AN ABSTRACT OF THE THESIS OF

BRUCE CONRAD ANDERSON   for the MASTER OF SCIENCE
_____   _____
(Name)   (Degree)

in Mechanical Engineering presented on _October 22, 1968_
_____   _____
(Major)   (Date)

Title: GAS-LIQUID CHROMATOGRAPHIC DETERMINATION OF

LOW MOLECULAR WEIGHT ALIPHATIC ALDEHYDES IN DIESEL

ENGINE EXHAUST

Abstract approved: *Redacted for Privacy*

J. G. Mingle

The study of aldehydes in diesel exhaust is important because

of their relationship to diesel odor, to air pollution, and to the de-

velopment of a theory of combustion.   Therefore, a study is made

of the low order aliphatic aldehydes using gas chromatography in

conjunction with standard wet chemical tests.

The engine is a two stroke-cycle GMC 3-71 RC diesel, with

standard injectors, connected to an eddy current dynomometer.   A

special ten foot insulated exhaust pipe is used for the sample collec-

tion.   Engine load and exhaust pipe length are used as variables, two

probes 6.7 feet apart being sampled simultaneously.

For the gas chromatographic analysis the aldehydes are con-

verted to 2, 4-dinitrophenylhydrazone derivatives in special tall form

bubblers.   The precipitates are then volumetrically dissolved in

carbon disulfide in preparation for the chromatographic separation.

The columns are ten percent SF 96 on 60-80 mesh acid washed DMCS treated Chromosorb W in 6 feet by 0.085 inch I.D. stainless steel. Nitrogen at 60 ml per minute is used as the carrier gas and the hydrogen flow for the flame ionization detector is 35 ml per minute. The column temperature is 230° C and the injector temperature 270° C. The sample injection size is 10 μl.

The chromotropic acid test is used as a wet test for the formaldehyde concentration in the exhaust, the MBTH test being used for total aliphatic aldehydes. The wet tests are used for correlation studies with the gas chromatograph and for comparison with literature values.

No correlation was found between the chromatograph and wet tests, the wet tests usually giving higher values. Both tests, however, indicate the concentration of aldehydes in the exhaust increases with load.

The average molecular weight of the lower molecular weight aldehydes in the diesel exhaust is found by gas chromatographic analysis to be approximately 35, 75-80 mole percent of the total aldehydes being formaldehyde. The average molecular weight decreases with probe length, as predicted by theory, and the concentration increases.

Gas-Liquid Chromatographic Determination of Low
Molecular Weight Aliphatic Aldehydes
in Diesel Engine Exhaust

by

Bruce Conrad Anderson

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

June 1969

APPROVED:

Redacted for Privacy

Professor of Mechanical Engineering
in charge of major

Redacted for Privacy

Head of Department of Mechanical Engineering

Redacted for Privacy

Dean of Graduate School

Date thesis is presented October 22, 1968

Typed by Marion F. Palmateer for Bruce Anderson

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

GAS-LIQUID CHROMATOGRAPHIC DETERMINATION OF LOW MOLECULAR WEIGHT ALIPHATIC ALDEHYDES IN DIESEL ENGINE EXHAUST

INTRODUCTION

Aldehydes are a group of oxygenated hydrocarbons which may exist in the gaseous state in the air. These highly reactive compounds have a very pungent odor and are irritating to the eyes (Berg, 1967; Linnell and Scott, 1962b; Fracchia, Schuette, and Mueller, 1967). The normal ambient air level is less than 0.1 ppm for rural areas and 0.2 ppm in urban areas, although concentrations in large cities have been measured at the 1 ppm level (Berg, 1967). There is also some indication that plant damage may be indirectly caused by aldehydes in the air because aldehydes are intermediates for peroxyacyl nitrate formation (Alperstein and Bradow, 1967).

There is some indication that diesel odor is related to the aldehydes in the exhaust. Rounds and Pearsall (1956) found a correlation at the 95 percent confidence level between the concentration of formaldehyde and higher aldehydes in diesel exhaust and the odor irritation intensity. Merrion (1968) also found a weak correlation between formaldehyde concentration and diesel odor. Hurn and Seizenger (1965, p. 128) state that there is a "---high aldehyde content, accounting for the 'diesel odor'" prominant at all levels of diesel operation. People tend to think of this odor as a serious air

pollutant and find it very irritating, and in some cases the odor of

diesel exhaust has restricted the use of this type of engine (Rounds

et al. , 1956).

Aldehydes are formed in many combustion processes and are

also formed photochemically in the atmosphere (Fracchia et al. ,

1967). Because of the low boiling point of these compounds (-21 to

103°C for C_1-C_5 aliphatic aldehydes, Shriner and Fuson, 1964) they

exist in the vapor phase in the air and tend to be very persistant air

pollutants (Berg, 1967). The additive effect of these factors could

put the concentration of the aldehydes above the odor threshold, which

is in the parts per billion range for some of the carbonyl compounds

(Fracchia et al. , 1967).

The knowledge of aldehyde concentration is also important in

the development of the theory of combustion. Frequently these

carbonyl compounds are both intermediates and products of the com-

bustion reactions of fuels (Minkoff and Tipper, 1962; and Griffiths

and Skirrow, 1968).

Aldehydes also influence other free radical reactions taking

place during combustion. Both formaldehyde and higher aldehydes

are believed to be active intermediates for degenerative branching

in the slow combustion of simple fuels (Minkoff et al. , 1962). Be-

cause of this relationship to the combustion reactions, the relative

concentration of aldehydes is sometimes taken as an indication of

the stage of reaction. During slow combustion oxidation, the higher

aldehyde concentration reaches its peak at the time of the maximum

rate (Minkoff et al., 1962). Linnell et al. (1962b) implies that the

acrolein and formaldehyde concentration in diesel exhaust could be

used in the same way as carbon monoxide as an indication of the

completeness of combustion.

The study of aldehydes as oxidation products is made more dif-

ficult by the number of factors which influence their concentration

and also their effect on other reactions. Temperature, molecular

weight and structure of the fuel, and the surface condition of the re-

action vessel are some of the factors which must be kept constant

during these studies (Griffiths et al., 1968; Minkoff et al., 1962).

This means that most of the data and theories of the combustion and

formation of aldehydes are based on experiments done under very

ideal conditions. What effect will factors such as the combustion

chamber, surface condition, and heterogeneous fuel dispersion in a

diesel engine have on these theories?

This study therefore is an effort to determine, using a gas

chromatograph, what effects certain diesel engine operating param-

eters will have on the concentration and type of aldehydes present

in the exhaust. In addition to checking agreement with the theory,

this information might be useful in determining the contribution of

the aldehydes to the odor problem and also the contribution of the

diesel engine to the aldehyde content in the air.

THEORY

Theory of Combustion

Aldehydes are oxygenated hydrocarbons which are formed during the combustion of many organic fuels (Fracchia et al., 1967). They are found in the pre-flame free radical reactions which take place in fuel-air mixtures. Up to 70 percent of the fuel can be oxidized before ignition takes place, leading to aldehydes and other oxygenated hydrocarbons (Pipenberg and Pahnke, 1957; and Alperstein et al., 1967). The aldehydes formed during these slow oxidation processes depend on such factors as the fuel, temperature, and state of reaction (Minkoff et al., 1962). Aldehydes are usually not considered as direct oxidation products of the hydrocarbons, but result from the breakdown of other intermediates such as peroxides, alkoxy, or higher order aldehydes (Minkoff et al., 1962).

Formation and Oxidation of High Order Aliphatic Aldehydes

The slow combustion reactions which take place inside the combustion chamber of a diesel take place in above the 350-400°C temperature region. However, the slow oxidation of the aldehydes in the exhaust pipe take place at a temperature which is borderline between the low and high temperature range. Below 350-400°C is usually considered as the region of low temperature for slow combustion

(Minkoff et al., 1962). In the high temperature range, the kinetics depend on the oxygen-fuel ratio and there is more thermal decomposition of the intermediates (Griffiths et al., 1968). Slow oxidation of stoiciometric n-heptane/air mixtures to aldehydes begins at 345° C, which is well below the peak temperature in a diesel engine combustion chamber (Pipenberg et al., 1957).

The mechanism of the slow oxidation of most organic fuels is a branched free radical chain reaction. Much of the charge in an engine is oxygenated by slow oxidation before the flame ever sweeps through it (Alperstein et al., 1967). Higher order aldehydes can be formed from the decomposition of peroxide intermediates, especially if there is a surface available to react on (Minkoff et al., 1962). The aldehydes are then oxidized further. The overall activation energy[1] for this oxidation is 15-25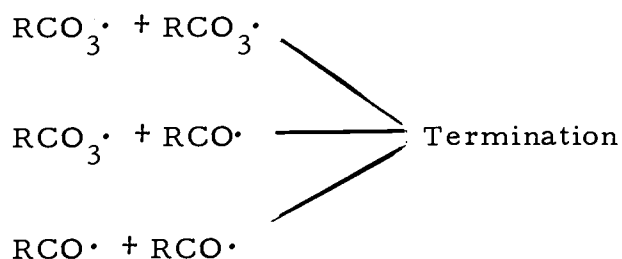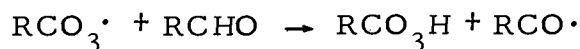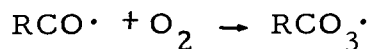 kilocalories per mole. Also, the higher carbonyl radicals decompose according to the equation $R'CO\cdot + M \rightarrow R'\cdot + CO + M$, which has a slightly higher activation energy (Minkoff et al., 1962).

A simplified reaction scheme for the oxidation of low order aldehydes other than formaldehyde is (Griffiths et al., 1968):

---

[1] The activation energy is a term in the Arrhenius equation, which is of the form $K = Ae^{-E^X/RT}$, where A and E are constants over a finite temperature range, K is the reaction rate constant, E^X is the experimental activation energy (Johnson, 1967).

Initiation → RCO·

$$RCO\cdot + O_2 \rightarrow RCO_3\cdot$$

$$RCO_3\cdot + RCHO \rightarrow RCO_3H + RCO\cdot$$

$RCO_3\cdot + RCO_3\cdot$

$RCO_3\cdot + RCO\cdot$ ——— Termination

$RCO\cdot + RCO\cdot$

Branching via peracyl → RCO·
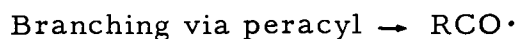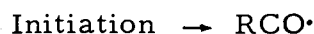
The proportional amount of each aldehyde is not constant during slow combustion reactions. There is a molecular weight shift both with time and temperature. At low temperatures (below 250-300°C) higher aldehydes oxidize readily but formaldehyde has a very slow reaction rate. As the temperature increases, this effect of molecular weight on reactivity decreases (Minkoff et al., 1962). Therefore as the temperature is raised, the yield of peracid decreases and the relative amount of formaldehyde increases. Minkoff et al., (1962, p. 144) similarly states that ". . . acetaldehyde and ethylene are formed furing propionaldehyde oxidation, the yields increasing as the temperature is raised, . . .". Thus, the molecular weight would seem to shift to a lower value as the

temperature is raised during slow oxidation. However, this effect

might become masked in the high temperature range by the increas-

ing complexity of the reaction scheme. In a motored engine,

Pipenberg (et al., 1957) also found a time effect on the molecular

weight. For a stoiciometric n-heptane/air mixture, he found that

oxidation begins at 345°C, forming higher aldehydes but formalde-

hyde doesn't start being formed until slightly higher temperatures.

There is also a variation within the cycle of the engine when burning

n-pentane (Malmberg et al., 1954). Acetaldehyde surpasses

formaldehyde in concentration beyond 20° after top dead center when

motoring the engine, the maximum carbonyl concentration being at

15° after top dead center.

There are other factors which effect the reaction kinetics. In

the high temperature region, the kinetics become dependent upon

the oxygen/fuel ratio. In the oxygen dependent region as the tem-

perature gets higher, the peracid begins to decompose and the reac-

tions become more complicated (Griffiths et al., 1968). The surface

condition of the reaction vessel also has a profound effect on the

aldehyde oxidation reactions. As the surface becomes coated, the

induction period falls and the maximum rate rises (Minkoff et al.,

1962). The surface also effects the order of the reactions. The

nitrogen oxides act as inhibitors for the slow oxidation of acetalde-

hyde, the induction period being proportional to the amount of NO_2

added (Minkoff et al., 1962). The molecular structure of the fuel

also has an effect on the oxidation of the carbonyls. Minkoff et al.,

1962, p. 215) states; "The yield of aldehydes from the oxidation of

straight chain hydrocarbons is much greater than from that of

branched chain ones."

The Formation and Oxidation of Formaldehyde

The theory of the slow thermal oxidation of formaldehyde is

much more controversial than that described above for higher

molecular weight aldehydes. Formaldehyde requires a higher oxida-

tion temperature (> 250°C) than do propionaldehyde and acetaldehyde

and also surface conditions have much more of an effect (Griffiths

et al., 1968). Thermal oxidation of formaldehyde takes place at a

measurable rate between 250 and 500°C. Griffiths et al. (1968)

states that this effect is due mainly to the differences in the branch-

ing effects between $HCO_3\cdot$ and $RCO_3\cdot$. The mechanism of forma-

tion with higher order aldehydes is: $RCHO + RCO_3\cdot \rightarrow RCO\cdot$

$+ RCO_3H$, where the peracid (RCO_3H) is a branching intermediate.

Formaldehyde, however, oxidizes to performyl, a non-branching

intermediate according to: $HCO_3\cdot + CH_2O \rightarrow HCO\cdot + HCO_3H$.

The rate can only become appreciable when the temperature gets

high enough for the $HO_2\cdot$ radical formed from the decomposition

of $HCO_3\cdot$ to attack the formaldehyde.

According to Minkoff et al. (1962) most of the formaldehyde

formed during the combustion of the high order paraffins (such as

diesel fuel) is due to the thermal breakdown of the alkoxy radical

intermediate according to: $CH_3CH_2O \cdot \rightarrow CH_3 \cdot + HCHO$. However,

formaldehyde is also formed from the oxidation of higher order

aldehydes, such as acetaldehyde, crotonaldehyde, and acrolein

(Minkoff et al., 1962).

As the temperature is raised in the high temperature region,

the yield of formaldehyde from the oxidation of higher order alde-

hydes increases (Minkoff et al., 1962). Increasing temperature also

has an effect on the subsequent oxidation of the formaldehyde. As

mentioned above, the rate of oxidation does not even become measur-

able until 250° C. The stoiciometry in this range is given by

$2CH_2O + O_2 = 2CO + 2H_2O$. However, with some surfaces above

330° C, the stoiciometry changes to $CH_2O + O_2 = H_2O_2 + CO$.

There is much controversy on the mechanism of the oxidation

of formaldehyde. This is partially due to the large effect of the re-

action vessel surface and also to the complications caused by the

decomposition of the peroxide intermediates. According to

Griffiths et al. (1968) most of the values for activation energy for

the slow oxidation of formaldehyde fall in the range of 20-28 kilo-

calories per mole; however, there is poor agreement between the

workers. Griffiths also gives a simplified kinetic scheme which

seems to predict most of the effects on this oxidation:

$$CH_2O + O_2 \rightarrow HCO\cdot + HO_2\cdot$$

$$CH_2O + HO_2\cdot \rightarrow HCO\cdot + H_2O_2$$

$$HCO\cdot + O_2 \rightarrow HO_2\cdot + CO$$

$$CH_2O + H_2O_2 \rightarrow HCO\cdot + OH\cdot + H_2O$$

$$CH_2O + OH\cdot \rightarrow HCO\cdot + H_2O$$

$$HCO\cdot + O_2 \rightarrow HCO_3\cdot$$

$$HCO_3\cdot + CH_2O \rightarrow HCOH_3 + HCO\cdot$$

$$HCO_3 \rightarrow OH\cdot + HCO_2\cdot$$

$$HCO_3H \xrightarrow{surface} Inert$$

$$CH_2O + HCO_2\cdot \rightarrow HCOOH\cdot + HCO\cdot$$

$$HCO_2\cdot + O_2 \rightarrow HO_2\cdot + CO_2$$

$$HO_2\cdot + HO_2\cdot \rightarrow Termination$$

$$HO_2\cdot \xrightarrow{surface} Inert$$

$$H_2O_2 \xrightarrow{surface} Inert$$
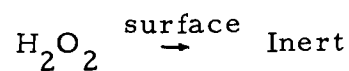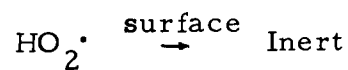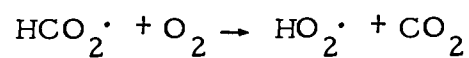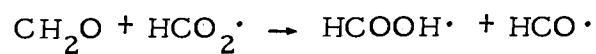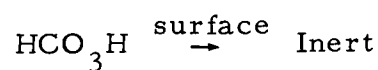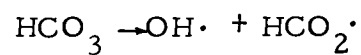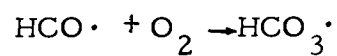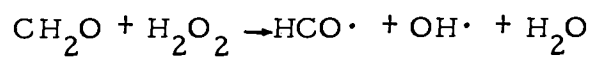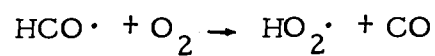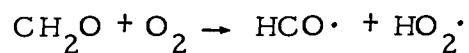
The relative importance of these reactions depends on the temperature (especially in the oxygen dependent region), and the surface condition (Griffiths et al., 1968).

Besides the effect of temperature on formaldehyde slow oxidation mentioned above, there is also a very strong surface effect on both the kinetics and the final products of reaction (Griffiths et al., 1968). The time the reaction has been going when it is quenched also has a marked effect. Minkoff et al. (1962) states that when formaldehyde is burned with an excess of oxygen at 480-580°C, there is an induction period of several minutes.

In summary in the 200-350°C temperature range formaldehyde tends to be more resistant to oxidation than higher order aliphatic aldehydes. It is formed from the oxidation of higher aldehydes plus the decomposition of the alkoxy radical, and is more influenced by surface effects than are higher aldehydes.

The Effect of Aldehydes on Free Radical Chain Reactions

Aldehydes are necessary intermediates for some of the free radical reactions which take place during the thermal oxidation of organic fuels. An important phase of some of the proposed reaction schemes is degenerate branching. Degenerate branching is not due to the free radical reaction between the fuel and intermediates, but instead is due to a relatively stable intermediate which is formed in

a nonbranching reaction. This stable intermediate, which may have a life time of seconds (Minkoff et al., 1962), then reacts to form radicals or products which can initiate a chain reaction leading to the formation of more of the stable intermediate.

According to Minkoff there are two candidates for the intermediate responsible for degenerate branching, these being peroxides and aldehydes. In the 350-500°C range with simple fuel, formaldehyde is mainly responsible for the branching. Below 450°C higher aldehydes are also active intermediates (Minkoff et al., 1962). Higher aldehyde concentration during slow combustion in the low temperature region usually reaches a maximum at the time of the maximum reaction rate, indicating they are active intermediates. Because the higher carbonyl compounds are more unstable, there are indications that they are more reactive intermediates than formaldehyde, causing the reaction to accelerate at a faster rate (Minkoff et al., 1962).

Cool flame reactions are also branched chain reactions. Formaldehyde and higher aldehyde concentration ". . . in a motored engine parallels the integrated cool flame intensity which is a measure of the extent of cool flame reaction at any time" (Minkoff et al., 1962, p. 208). The flourescent spectra of a cool flame is actually identical to that of excited formaldehyde, which is believed to be produced by the reaction:

$$CH_3O_2\cdot + HO_2\cdot \rightarrow CH_2O + H_2O + O_2$$
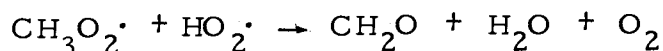
(Minkoff et al., 1962).

Thus even though carbonyl compounds are partially oxidized intermediates of the combustion reactions of organic fuels, they appear to be necessary to the overall reaction and are indeed relatively stable intermediates. It is, therefore, unlikely that it would be possible to reduce the aldehyde content of the exhaust of these reactions to zero unless the reaction is allowed to go to completion.

Theory of the Gas Chromatograph

The gas chromatograph was introduced in 1952 and has since come into wide use for chemical analysis (McNair and Bonelli, 1966). A sample is carried through a column on an inert carrier gas. The sample components are selectively retarded by the stationary phase within the column (a nonvolatile liquid on a solid support) and are eluted as bands, which can then be indicated by an appropriate detector. For compounds with the same general structure, the amount of time the components are retarded is directly proportional to the molecular weight. The instrument can be used both for qualitative and quantitative analysis by comparing the retention time and peak area (respectively) with those generated by known standards. Liquid samples can be introduced into the chromatograph by injecting the sample with a calibrated syringe into an injection port

where the sample is vaporized and swept through the column by the carrier gas.

The operation of the chromatograph is very sensitive to the temperature of the column, which is usually in a carefully controlled oven. The temperature has to be high enough so the components will elute in a reasonable time but must be low enough that the peaks are separated.

Another factor to which the operation of the chromatograph is very sensitive is the stationary phase used. The selection of the column material seems to be more of an art than a science, since there is no fool-proof way to select a liquid phase. The amount of liquid phase on the solid support is also important. Low liquid loading should be used for low volatility compounds and when short retention times are desired (McNair et al., 1966).

The detector most widely used with the gas chromatograph is the flame ionization detector. The carrier gas and the eluted sample are burned with hydrogen in a jet below a collector at 200-300 volts. As the organic materials burn, the current carried through the collector increases because of the ions produced. The current is then used as an indication of oxidizable materials present. The minimum detectable quantity for this detector is 10^{-6} μg with good linearity. Another good feature of the flame ionization detector is that it is insensitive to fixed gases and water vapor (McNair et al., 1966).

PROCEDURE AND APPARATUS

In this study, a gas-liquid chromatographic determination of the low molecular weight aliphatic aldehydes in diesel exhaust is made. The C_1 to C_5 aldehydes are the only ones considered because they have high vapor pressures and because the literature indicates they will be in the highest concentration (Fracchia et al., 1967). Also, there has to be a limit set on the number of compounds considered because of the difficulty of resolution in a gas chromatograph.

Wet tests for formaldehyde and total aliphatic aldehydes are made simultaneously with the gas chromatographic tests using standard methods. The chromotropic acid test (Reckner, Scott and Biller, 1965; Linnell et al., 1962b; Hurn et al., 1965) is used for formaldehyde and the 3-methyl-2-benzo-thiazone hydrazone hydrochloride (MBTH) method is used for total aliphatic aldehydes (Reckner et al., 1965; Merrion, 1968; Hauser, 1965). These tests are made for correlation with the data obtained by gas chromatograph and also to check the wet test data from the engine with literature values.

Two variables are used. Load is varied at constant speed. Zero, one-half, and full load are measured at 1800 RPM. Since the diesel is a constant air consumption engine at constant speed, varying

load is the same as varying fuel-air ratio and consequently the combustion temperatures.

The other variable is the exhaust pipe length from the exhaust manifold to the probe. Two probes are used and are sampled at the same time. The exhaust pipe between these two probes can be considered as a steady flow reaction chamber. The effect of the difference in reaction time between the probes (about 50 milli-seconds at 1800 RPM) is then checked against what the theory predicts.

The engine used is a two stroke-cycle General Motors Model 3-71 RC diesel. This model has a 213 cubic inch displacement with a $4\frac{1}{4}$ x 5 inch bore and stroke and a 16:1 compression ratio. Although this is a rather old engine, having been received at the University in 1945, it has only approximately 350 hours of operation and is in good mechanical shape. The injectors are the standard 60 mm models and the pump is also standard. The tachometer reading was checked with a strobe light. The engine, control panel, and water cooled eddy current dynometer are shown in Figure 1. The GMC 71 series diesel is often used in buses and trucks.

There is some controversy on the effect of fuel on the aldehyde content of a diesel (Marshal and Hurn, 1968; Perez and Landon, 1968). The fuel used is #2, 50 cetane to agree with the fuel used by other experimentors in the field (Reckner et al. 1965; Linnell et al. 1962b; Linnell and Scott, 1962a). The API gravity, as determined
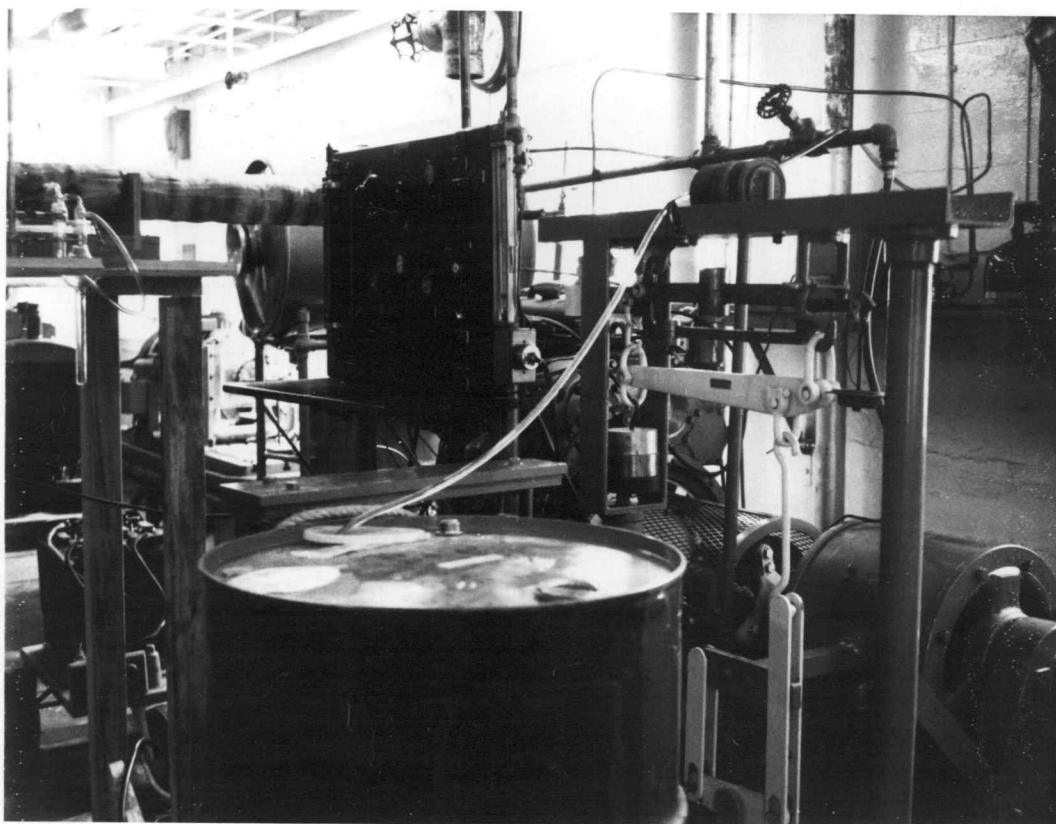
Figure 1. GMC 3-71 engine and eddy current dynamometer.

by ASTM test #D287-55 is 34.7. ASTM test #86 for the distillation curve of the fuel gives: 10 percent - 425° F, 50 percent - 523° F, and 90 percent - 613° F. According to ASTM test #D1319, 89 percent of the fuel is saturates, five percent is olefins and six percent aromatics.

The special exhaust pipe used in the study is shown in Figure 2 and the top of Figure 3. A horizontal three inch nominal diameter steel pipe is used and wrapped with $1\frac{1}{2}$ inches of fibreglass insulation. The tip of probe one is 30 inches down the pipe, and 50 inches from the exhaust manifold. This 30 inch length is necessary to decrease the turbulence of the exhaust caused by the curved section of exhaust coming out of the manifold (see Figures 1 and 2). The tip of probe two is 80 inches further down the pipe from probe one. This 80 inch length represents retention times of 0.0479 seconds at zero load, 0.0415 seconds at one-half load, and 0.0368 seconds at full load.

Four iron-constantan thermocouples on the exhaust pipe are monitored during testing. One is located in the exhaust stream one inch behind the tip of the first probe. Another is located one inch beyond the second probe tip, and the last is imbedded in the steel pipe by the second probe. The temperature is read with a Leeds and Northrup potentiometer indicator. Because of the effect of surface conditions on the reaction of aldehydes, the engine was run for 30 hours at all loads at 1800 revolutions per minute to coat the
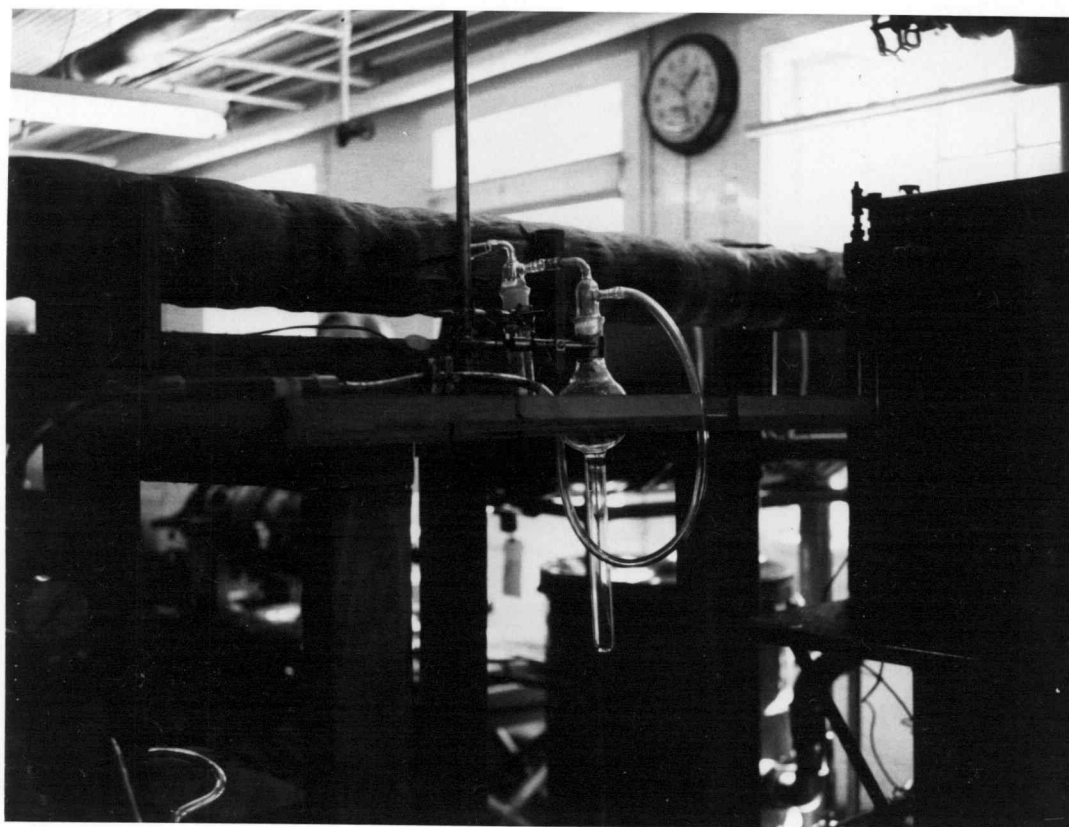
Figure 2. Water trap and tall form bubbler at probe one.
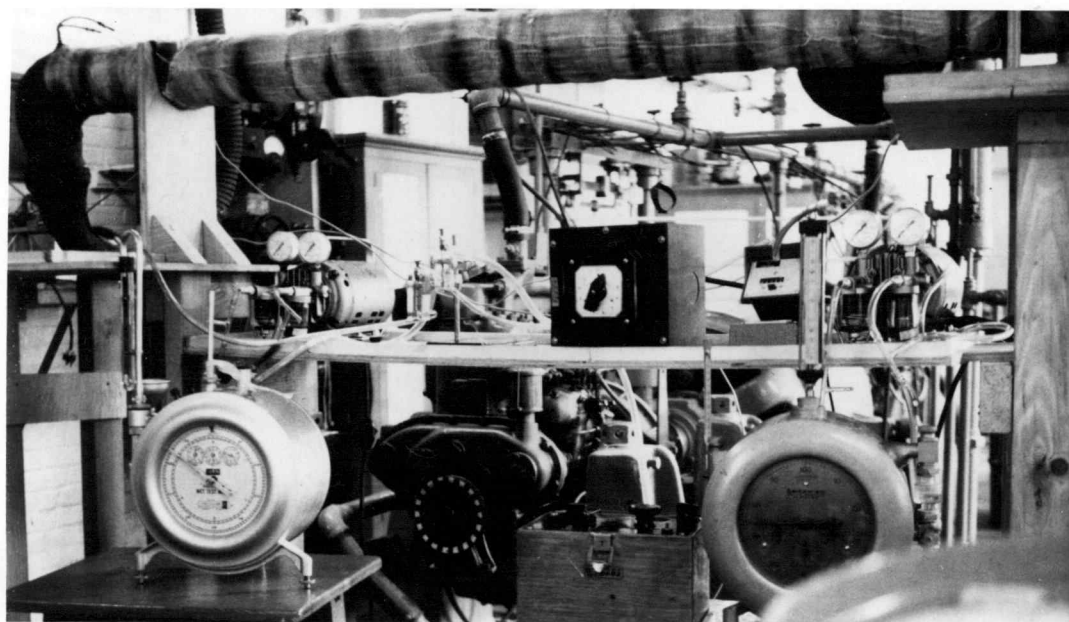
Figure 3. Test equipment. Exhaust pipe in upper part of picture, probe one and engine to the right.

exhaust to a condition of equilibrium deposits.

The probes are of the type described by Linnell et al. (1962) and Reckner et al. (1965). They consist of $\frac{1}{4}$ inch stainless steel tubing with a 1/16 x 3 inch slot in the end. The probes are pictured in Figure 4. Probe one, on the left in Figure 4, is $12\frac{1}{4}$ inches long, with a 90° bend $5\frac{1}{2}$ inches from the slotted end. Probe two is 16 inches long and is straight. Both have a 10-30 standard taper joint for connecting the first bubbler. The probes are connected to the exhaust pipe with Swagelock fittings. Because of the danger of condensing the aldehydes in the sampling lines (Linnell et al., 1962a, 1962b; Perez et al., 1968) the distance from the exhaust pipe to the first joint is only eight inches. These probes are not suitable for isokinetic sampling; however, only a slight amount of aldehydes is absorbed on the particulates (Linnell et al., 1962b).

The sampling train for the gas-liquid chromatographic analysis is described by Fracchia et al. (1967). There is one complete sampling line for each probe. A water trap is connected to the 10-30 standard taper joint on the probe. This trap consists of a standard 30 ml midget impinger with a standard-taper glass joint. A tall form bubbler, also of the type used by Fracchia (see Figure 5) is fastened to the water trap with a butt joint using Tygon tubing. The special form is needed because of the foaming characteristics of the reagent.
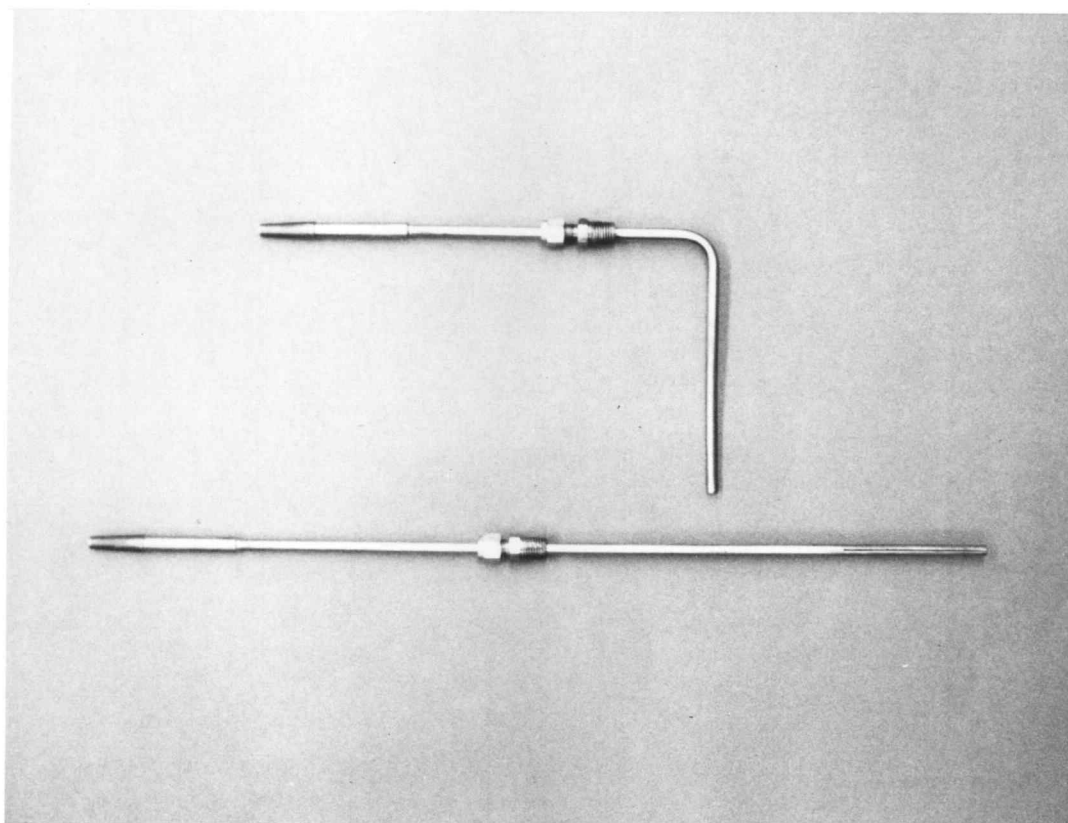
Figure 4. Stainless steel exhaust probes. Probe one at top.
Note slot in end of probe two.
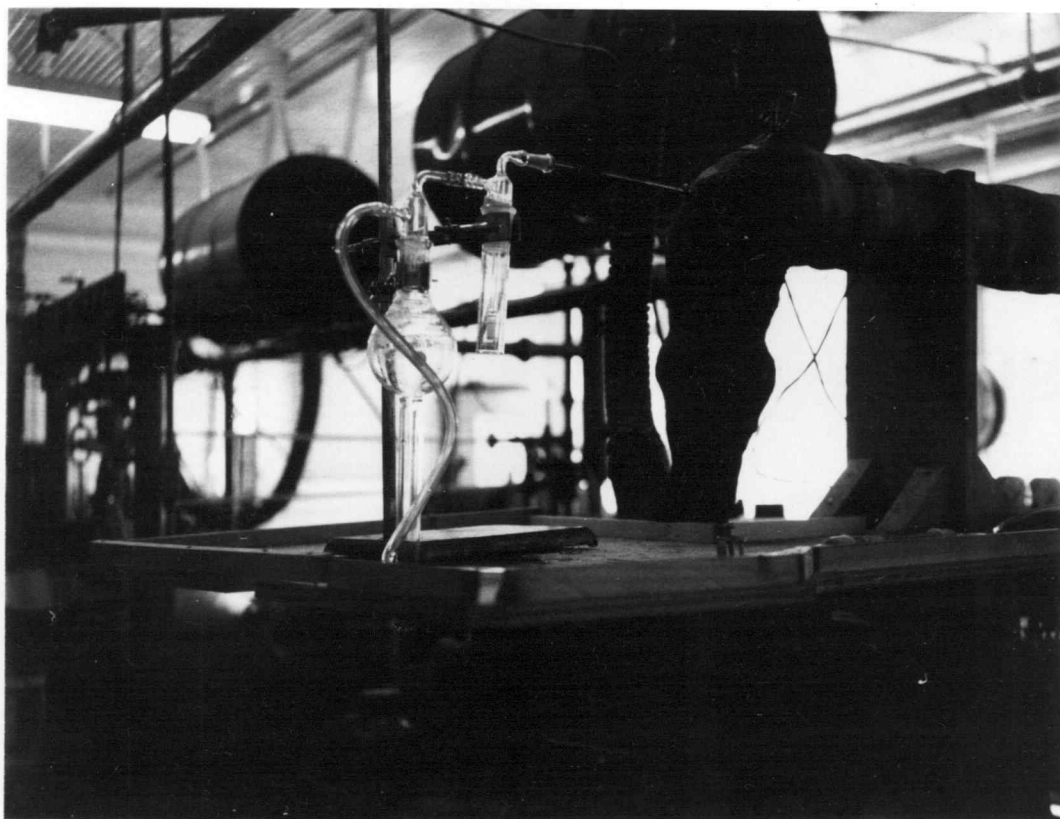
Figure 5. Water trap and tall form bubbler at probe two.

Following the bubblers is a silica gel desiccant tube with a filter. These are needed to protect the in situ flowmeters which follow the desiccant tube. These Dwyer flowmeters are of the rotameter type, with a flow capacity of four standard cubic feet per hour, and are used to get an estimate of the flow rate through the bubblers. The actual volume of gas which goes through the bubbler is measured by the last instrument in the sampling train, a wet test flowmeter manufactured by Precision Scientific Company. No pumps are required because a six inches of mercury pressure head exists in the exhaust pipe due to restrictions in the laboratory exhaust system.

The bubblers used in the wet test are 30 ml all glass midget bubblers, course frit, manufactured by Mine Safety Appliance Company. The first bubbler has one 10-30 standard-taper joint to fit the probe. The second bubbler is butt jointed to the first by Tygon tubing. Again, there is one complete sampling train for each probe, the rest of the train being identical to the one described above for the gas chromatographic bubblers.

The gas chromatographic analysis is generally the one described by Fracchia et al. (1967) for spark ignition engines. The sampling reagent is a solution of 2, 4-dinitrophenylhydrazine. A 600 milligram quantity of the phenylhydrazine is dissolved in 6 ml of concentrated sulfuric acid. After five minutes 20 ml of double

distilled water are added dropwise and the solution is then diluted

to 100 ml with double distilled water using tap water cooling. Fifteen

ml of the sampling reagent is used in each bubbler. The 2, 4-dini-

trophenylhydrazine reacts with the carbonyl compounds in the

exhaust to form precipitates, which are easier to work with than the

reactive carbonyl compounds. The reaction is:

$$\begin{matrix} R \\ \diagdown \\ \diagup \\ H \end{matrix} C{=}O \ + H_2NH{-} \underset{NO_2}{\diagup\!\!\!\diagdown} {-}NO_2 \ \overset{H_2SO_4}{\rightarrow} \ \begin{matrix} R \\ \diagdown \\ \diagup \\ H \end{matrix} C{=}NNH{-} \underset{NO_2}{\diagup\!\!\!\diagdown} {-}NO_2 {+}H_2O$$
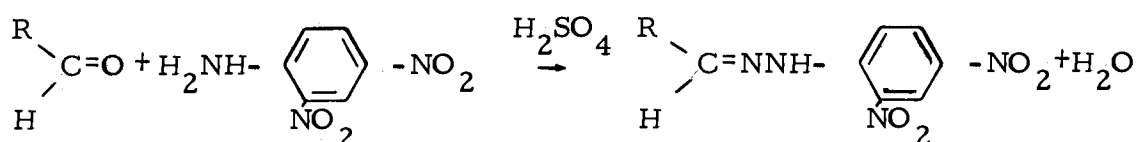
Fracchia et al. (1967) recommends a sampling rate of one liter

per minute based on trapping and hydrazone recovery efficiency

studies. Because of the difficulty and expense involved in generating

the calibrated gas streams necessary for such an efficiency study,

Fracchia's efficiencies are used (listed in the results) and Fracchia's

method followed as closely as possible. Approximately 60 minutes

sampling time is required for reproducible results.

The hydrazone recovery method used is similar to the one

described by Fracchia et al. (1967). Immediately after each test

the water trap is washed with double distilled water and then added

to the phenylhydrazone bubbler. This is done to recover the formal-

dehyde dissolved in the water trap.

The tall form bubbler and frit are then washed with double

distilled water, keeping the volume to less than 25 ml, and the

entire reagent volume extracted twice with two 10 ml aliquots of

dichloromethane. The bubbler and frit are washed carefully with

the dichloromethane extractant and then are washed again with fresh

dichloromethane. The combined washings are then filtered through

Wattman #12 fluted filter paper. The filter paper is washed well

with more dichloromethane, keeping the total volume of dichloro-

methane solution to less than 50 ml. The solution is then concen-

trated to near dryness in a water bath using boiling beads to prevent

bumping, leaving only enough solvent to maintain solution. The

dichloromethane is then allowed to air evaporate to dryness, being

careful not to allow any longer time than necessary for complete

evaporation. Immediately 10-15 ml of carbon disulfide is added and

placed back in the water bath until solution of the phenylhydrazones

is attained. The solution is then transferred to a volumetric tube

and evaporated to volume. This is then chromatographed imme-

diately.

The chromatograph is a Perkin Elmer 810, pictured in Figure

6. The flame ionization detector included with the unit is used in

conjunction with a Minneapolis Honeywell Electronik -0. 5 to 1. 05

millivolt recorder.

The chromatographic columns are ten percent SF 96 on 60-80

mesh acid washed dimethyldichloroselane treated Chromosorb W
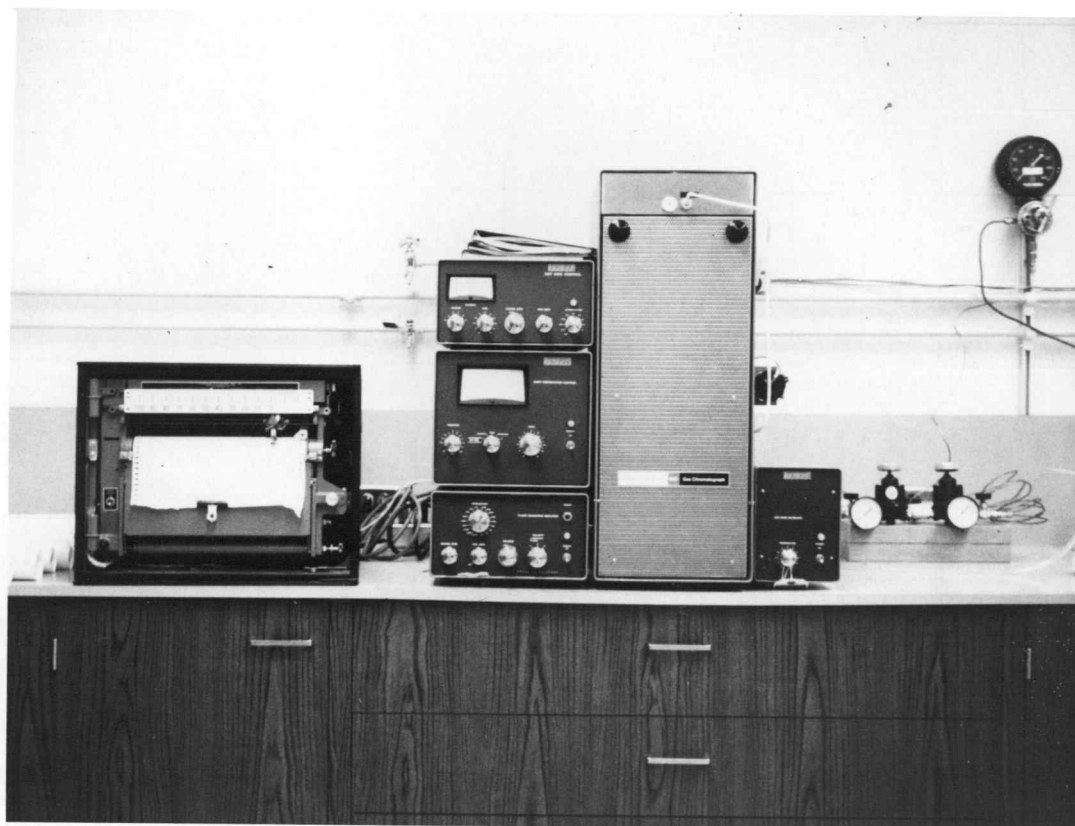
Figure 6. Perkin Elmer 810 gas chromatograph with Brown-Honeywell Electronik Recorder at left.

in 6 feet by 0.085 inch I. D. stainless steel tubing. The carrier gas

is nitrogen at 60 ml per minute and the hydrogen flow for the flame

ionization detector is 35 ml per minute. The column temperature for

the phenylhydrazones of the lower order aldehydes is 230 degrees

centigrade with a 270 degree centigrade injector temperature, as

suggested by Fracchia et al. (1967). The ten microliter liquid

samples are injected using a Hamilton 701 syringe with a Chaney

adaptor.

The 2, 4-dinitrophenylhydrazone derivatives of the C_1 to C_5

aliphatic aldehydes are prepared by the method of Shriner and Fuson

(1964) and the precipitates recrystallized until the melting points

agree with literature values (Shriner et al., 1964). The precipitates

are then dried to constant weight in a vacuum over phosphorous

pentoxide and the standard solutions prepared gravitimetrically.

These solutions ranged from 0.05 to 3.0 grams per liter of the

phenylhydrazone derivative in carbon disulfide. Three dilutions are

made of each solution for a linearity check on the flame ionization

detector. Fracchia et al. (1967) found good linearity, the correlation

coefficients between concentration of the derivative solution and

detector response ranging from 0.924 to 0.997. To find the flame

ionization detector response, a 10 μl injection of a known concentra-

tion of the phenylhydrazone is chromatographed and the area under

each peak measured with a polar planimeter. The ratio of the area

to the standard concentration is then known as the flame ionization response. There is a ± 15 percent variation in response from injection to injection but no detectable variation in response from day to day. Therefore, each standard solution and exhaust test solution is chromatographed from two to four times and the average response used. The retention time for each phenylhydrazone derivative is constant from injection to injection but increases as the column wears. The chromatograph calibration data is listed in the results.

The base line of the exhaust test chromatogram does not return to zero before the aldehyde retention times. Thus the aldehyde-phenylhydrazone peaks appear as trace components after a major peak (see Figure 7). To measure these peaks, the base line is drawn in and the peak area measured with a polar planimeter (McNair et al. , 1966).

For the wet tests, the samples are collected in 10 ml of 0.06 percent aqueous sulfamic acid solution immediately after the collection of the gas chromatograph sample. The sulfamic acid solution is used to reduce interference from NO_2 (Reckner et al. , 1965). Two bubblers with identical sampling solutions are used for each probe. The sampling rate is one liter per minute for three minutes.

For formaldehyde, a slightly modified version of the chromotropic acid method described by Reckner et al. (1965) is used. One ml of solution from each bubbler is placed in separate test tubes.

Figure 7

EXACT COPY OF CHROMATOGRAM FROM
TEST #16, 0 LOAD, PROBE 1

Note: Dashed line is artificial baseline used
in measuring areas under peaks. Peak
numbers are circled.

Retention Time, Minutes
(Minutes After Injection)

1.5   2.0   2.5   3.0   3.5   4.0   4.5   5.0   5.5   6.0
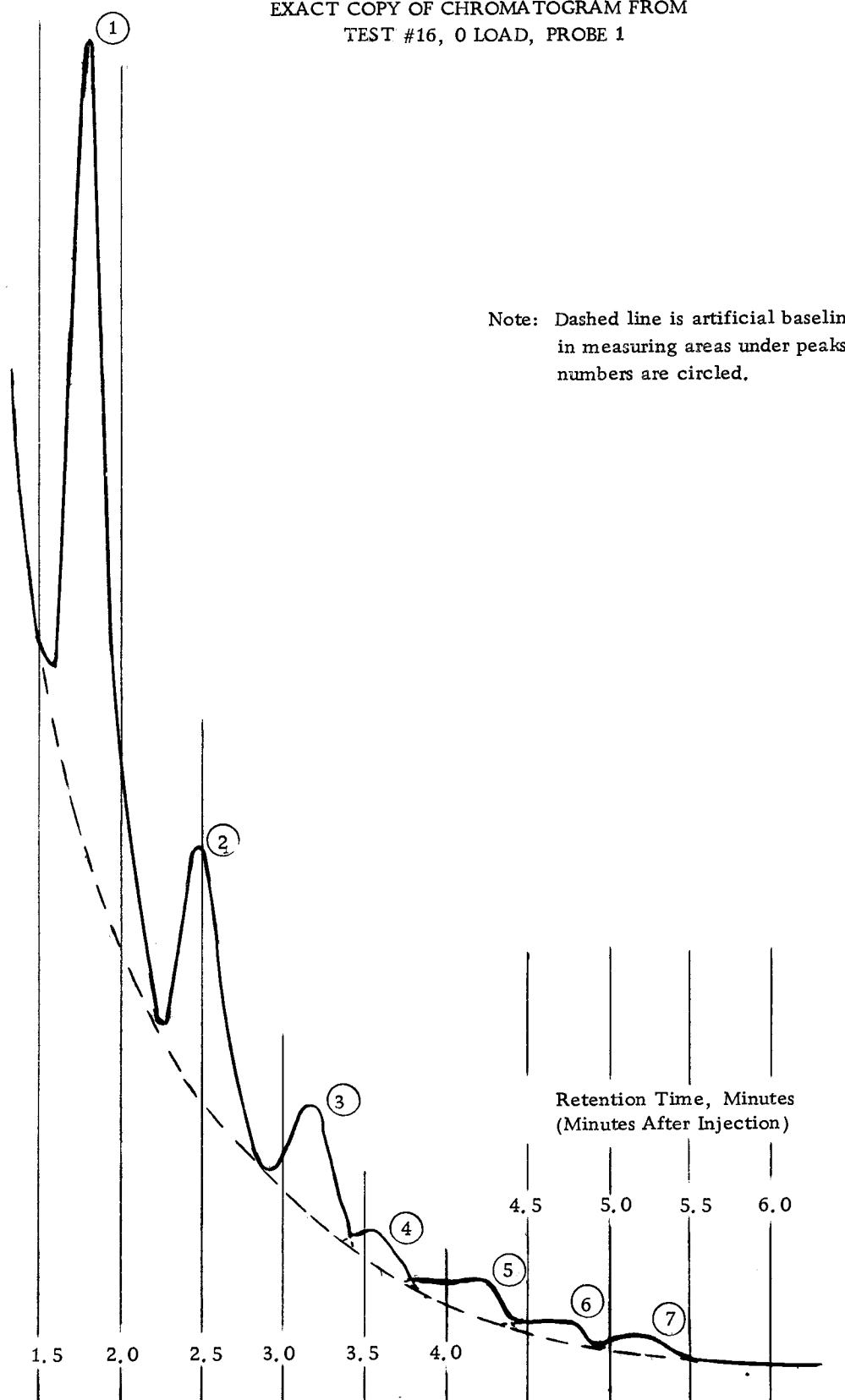
One ml of one percent chromotropic acid in sulfuric acid and 6 ml of reagent grade concentrated sulfuric acid are then added to the tube. After 45 minutes the solution is stirred and the absorbance measured immediately. If the transmissivity is less than one percent, the solution is diluted one to three and measured again. The transmissivity is measured with a Bausch and Lomb Spectronic 20 colorimeter at 580 mμ against a reagent blank.

Total aliphatic aldehydes are measured by the 3-methyl-2-benzo-thiazone hydrazone hydrochloride method described by Reckner et al. (1965). To $\frac{1}{2}$ ml from each bubbler is added 1 ml of 0. 4 percent aqueous MBTH solution in separate 25 ml volumetric flasks. Five ml of 0. 2 percent aqueous ferric chloride solution is added to each flask after 20 minutes, and after five more minutes, the solutions are made to volume with reagent grade acetone. After stirring carefully, the transmissivity is measured at 635 mμ against an identically prepared blank.

Both wet methods are calibrated by a stock formaldehyde solution standardized by the dimedon method (Hauser, 1965). From this stock solution, five calibration solutions with concentrations ranging from 0. 3925 x 10^{-3} g/l to 3. 0 x 10^{-3} g/l are made. The calibration is checked often during the test using one of these calibrating solutions. The curve for percent transmissivity versus concentration for each test is included in the Appendix.

RESULTS

The testing and calibration was done according to the procedure

described previously. The calibration results for the gas chromato-

graph are shown in Table 1. The compound and peak number with the

corresponding retention time and flame ionization response are

listed. More than one compound is represented in a peak when the

retention time of the carbonyl phenylhydrazone derivatives are not

separable enough for distinct peaks. There is a range for the re-

tention times because of the tendency for the retention time to in-

crease as the column wears. The smaller times represent the first

tests made. The standard solutions are injected from time to time

to check the effect of column wear on retention time and detector

response. As described above, the flame ionization response for

each peak is the ratio of the concentration of the hydrazone to the

area under the peak as measured by a polar planimeter. Fracchia's

et al. (1967) retention times are also listed and appear to be much

longer than the ones found during this test.

The raw data from the gas chromatographic and wet tests are

in the Appendix. Table 2 is a summary of this data. The concentra-

tions listed are in terms of parts per million of the aldehydes in the

exhaust. Sample calculations for the conversion of concentration in

the test sample to concentration in the exhaust are shown in the

Table 1. Chromatographic calibration data.[*]

Compound	Peak No.	Retention Time (Minutes)	Flame Ionization Resp. $(g/1\text{-}in^2$ Phenylhydrazone)	Fracchia, et. al. (1967) Retention Time
Formaldehyde	1	1. 7--1. 9	3. 320	3. 1
Acetaldehyde	2	2. 5 -2. 7	1. 880	4. 6
Acrolein	3			
Acetone	3	3. 1 -3. 45	1. 742	6. 1
Propionaldehyde	3			
iso-Butyraldehyde	4	3. 5 -4. 0	1. 255	6. 8
n-Butyraldehyde	5	4. 1 -4. 4	1. 342	8. 2
iso-Valeraldehyde	6	4. 35-4. 8	1. 210	---
Crotonaldehyde	7			10. 2
		5. 3 -5. 6	1. 710	
n-Valeraldehyde	7			---

[*]Refer to Figure 7

Table 2. Average Concentration of Aldehydes

| | | Engine Load Condition @ 1800 RPM | | | | | |
| | | 0 Load | | 1/2 Load | | Full Load | |
		Probe 1	Probe 2	Probe 1	Probe 2	Probe 1	Probe 2
Wet Test							
Total Aliphatic Aldehydes	Conc. PPM[1]	16.48	17.84	54.50	84.39	59.28	68.20
	Std. Dev.	2.71	2.36	8.75	13.12	8.51	10.65
	Coef. Var. %	16.43	12.52	16.05	15.54	14.36	15.61
Formal	Conc. PPM[1]	13.15	13.08	36.89	59.41	53.34	65.82
	Std. Dev.	1.24	1.28	5.97	11.93	9.37	11.56
	Coef. Var. %	9.46	9.81	16.18	20.07	17.56	17.57
GLC.							
Total Aldehydes 5 Carbon	Conc. PPM[1]	17.73	15.89	26.41	32.34	53.38	55.84
	Std. Dev.	2.37	2.73	10.21	4.71	8.31	15.36
	Coef. Var. %	13.36	17.16	38.67	14.57	15.58	27.50
Formal	Conc. PPM[1]	13.90	12.55	19.53	24.87	42.73	49.63
	Std. Dev.	1.74	1.97	8.62	4.66	7.25	10.00
	Coef. Var. %	12.52	15.68	44.16	18.73	16.97	20.16
Molecular Weight Index	M.W.I.	34.42	34.46	36.05	34.89	34.18	33.41
	Std. Dev.	0.70	0.63	1.32	1.19	0.31	0.49
	Coef. Var. %	2.05	1.81	3.67	3.40	0.90	1.47
Normalized Mol. Wt. Index	N.M.W.I.	4.42	4.46	6.05	4.89	4.18	3.41
	Std. Dev.	0.70	0.63	1.32	1.19	0.31	0.49
	Coef. Var. %	15.85	14.10	21.85	24.37	7.41	14.37

[1] Although two digets are shown to the right of the decimal, only one is significant.

Appendix. The mean concentration for each load and probe condi-
tion, and the standard deviation around this mean are shown in
Table 2. The coefficient of variation is the percentage ratio of the
standard deviation to the mean. Since for a normal distribution 68
percent of the points should be within ± one standard deviation of the
mean, the coefficient of variation is a good indication of the relative
spread of points around the mean concentration. The total aldehyde
concentration using gas-liquid chromatography is the summation of
the concentrations of the aliphatic aldehydes up to five carbon atoms,
as listed in Table 1.

The molecular weight index in Table 2 is the mole average of
the molecular weight. The normalized molecular weight index is
the molecular weight index minus 30, the molecular weight of
formaldehyde. This is done so that the molecular weight index can
go to zero instead of having a minimum of 30. The coefficients of
variation for the normalized molecular weight index are similar to
the coefficients for the concentrations.

Tables 3, 4 and 5 list the effects of load, probe location, and
test type on the various concentration and molecular weight index
values. The 't' test is used to determine if the difference of the
means between two conditions of a variable are significant. If the
difference is not significant at the 90 percent level or greater, N. S.
for not significant is entered in the table. The computer printout

Table 3. Effect of Load

Test Condition		Value at 0 Load	C. L.[1] 0-1/2 Load	Value at 1/2 Load	C. L.[2] 1/2-Full Load	Value at Full Load
Wet Test						
Total PPM[4]	Probe 1	16.48	>99%	54.50	N.S.[3]	59.28
	Probe 2	17.84	>99%	84.93	95%	68.20
Formal PPM[4]	Probe 1	13.15	>99%	36.89	>99%	53.34
	Probe 2	13.08	>99%	59.41	N.S.[3]	65.82
GLC						
Total PPM[4]	Probe 1	17.73	95%	26.41	>99%	53.38
	Probe 2	15.89	>99%	32.34	>99%	55.84
Formal PPM[4]	Probe 1	13.90	90%	19.53	>99%	42.73
	Probe 2	12.55	>99%	24.87	>99%	49.63
MWI	Probe 1	34.42	99%	36.05	>99%	34.18
	Probe 2	34.46	N.S.	34.89	98%	33.41

[1] Confidence Limit at which difference between 0-1/2 load is significant.

[2] Confidence Limit at which difference between 1/2-full load is significant.

[3] Not significant at 90% confidence level.

[4] Concentrations are significant to only one place after the decimal.

Table 4. Effect of Probe Location

Wet Test

	Total Aldehydes as HCHO, PPM[1]			Formaldehyde, PPM[1]		
	0 Load	1/2 Load	Full Load	0 Load	1/2 Load	Full Load
Probe #1	16.48	54.50	59.28	13.15	36.89	53.34
% Confidence of Difference	N.S.	>99%	90%	N.S.	>99%	95%
Probe #2	17.84	84.39	68.20	13.08	59.41	65.82

Gas-Liquid Chromatography

	Total Aldehydes, PPM[1]			Formaldehyde, PPM[1]			Molecular Weight Index		
	0 Load	1/2 Load	Full Load	0 Load	1/2 Load	Full Load	0 Load	1/2 Load	Full Load
Probe #1	17.73	26.41	53.38	13.90	19.53	42.73	34.42	36.05	34.18
% Confidence of Difference	N.S.	90%	N.S.	N.S.	80%	N.S.	N.S.	90%	>99%
Probe #2	15.89	32.34	55.84	12.55	24.87	49.63	34.46	34.89	33.41

[1] Concentration values are significant to only one place after the decimal.

Table 5. Effect of method on concentration.

	Total Aldehydes, PPM[1]						Formaldehyde, PPM[1]					
	0 Load		1/2 Load		Full Load		0 Load		1/2 Load		Full Load	
	Probe 1	Probe 2	Probe 1	Probe 2	Probe 1	Probe 2	Probe 1	Probe 2	Probe 1	Probe 2	Probe 1	Probe 2
Wet Test	16.48	17.84	54.50	84.39	59.28	68.20	13.15	13.08	13.89	59.41	53.34	65.82
% Confidence of Difference	N.S.	N.S.	>99%	>99%	N.S.	90%	N.S.	N.S.	>99%	95%	95%	98%
Chromatography	17.73	15.89	26.41	32.34	53.38	55.84	15.90	12.55	19.53	24.87	42.73	49.63

[1] Concentration values are significant to only one place after the decimal.

for the 't' test is in the Appendix.

Table 3 shows the effect of load on the aldehyde concentrations in the exhaust and the molecular weight index. In the table the confidence limits are between the two load columns they compare. This information is presented graphically in Figures 8 A-E. A dotted line on the graphs in Figures 8 A-E means the difference between the two points is not significantly different at the 90 percent confidence level.

Table 4 lists the effect of probe location. Again the confidence limits for a significant difference in the two values are between the rows being compared. Figures 8 F-J portray these values graphically, probe one being four feet from the exhaust manifold and probe two being 10. 7 feet.

Table 5 shows the effect of the test method on the two concentrations measured, total aliphatic aldehydes and formaldehyde. Once again, the statistical significance of the difference in the values is listed between the respective values. Figures 8 K and L are bar charts portraying the same information. If the differences between the two tests are significant at the 90 percent confidence level or greater, the difference is shaded.

A correlation study was made between the various engine, probe, and test method conditions. The computer printout of the correlation matrix is in the Appendix. Table 6 lists the correlations of interest in this study. Only correlations at the 90 percent

Table 6. Correlations Significant at the 90 Percent Confidence Level.

Correlation between:	Confidence Level, %	Sign
(1) GLC Total vs. Wet Test Total at same load and probe		
None		
(2) GLC Formaldehyde and Wet Test Formaldehyde at same load and probe		
None		
(3) Probe #1 and Probe #2 at same load and test		
GLC Total PPM 1/2 Load	95%	+
GLC Formaldehyde PPM 1/2 Load	90%	+
Wet Test Total PPM Full Load	98%	+
Molecular Weight Index Full Load	98%	+
(4) Loads at same probe and test		
GLC Total PPM Probe #2 0-1/2 Load	98%	−
GLC Total PPM Probe #2 1/2-Full Load	95%	−
Wet Test Formaldehyde Probe #1 0-1/2 Load	99%	+
Molecular Weight Index Probe #1 0-1/2 Load	95%	+
(5) Wet Test for Total and Formaldehyde PPM at same load and probe		
Probe #1 0 Load	90%	+
Probe #1 1/2 Load	98%	+
(6) GLC Formaldehyde and CLC Total PPM at same load and probe		
All Loads and Probes	98%	+
(7) Wet Test Total PPM and Molecular Weight Index at same load and probe		
Probe #1 1/2 Load	98%	−
Probe #2 Full Load	99%	−
(8) Wet Test Formaldehyde PPM and Molecular Weight Index at same load and probe		
Probe #1 0 Load	95%	−
Probe #1 1/2 Load	99%	−
(9) GLC Total PPM and Molecular Weight Index at same load and probe		
None		
(10) GLC Formaldehyde PPM and Molecular Weight Index at same load and probe		
None		

confidence level or higher are listed. The sign of the correlation is also given.

Table 7 lists the average concentrations and mole percent of each of the peaks in the gas chromatographic analysis. The raw data is in the Appendix, with the outliers circled. The mole percent is the percentage of the total concentration of the aldehydes measured which that particular peak represents.

Because of the difficulty involved in determining the sampling efficiency for the gas chromatograph, the values determined by Fracchia et al. (1967) for automotive sampling using the same procedure are used. These efficiencies are listed in Table 8. The first column lists the compound under consideration, the second the trapping efficiency of the bubbler, the third the hydrazone recovery efficiency, and the fourth the overall sampling efficiency. The efficiencies are seen to be near 100 percent for aldehydes, but lower for the ketones. For the purpose of this study, collection efficiency is assumed to be 100 percent.

The exhaust temperatures and pressure, and the horsepower corresponding to each load condition are shown in Table 9.

EFFECT OF LOAD

Note: Dashed line designates differences not significant at the 90 percent confidence level.

A

Total Aliphatic
Aldehyde, Wet Test

B

Formaldehyde,
Wet Test

C

Chromatographic
Total Aldehydes

D

Chromatographic
Formaldehyde

E

Molecular Weight
Index
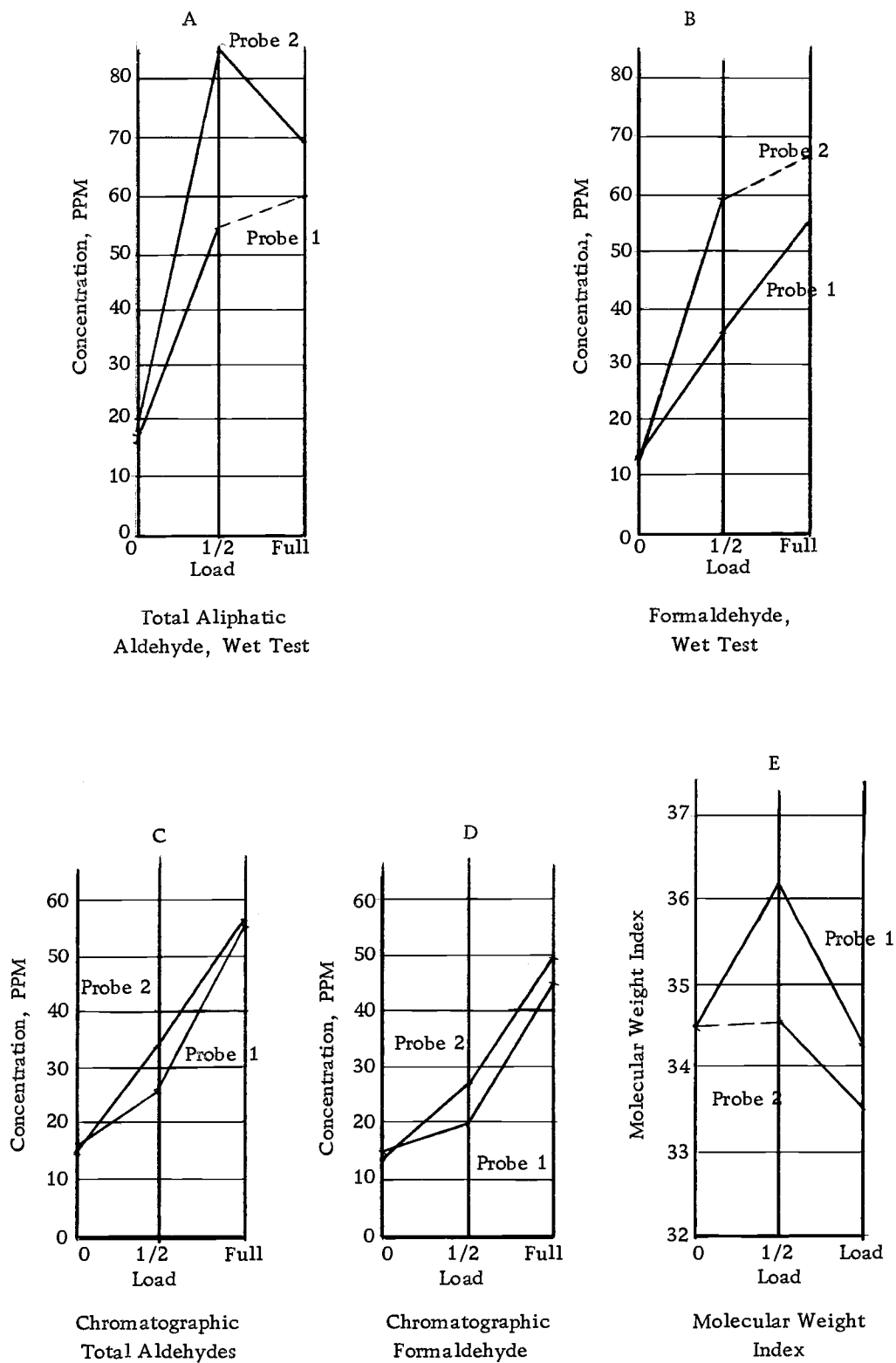
Figures 8F-J

EFFECT OF PROBE

Note: Dashed lines designate differences not significant at the 90% confidence level.

F

Total Aliphatic Aldehydes,
Wet Test

G

Formaldehyde,
Wet Test

H

Chromatographic
Total Aldehydes

I

Chromatographic
Formaldehyde

J

Molecular Weight
Index
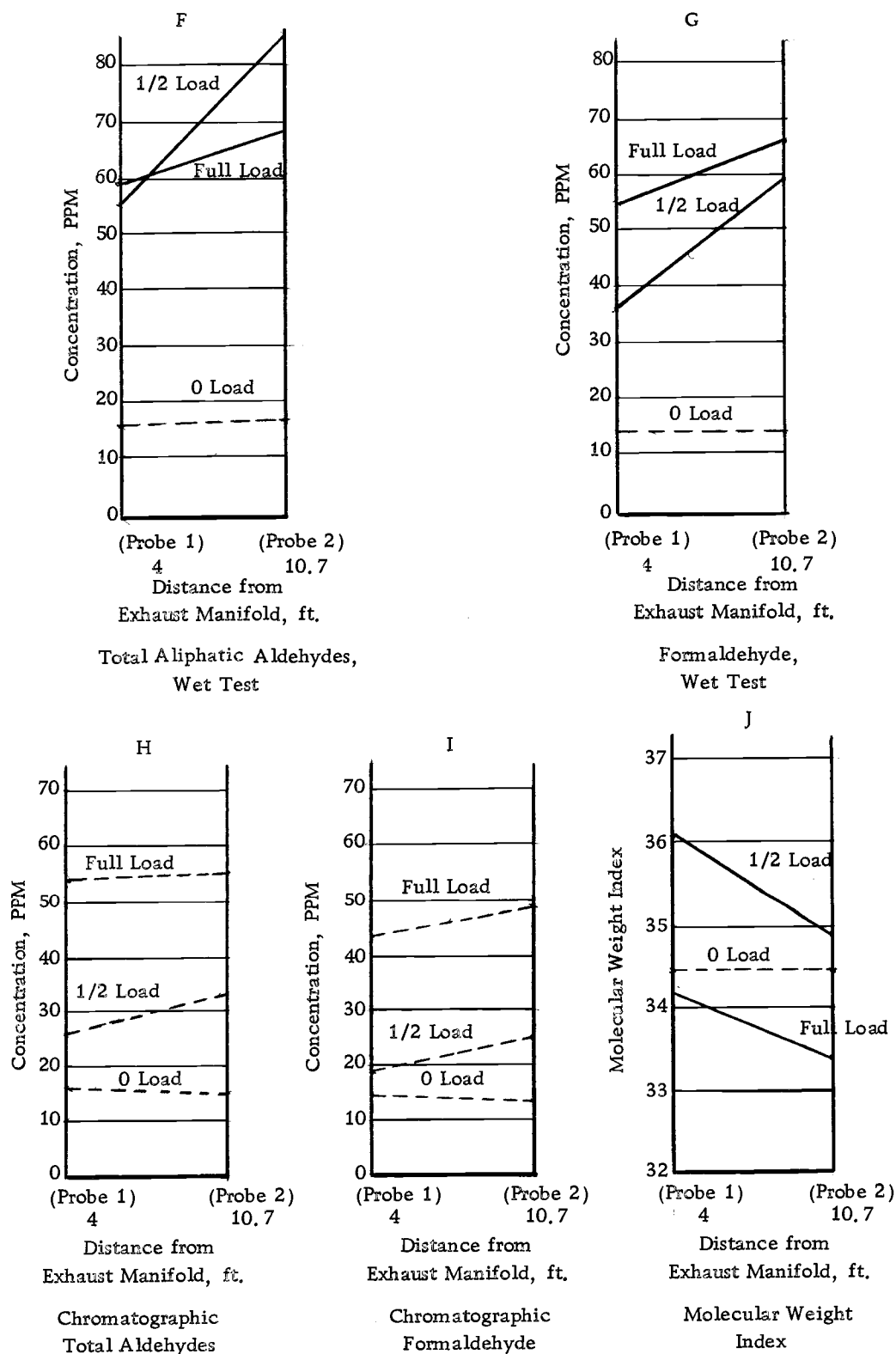
Figures 8 K-L

EFFECT OF TEST METHOD

Total Aliphatic Aldehydes
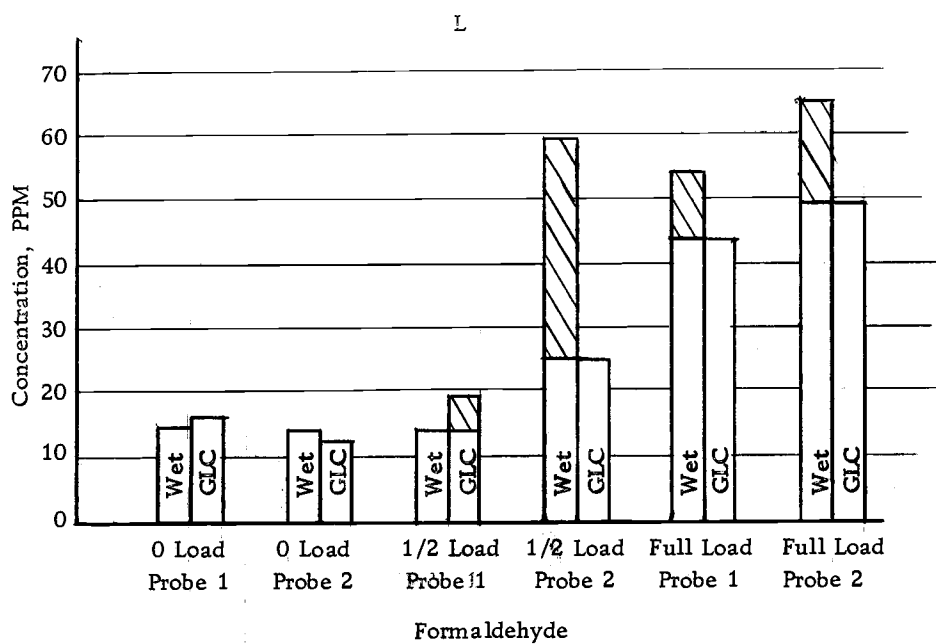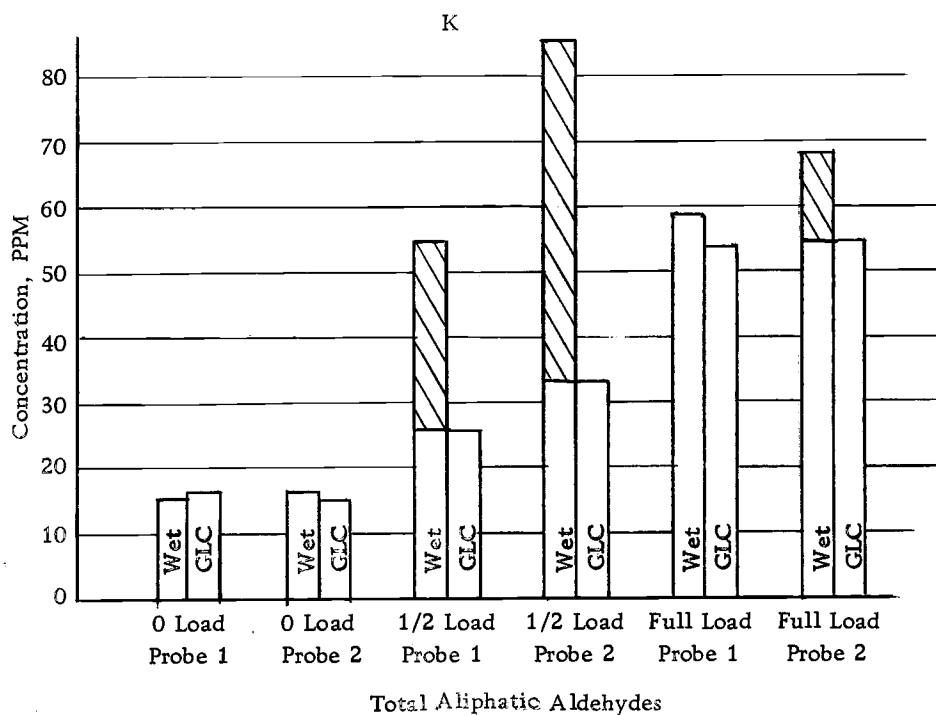
Formaldehyde

Note: Cross-hatched areas designate significant differences at the 90 percent confidence level.

45

Table 7. Average Concentration and Mole % of Aldehydes in Exhaust

Component	Formal-dehyde		Acetal-dehyde		Propional-dehyde Acetone, Acrolein		iso Butyral-dehyde		n Butyral-dehyde		iso Valeral-dehyde		n Valeral-dehyde, Crotonal	
Peak #	1		2		3		4		5		6		7	
Mol. Wt.	30		44		57.3		72		72		86		78	
Probe #	1	2	1	2	1	2	1	2	1	2	1	2	1	2
0 Load														
PPM[1]	13.91	13.51	2.52	2.27	0.68	0.74	0.14	0.09	0.19	0.15	0.08	0.09	0.21	0.16
Mole %	78.45	79.42	14.21	13.35	3.84	4.35	0.79	0.53	1.07	0.88	0.45	0.53	1.18	0.94
1/2 Load														
PPM[1]	21.61	24.07	4.44	4.82	1.90	1.49	0.10	0.03	0.62	0.53	0.07	0.04	0.45	0.54
Mole %	74.44	74.43	15.30	14.90	6.55	4.61	0.34	0.09	2.14	1.64	0.24	0.12	1.55	1.67
Full Load														
PPM[1]	42.73	49.63	6.81	6.66	2.41	2.12	0.06	0.06	0.45	0.39	0.04	0.01	0.86	0.74
Mole %	80.05	83.27	12.76	11.17	4.51	3.56	0.11	0.10	0.84	0.65	0.07	0.02	1.61	1.24

[1] Concentration values are significant to only one place after the decimal.

Table 8. Collection Efficiency Data as Determined by Fracchia et al. (1967, p. 918)

Compound	Concentration PPM	T. E.[1] %	H. R. E.[2] %	E.[3] %
Formaldehyde	18.50	-	-	90
Acetaldehyde	5.35	97	102	99
Acetone	3.50	18	128	23
Acrolein	3.17	97	78	75
Propionaldehyde	3.95	92	92	85
2- Butanone	3.30	34	90	30
Butyraldehyde	7.85	99	103	102
Crotonaldehyde	3.93	100	97	97
2- Pentanone	3.51	71	111	79
Benzaldehyde	4.17	100	80	80

[1] Trapping efficiency of the bubbler

[2] Hydrazone recovery efficiency

[3] Overall efficiency

Table 9. Average Engine Operation Data

		0 Load	1/2 Load	Full Load
Horsepower		0	32.7	66.2
Exhaust Pressure, in. Hg.		4.6	5.4	6.3
Exhaust Gas Temp., Probe #1	°F	499	684	906
	°C	260	366	485
Exhaust Gas Temp., Probe #2	°F	451	633	832
	°C	232	334	439
Exhaust Gas Temp., Manifold	°F	495	703	946
	°C	257	373	507
Exhaust Pipe Temp., Probe #2	°F	454	647	823
	°C	235	341	440

DISCUSSION

The retention times listed in Table 1 are approximately one-half those given by Fracchia et al. (1967). The column material, length, and temperature are identical to his. This difference could be due to column packing. The flame ionization detector response is an average of the chromatograms of the calibration solutions. The exhaust phenylhydrozone extracts are chromatographed from two to four times to take the variation in the response (± 15 percent) into account. This variation could be the effect of column loading, a small amount of each compound being held in the column after elution.

The total aliphatic aldehyde concentrations as formaldehyde determined by the MBTH wet test method are listed in Table 1. The values seem to be higher than some values cited in the literature for the GMC 71 series two cycle diesel. The full load value at probe one is 59 ppm as formaldehyde. Using the same method but a newer engine, Hurn and Marshal (1968) found the total aldehyde content at full load, 1800 RPM, to be 5.5 ppm. Rounds et al. (1956), using a different method, found the total aldehyde concentration to be 65 ppm for a 6-71 at full load, 1600 RPM, and 80 ppm at 2000 RPM. Rounds' data seems to be in agreement with the data from this study. In the GMC 6-71 E two cycle diesel using the MBTH method,

Merrion (1968) found 25 ppm at no load. With the 6-71 N engine,
Merrion found only 5 ppm at full load, and 2 ppm at zero and half
load.

Some of the variation between the test and literature concen-
trations might be explained theoretically. The test engine is 23 years
old with 350 hours on it. During this time, a stable film of deposits
would have built up in the combustion chamber and exhaust manifold.
The test exhaust pipe was run for some time in an attempt to develop
a layer of stable deposits. Marshal et al. (1968) and Merrion (1968)
used new engines in their studies. This may explain the difference
in concentrations. Merrion (1968) reported a reduction of two to six
times in the total aldehyde concentration between the "E" and "N" series.
The engine used in this test is a model "RC". The surface conditions
in the engine and exhaust pipe can also effect the concentrations of
the aldehydes in the exhaust (Minkoff et al. , 1962). Alperstein et al.
(1967) found that the aldehyde concentration in the exhaust of iso-
octane was 2. 5 ppm for a clean engine and 5. 0 ppm for an engine
with stable deposits.

The formaldehyde concentration determined by the chromo-
tropic acid method is listed in Table 2 as increasing from 13 ppm
at zero load to 53 ppm at full load for probe one. Again this does
not agree with most of the literature values. Hurn et al. (1965) re-
ported 32 ppm for the same engine type at full load and rated speed.

Linnell et al. (1962b) found 20. 2 ppm for full load at 1600 RPM, and 13. 7 ppm at 2000 RPM using the chromotropic acid method. Reckner et al. (1965) gave the formaldehyde concentration for the same test and engine type as 19 ppm for 1600 RPM and full load. Rounds et al. (1956) reports the formaldehyde concentration as 51 ppm for full load at 1600 RPM, and 53 ppm at 2000 RPM. Thus Rounds once again is in substantial agreement with the test values given here.

The same effects listed above for total aldehydes can also effect the formaldehyde concentration. Formaldehyde is more sensitive to surface effects than are the higher order aldehydes (Griffiths et al. , 1968).

The total aliphatic aldehyde concentration as determined by gas-liquid chromatography listed in Table 2 is the total of the seven individual peaks listed in Table 1. The total is 53 ppm at full load for probe one and 26 ppm at half load. Fracchia et al. (1967) found 59. 2 to 92. 9 ppm total carbonyls for an automobile at part load using the same gas chromatographic method.

The gas chromatographic formaldehyde concentration in the exhaust is determined from the first peak on the chromatogram. Probe one at zero load, 1800 RPM, gave 13. 90 ppm of formaldehyde, half load giving 19. 53 ppm. Fracchia et al. (1967) found formaldehyde concentrations in automobile exhaust ranging from 28. 8 ppm for fast idle to 69. 3 ppm at 40 miles per hour cruise.

The molecular weight index is the volume weighted average of
the molecular weights of the C_1 to C_5 aliphatic aldehydes measured
with the gas chromatograph. If the index gets larger, it indicates a
shift towards the higher molecular weight aldehydes. Since the
molecular weight of formaldehyde is 30 and the molecular weight
index is between 33 and 36, this indicates formaldehyde predominates
the aldehydes in diesel exhaust. Fracchia et al. (1967) reported an
average molecular weight of 42 for all the automobile samples. This
difference could partially be due to the inclusion of benzaldehyde and
n-decanal in Fracchia's data. As mentioned in the results, the co-
efficients of variation for the molecular weight index are artificially
low, and the variability of the normalized molecular weight index is
more in line with the variation in the mean concentration. The
normalized molecular weight index has the highest scatter at half
load and the lowest at full load.

The coefficient of variation is 38.67 percent and 44.16 percent
for the chromatographic concentration of total aldehydes and formal-
dehyde, respectively, on probe one for half load. This is a very
large scatter. Other half load variations are more reasonable.

For several reasons, it is not likely the entire variation in
the test results is due to an actual variation in exhaust concentration.
The engine temperatures and operating conditions were fairly stable
before each test was begun. The combustion chamber and exhaust

pipe deposits should be stable. Any short range variation in operating conditions should be overcome because of the test being an hour long. The testing method is the same throughout the test period reported. Therefore, the variation must be due to the chemical analysis. Rounds et al. (1956) found coefficients of variation of 13.69 percent for total aldehydes and 38.55 percent for formaldehyde using a similar engine but different wet tests.

Figure 8A and Table 3 show the effect of load on the total aldehydes determined by the MBTH method. Probe two has a maximum concentration of 85 ppm at half load, and a minimum of 18 ppm at zero load. Probe one has a minimum at zero load of 16.5 ppm but no significant difference between half and full load, the full load concentration being 59 ppm. Most workers have found the minimum concentration at part load, and the maximum at full load for similar engines and speeds (Reckner et al. 1965; Merrion, 1968; and Rounds et al., 1956). Merrion (1968) and Rounds et al. (1956) found the actual minimum at one-fourth load with the one-half load concentration being near that of zero load. It is beyond the scope of this paper to predict the effect of load on total concentration using theory because of the surface effects and thermal decomposition of intermediates. Table 9 shows the exhaust temperature at full load to be in the high temperature region and at zero load to be in the low temperature region of slow oxidation. However, the effects of the high

temperatures and pressures during combustion itself are again beyond the scope of this study to predict.

The effect of load on the formaldehyde concentration as determined by the chromotropic acid method is graphically presented in Figure 8B and in Table 3. Probe two increases from 13 ppm to 66 ppm at full load with no significant variation between half and full load. Probe one increases linearly to 53 ppm at full load. According to the literature, the minimum concentration should occur between one-quarter and one-half load and the maximum at full load (Rounds et al., 1956; Linnell et al., 1962b; Reckner et al., 1965). Hurn et al. (1965) found the concentration decreases with load from 70 ppm at zero load to 32 ppm at full load.

According to the theory, both the rate of formation and the rate of oxidation of formaldehyde should rise with temperature (Griffiths et al., 1968; Minkoff et al., 1962). The exhaust temperature in the exhaust pipe is below the minimum oxidation temperature range of formaldehyde at zero load. Again, in the high temperature range the surface conditions and decomposition are difficult to work with. However, because of the relative unreactivity of formaldehyde and its primary role in the free radical oxidation reactions, the concentration would be expected to increase with temperature (load) as long as the same reaction mechanism is used.

Comparing Figures 8A and B beyond half load, the higher order

aldehydes must be decreasing at a faster rate than the formaldehyde

is increasing because of the greater reactivity and oxidation rate of

the higher aldehydes, this is not unreasonable.

Figure 8C shows the effect of load on the total C_1 to C_5 ali-

phatic aldehydes as determined by gas chromatograph. Probe two

increases almost linearly with load from 16 ppm at zero load to 56

ppm at full load. Probe one increases more slowly to a half load

concentration of 26 ppm with the other two load points similar to

probe two. The formaldehyde curves on Figure 8D are of the same

shape. This agrees more with the literature than the wet tests do

(Rounds et al. , 1956; and Merrion, 1968).

Figure 8C gives the effect of load on the molecular weight

index. Probe two has essentially no change between zero and half-

load, but there is a significant decrease to a minimum of 34 at full

load. Probe one also shows a decrease from half load to full load,

but there is a significant increase from zero load to a maximum of

36 ppm at half load.

As the load increases in a diesel engine, the combustion tem-

perature rises. Also as the load increases for the test engine, the

exhaust back pressure increases from 4. 6 to 6. 3 inches of mercury.

Higher aldehydes form first and at a lower temperature than

formaldehyde in an engine (Ripenberg et al. , 1957). As the tem-

perature is raised, the rate of the combustion reaction becomes

greater as long as the same reaction mechanism is used. Also the

effect of the molecular weight is more pronounced in the lower tem-

perature ranges (Minkoff et al. , 1962). Thus between zero and half

load the temperature of combustion might be low enough that the

formation of formaldehyde is restricted and the formation of the

higher aldehydes becomes greater, mainly due to the increased

breakdown of the peroxide intermediates. However, as the tempera-

ture rises further, the mechanism of reaction changes, the effect of

the molecular weight becomes smaller, and the breakdown of the

alkoxy radicals increases. Also the oxidation of the higher aldehydes

to formaldehyde and other lower molecular weight aldehydes would

increase in importance with rising temperature (Minkoff et al. , 1962).

Still another reason for the increased proportion of formaldehyde with

load from half to full load might be the effect of the increased resid-

ual gas, which could act as extra intermediates to catalyze the degenerate

branching reactions forming more formaldehyde.

Table 4 and Figures 8F and G show the effects of probe loca-

tion on the total aldehyde and formaldehyde concentrations as deter-

mined by wet test methods. Probe one is four feet from the exhaust

manifold and probe two is 10. 7 feet. The reaction time of approxi-

mately 40 milliseconds this distance represents has the same effect

on both test methods. Zero load gives no difference between probes.

Both half and full load give significant increases in concentration

with reaction time, the largest difference being at half load.

Total C_1 to C_5 aliphatic aldehydes and formaldehyde concentrations as determined chromatographically are shown by Figures 8H and I to be effected by probe location similar to the way the wet rests are effected. However, there is no change statistically significant at the 90 percent confidence level. The half load increases for the gas chromatographic analysis are significant at the 80 percent confidence limits.

It is of interest to note that the increases in total aldehyde concentration with reaction time for both tests is exactly paralleled by almost identical increases in formaldehyde concentration. This would seem to indicate that most of the change in total concentration is due to formaldehyde and the change in higher order aldehydes is relatively small.

As would be assumed from the preceding discussion, Figure 8J shows no change in molecular weight index with reaction time for zero load, and significant decrease at full load and half load.

At zero load, the exhaust temperature is approximately $250°$ C. This is the borderline temperature for oxidation of formaldehyde (Griffiths et al., 1968). Also at this temperature, the oxidation of higher order aldehydes to formaldehyde is taking place at a rate much slower than is necessary to produce a significant molecular weight shift in the 0. 0479 seconds between probes (see Griffiths,

et al., 1968, Figure 10, p. 76). It is therefore plausible that at this

temperature, the aldehydes are being formed as fast as they are

being oxidized.

However at half load the temperature increases to 350° C.

Formaldehyde is being oxidized at a measurable rate but is also

being formed both by the decomposition of the alkoxy radical and by

the oxidation of higher order aldehydes (Minkoff et al., 1962). As

the temperature increases during oxidation of higher order aldehydes,

the peracid yield decreases and the formaldehyde yield increases.

Other low molecular weight aldehydes are similarly being formed.

Because of the difference in the way the $HCO_3 \cdot$ and $RCO_3 \cdot$ radicals

react, formaldehyde is much more resistant to slow oxidation in the

low temperature region than are the higher aldehydes (Griffiths et al.,

1968). There is also some changes in the reaction mechansims be-

tween 250 and 350° C. The combined effect is a reduced molecular

weight.

Full load also produces a decrease in the molecular weight in-

dex between probes, the decrease being of the same magnitude as at

half load. However, simple theory would seem to predict a greater

decrease than at half load. The full load exhaust temperature is ap-

proximately 460° C, which is in the high temperature region of slow

oxidation. Thus, the mechanisms of reaction are not the same as

at half load. Also, the residence time between probes has decreased

from 0.0415 seconds to 0.0368 seconds at full load. As the temperature increases, the difference in the oxidation reactivities of the aldehydes with molecular weight decreases. Thus formaldehyde is reacting at a relatively faster rate than at 350°C (Minkoff et al., 1962). One other factor which might tend to decrease the difference at full load is the effect of the increasing NO_x concentration. Both NO and NO_2 retard the slow oxidation of acetaldehyde, thus decreasing one source of molecular weight shift (Minkoff et al., 1962).

Table 5 and Figures 8K and L list the effect of the test on the two concentration values at the load and probe position. If the difference between the tests is statistically significant at the 90 percent confidence limit, the difference is shaded in Figures 8K and L. For total aldehydes the biggest difference between tests is at half load, the wet test value being significantly larger than the chromatographically determined concentration. The only other significant difference is at probe two, full load. Again the wet test gives the larger value.

The formaldehyde concentration is not significantly different between tests at zero load; however all other load-probe conditions are different. Except for probe one at half load, the wet test gives the larger values.

The discrepancy between tests varies from zero to 250 percent; thus, the two tests are not good predictors of each other. Only C_1

to C_5 aldehydes are measured by the gas chromatograph, which is bound to have the effect of lowering the indicated total concentration. Fracchia et al. (1967) found the mole percent of carbonyl compounds greater than C_5 to be from 6.8 to 13.8 mole percent. Orberdorfer (1967, as cited by Fracchia et al., 1967) found 11 mole percent of the total concentration to be of a greater molecular weight than valeraldehyde (molecular weight -- 86).

The wet tests have interferences which might effect the concentrations. NO_2 interferes but the sulfamic acid solution should minimize this effect. Fracchia et al. (1967) noted that there are negative interferences in exhaust gases for the chromotropic acid method. However, negative interferences do not explain the larger concentrations indicated by the wet tests.

Since the concentration of total aliphatic aldehydes by the MBTH method is given as parts per million of formaldehyde, the gravitimetric calibration of this test gives concentrations larger than they should be. The average molecular weight of the aldehydes is at least 35, if not higher, instead of 30 as the wet test assumes it to be (see sample calculation in Appendix). This means the concentration reported as ppm of formaldehyde is at least 17 percent too large. Reckner (1965) however, reports the absorbtivities of the higher aldehydes in the colorimeter are 30 - 85 percent of formaldehyde, which would tend to counteract the effect of molecular weight

mentioned above. Hurn et al. (1968) found the MBTH method to be

inadequate. He reported the total aldehyde concentrations to be

typically less than the concentration of formaldehyde as determined

by the chromotropic acid method. This was not found during the

testing but it does cause suspicions about the wet tests.

The chromatographic analysis is not 100 percent efficient. As

listed in Table 8, the collection efficiencies for aldehydes range from

75 to 102 percent. This would tend to cause a lowering of the con-

centrations reported by the chromatographic technique.

Table 6 gives the correlations of interest generated from a

correlation matrix. As would be suspected from Figures 8K and L,

there is no correlation significant at the 90 percent confidence level

between the wet test and chromatographic concentration of either

total aldehydes or formaldehyde.

There is a correlation at the 90 percent level or greater be-

tween the probes at the same load and test method in four cases.

These correlations are positive, indicating the same factors are

effecting both probes. It is possible this correlation is an indication

of changing exhaust conditions, but it could also be due to improved

chemical technique.

Correlation is also found between some loads at the same

probe and test method. However, this is difficult to explain be-

cause even though the loads correlated are consecutively tested,

they are completely separate tests.

Only two points show correlation at the 90 percent level or greater between the wet test for total aldehydes and formaldehyde at the same load and probe. Both are positive correlations. Because of the proportion of total aldehyde concentration represented by formaldehyde, a positive correlation is expected.

Total aldehyde and formaldehyde concentrations as determined by gas-liquid chromatography are all correlated at the 98 percent confidence level or greater. This indicates that formaldehyde concentration is a good indicator of the total aldehydes.

There is a negative correlation in two cases between the wet test total aldehyde concentration and the molecular weight index at the same load and probe. The negative correlation means as the total concentration increases the molecular weight decreases. This indicates the concentration increase is due mainly to the lower molecular weight aldehydes, mainly formaldehyde. However, between the formaldehyde concentration as determined by the chromotropic acid method and the molecular weight index at the same load and probe only two conditions are correlated, also negatively.

There is no correlation at the 90 percent level between either total aldehydes or formaldehyde determined chromatographically and the molecular weight index. This is surprising since both concentrations are used in the computation of the molecular weight

index (see sample calculation in the Appendix). The lack of correlation may be due to the variation of the higher molecular weight aldehyde concentrations.

Table 7 lists the average concentrations and mole percents of the C_1 to C_5 aliphatic aldehydes in the exhaust. Formaldehyde represents 75 to 80 mole percent of the aldehydes measured. Acetaldehyde is next in concentration with 11 to 15 percent. All of the peaks are found at each load. Peak 7, including n-valeraldehyde and crotonaldehyde, is usually very wide on the chromatogram (see Figure 7) and it represents 0.94 to 1.67 mole percent.

For a similar engine, Linnell et al. (1962b) found 10.6 ppm of acrolein at 1600 RPM, full load, and 7.8 ppm at 2000 RPM. For probe one at full load, 1800 RPM, the chromatographic test gave only 4.5 ppm as the total concentration of propionaldehyde, acetone, and acrolein. Reckner et al. (1965) found 5.1 ppm of acrolein at 1600 RPM, full load for the same engine. However, both Linnell and Reckner used wet tests to determine the acrolein concentration. The average collection efficiency for propionaldehyde, acetone, and acrolein listed in Table 8 is only 61 percent, the efficiency for a acrolein being 75 percent. This could account for some of the discrepancy between the test and literature values. Fracchia, et al. (1967) found the acetone concentration in automobile exhaust to be one percent or less, and propionaldehyde to be less than 0.1 mole

percent. If this is also true in diesel exhaust, the actual acrolein concentration in the exhaust at probe one, full load, is 4.51/0.75 = 6 ppm. Fracchia et al. (1967) and Orberdorfer (1967, as cited by Frachhia et al., 1967) found the formaldehyde to be between 67. 3 to 75. 6 mole percent of the total C_1 to C_5 carbonyls in automotive exhaust. This is slightly lower than the 75 to 80 mole percent found in the diesel; however, part of this difference is due to the lack of C_5 to C_{10} carbonyls in the chromatographic tests. Acetaldehyde concentrations in automobile exhausts are similarly found (Fracchia et al., 1967) to range from 4 to 10 ppm--slightly higher than the concentration found in the diesel exhaust.

Table 7 lists some average concentrations below 0. 1 ppm, which Fracchia et al. (1967) reports as the detectable limit of the gas chromatographic procedure. These values therefore should be considered as trace concentrations instead of actual reproducible values.

Table 9 gives the engine power, temperature, and pressure data. The zero load exhaust temperatures are at the borderline oxidation temperature for higher aldehydes (Griffiths et al., 1968). Half and full load temperatures are in the high temperature range of slow oxidation (Minkoff et al., 1962). The exhaust back pressure increases slightly with load, probably due to an increase in the exhaust mass flow rate. This has some effect on the scavanging

efficiency and thus increases the amount of residual in the combustion chamber with load. The aldehydes and other active intermediates in the residual could effect the reaction mechanism.

CONCLUSIONS AND RECOMMENDATIONS

1. No correlation at the 90 percent confidence level is found between wet test and chromatographically determined concentrations of aldehydes in diesel exhaust. Significant differences in the means of the two tests are also found.

2. The mole percentages of the various aldehydes for diesel exhaust are similar to those reported for automobile exhaust. Seventy-five percent of the total concentration is formaldehyde.

3. The aldehyde concentration found is ten times that reported by Hurn et al. (1968). This difference possibly is due to the effect of design changes and stable deposits in the engine, Hurn having used new engines in his work.

4. The total aldehyde and formaldehyde concentration for both tests tend to increase with load. This does not agree with the literature.

5. The concentration of aldehydes in diesel exhaust tends to rise with increasing reaction time in the exhaust pipe except at zero load. It is beyond the scope of this work to check this with theory because of the effect of the surface conditions and intermediate decomposition.

6. The average molecular weight of the aldehydes tends to decrease with increasing reaction time in the exhaust except at zero

load. This agrees with theory.

7. It is unlikely the aldehyde concentration in diesel exhaust can be reduced to zero because they are needed as intermediates in oxidation reactions.

8. More tests are needed for the carbonyl content in diesel engines. These should include the aldehydes above C_5.

9. A more direct gas chromatographic method is needed for the study of carbonyl compounds in diesel exhaust.

10. This thesis studies the effect of load and exhaust residence time on aldehyde concentrations as determined by two test methods. It is beyond the scope of this paper to reach any conclusions about the effect of aldehydes on diesel odor or the contribution of the diesel to air pollution.

BIBLIOGRAPHY

Alperstein, M. and R. L. Bradow. 1967. Exhaust emissions related to engine combustion reactions. Transactions of the Society of Automotive Engineers 75:876-884.

Berg, Neil. 1967. Unpublished research on formaldehyde. Portland, Ore. , Air Quality Control Board. 10 numb. leaves.

Beyer, W. H. (ed.). 1966. CRC handbook of tables for probability and statistics. Cleveland, Chemical Rubber Company. 502 p.

Crow, E. L. , F. A. Davis and M. W. Maxfield. 1955. Statistics manual. China Lake, Calif. 292 p. (U. S. Naval Ordnance Test Station. NAVORD Report no. 3369)

Fracchia, M. F. , F. J. Schuette and P. K. Mueller. 1967. A method for sampling and determination of organic carbonyl compounds in automobile exhaust. Environmental Science and Technology 1:915-922.

Griffiths, J. F. and G. Skirrow. 1968. The low temperature gas-phase oxidation of lower aliphatic aldehydes. Oxidation and Combustion Reviews 3:47-96.

Hurn, R. W. and D. E. Seizinger. 1965. Air pollution inventory-enter the diesel. Proceedings of the American Petroleum Institute 45:127-132.

Hurn, R. W. and W. F. Marshall. 1968. Techniques for diesel emissions measurement. Paper presented at the Mid-Year Meeting of the Society of Automotive Engineers, Detroit, Mich. , May 20-24, 1968. New York, 10 p. (S. A. E. paper no. 680418) (Pre-print)

Johnson, H. S. 1967. From notes of chemistry and chemical kinetics section of a short course on Combustion-Generated Air Pollution, University of California, Berkley, June 21-30, 1967.

Lingren, B. W. and G. W. McElrath. 1959. Introduction to proba-bility and statistics. New York, Macmillan. 277 p.

Linnell, R. H. and W. E. Scott. 1962a. Diesel exhaust analysis. Archives of Environmental Health 5:616-625.

Linnell, R. H. and W. E. Scott. 1962b. Diesel exhaust composition and odor studies. Journal of the Air Pollution Control Association 12:510-515.

McNair, H. M. and E. J. Bonelli. 1966. Basic gas chromatography. Walnut Creek, Calif., Varian Aerograph. 105 p.

Malmberg, E. W. et al. 1954. A study of cool flames and associated reactions in an engine. In: Combustion in engines and combustion kinetics. Fifth Symposium (Internation) on Combustion, Pittsburg, 1954. New York, Reinhold. p. 385-392.

Marshall, W. F. and R. W. Hurn. 1968. Factors influencing diesel emissions. Paper presented at the West Coast Meeting of the Society of Automotive Engineers, San Francisco, Calif., August 12-15, 1968. New York. 9 p. (S. A. E. paper no. 680528) (Pre-print)

Merrion, D. F. 1968. Effect of design revisions on two stroke cycle diesel engine exhaust. Paper presented at the Mid-Year Meeting of the Society of Automotive Engineers, Detroit, Mich., May 20-24, 1968. New York. 10 p. (S. A. E. paper no. 6804220) (Pre-print).

Minkoff, G. J. and C. F. H. Tipper. 1962. Chemistry of combustion reactions. London, Butterworths. 393 p.

Perez, J. M. and E. W. Landen. 1968. Exhaust emission characteristics of precombustion chamber engines. Paper presented at the Mid-Year Meeting of the Society of Automotive Engineers, Detroit, Mich., May 20-24, 1968. New York. 13 p. (S. A. E. paper no. 680421)(Pre-print).

Pipenberg, K. J. and A. J. Pahnke. 1957. Spectrometric investigations on n-heptane preflame reactions in a motored engine. Industrial and Engineering Chemistry 49:2067-2072.

Reckner, L. R., W. E. Scott and W. F. Biller. 1965. The composition and odor of diesel exhaust. Proceedings of the American Petroleum Institute 45:127-132.

69

Rounds, F. G. and H. W. Pearsall. 1957. Diesel exhaust odor--its evaluation and relation to exhaust gas composition. Transactions of the Society of Automotive Engineers 65:608-627.

Shriner, R. L., R. C. Fuson and D. Y. Curtain. 1964. The systematic identification of organic compounds. 5th ed. New York, Wiley. 458 p.

APPENDIX

SAMPLE CALCULATIONS

1. Concentration of formaldehyde by chromatography, test #16, 0 load, probe one.

1.43 polar planimeter units of area (in.^{2}).

(1.43 in.^{2})(3.32 g/1/in.^{2}) = 4.75 g/1 of phenylhydrazone in the 10 μl aliquote injected into the chromatograph.

30/223 = 13.47% of the molecular weight of the phenylhydrazone is the aldehyde.

(4.75 g/1)(0.1347) = 0.639 g/1 of aldehyde.

$$\text{ppm} = \frac{(g/1)(ml \text{ of solvent}) (22.4 \text{ 1/g-mole})(10^6)}{(molecular \text{ weight})(1._{exhaust})}$$

$$= \frac{(0.639)(2 \times 10^{-3})(22.4)(10^6)}{(30)(59.7)} = \underline{15.98.}$$

Molecular weight index = $\sum$(mole %)(mol. wt).

$$MWI = \frac{(15.98)(30) + (3.04)(44) + (0.75)(57.3) + (0.16)(72)}{20.65}$$

$$+ \frac{(0.23)(72) + (0.16)(86) + (0.33)(78)}{20.65} = \underline{35.05}$$

2. Formaldehyde concentration in exhaust from wet test.

g/1 in test solution found from percent transmissivity by using the calibration curve for the chromotropic acid method developed with stock formaldehyde solutions.

$$\text{ppm} = \frac{(g/1)(10 \times 10^{-3} \text{ 1. of test soln. })(22.4 \text{ 1/g-mole})(10^6)}{(30 \text{ g/g-mole})(1._{exhaust})}$$

Bubbler #1:

$$\text{ppm of formaldehyde} = \frac{(5.1 \times 10^{-3})(10)(22.4)(10^3)}{(30)(3.2)} = \underline{11.90}$$

Bubbler #2:

$$\text{ppm of formaldehyde} = \frac{(0.2)(10)(22.4)(10^3)}{(30)(3.2)} = \underline{0.47}$$

Total ppm of formaldehyde = 11.90 + 0.47 = $\underline{12.37}$

3. 't' test for significant difference between mean concentrations.

Between probe one and two, wet test formaldehyde, 0 load.

$$t = \frac{\overline{X}_1 - \overline{X}_2}{s_{\underline{1}}^2 + s_{\underline{2}}^2} = \frac{13.1462 - 13.078}{\frac{(1.2439)^2}{8} + \frac{(1.2832)^2}{8}} = \underline{0.1068}$$

Since 0.1068 is less than 1.76, which is the critical limit for rejection of the hypothesis that $\mu_1 = \mu_2$ at 90% confidence and $\underline{8 + 8 - 2 = 14}$ degrees of freedom, the difference between $\overline{X}_1$ and $\overline{X}_2$ is not significantly different at the 90% confidence limits (Lingen and McElrath, 1959).

4. Calculation of the correlation coefficient

Between probe one and two, wet test formaldehyde, full load.

$$r = \sum \frac{(X_i - \overline{X})(Y_j - \overline{Y})}{(n-1)s_x s_y}$$

where X is probe one and Y is probe two. (Crow, Davis, and Maxfield 1955).

$\overline{\overline{X}}$ = 51.27 ppm, s_x = 9.00

$$\overline{Y} = 65.78 \text{ ppm}, \quad s_y = 12.83$$

$$r = \frac{+210.9}{(6-)(9.00)(12.83)} = \underline{+0.365}$$

Since 0.365 is less than 0.792, which is the percentile of the distribution of he correlation coefficient for 90 percent confidence at n - 2 = 4 degrees of freedom (Beyer, 1966), probe one and two for wet test formaldehyde at full load are not significantly correlated at the 90 percent level of confidence.

MBTH WET TEST FOR ALIPHATIC ALDEHYDES
CALIBRATION CURVE

Percent Transmissivity

g/l x 10^{-3} as HCHO
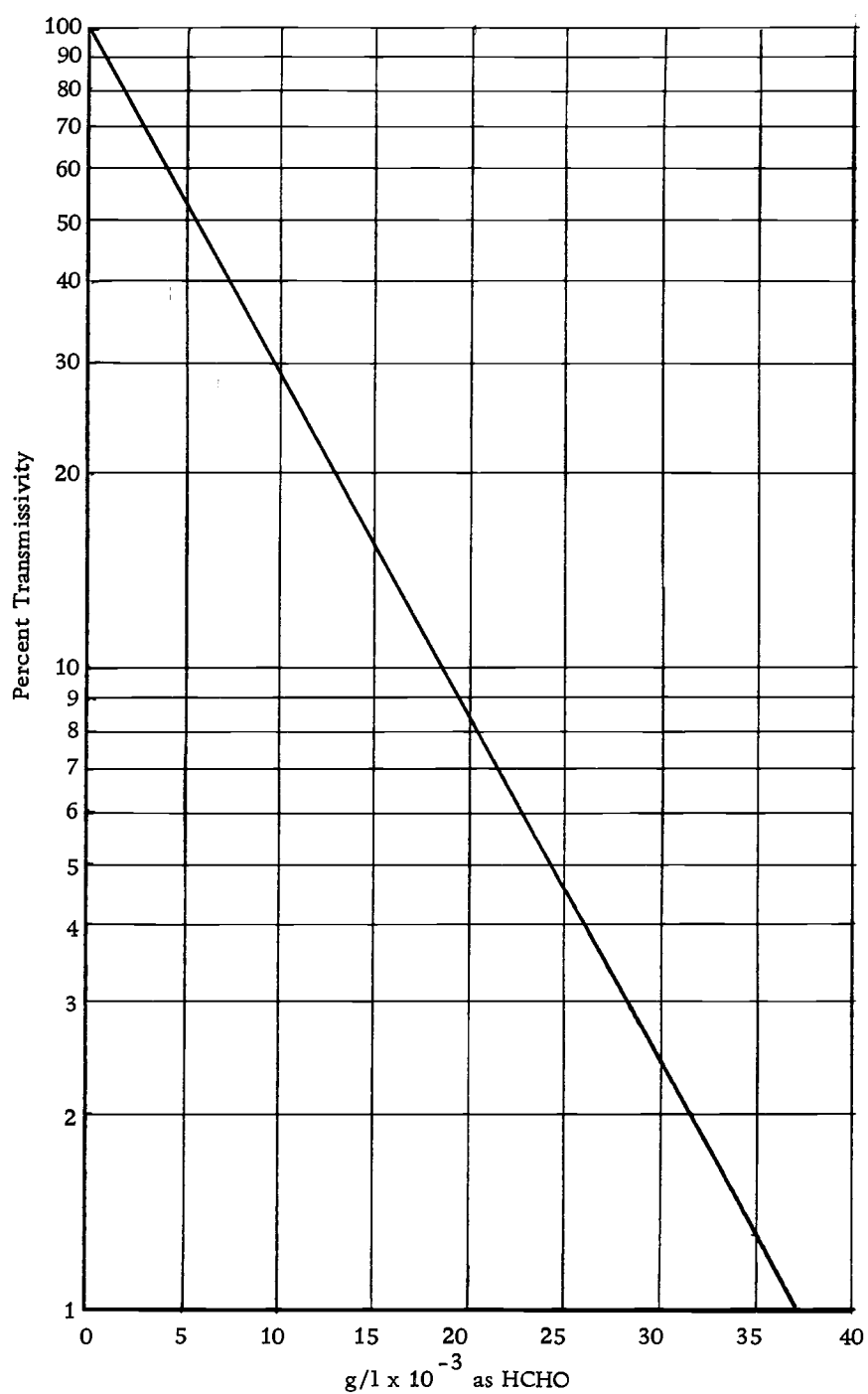
CHROMOTROPIC ACID WET TEST FOR FORMALDEHYDE
CALIBRATION CURVE

Percent Transmissivity

g/l x 10^{-3} of Formaldehyde
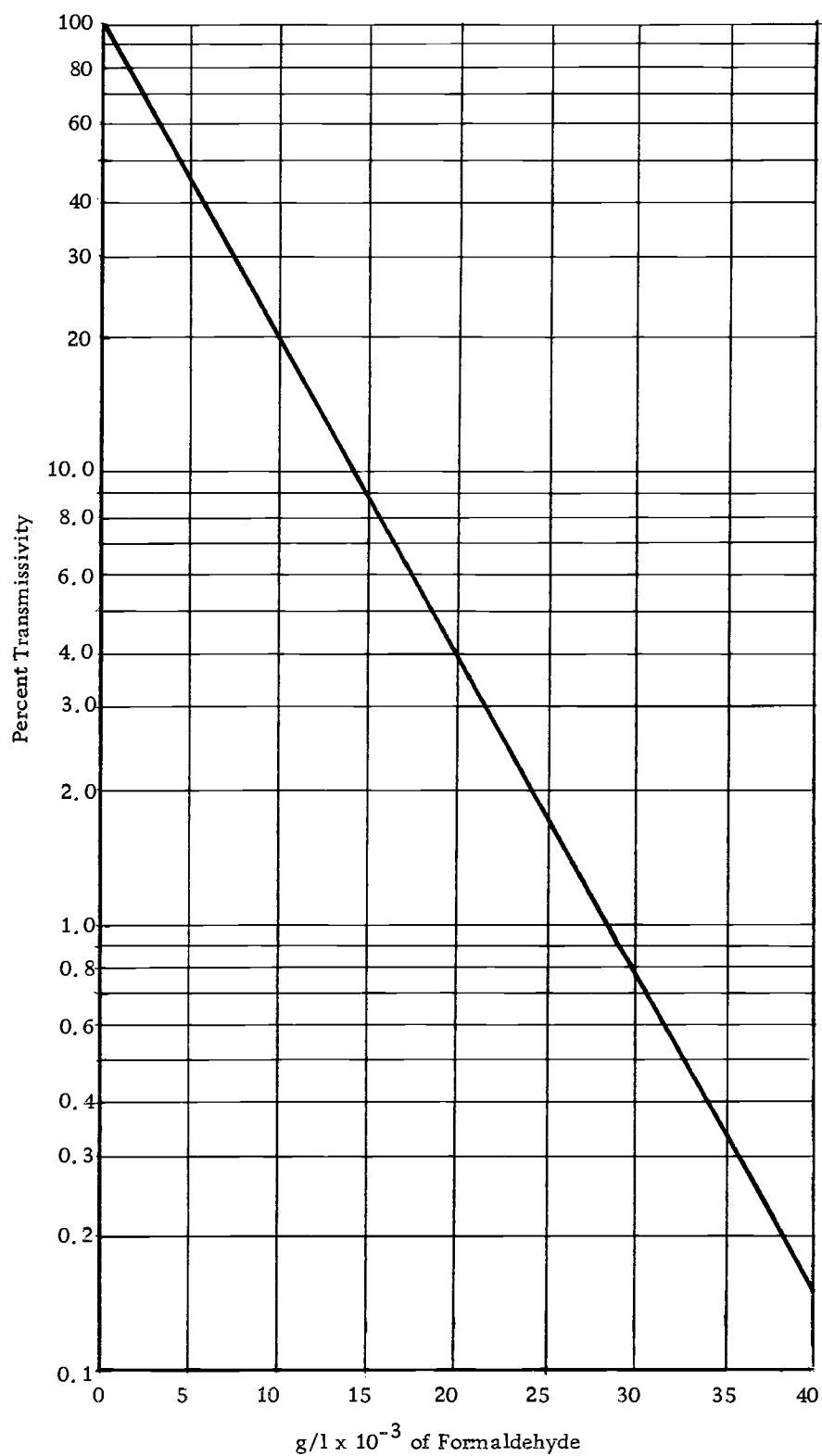
Appendix Table 1. PPM Aldehydes in Diesel Exhaust

Peak #	Formal. 1		Acetal. 2		Propanal. Acetone Acrolein 3		iso Butyral. 4		n Butyral. 5		iso Valeral. 6		n Valeral. Crononal. 7		Total Aldehydes	
Probe #	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
0 Load																
Test #																
2	8.54	8.38	1.16	1.65	0.20	0.27	0.14	0.09	-	-	0.13	0.17	-	0.17	10.18	10.72
5	13.26	10.99	3.00	2.07	0.78	0.37	0.21	0.05	0.37	0.14	-	0.12	0.16	0.12	17.77	13.85
8	13.03	10.19	2.06	1.73	0.73	0.41	0.18	0.03	0.11	0.16	0.14	0.15	0.18	0.18	16.43	12.86
10	11.25	14.13	1.94	2.53	0.50	0.59	0.05	0.07	0.11	0.14	0.06	0.10	T	0.05	13.91	17.61
13	14.49	12.66	2.45	1.85	0.61	0.59	0.14	0.13	0.15	0.20	0.14	0.07	0.14	0.07	18.13	15.57
16	15.98	14.78	3.04	2.42	0.75	1.74	0.16	0.13	0.23	0.15	0.16	0.12	0.33	0.19	20.65	19.54
22	15.46	18.32	2.63	3.03	0.72	0.71	0.09	0.10	0.15	0.11	-	-	0.45	0.35	19.49	22.67
1/2 Load																
3	35.04	26.46	3.97	2.93	1.08	0.76	-	0.07	0.59	0.40	0.17	0.05	0.35	0.32	41.20	30.99
6	15.93	22.56	5.49	7.04	2.16	2.10	0.07	0.07	0.63	0.69	-	-	0.60	0.87	24.88	33.33
9	14.86		3.38		1.00		0.03		0.48		-		0.68		20.43	
12	31.57	31.93	6.39	5.14	3.46	1.44	0.45	-	1.40	0.66	0.19	0.16	0.37	0.45	43.83	39.78
15	12.71	8.48	2.35	0.86	0.72	0.32	0.04	0.03	0.34	0.24	-	-	0.59	0.32	16.73	10.24
18	16.24	9.74	1.87	1.37	1.73	0.67	-	-	0.32	0.23	T	0.02	0.51	-.36	20.66	12.38
20	15.31	23.81	3.95	4.04	1.56	1.42	-	-	0.42	0.42	0.03	-	0.62	0.72	21.90	30.57
24	14.54	19.58	4.94	4.96	1.43	1.72	0.07	T	0.38	0.50	-	-	0.27	0.36	21.63	27.11
Full Load																
4	83.36	22.19	10.4	7.56	1.91	1.73	0.05	0.07	0.66	0.82	0.20	-	0.34	0.87	96.92	33.25
7	19.64	21.42	4.10	1.56	1.25	0.49	-	-	0.28	0.18	-	-	0.40	0.43	25.66	24.07
11	37.05	44.23	4.61	6.05	2.47	1.91	-	-	0.42	0.19	0.13	-	0.47	0.34	45.14	52.73
14	50.11	31.81	6.71	2.76	2.41	0.89	0.21	0.08	0.64	0.25	-	-	0.70	0.77	60.79	36.55
17	49.34	59.12	7.42	6.54	2.35	2.21	-	0.07	0.43	0.50	0.09	-	1.12	0.53	60.76	68.99
19	43.92	54.98	7.74	9.09	2.53	3.42	0.08	0.11	0.40	0.60	0.03	-	1.28	0.90	56.07	69.10
21	44.55	53.65	8.07	6.85	2.51	2.30	-	0.04	0.41	0.28	-	0.03	0.89	1.05	56.43	64.20
23	31.43	53.98	6.32	8.66	2.16	1.98	0.07	0.06	0.38	0.51	-	-	0.71	0.84	41.06	66.04

Appendix Table 2. Test Results

		Wet Tests				Gas Liquid Chromotography					
		Formal.PPM		Total PPM		Total PPM		Formal. PPM		Mol. Wt. Index	
Probe #		1	2	1	2	1	2	1	2	1	2
Condition #		1	2	3	4	5	6	7	8	9	10
0 Load											
Test #	1	15.07	12.03	28.22	23.83						
	2	11.65	12.80	18.05	20.93	10.18	10.72	8.54	8.38	33.40	34.81
	5	12.19	12.20	16.58	19.84	17.77	13.85	13.26	10.99	35.36	34.31
	8	12.01	15.11	11.59	16.47	16.43	12.86	13.03	10.19	34.69	34.73
	10	14.20	13.69	20.51	19.62	13.91	17.61	11.25	14.13	33.67	33.88
	13	13.91	12.56	16.99	17.74	18.13	15.57	14.49	12.66	34.29	34.05
	16	12.37	11.57	15.52	14.81	20.65	19.54	15.98	14.78	35.05	35.59
	22	39.37	57.82	47.71	66.71	19.49	22.62	15.41	18.32	34.51	33.87
	25	13.77	14.67	16.10	15.47						
1/2 Load											
Test #	3	69.36	93.00	72.76	105.3	41.20	30.99	35.04	26.46	33.30	33.21
	6	31.54	59.45	45.99	86.48	24.88	33.33	15.93	22.56	37,81	36.89
	9	29.09	40.73	46.11	64.75	20.43		14.86		36.30	
	12	34.81	71.06	48.80	70.67	43.82	39.78	31.57	31.93	36.63	34.26
	15	43.64	48.04	59.78	87.73	16.73	10.29	12.71	8.48	35.75	34.16
	18	44.11	65.16	70.23	94.88	20.66	12.38	16.24	9.74	35.39	35.24
	20	34.25	57.74	53.39	102.6	21.90	30.51	15.31	23.81	36.73	34.74
	24	15.51	12.01	17.10	16.58	21.63	27.11	14.54	19.58	36.49	35.69
	27	40.79	73.68	57.19	83.63						
Full Load											
Test #	4	69.04	78.70	61.63	75.11	96.92	33.25	83.36	22.19	32.63	37.00
	7	48.56	58.76	52.35	57.15	25.66	24.07	19.64	21.42	34.76	32.62
	11	57.42	86.74	60.71	74.95	45.14	52.73	37.05	44.23	33.97	33.07
	14	40.71	68.02	63.77	72.17	60.79	36.55	50.11	31.81	33.77	33.09
	17	65.05	69.51	69.24	82.43	60.76	68.99	49.34	59.12	34.03	32.93
	19	49.28	59.54	44.11	49.14	56.07	69.10	43.92	54.98	34.60	34.25
	21	51.73	49.77	62.30	67.83	56.43	64.20	44.55	53.65	34.28	33.49
	23	43.43	60.20	66.61	97.03	41.06	66.04	31.43	53.98	34.41	33.62
	26	54.80	60.27	55.81	67.21						