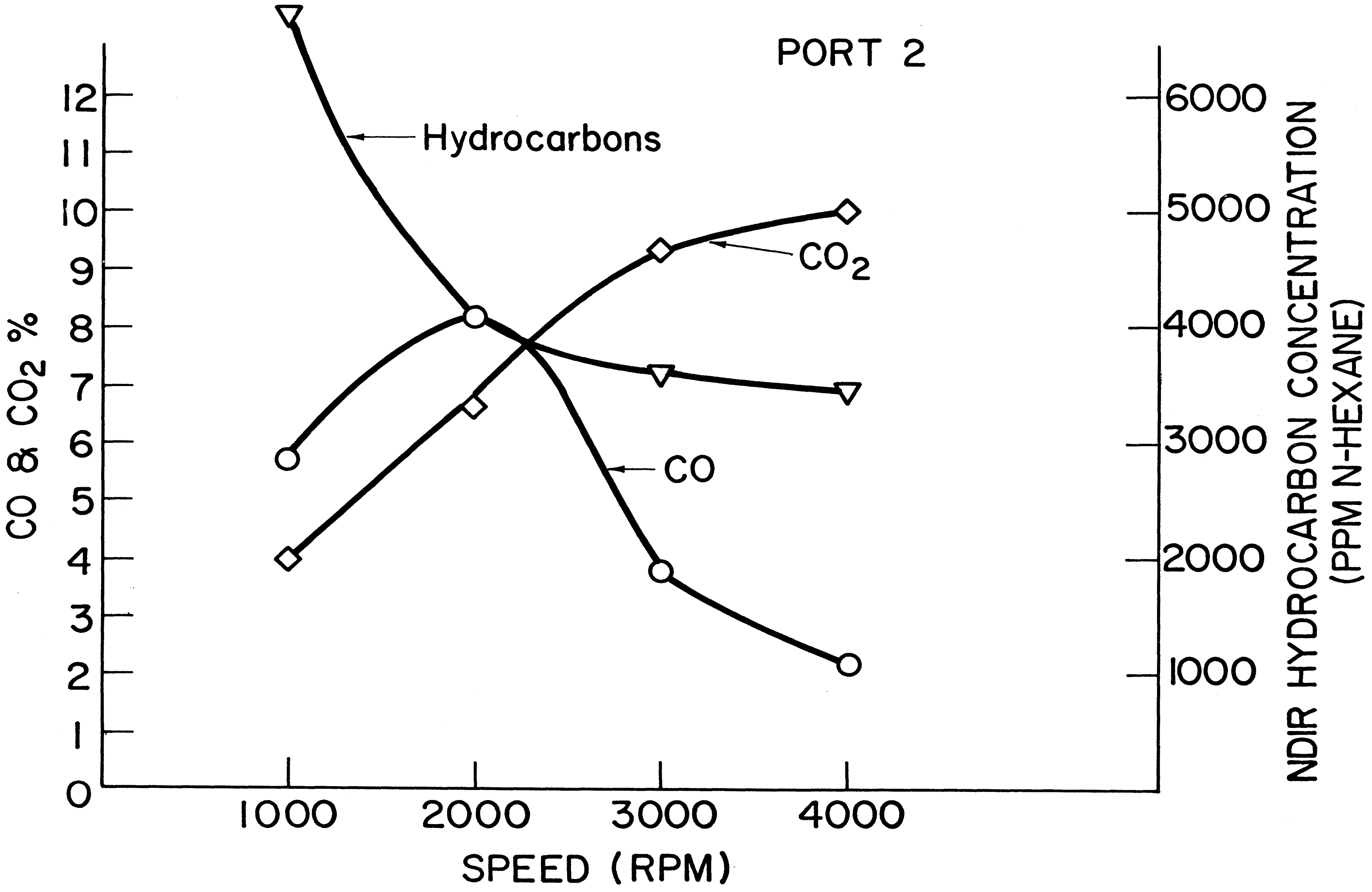

Figure 25. Hydrocarbon (NDIR), CO, and CO_2 exhaust emissions from cylinder 2 at the boat load test conditions.

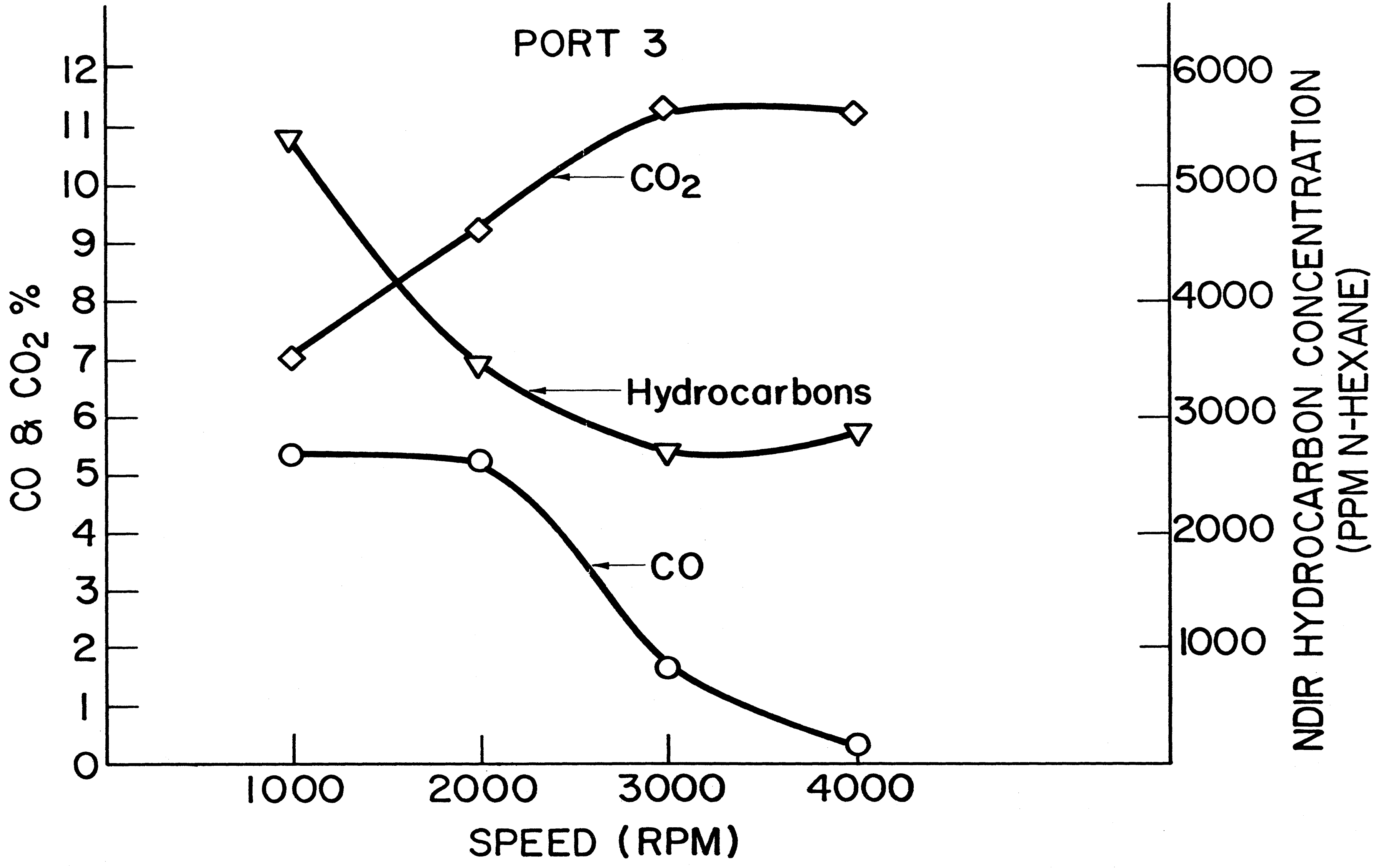

Figure 26. Hydrocarbon (NDIR), CO, and CO_2 exhaust emissions from cylinder 3 at the boat load test conditions.

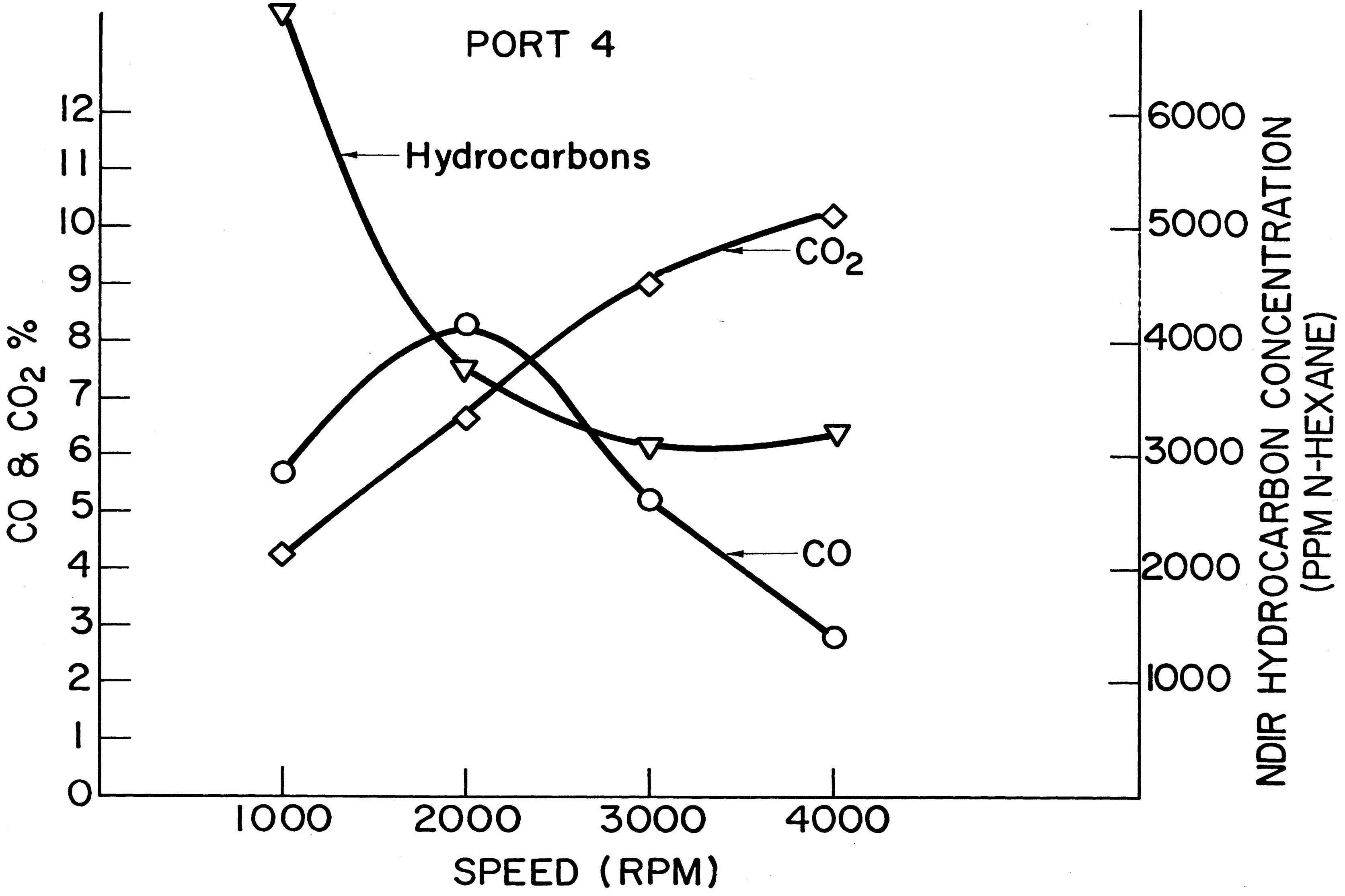

Figure 27. Hydrocarbon (NDIR), CO, and CO_2 exhaust emissions from cylinder 4 at the boat load test conditions

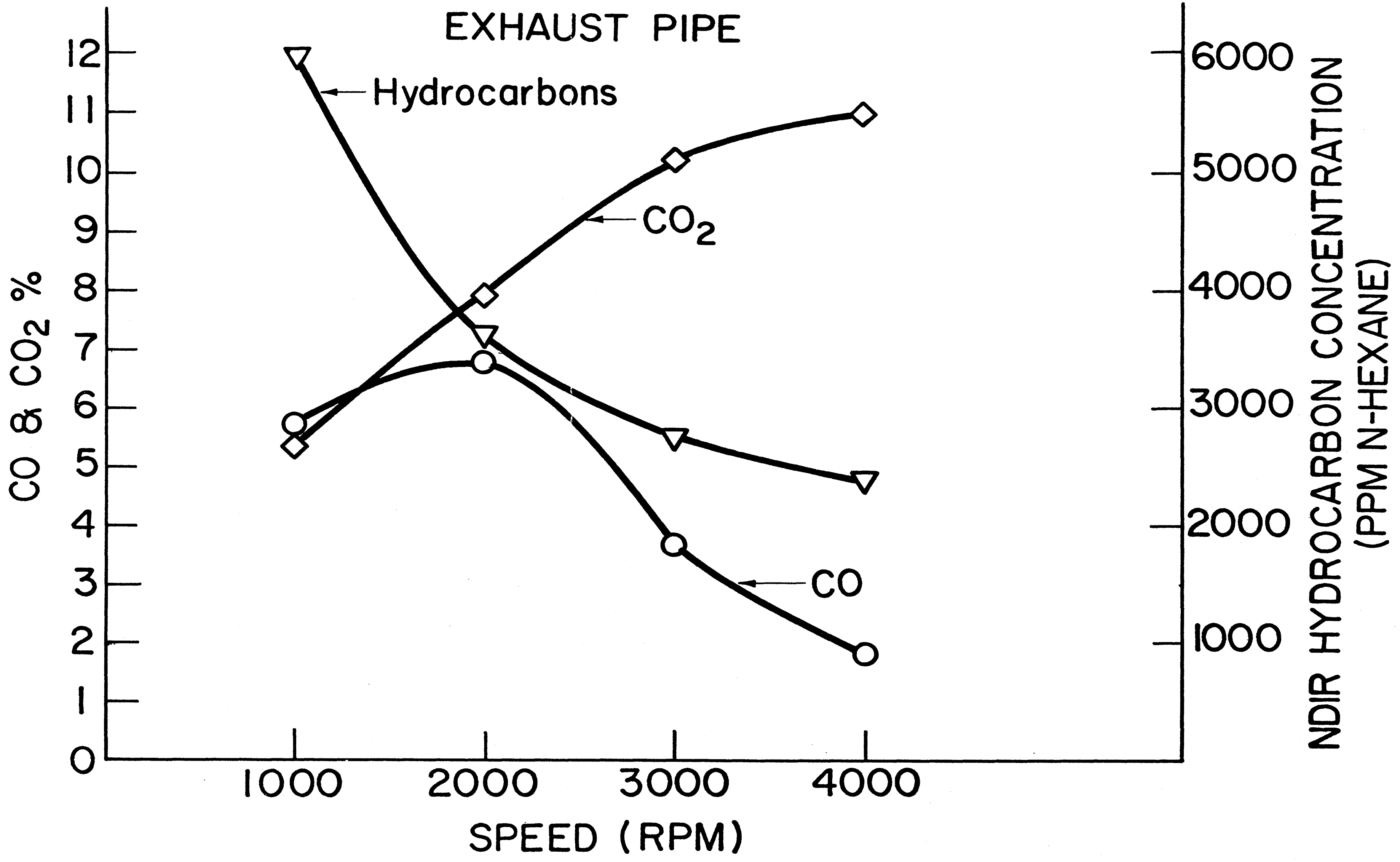

Figure 28. Hydrocarbon (NDIR), CO, and CO_2 exhaust emissions from the exhaust pipe at the boat load test conditions.

discrepancy from the baseline test occurred at 1000 rpm and probably relates to either random misfiring or a change in the low-speed mixture ratio.

2. NITROGEN OXIDES - NO_x

Atmospheric pollution from the many oxides of nitrogen is increasing as a national problem. Even moderate concentrations can be a health hazard because of the formation of nitric acid when ingested into the body and also because of a physiological reaction similar to CO which hinders the bloods ability to transport oxygen. Furthermore, in some localities, notably Los Angeles, NO_x is an important part of the photochemical smog reaction.

Legal NO_x emission limits from automobiles have been proposed and will be implemented in the early 1970's. California has set a limit of (4.0) grams/mile in 1971 and this will be reduced to (1.3) grams/mile in 1974. Actually only one oxide of nitrogen, NO, is formed during the combustion process. However, after nitric oxide, NO, enters the atmosphere it reacts readily with oxygen to form the other oxides of nitrogen,the collection of which are commonly called NO_x.

The concentration of NO in the exhaust is directly related to the equilibrium composition at the maximum flame temperature in the engine cylinder (11,12) and therefore the higher the combustion temperatures the higher the exhaust NO concentration.

Control of NO_x can be partially achieved in automotive engines by limiting the peak cycle temperatures through fuel/air ratio enrichment (or leaning from the fuel/air ratio which gives maximum temperature), water injection or exhaust recirculation. The two-stroke engine with its inherent high exhaust dilution and usually rich mixture ratio has built-in control of the maximum flame temperature. The results of this are borne out by the moderately low NO measurements observed in this investigation. Also, even though NO is relatively insoluble in water some will likely be retained during the underwater exhaust process and further reduce the atmospheric emission.

The results of the NO_x emission test for the four engine cylinders and the exhaust pipe are plotted in Figures 29-33 with NO_x measured as NO. In every case the NO concentration was observed to increase exponentially with increasing speed and load.

At the 1000 and 2000 rpm test conditions the NO concentration was extremely low, less than 50 ppm, from each cylinder. At 3000 rpm the NO emissions from cylinders 2 and 4 were slightly less than 100 ppm whereas from cylinders 1 and 3 they were slightly greater than 100 ppm. The NO emissions then increased very rapidly, and were approximately 250 ppm from cylinders 2 and 4, and over 500 ppm from cylinders 1 and 3. Even these seemingly high NO results were still much lower than those observed from typical modern automotive engines (≈2000 ppm). Although data was not obtained at 5000 rpm it can be speculated that the NO concentration could exceed 1000 ppm.

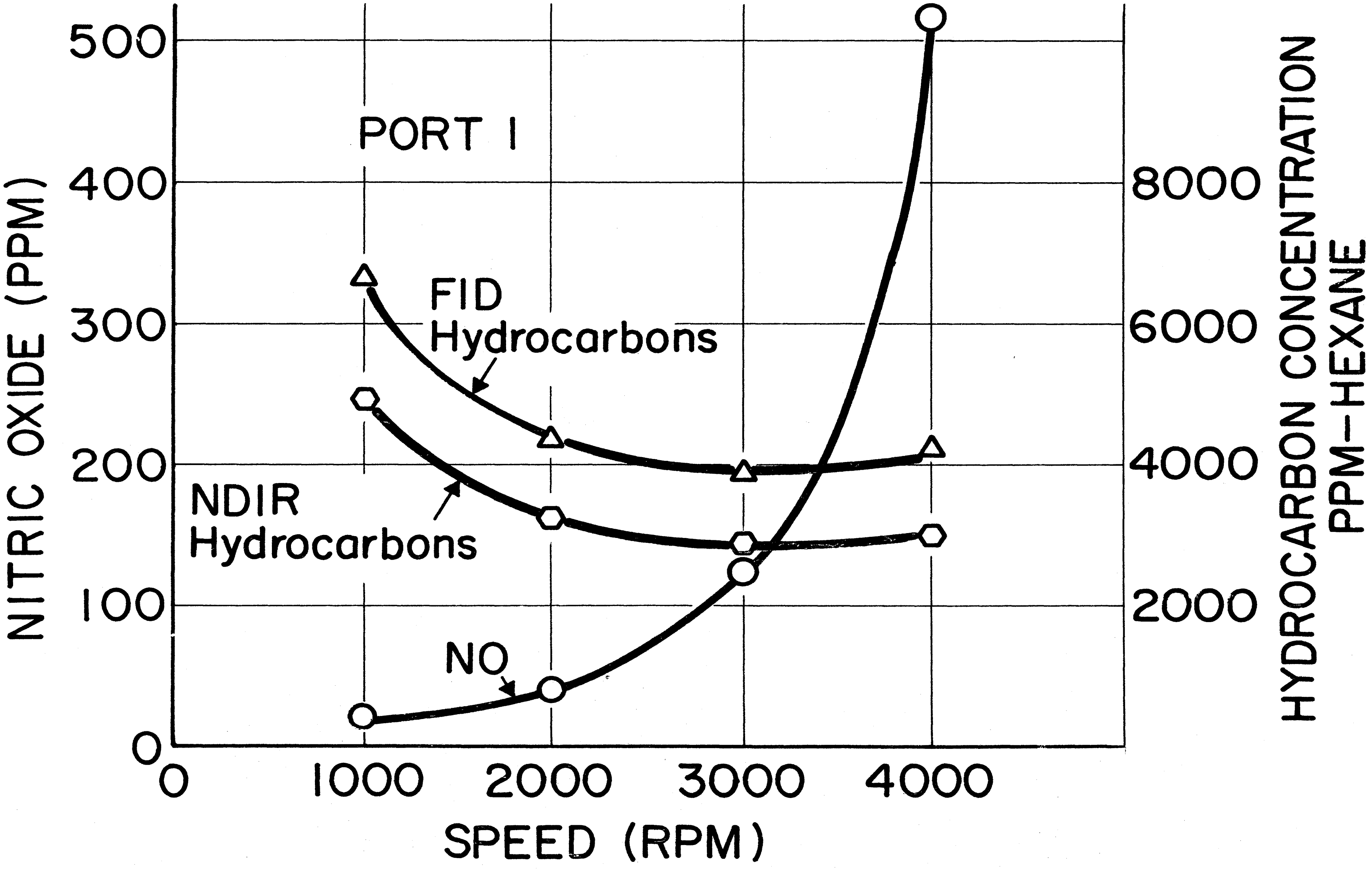

Figure 29. Hydrocarbon (FID and NDIR) and NO exhaust emissions from cylinder 1 at the boat load test conditions.

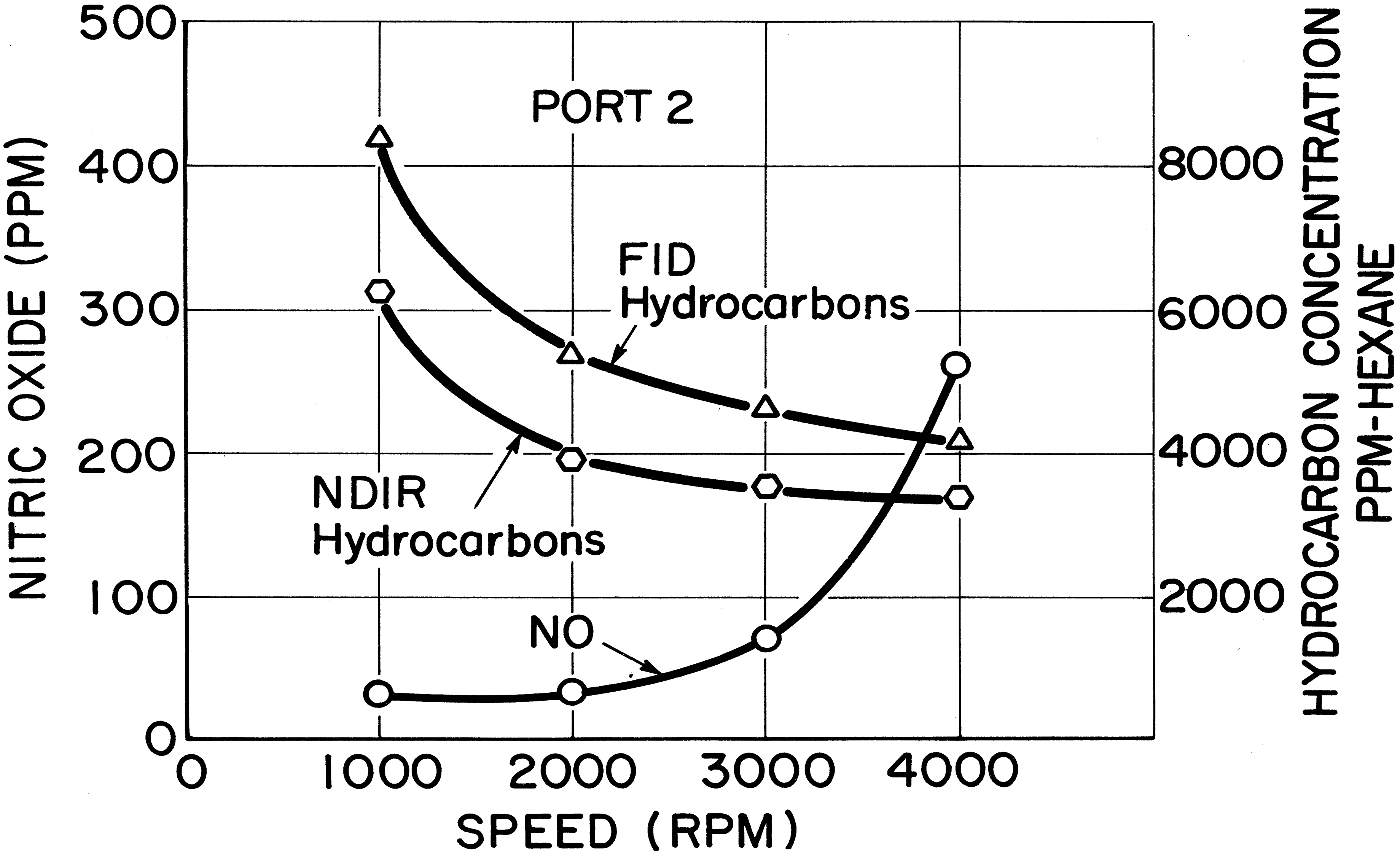

Figure 30. Hydrocarbon (FID and NDIR) and NO exhaust emissions from cylinder 2 at the boat load test conditions.

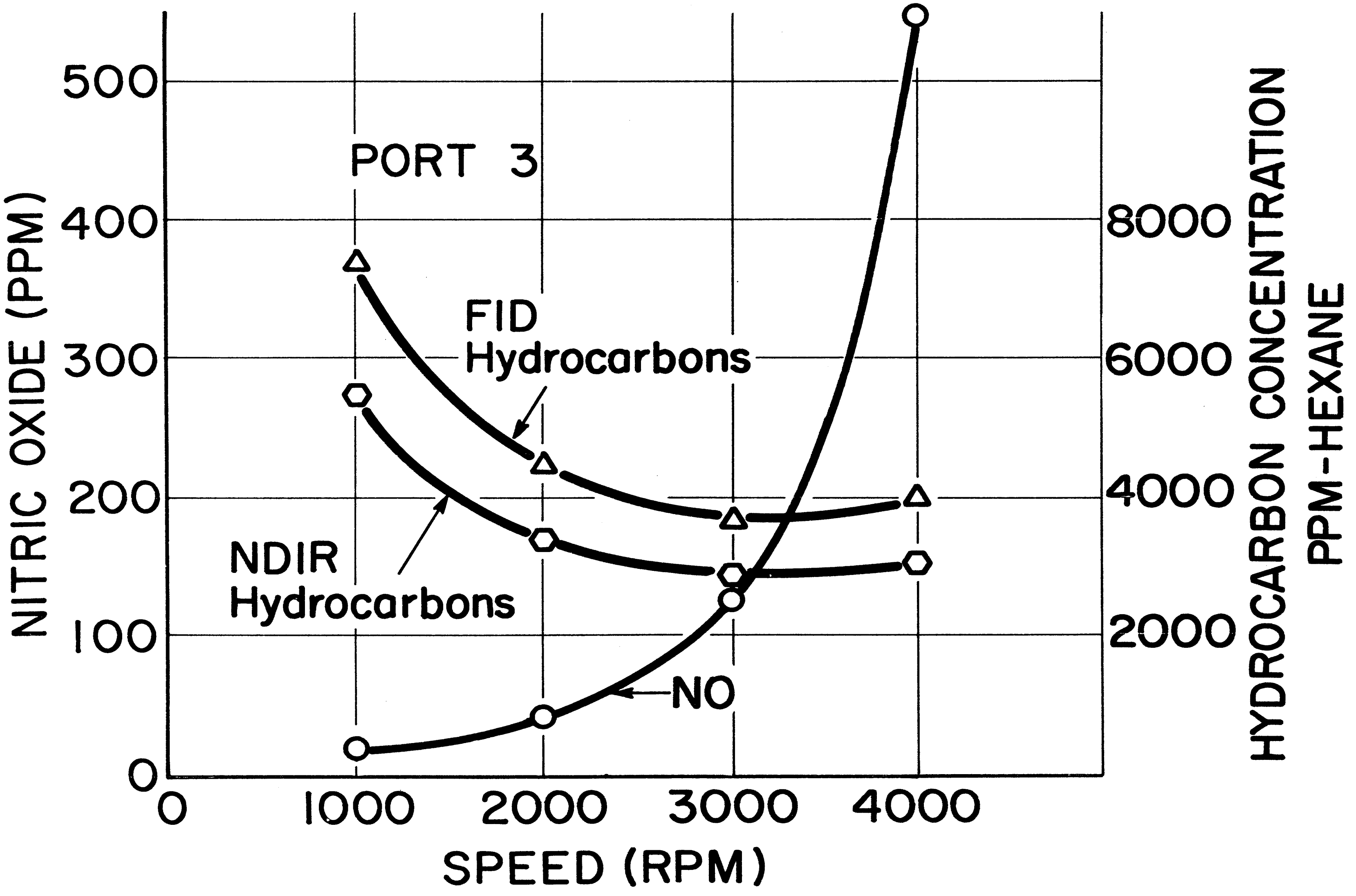

Figure 31. Hydrocarbon (FID and NDIR) and NO exhaust emissions from cylinder 3 at the boat load test conditions.

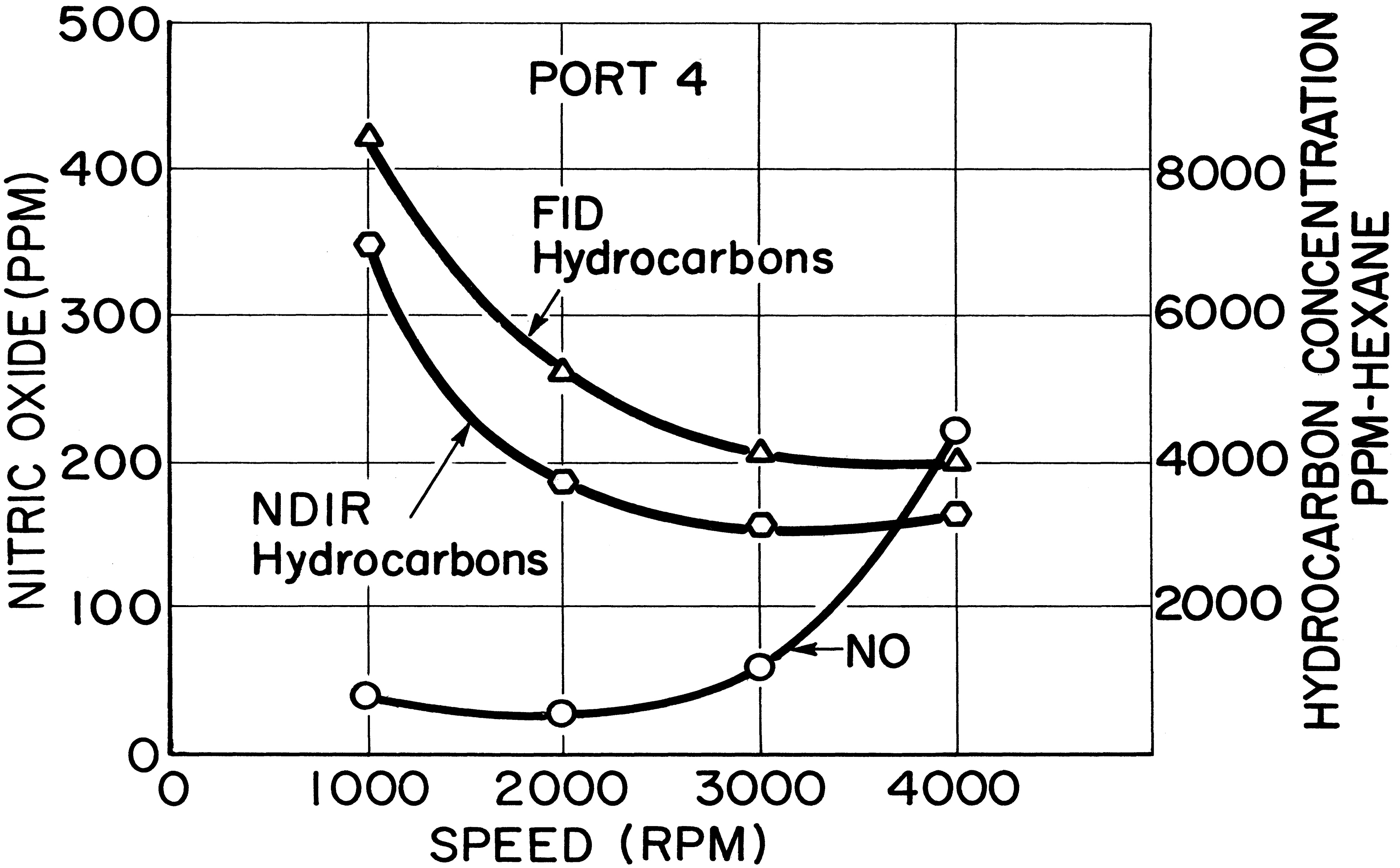

Figure 32. Hydrocarbon (FID and NDIR) and NO exhaust emissions from cylinder 4 at the boat load test conditions.

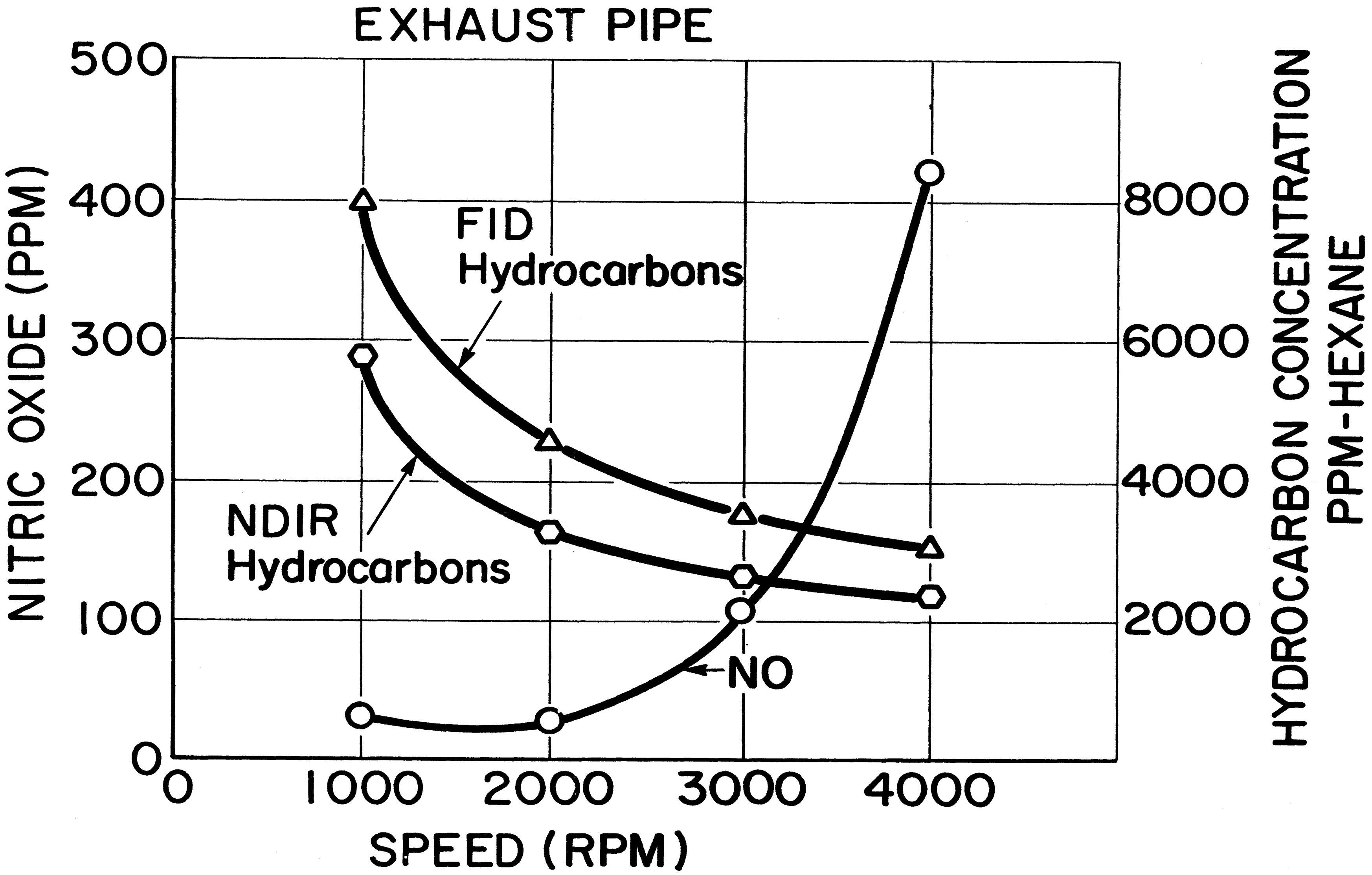

Figure 33. Hydrocarbon (FID and NDIR) and NO exhaust emissions from the exhaust pipe at the boat load test conditions.

The NO increase observed with the speed and load increase is quite reasonable when we realize that the average combustion temperatures have significantly increased due to improved scavenging, decreased misfiring, perhaps leaner mixture ratios, decreased time for heat transfer from the working fluid, and increased charge density per cycle.

The higher NO emissions from cylinders 1 and 3 (compared to 2 and 4) at 3000 and 4000 rpm are consistent with the CO and CO_2 data. The higher CO_2 concentration found in cylinders 1 and 3 indicate that the mixture ratio was closer to stoichiometric resulting in higher temperatures and therefore increased NO emissions.

As in the case of the CO and CO_2 exhaust emissions, the NO measured in the exhaust pipe, Figure 33, is essentially the average of the individual cylinder NO emissions. No noticeable after-reaction of NO was observed in the exhaust plenum.

3. HYDROCARBONS—FID and NDIR

The unheated FID and NDIR exhaust hydrocarbon emissions are also plotted in Figures 29-33 to show the comparison between the measurements made with the two instruments. Note that there is almost an inverse relationship between the NO and hydrocarbon emissions. The lower hydrocarbon concentrations result from the increased trapping efficiency, decreased misfiring and higher temperatures as the speed and load are increased, some of the same factors which can result in increased NO concentrations.

4. MASS EMISSIONS OF CO, NO AND NDIR HYDROCARBONS

The mass rate of exhaust pipe CO, NO, and NDIR hydrocarbon emissions are shown in Figure 34* at the boat-load test conditions. The mass emission data was determined according to techniques illustrated in the Appendix. Generally the mass emissions increase with increasing speed and load. The CO emissions, however, peak at 2000 rpm because of the high concentration at this condition. Both the CO and hydrocarbon mass emissions are much higher than found in a similar sized four-stroke engine operated at the same test conditions.

To provide some measure of comparison to the automotive emission standards, the mass emissions in lb/hr from the 100 hp Johnson engine may be converted to grams/mile. The lb/hr data is multiplied by a mass conversion factor (453.6 grams = 1 lb) and divided by an estimated boat velocity, V, in mph. The total conversion factor is:

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*The mass rate of air and fuel flow in the mass emission calculations were determined experimentally.

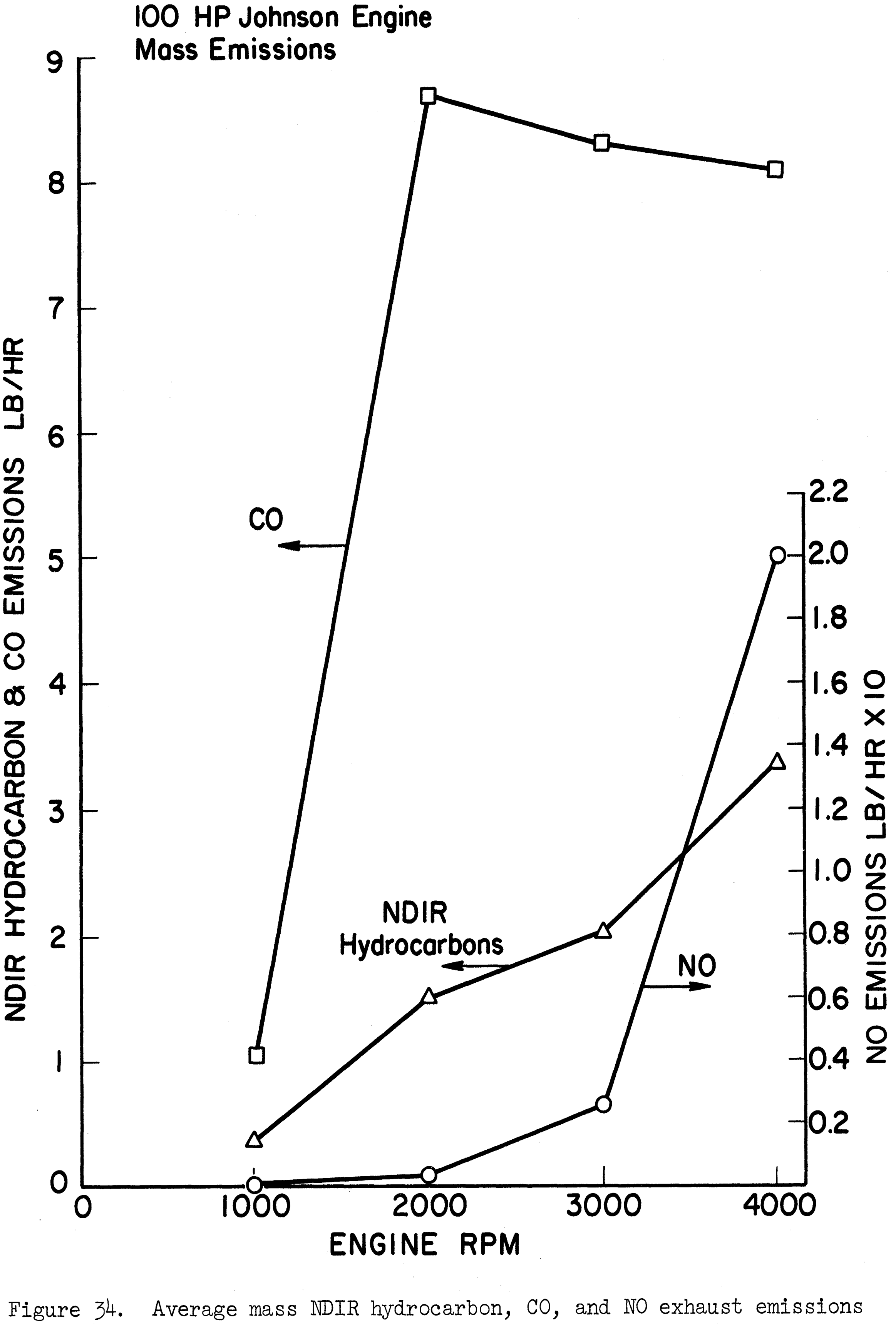

Figure 34. Average mass NDIR hydrocarbon, CO, and NO exhaust emissions from the exhaust pipe at the boat load test conditions—lb/hr.

$$\frac{\text{gram}}{\text{mile}} = \frac{\text{lb}}{\text{hr}} (453.6) \frac{\text{gm}}{\text{lb}} \frac{\text{hr}}{(V)\ \text{mile}}$$

The estimated boat velocities and the calculated conversion factor at the boat-load test conditions are given in Table IV.

TABLE IV

BOAT VELOCITY AND MASS CONVERSION FACTOR FOR A TYPICAL HULL AT THE BOAT-LOAD TEST CONDITIONS

Engine, rpm	Engine bhp	V, mph	Conversion Factor, lb/hr to grams/mile
1000	1.5	3.5	130.0
2000	9.0	5.9	77.0
3000	24.0	12.0	37.8
4000	50.0	22.0	20.6

The exhaust pipe mass emission data in grams/mile is plotted in Figure 35 at the boat-load test conditions and shows that the hydrocarbon and CO emissions peak at 2000 rpm because of a combination of high emission concentrations and low speeds caused by the significant motion resistance of the not yet planing hull. Both the CO and hydrocarbons significantly exceed the composite Federal emission standards for automobiles. At higher engine and boat speeds, the NO emissions are in the range of future Federal NO_x standards. It must be recognized that this presentation of our data is rather questionable and is only done for comparative purpose. Different hulls will exhibit widely different drag resistances and therefore show wide variation in grams/mile emission levels.

B. Source of Exhaust Hydrocarbon Emissions

To increase our understanding of the physical processes within the engine which result in the formation of the exhaust hydrocarbons, a series of tests were conducted using two fuels of widely varying composition. Regular gasoline and iso-octane (2,2,4 trimethyl pentane) were selected because we had obtained much data using the gasoline and the pure paraffinic fuel, iso-octane, would respond almost equally to both the NDIR and FID analyzers if its composition is not changed by combustion. A gross hydrocarbon family analysis of the two fuels is shown in Table V. It must be noted that the regular gasoline composition may vary some with geographic location, time of the year, and brand.

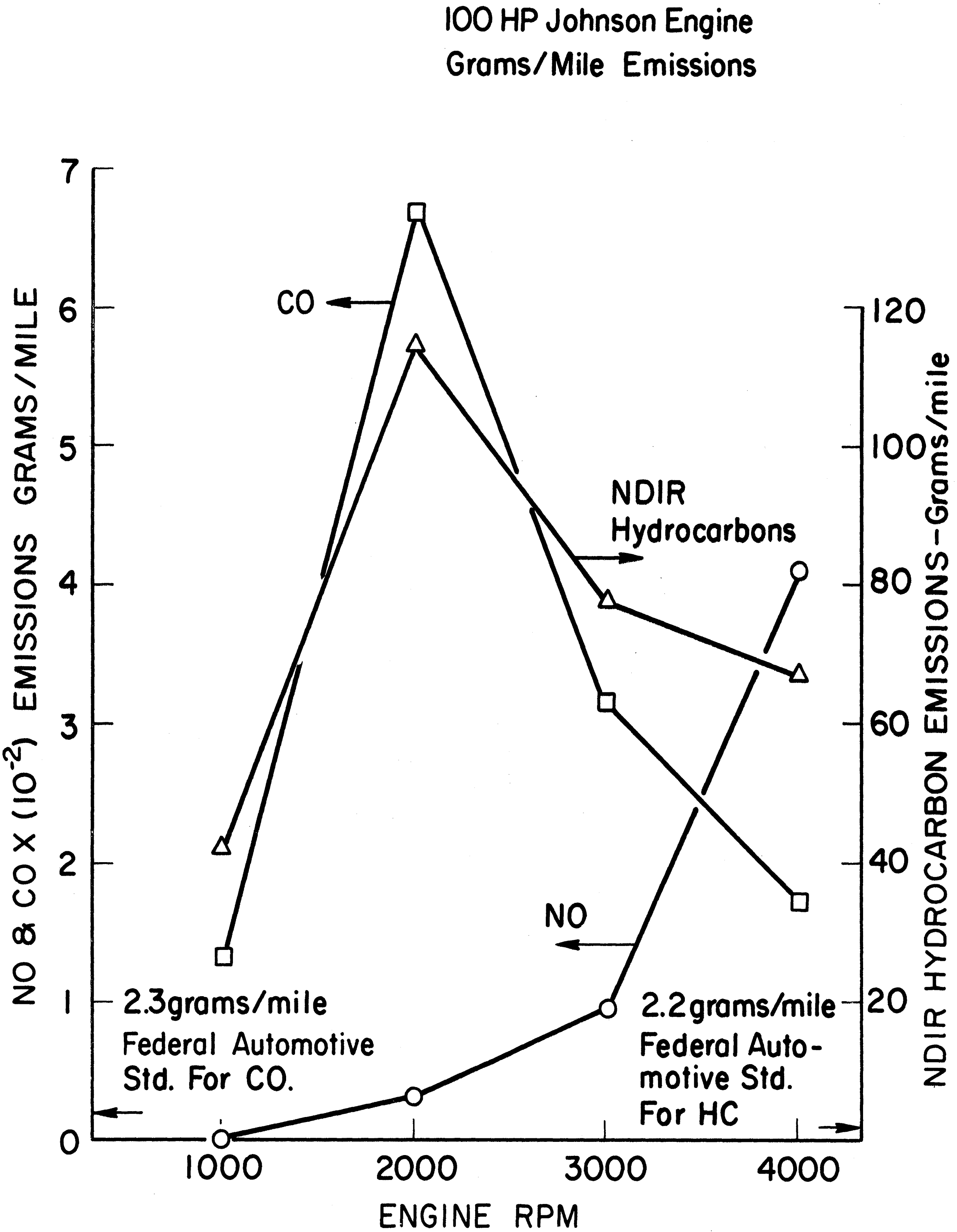

Figure 35. Average mass NDIR hydrocarbon, CO, and NO exhaust emissions from the exhaust pipe at the boat load test conditions—grams/mile.

TABLE V*

TEST FUEL COMPOSITION

Components	Regular Gasoline*	Iso-Octane
Paraffins	65%	100%
Olefins	10%	0
Aromatics	25%	0
Octane No.	95.5	100
Lead Content	2.4 gm/gal	0

*Standard - American Oil Company.

The fuel-air mixture flow and its relationship to the hydrocarbon emission formation processes within the engine is shown schematically in Figure 36. This diagram will aid in our understanding of the observed results. The scavenging and misfiring unburned hydrocarbons are closely related to the fuel whereas the combustion products are not. The closer the measured exhaust hydrocarbons compare with the fuel-air mixture, the more important misfiring and "through scavening" are as the emission sources.

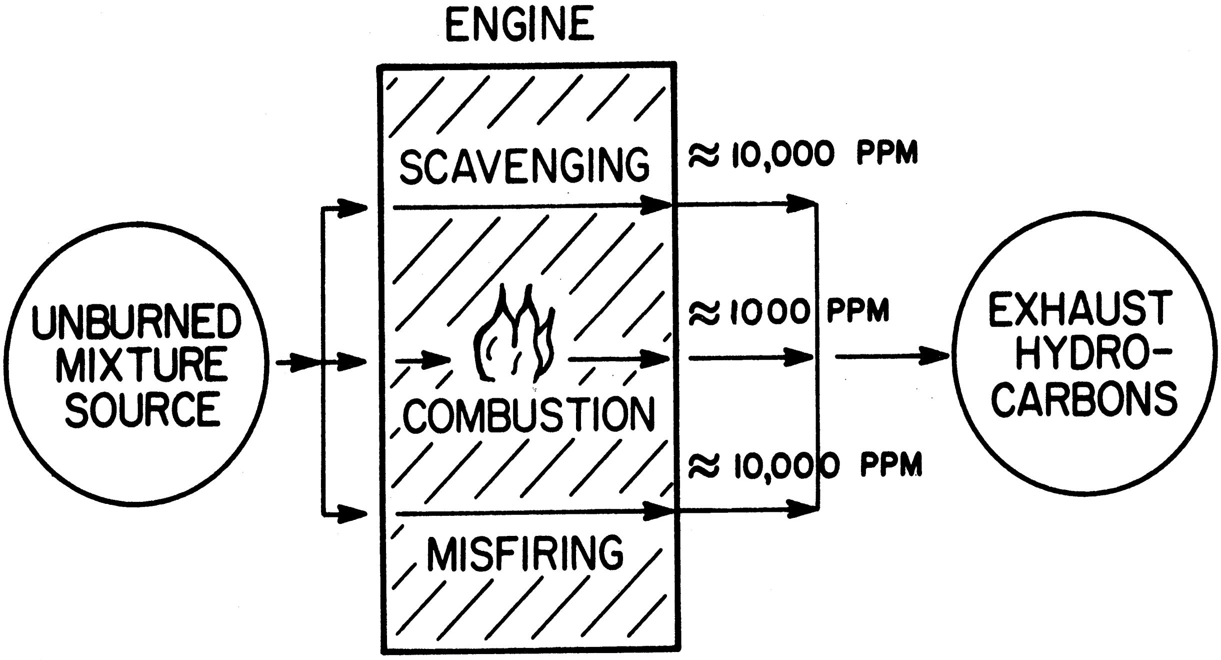

Figure 36. Schematic diagram showing the sources of the hydrocarbon emissions in the two-stroke engine.

1. GASOLINE

The paraffinic and aromatic hydrocarbon compounds in gasoline are relatively stable at elevated temperatures (800-1200°F) compared to the unsaturated hydrocarbons (olefins). Consequently, the paraffinic and aromatic components of the fuel lost during scavenging and misfiring should not be greatly affected by the temperatures found in the exhaust plenum and in the cylinder during the scavenging and misfiring processes. On the other hand, the unsaturates are more easily oxygenated and therefore only part of the original fuel-type olefins are drawn into the analysis system. The oxygenated hydrocarbons formed, which are principally aldehydes, are not measured in either the NDIR or FID instruments because, due to their high water solubility, they are trapped out of the sample in the wetted-wall condensing coil which precedes the FID and NDIR analyzers. Thus one would expect that the FID/NDIR hydrocarbon ratio would be close to 1.3* if the exhaust consisted of 100% fuel-air mixture.

Of course, it must be recognized that because of the complex nature of the fuel, the FID and NDIR will not respond exactly on a one-to-one basis to each carbon atom. Since calibration of the instruments is done with a single

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*With regular gasoline of the test fuel's composition in a fuel-air mixture, the FID/NDIR response ratio can be estimated as follows:

Paraffins - 65% of the fuel

$$\frac{\text{FID}}{\text{NDIR}} = \frac{100}{95}$$

Olefins - 10% of the fuel

$$\frac{\text{FID}}{\text{NDIR}} = \frac{100}{50}$$

Aromatics - 25% of the fuel

$$\frac{\text{FID}}{\text{NDIR}} = \frac{100}{20}$$

If we assume one-half of the olefins are oxygenated, the base is 100 - .5 x 10 = 95 and the total FID/NDIR ratio can be approximated as:

$$\frac{\text{FID}}{\text{NDIR}} = \frac{100}{65 \times \frac{95}{100} + 10 \times \frac{50}{100} + 25 \times \frac{20}{100}} = \frac{100}{61.5 + 5 + 5} = \frac{100}{71.5} \cong 1.4$$

If we then allow for a negative oxygen response in the FID of -6%, which was found to be an average number for the composition of the two-stroke exhaust, the measured FID/NDIR ratio should be approximately 1.3.

component gas, either n-hexane or propane (the NDIR and FID are set to a FID/NDIR ratio of 1.0 for this single component with no O_2 present), and since the relative response of the FID and NDIR to various hydrocarbons in the fuel is different, as shown in Tables I and II of the previous chapter (for example, the relative response of ethane is 100 for the NDIR and 106 for the FID), the FID/NDIR ratio will not be exactly 1.3. It would be impossible to theoretically predict the ratio based on unburned fuel alone unless one knew its exact composition and full range of relative response information.

When the engine is firing normally and misfiring is not significant, approximately 70% of the supplied mixture is burned. If we assume that the combustion products show about 1000 ppm, C_6H_{14} (NDIR), and the unburned mixture about 10,000 ppm C_6H_{14} (NDIR) the average NDIR hydrocarbon concentration in the exhaust will be approximately

$$.3 \times 10,000 + .7 \times 1000 = 3000 + 700 = 3700 \text{ ppm.}$$

About $\frac{700}{3700} \times 100 \cong 19\%$ will be related to the combustion products and $\frac{3000}{3700} \times 100 \cong 81\%$ will be derived from the unburned mixture. If we assume that the combustion products FID/NDIR ratio is about the same as found in the four-stroke engine, 2.0/1, and that the unburned fuel-air mixture FID/NDIR ratio is about 1.3/1, (uncorrected for oxygen) then the expected total FID/NDIR ratio should be approximately $.19 \times 2.0 + .81 \times 1.3 \cong 1.4$. This number is quite close to the average measured ratio of 1.3. The measured FID/NDIR ratio data was shown in Table III in the previous chapter. It is interesting to note that as the speed and load are increased, the exhaust plenum temperature increases. This temperature increase would be expected to increase the oxygenation of the olefins and thereby decrease the FID/NDIR ratio. However, the trapping efficiency is increasing and misfiring frequency decreasing with increasing speed tending to cause an increase in the FID/NDIR ratio.

In the four-stroke engine which burns almost all of the inducted charge, it has been found that the fuel type has little influence on the unburned hydrocarbon composition of exhaust gas. Even if a totally paraffinic fuel is burned, the exhaust hydrocarbons will still consist of many olefins, aromatics, etc., as well as paraffins. The FID/NDIR ratio remains about 2.0/1 regardless of the fuel composition.

2. ISO-OCTANE

One would expect the FID/NDIR ratio to be much smaller with iso-octane than with regular gasoline if the majority of exhaust hydrocarbons are a result of unburned fuel. Iso-octane is totally paraffinic and therefore the FID and NDIR analyzers should respond almost equally to the fuel, FID/NDIR ratio $\cong 1.0$. As the proportion of iso-octane which burns in the combustion chamber increases, due perhaps, to increased trapping efficiency or decreased misfiring, an increase in the FID/NDIR ratio should be observed. Substantial concentrations of aromatic and olefinic compounds are formed during the burning of even a pure paraffinic fuel.

The results of this testing are shown in Table VI. The FID/NDIR hydrocarbon ratios are tabulated at all four engine test conditions from cylinders 1 and 2.

TABLE VI*

RELATIVE RESPONSE OF THE FID AND NDIR ANALYZERS TO TWO-STROKE ENGINE EXHAUST HYDROCARBONS—ISO-OCTANE FUEL

Boat-Load Test Condition, rpm	FID/NDIR Ratio Cylinder No. 1	2
1000	1.18	1.24
2000	1.02	1.07
3000	1.13	1.05
4000	1.05	1.11

*Uncorrected for oxygen in the exhaust.

The ratio is significantly less than found in the regular gasoline test which is a strong indication that the "combustion" hydrocarbon source is small. Interestingly enough the FID/NDIR ratio is highest at the lowest speed which is contrary to what one would expect because of the lower trapping efficiency and greater misfiring at this condition. As yet we have no explanation for this phenomenon.

The comparison between the iso-octane and regular gasoline data could provide a measure of engine trapping efficiency if we were able to obtain an analysis of only the "combustion products" from the two-stroke engine. Unfortunately, this is very difficult to do in our engine and if we use a four-stroke engine of similar compression ratio and geometry, too many variables will be different from the two-stroke engine to permit a valid comparison. Qualitatively, however, we can use the measurement of FID/NDIR hydrocarbon ratio as rough indicator of the scavenging and trapping efficiencies.

The test with the pure paraffinic fuel, iso-octane, suggests a method for controlling the smog forming capability of the exhaust. As indicated by the low FID/NDIR ratio, the exhaust hydrocarbons must consist of relatively few olefins and other highly reactive species (with respect to their photochemical smog forming potential) and suggests that a blended paraffinic fuel may substantially reduce the contribution of the two-stroke engine to the smog formation process.

Even with regular gasoline the relatively low FID/NDIR ratio is an indication of a low exhaust hydrocarbon reactivity.

IV. CONCLUSIONS AND OBSERVATIONS

1. The carbon monoxide emissions from the 100 hp Johnson engine range from approximately 5-8% at 1000 and 2000 rpm boat-load to 1-2% at the higher speeds and loads. On a mass basis (lb/hr) the CO emissions were lowest at 1000 rpm, 1 lb/hr, and increased significantly to 8-9 lb/hr at the other test conditions.

2. The nitric oxide concentration in the exhaust was quite low in comparison to a typical automotive four-stroke engine and ranged from less than 100 ppm at 1000 and 2000 rpm to approximately 100 ppm at 3000 rpm and to 300-500 ppm at 4000 rpm. The mass NO emissions ranged from a low of .001 lb/hr at 1000 rpm to .2 lb/hr at 4000 rpm.

3. The FID exhaust hydrocarbon concentration was greater than the NDIR measured hydrocarbon concentration by a factor of approximately 1.3.

4. The studies using two fuels of widely varying composition with both the FID and NDIR analyzers strongly suggest that the major portion of the exhaust hydrocarbons are directly related to the fuel. A minor source is related to the hydrocarbons formed during burning of the charge.

5. The misfiring studies show that misfiring or incomplete combustion is a major source of unburned hydrocarbons at 1000 rpm and moderately important at 2000 rpm. At higher speeds the combustion appears to be very reproducible.

6. The ionization probe and phototube sensing of combustion generated light are reasonably good techniques for measuring misfiring frequency.

7. The heated Flame Ionization Detector with a heated sample line is a superior hydrocarbon measurement system because it prevents retention or "hang-up" of most heavy hydrocarbon molecules in the system plumbing. However, this device is difficult to use and is sensitive to oxygen which causes a negative hydrocarbon interference.

8. The minimum sample line temperature which should be used with the heated FID is 150°F.

9. It is possible to determine the combustion fuel/air ratio in a given cylinder if the CO and/or CO_2 and O_2 concentration are measured in that cylinder.

APPENDIX

CONVERSION OF CONCENTRATION HYDROCARBON, CO, AND NO EMISSIONS (DRY BASIS) TO MASS RATE OF EMISSIONS

It is reasonable to assume that the dry exhaust gas* is composed primarily of the following components shown with their respective molecular weights: CO_2 - 44, N_2 - 28, and C_6H_{14} - 86.

For each mole of CO_2 there are approximately six moles of N_2, therefore the molecular weight of the CO_2 and N_2 mixture $\cong \frac{(1 \cdot 44) + (6 \cdot 28)}{7} = 30.3$. If x = ppm C_6H_{14} (n-hexane), then $86x$ is proportional to the mass of C_6H_{14}, and $30.3 (10^6 - x)$ is proportional to the mass of $CO_2 + N_2$ and $\frac{\text{Mass } C_6H_{14}}{\text{Mass of Dry Exhaust}} \cong \frac{86x}{30.3 (10^6 - x) + 86x}$ which can be simplified to $\frac{86x}{30.3 (10^6)}$. This simplification introduces less than 1% error for $x < 10{,}000$ ppm.

Since $\frac{\text{Total Mass of Exhaust}}{\text{Mass of Dry Exhaust}} = 1.1$ for the average hydrocarbon fuel, the

$$\frac{\text{Mass } C_6H_{14}}{\text{Mass (of Total Exhaust)}} \cong \frac{86x}{30.3 \cdot 10^6 \cdot 1.1} = \frac{78x}{30.3 \cdot 10^6} .$$

The total mass flow rate of air and fuel through the engine is:

$$\dot{M}_T = \dot{M}_A + (F/A)\,\dot{M}_A = (1 + F/A)\,\dot{M}_A$$

where

$\dot{M}_T$ = Total mass flow rate - lb/hr

$\dot{M}_A$ = Air flow rate - lb/hr

F/A = Fuel/air ratio

Thus the mass rate of unburned hydrocarbon emissions (measured as C_6H_{14}) is:

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*The water vapor can be assumed to be totally condensed in the analysis system condenser and the unburned hydrocarbons to have negligible mass compared to the other constituents.

$$\dot{M}_{C_6H_{14}} \cong \dot{M}_A(1 + F/A) \frac{78x}{(30.3 \cdot 10^6)} \text{ lb/hr n-hexane.}$$

Similarly it can be shown that the mass rate of the CO, molecular weight 28, and NO molecular weight 30, exhaust emissions are approximated by the following relationships:

<u>CO</u>

$$\dot{M}_{CO} = \dot{M}_A(1 + F/A) \frac{28(CO_{ppm})}{(30.3 \cdot 10^6)1.1} = .84\, \dot{M}_A(1 + F/A)\ (CO_{ppm})\ 10^{-6}$$

or if the CO concentration is expressed in percent as is usually the case

$$\dot{M}_{CO} \cong .84\, \dot{M}_A(1 + F/A)\ (CO_{\%})\ 10^{-2} \quad \text{- lb/hr}$$

<u>NO</u>

$$\dot{M}_{NO} \cong \dot{M}_A(1 + F/A) \frac{30(NO_{ppm})}{(30.3 \cdot 10^6)1.1} = .9\, \dot{M}_A(1 + F/A)\ (NO_{ppm})\ 10^{-6} \text{ - lb/hr}$$

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