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# A STUDY OF THE RELATION OF COMBUSTION TO THE EMISSION OF ATMOSPHERIC CONTAMINANTS

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# I. INTRODUCTION

A statement of the program objectives and proposed investigation was outlined in a previous report, "Outline of Tentative Program to Study the Relation of Internal Combustion Engine Combustion to the Emission of Atmospheric Contaminants." The present report describes the work during the period from March, 1962, to January, 1963.

Activity has been concentrated in three broad areas. These are:

1. a literature search of topics related to the production of atmospheric contaminants from internal combustion engines.
2. initiation of an experimental program to study the flame quenching process in both a steady-state "bench-type" apparatus and a single cylinder CFR engine.
3. development of proper gas sampling and gas analysis techniques following the procedures outlined in the literature (I-3).

Current objectives and plans for the immediate future are outlined in Section III - D of this report.

An appropriate statement about the complexity of the smog problem was given by L. G. Wayne in 1959, (N-1). "It might not be easy to know the cause-and-effect relationships in smog, because in a system as complex as the polluted atmosphere, variable amounts of a large number of substances of widely differing reactivity are mixed together and irradiated under incompletely predictable weather conditions to undergo inadequately understood reactions yielding unidentified products of unknown stability which cause numerous different physical and physiological manifestations." The problem is as complex as this statement.

For the benefit of new students who will be working in this and related studies, a survey of the literature covering the effects of engine operating conditions on emission products and on methods currently being considered for their control is given in Appendix A.

## II. THE FLAME QUENCHING PROBLEM

It has been observed that a flame in a combustible mixture will be extinguished if it is forced to propaget through a constriction or next to a wall. The walls are evidently able to exert some repressive influence on the flame. The quenching effect of the walls on flame propagation is termed "wall quenching". The minimum diameter or the minimum rectangular opening through which a flame will travel is called the "quench distance". The minimum distance between a wall and the flame propagating along the wall is called the "dead space" and is approximately half the quench distance. In order to interpret the observed ability of walls to quench flames in terms of fundamental processes, it is necessary to decide upon the mechanism by which a flame is presumed to propagate and then to examine the influence of the presence of walls upon this mechanism.

The flame is a zone of intense chemical reactions accompanied by the evolution of heat and the formation of products from the reacting fuel and air. There exist steep gradients of temperature and concentration from the flame to the unburned gases. The effect of the walls in stopping the flame propagation is understood to occur because the walls absorb heat and free-radial chain carriers, one or both of which must be transferred ahead of the flame to the unburned gas in sufficient quantity if the flame is to continue propagating (D-6).

There is also a suggested possibility that a flame might be quenched by the combustible gas itself. Such homogeneous quenching might occur, for example, in a flame propagating in a turbulent mixture. If the turbulent intensity were sufficiently high, the dilution of the flame zone with cold unburned gas might overwhelm the transfer of heat and chain carriers from the burning zone to the surrounding fresh gas, and the flame would then be extinguished.

Although both heat and active particles must flow from the flame because of the gradients that exist, it is common to choose either the thermal or the diffusion process as the most important for an analytical study, in order to make the basic differential equation amenable to solution in closed form, (D-6).

## A. Theoretical Survey

### 1. Thermal Theory

#### a. Work of R. Friedman (A-5)

A simplified model for flame quenching based on thermal effects was developed. A flame propagating between two parallel plates is assumed to be quenched when the rate of heat generation in the reaction zone is equal to the rate of heat transfer from the flame to the walls. The rate of heat generation is given by (see Fig. 1),

$$(2\ x\ SL)\ C\ (T_f - T_o)$$

and the rate of heat transfer to the walls may be roughly represented by

$$2\ k\ (Ld)\ \frac{(T_f - T_o)}{f\ x}$$

where

f = geometric factor ≃ 1.0.

By equating both equations, the quench distance is given by

$$x^* = 2x = 2\ (\frac{k}{fSC}\ .\ d)^{1/2}.$$

It is possible to eliminate "d" by using the Mallard-LeChatelier equation for burning velocity,

$$S = \frac{k}{C}\ \ \frac{T_f - T_i}{T_i - T_0}\ \ \frac{1}{d}.$$

Solving for d and substituting in the equation for $x^*$ we get

$$x^* = \frac{2k}{SC}\ \left(\frac{1}{f}\ \frac{T_f - T_i}{T_i - T_0}\right)^{1/2}.$$

This indicates that the quench distance is a function of the geometry, flame temperature, ignition temperature, initial temperature, thermal conductivity, flame speed and heat capacity.

#### b. Work of Potter and Berlad (A-3)

This development was based on the assumption that for a flame to exist the heat retained by it must be greater than a critical amount which is assumed to be a constant fraction of the total heat produced in the flame.

$$\frac{H_r}{H_T} \geqslant F$$

where

$$H_T = x_f \cdot \Delta H$$

and

$x_f$ = mole fraction of fuel in the fresh mixture

$\Delta H$ = heat of combustion per mole of fuel (assuming complete combustion)

$$H_r = \bar{c}_p (T_f - T_o).$$

Therefore,

$$\bar{c}_p (T_f - T_0) > F\, x_f \cdot \Delta H. \quad \text{------------} \quad (1)$$

Assuming heat transfer by conduction only to the walls, where $T = T_o$,

$$\frac{\partial T}{\partial \theta} = \frac{k}{\rho \bar{c}_p} \frac{\partial^2 T}{\partial x^2}.$$

Integrating and averaging

$$\bar{T}_f - T_o = \frac{d^2}{G_i} \frac{\partial T / \partial \theta}{k/\rho \bar{c}_p} = \frac{d^2}{G_i} \cdot \frac{q}{a} \quad \text{--} \quad (2)$$

$a$ = thermal diffusivity

$G_i$ = geometric factor

$q = \frac{dT}{d\theta}$ (assumed constant)

From (1) and (2)

$$d^2 = \frac{F\, G_i\, a\, x_f \cdot \Delta H}{\bar{C}_p \cdot q}$$

Substituting for q

$$q = \frac{RT}{p} \cdot \frac{\Delta H \cdot w}{\bar{c}_p \cdot N}$$

where w is the rate of disappearance of fuel.

In order to apply the equation using experimental data, the rate controlling reaction must be specified. Two choices were made:

(1) The reaction between active particles and fuel (corresponding to the diffusion theory).

(2) The reaction between $O_2$ and fuel.

The two equations were tested using published data for the quenching of propane-oxygen-nitrogen flames. The data selected included the effect on quench distance of $O_2 - N_2$ ratio, propane concentration, and initial temperature and pressure.

The equation using the active particle-fuel reaction did not correlate data for rich mixtures; the equation using the $O_2$-fuel reaction, while correlating data for rich and lean mixtures, showed a larger deviation from the predicted relation then the other equation. The quenching diameter is given by either of the two equations depending upon how "w" is defined.

1. If the collision theory is used,

$$w = B_t \cdot a_r \Sigma_i c_{i,r} T_r^{1/2} \exp.\left(\frac{-E_r}{RT_r}\right)$$

where

$$T_r = 0.7\, T_f$$

so that

$$d^2 = \frac{F\, G_i\, N\, k_r\, x_f}{\bar{c}_{p,r}\, B_t\, a_r \Sigma_i c_{i,r} T_r^{1/2} \exp.\left(\frac{-E_r}{RT_r}\right)} = \frac{F}{B_t} \cdot \Psi_t$$

2. If the reaction in the combustion zone is assumed to be bimolecular and first order with respect to fuel and oxygen, although it is probably that the real reacting species are not fuel and oxygen molecules, then such an assumption is satisfactory if the concentration of the reacting species are proportional to the fuel and oxygen concentrations. In this case, the rate of the reaction is given by,

$$w = k_s\, a_r\, b_r$$

where

$$k_s = B_s T_r^{1/2} \exp.\left(\frac{-E_s}{RT_r}\right)$$

so that

$$d^2 = \frac{F\,G_i\,N\,k_r\,x_f}{C_{p,r}\,B_s\,a_r\,b_r\,T_r^{\,1/2}\exp.\left(\frac{-E_s}{RT_r}\right)} = \frac{F}{B_s}\cdot\Psi_s.$$

c. Work of Von Kármán (A-4)

In this derivation diffusion and the possible wall effect of breaking up chain reactions were neglected. The wall was assumed to modify the flow through friction and the temperature distribution through heat conduction.

In order to eliminate the complications resulting from the friction effect that extends ahead of the flame and the existence of a secondary motion caused by the flame front, the flame was considered as progressing in a large tube filled with the unburned mixture. The flow was considered in two dimensions near the wall and in one dimension in the tube.

To facilitate the solution the viscous forces and pressure gradients were neglected, the reaction was assumed to be first order and the rate assumed to follow the Arrhenius Law. Two domains were considered in the solution for the temperature profile. The first was where the temperature is below the ignition temperature so that the problem was reduced to one of pure heat conduction and convection. The second domain covered the region in which the temperature is above the ignition temperature and where chemical reactions take place.

From the continuity, momentum, energy and reaction equations a solution was numerically computed for the temperature distribution. The most important conclusion drawn from Table I, is that the ratio between the dead space $\delta$ and the characteristic length $l = (k/\rho C_p \mu)$, which is equal to flame thickness, appears to be almost independent of the nature of the gas used. This may indicate that the thermal conduction is the fundamental characteristic which determines the behavior of the flame near the wall.

Table I

| Gas | (mm.) | l | δ/l |
|---|---|---|---|
| $CH_4$ | 0.3 | 0.05 | 5.9 |
| Propane | 0.28 | 0.044 | 6.36 |
| Ethelyne | 0.18 | 0.227 | 6.66 |

It was stated that the values of the dead space measured by Kaskan and reported in a personal communication* agreed with those calculated.

d. Work of Kurt Wohl (A-2)

By establishing a flame front parallel to a cool wall by passing a combustible gaseous mixture through a cooled porous plate the dead space (which is taken here to be the minimum distance between the visible zone and the plate) can be obtained by reducing the flow velocity, causing the flame to approach the plate until the cooling effect extinguishes the flame. Only thermal conduction was assumed between the flame and the plate. Referring to Fig. 2 and applying the conservation of energy and heat transfer equations, the relations

$$\frac{X_1}{\Delta} = \frac{S_u}{S} \ln \left(1 + \frac{1}{\phi}\right)$$

and

$$\frac{S}{S_u} = \left(\frac{1 - \phi}{1 + \phi}\right)^{1/2} e^{-\frac{A}{\frac{11}{3\phi} - 1}}$$

where obtained, where

$$\phi = \frac{T_f^a - T_f}{T_i - T_u} = \text{degree of flame cooling}$$

$$A = \frac{7E}{11\ R\ T_f^a} .$$

Plotting $\frac{S}{S_u}$ against $\frac{X_1}{\Delta}$ yields two real values of $\frac{S}{S_u}$ greater than a critical "reduced distance" $\frac{X_1}{\Delta}$ and no real values below this distance. Thus a well defined dead space is obtained which

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*Also obtained by Univ. of Mich.

limits the approach of a flame front to a cool wall.

The curves in Fig. 3 indicate that with decreasing velocity of flow through the plate, the flame front approaches the plate to a minimum distance and then moves away from it. As the velocity approaches zero, the distance approaches infinity.

The physical reason for this behavior may be described as follows. When the gas velocity, which is equal to the burning velocity, is gradually reduced, the distance "$X_1$" decreases. The portion of the flame heat which is transferred to the plate increases with decreasing $X_1$. Below a certain gas velocity the heat loss to the plate will become so large that the gas cannot be heated to the ignition temperature so that a flame will not be possible. In order to establish a flame at this gas velocity, the heat transferred to the plate has to be reduced by increasing the distance $X_1$.

## 2. Diffusion Theory - Laminar Flames

### a. Work of Simon and Belles (B-1)

An approximate equation was derived for quench distance based on the effect on the chemical reaction and on flame propagation of the distruction of atoms and free radicals by the surface.

The derived equation is used in two ways to predict quench distances for propane-air flames,

1. With one empirical constant derived from quenching data.
2. With a constant which is the quotient of the lean flammability limit and a rate constant from flame velocity measurements.

A simple active particle mechanism of quenching is examined in which active particles are considered to be generated in the gas and destroyed on the container walls. Such a mechanism is shown to predict the existence of a limiting diameter for flame propagation.

The equation for the quench diameter was derived from the assumption that in order for the flame to propagate through the tube, the number of effective collisions per unit volume necessary for the flames to propagate. By equalizing these two expressions, the general equation for the quench diameter is obtained and is given by

$$d = \left( \frac{32\,A\,P}{\sum_i \frac{p_i}{D_i \tau_i \epsilon_i}} \right)^{1/2}$$

This mechanism of quenching indicates the importance of the nature of the surface. The results of experiments to determine the effect of the nature of the surface on the quench distance are conflicting. In general, either no surface effect or only a slight surface effect has been observed.

## B. Comparison of Thermal and Diffusion Theories with Experimental Results (E-2)

An experimental study was made of the quenching of helium and argon-oxygen-propane flames.

It was found that a thermal quenching equation satisfactorily predicted the effect of replacement of argon by helium on quench distance. A similar equation based on diffusion effects did not give satisfactory results.

The success of the thermal theory should not be interpreted as conclusive evidence that flame quenching is entirely a thermal process because both thermal and diffusion equations are, in reality, quite approximate.

The true relative importance of thermal and diffusion effects can only be evaluated when a complete theory of quenching, including both heat and mass transfer, becomes available.

## C. Factors Affecting Flame Quenching

It has been found that flame quenching depends on many variables, mainly:

1. Geometry of Quenching Surface
2. Fuel Type
3. Inert Diluents
4. Temperature
5. Pressure
6. Oxygen Concentration

### 1. Geometry of Quenching Surface

Various cylindrical tubes and rectangular slits were used in studying the effect of geometry on flame quenching (D-4).

Fuels used were methane and propane in air at room temperature and atmospheric pressure.

A geometric factor B was defined as:

$$B = \frac{\text{tube diameter}}{\text{slit diameter}} = \frac{d_{tube}}{d_{slit}}$$

The data of Ref. (D-4) shows that for lean to stoichiometric mixtures the average value of B is 1.25 for methane-air mixtures and 1.45 for propane-air mixtures.

An extension of the study of geometry effects to include annuli and rectangular slots for various length-to-width ratios is reported in Ref. (E-4). It was found that a very small center body has a large quenching action in the annular case.

### 2. Fuel Type

The quenching distances of mixtures of propane, benzene, n-heptane, and iso-octane in air have been measured, by determining the smallest opening of a rectangular burner that will permit a flame to flash back when the mixture flow is stopped (D-9). It is shown that for lean and stoichiometric mixtures the quenching distances decrease in the following order:

iso-octane > n-heptane > propane > benzene.

It was noted that this order is the same as the order of increasing burning velocities for the four compounds.

In the case of rich mixtures, no simple relation between quench distance and burning velocities was found. However, results indicate that the quench distances for the various compounds were a function of the molecular weights.

### 3. Inert Diluents

The effect of inert gases on quenching is reported in Ref. (A-5). Inert gases used were helium, argon, nitrogen and carbon dioxide.

Mixtures of hydrogen and oxygen and inert gas were prepared such that the calculated flame temperatures of the stoichiometric mixtures were the same in all four cases. It is shown that for a given mixture, the quench distance decreases with inert diluent used in this order:

helium > argon > nitrogen > carbon dioxide.

Analogous results for hydrocarbon fuels were found for methane (D-4) and for propane (D-2).

Replacement of rare gases by nitrogen affects not only the transport coefficients but also the temperature and reaction rates in the flame. In this case not only the transport process but also the rate controlling reactions must be specified.

For the oxy-hydrogen quenching it was considered unlikely that low concentrations of $H_2O$ have any abnormal effect on the results.

It has been stated that no conclusion could be drawn as to the true mechanism of quenching and that diffusion of active particles to the walls might be important (A-5). In Ref. (D-2) it was hoped that a decision could be reached as to the importance of loss of heat as opposed to loss of active particles at the walls.

Table II compares the observed ratios of quenching distances at atmospheric pressure for propane-oxygen-argon and propane-oxygen-helium mixtures with ratios predicted by diffusion and thermal theories.

Table II

| Stoichiometric Fuel-Oxident Ratio | $\frac{d_{slit\ (argon)}}{d_{slit\ (helium)}}$ | | |
|---|---|---|---|
| Percent | Observed | Thermal | Diffusion |
| 73.8 | 0.35 | 0.47 | 0.67 |
| 100. | 0.41 | 0.48 | 0.68 |
| 149. | 0.44 | 0.50 | 0.72 |

The observed ratios are in better agreement with the results of the thermal theory than with the diffusion theory.

## 4. Temperature

The effect of temperature on quenching distance has been studied (D-1). Increased temperature decreases the quench distance. The results given for propane-air mixtures at about 1 atmosphere are consistent with the general observation that chemical reactions are promoted by increase in temperature. The magnitude of the temperature effect varies with mixture composition.

For rich and stoichiometric propane-air mixtures, quench distance is approximately proportional to the -0.5 power of the absolute temperature, while for lean mixtures the exponent increases.

## 5. Pressure

Quenching distance increases with decreasing pressure (D-2). It is pointed out that: $d \propto p^n$ where n is a negative number, increasing from lean to stoichiometric mixtures and reaching a maximum somewhat rich of stoichiometric. "n" usually decreases again as the mixture becomes very rich.

The pressure exponent of the quench distance is the sum of two terms: one is one-half the order of the reaction and the other is a function of the pressure dependence of the flame temperature. The effect of the pressure on quench distance of propane, benzene, n-heptane and iso-octane-air flames was reported in Ref. (D-1).

The value of n for the propane concentration corresponding to the minimum quench distance was 0.91.

Table III shows the variation of the pressure dependence of quench distance of propane-air flames with fuel concentration.

Table III

| Stoich. Fuel-Air Ratio (percent) | n | Reference |
|---|---|---|
| 74 | -0.83 | K-11 |
| 74 | -0.85 | D-2 |
| 86 | -0.84 | D-2 |
| 87 | -0.85 | K-11 |
| 100 | -0.88 | K-11 |
| 100 | -0.89 | D-2 |
| 110 | -0.91 | D-1 |
| 124 | -0.95 | D-2 |
| 149 | -0.98 | D-2 |

### 6. Oxygen Concentration

The effect of pressure on the quench distance of flames in various propane-oxygen-nitrogen systems is reported in Ref. (D-2).

Five oxident atmospheres were used, containing 17, 21, 30, 50, and 70 percent oxygen by volume.

At any given pressure and percent stoichiometric propane, the quenching distance decreases as the oxygen concentration is increased.

## III. EXPERIMENTAL PROGRAM

### A. Phase I - Steady State Burner

This part of the investigation is a study of the steady-state wall quenching process. There are numerous experimental techniques that may be used for a steady-state investigation. Two approaches were chosen for this problem. In one case, a flat quench plate was selected, upon which a flame impinges, and the second choice was a porous plate, flat flame burner. In the later case, the porous plate functions as the quenching surface, the porous material allowing the combustible mixture to flow through it. The fuel and air burn as a flat flame just above the plate and the distance between the flame and the surface is taken as the quench distance. The natural objection to this model is that the walls of a reciprocating engine are not porous and consequently the same quench process may not occur on the porous surface. However, the quench process, whether it be thermal or chemical or both, seems to be analogous in both cases. In addition, the flat flame burner offers the decided advantage of being one-dimensional and thus easier to investigate and analyse.

To date, the design and construction of a thick walled cylinder which is provided with four identical viewing and access ports has been completed. This chamber is shown in Fig. 4. Two ports are covered with pyrex windows and are used for viewing the flame. The other two ports are covered with plates which support the quench plate and provide access for thermocouple leads, cooling tubes, gas sampling probes and the electrical ignition system. The fuel-air mixture enters the burner through a mixing tube packed with glass beads.

The flow of the fuel and the air are individually controlled by needle valves. Pressure regulators and flowmeters for the fuel and air are located on the rack to the right of the chamber shown in Fig. 5. The exhaust from the chamber is removed through a tube in the top which is connected to the laboratory exhaust system through a throttling valve.

A bunsen burner with a rectangular opening used with the quench plates may be interchanged with the flat flame burner. These two burners can be adjusted vertically by means of a knob at the bottom of the burner chamber. In addition, the bunsen burner may be rotated about its vertical axis to make it possible to align the flame with the quench plate.

### 1. Quench Plate

The first quench plate and the adjustment assembly is illustrated in Fig. 6. The quench surface is the narrow area of the plate shown at the extreme left. This surface has a thermocouple embedded parallel to the surface with the junction 1/16 inch from the point where the hypodermic sampling tube reaches the surface. The hypodermic tube has an inside diameter of 0.010 inches. The plate also contains machined passages for water cooling. The three arms which support the plate can be adjusted in length individually to change the position and angle of the quench plate.

Efforts to produce a quench zone with this plate were unsuccessful. The region between the luminous zone of the flame and the plate consisted entirely of the products of combustion. When the plate was moved toward the flame, the flame merely receded until it finally went out. Thus, a quench region could not be obtained with this arrangement.

A solution was to change the quench surface to a wedge. An included angle of 45 degrees was selected for the wedge by a trial and error procedure in which brass sheets bent to various angles were placed over the burner and photographed to show the position of the quench region.

The wedge was constructed from 1/8 inch brass plates which were silver soldered together so that a coolant could be passed through it. The sampling port was modified to allow faster sampling than was obtained with the first quench plate. A hypodermic tube of 0.020 inch inside diameter was used for the sampling port. The pressure drop through the sampling line was thereby reduced and the rate of sampling increased.

To date, only a few gas samples have been taken. Analysis of these samples indicated the presence of only unburned fuel (i.e. natural gas) and air. There appears to be two explanations for this. First, the best columns or settings on the gas chromatograph for optimum separation and sensitivity may not have been used. Second, the quench region is very narrow and the flame has not been as steady as desired. Thus the quench zone does not remain over the sampling hole throughout the sampling process. The stability has been improved somewhat by covering half of the burner slit and using only one side of the wedge. Figure 7 shows the configuration of the flame in the burner with the wedge assembly.

Somewhat more encouraging results have been very recently obtained with the porous plate apparatus.

## 2. Flat Flame Burner

In order to thoroughly analyse the observed quenching of flames on internal combustion engine walls, it is necessary to first examine the influence of the wall upon the flame and then to develop the mechanism by which a flame is presumed to propagate under these conditions.

A one-dimensional steady-state flame using a flat flame burner is an idealization of the behavior of the gases in the internal combustion engine and was chosen as the model for this study.

The burner was constructed from a 2" diameter tube, 6" long, having at the upper and lower ends two 1/4" thick porous discs. The space between these two discs is filled with 3 mm glass beads.

In operation, this unit is placed in the burner atop the mixing tube. When the gases are ignited, a flat disc of flame burns steadily above the porous disc as shown in Fig. 8.

The top porous plate serves both as a flame holder and quench plate.

### a. Structure of the Flame Front

The equations describing the propagation of the flame are the one-dimensional steady-state equations of motion and the reaction equations. These equations along with the boundary conditions possess a solution for one value of mass rate of flow. This solution describes the structure of the flame front.

Flame structure is generally used to describe two properties of flames, the macroscopic structure or flame front and the microscopic structure as described by temperature and composition profiles.

In order to study flame fronts, it is necessary to determine the state of the gas at each point in the flame. A complete description in this case (one-dimensional, steady-state) can be given by two sets of profiles, temperature and composition.

For the measurement of temperature profiles Friedman, Ref. H-1, recommends the use of a 0.0005" diameter ceramic coated platinum, platinum-rhodium thermocuple to operate at the high temperatures, avoid disturbing the flame and to minimize the radiation and convection losses. Attempts are being made to construct thermocouples of this size to obtain temperature profiles.

The composition profiles are of primary importance in understanding the chemical process that occurs in flames. A qualitative interpretation of these data could provide clues to the course of the reaction, and kinetic constants can be obtained from quantitative interpretation of the data.

A 30 micron quartz probe has been made and is being mounted in the burner so that gas samples in any region of the flame may be obtained. A very recent analysis of the gases before and after the flame has shown a complete change in the mixture when it passes through the flame. Commercial city gas containing methane, ethane, propane and normal butane was used and good separation was obtained with a Perkin-Elmer Model 800 gas chromatograph with modified silica gel columns, type "S".

The luminous zone and the dead space are presently being measured with an eye micrometer which reads to 0.001".

## B. Phase II - Single-Cylinder Engine

This phase is concerned with the study of the quench zone in the engine combustion chamber. A technique similar to the one described by Daniel and Wenworth (L-1) is being used. The objective is to establish some correlation between the quench zone in the combustion chamber and that in the one-dimensional model.

The engine, shown in Fig. 9, is a single-cylinder CFR engine. A special cylinder and head to accommodate a quartz window, previously obtained from General Motors, is being used. Air flow is measured by critical flow nozzles. Modifications are underway to convert the engine to use gaseous fuels which will be used in the steady-state apparatus.

A solenoid type Cox sampling valve is being used for gas sampling. It's lift can be easily varied to any fraction of the quench zone thickness and it remains open for about 1 millisecond. The valve at present fits into one of the engine spark plug holes. The valve seat has been made level with the combustion chamber wall so that as little surface irregularities as possible are introduced when the valve is in place.

It was noticed that after the valve has been in operation for a short time, its lift changes somewhat. This is believed to be due to thermal expansion of parts of the valve in contact with the hot gases. It was therefore decided to measure the valve lift continuously while the engine is in operation. A solar cell was found suitable for this purpose. A small flag was attached to the valve stem, so that when the valve is in operation, the flag moves with the valve stem and modulates a light beam which shines on the solar cell. A solar cell output proportional to the valve lift is obtained. The solar cell output is displayed on an oscilloscope. Deflections on the scope of about 1 cm. per .001 in. of valve lift have been obtained. This method also makes it possible to measure valve opening time at various lifts.

A breaker point mechanism which enables operation of the valve at any point in the cycle has been designed and built.

Sampling of exhaust gases and quench zone gases from the combustion chamber was made to conform as closely as possible to the sampling technique described in Ref. (I-3). The sampling valve is connected by a short stainless steel tube to a stainless steel or glass bottle. When a sample is being taken, this line is heated slightly to prevent condensation. A stainless steel line branches to a mercury manometer and a connection is made to a vacuum pump by means of a rubber hose. All valves and fittings used in the above system are made of stainless steel.

A sample is collected at approximately atmospheric pressure. When taking a sample for analysis on the infrared absorbtion spectrometer, it is important to eliminate water from the sample. As recommended by Ref. (K-3) indicating Drierite heated to about

150 degrees can be used to absorb water. The Drierite, it was reported, absorbs approximately a constant amount, about 10%, of hydrocarbons. It is soon saturated and no further absorbtion takes place. Some absorbtion of $CO_2$ by Drierite has also been noticed.

Another procedure presented in Ref. (K-3) is to collect the sample in an intermediate bulb and then transfer it to a measuring cell. It was reported that sufficient water was removed so that no further condensation of water will occur when the sample is transferred to the spectrometer cell. No important amount of hydrocarbons was reported lost in the intermediate sample bulb. It is necessary, however, to transfer the exhaust sample from the sampling flask to the measuring cell in one hour or less.

Daniels and Wentworth (L-1) have shown that there is considerable variation of hydrocarbon concentration of exhaust gases, depending on the location of the tap in the exhaust pipe. Timewise variation at a particular location in the exhaust pipe has also been reported. Therefore, a mixing tank is provided to collect exhaust gases before they are sampled.

## C. Methods of Gas Analysis

The gas analysing equipment includes a Perkin-Elmer Model 112 single beam infrared spectrometer and a Model 800 Perkin-Elmer dual column gas chromatograph.

The infrared spectrometer has been calibrated to give concentrations of CO and $CO_2$ in the sample gas. (Figs. 10 and 11). It is anticipated that the spectrometer will also be used to identify individual peaks from the gas chromatograph.

The Model 800 Perkin-Elmer gas chromatograph is a dual column, temperature programed chromatograph which can be operated with either one or two columns under isothermal conditions. A differential hydrogen flame ionization detector is incorporated for high sensitivity over the entire temperature range. The use of the differential detector compensates for base line drift due to substrate elution. This detector is sensitive to all hydrocarbons but is insensitive to inorganic fixed gases. A thermal conductivity detector is on order for this purpose. The instrument is equiped with a gas sampling valve to introduce gaseous samples into the carrier gas which flows into the sensing column.

To date some pure hydrocarbons such as propane, methane, n-heptane and iso-octane have been examined using the gas sampling valve for the gaseous fuels and a microliter syringe for liquid fuels.

In addition, several dead space gas samples from the wedge-plate have been analysed but as yet only the presence of natural gas and air is indicated. Better results have recently been obtained with the dead space gas from the flat flame burner. However, these results are very recent and no conclusions can be drawn at this time.

In an effort to improve our analytical technique, runs were made to determine optimum operating conditions for the gas chromatograph. Test runs were made to determine the following:

1. Best combination of the detector $H_2$ and dry air pressure for maximum sensitivity. (Figs. 12, 13, 14).
2. Best column temperature for maximum sensitivity. (Fig. 15)
3. Tests to determine best column flow rate for optimum HETP are in progress.

## D. Immediate Objectives of the Experimental Program

Current efforts in the experimental program are in the general area of gas sample collection and analysis with the immediate objective being the development of acceptable working techniques. Additional work to obtain accurate dead space and temperature profile measurements in the flat flame region is also underway. The sampling apparatus for the single cylinder engine is felt to be adequate for the time being. However, the engine is being modified to use gaseous fuels so that a meaningful correlation between the data for the engine and steady-state burner might be obtained.

Latest efforts to obtain and analyse gas samples from different regions in the flat flame have been somewhat successful. Samples from a city-gas flame (this gas is being used while the various measurement techniques are being developed) were collected with a small quartz probe mounted vertically above the flame. The analysis of these samples using gas chromatography shows marked differences in composition in the various regions. As would be expected the peaks for methane, ethane, propane and normal butane which appear in the unburned mixture are absent from the burned mixture. However, the downstream gases have not as yet been thoroughly analysed at maximum sensitivity settings on the instrument and no peaks have been observed for this gas. It is possible that those products which are present cannot be detected by the flame ionization detector. A thermal conductivity detector, which is to be delivered soon, may have to be used along with the flame ionization detector for these tests.

As soon as this technique is perfected, concentration profiles through the flame will be measured and analysed under various operating conditions. It is anticipated that a procedure for trapping the separate eluted peaks from the gas chromatograph will have to be developed soon so that identification of the unknowns can be attempted with the infrared spectrometer.

A rig for holding and positioning fine thermocouples has been designed and is being constructed. This will be used for measuring temperature profiles through the flat flame. Initial measurements will be made with a commercial, uncoated platinum, platinum-rhodium thermocouple made of 0.001 inch wires. The development of a technique for making thermocouples from 0.0005 inch wires and coating them with a ceramic to prevent catalytic effects will be started soon.

Conversion of the single cylinder engine to gaseous fuels is about half completed at this time. When completed, gas samples will be taken from the quench zone under various engine operating conditions.

The main objective of this program for the immediate future will be to compare and attempt to analyse variations in trends of gas composition changes with changes in operating variables for both the flat flame burner and single cylinder engine.

## IV. MISCELLANEOUS ACTIVITIES

In August, 1962, Mr. Gad El Mawla and Prof. William Mirsky attended the Ninth International Combustion Symposium which was held at Cornell University, Ithica, New York.

Prof. William Mirsky also attended the American Society for Testing Materials, Committee E-19 session on "The Practice of Gas Chromatography" held in September, 1962, at Michigan State University, East Lansing, Michigan.

## V. PERSONNEL

The following persons are presently engaged on this project.

1. Prof. Gordon Van Wylen, Chairman of the Department of Mechanical Engineering, co-director of this project.
2. Prof. William Mirsky, Associate Professor of Mechanical Engineering, co-director of this project
3. Mr. A. Gad El-Mawla, doctoral student, is presently working with the flat flame burner and the mathematical analysis of this flame, with special regard to the effect of the surface on the dead space gases. He will be soon selecting a thesis subject involving a portion of this study.
4. Mr. A. Kurkov, is studying for his master's degree and working on the single cylinder engine. He is concerned with all phases of gas sampling and analysis related to the engine. He plans to continue at The University of Michigan for a Ph.D. degree and it is hoped that he will also select a thesis subject from some phase of this work.
5. Mr. J. Steiner, a doctoral student, is involved primarily with the development of our gas chromatography techniques, but is also assisting on the flat flame burner and single cylinder engine. Mr. Steiner is in the terminal stages of his Ph.D. program where he has been studying the relative influence of the capacitive and inductive components of a spark in supplying the ignition energy for igniting lean mixtures. He will start working sometime this summer for the Mechanical Development Dept, GM Engineering Research, General Motors Technical Center.

# VI. NOMENCLATURE

$a$ = $k/\rho c_p$, thermal diffusivity

$a_r$ = fuel concentration at the reaction temperature

$A$ = fraction of molecules which must react for flame to continue to propagate.

$b_r$ = oxygen concentration at the reaction temperature

$B_t$ = Arrhenius constant

$C$ = heat capacity per unit volume

$c_{i,r}$ = concentration of active particles at the reaction temperature $T_r$

$d$ = quench diameter, distance

$D_i$ = diffusion coefficient

$E$ = activitative energy

$G_{i,f}$ = geometric factor

$H$ = heat of combustion per mole of fuel

HETP = height equivalent of theoretical plates (efficiency index of a gas chromatographic column).

$k$ = heat conductivity

$k_s$ = rate of reaction

$L$ = distance

$N$ = Avogadro's Number (molecules fuel/mole fuel)

$p$ = total pressure

$p_i$ = partial pressure

$q$ = $dT/dQ$

$S$ = burning velocity

$T_a$ = wall temperature

$T_f$ = flame temperature

$w$ = rate of disappearance of fuel (molecules/cc-sec.)

$X$ = distance

$x^*$ = quench distance

$x_{\prime}$ = dead space

$x_f$ = mole fraction of fuel

## NOMENCLATURE con'd

$\Delta$ = flame thickness

$\rho$ = density

$\theta$ = time

$\tau_i$ = frequency of collison

$\epsilon_i$ = efficiency of the wall to prevent active particles which collide with it from rereturning to gas phase as chain carrier

$\mu$ = velocity

### Subscript

r = conditions at the reaction temperature $T_r$

# VII. APPENDIXES

## Appendix A - Literature Search

### A. Effect of Engine Operating Variables on Emission

#### 1. Unburned Hydrocarbons (E-1, L-3, L-9)

About one-third of the total amount of unburned hydrocarbons exhausted by automobiles is emitted during deceleration at which time the concentration of unburned hydrocarbons in the exhaust gas may be as high as 60% by weight of the fuel supplied. The other two-thirds of the total amount of unburned hydrocarbons is exhausted during full-throttle, road-load, and idle operation. Under these conditions the hydrocarbon concentrations are usually less than 5%.

Some possible explanations for these low concentrations are given in the literature.

Hydrocarbons are equilibrium products of the combustion reactions.

The highly turbulent gases in the combustion chamber enable small pockets of the unburned mixture to pass through the reaction zone without igniting.

Flame quenching at the relatively cool walls of the combustion chamber may prevent a portion of the fuel-air mixture from reacting.

Engine operating variables, which have greater influence on exhaust gas composition than fuel and lubricant variables are manifold vacuum and engine detuning. High manifold vacuum (above approximately 21.5 inches of mercury absolute) accounts for high concentrations of hydrocarbons during deceleration. This effect is accentuated by high speeds at the start of deceleration and by manual transmissions as compared to automatic transmissions.

Enriched carburetor idle settings also increase the hydrocarbon emission during deceleration.

Accelerating and cruising conditions at various engine speeds produce similar hydrocarbon concentrations, generally in the range of one to five percent of the supplied fuel, with the hydrocarbon concentrations tending to decrease with increasing engine speed.

Enriched carburetor idle settings increase hydrocarbon emission during cruise up to about 30 m.p.h.

The idle air-fuel ratio as determined by the carburetor setting effects hydrocarbon concentration during idle as well as during deceleration.

Lower hydrocarbon concentrations are exhausted after a car is warmed up than during the starting and warm-up periods. The average hydrocarbon concentration for a "cold" car is around five times greater than that for a "hot" car and this is believed due to the action of the automatic choke, poor mixture distribution within the cold manifold, misfiring, and cold wall quenching. Reference L-3 shows that the percentage of hydrocarbons emitted increases as the coolant temperature decreases.

Spark plug condition is of great importance. One misfiring may more than double the average hydrocarbon emission. Fouled spark plugs can increase the rate of hydrocarbon emission during wide open throttle acceleration more than two and one-half times.

### 2. Oxides of Nitrogen (L-4)

Among variables which affect the emission of oxides of nitrogen, air-fuel ratio is of primary importance. Lean mixtures promote the formation of oxides of nitrogen and increase the relative effects of other engine variables.

Under full throttle and rich mixture conditions, concentrations of oxides of nitrogen are relatively low. Under part throttle conditions, however, mixtures are sufficiently lean to permit varying degrees of importance to be attached to ignition during advance, manifold pressure increase, and compression ratio increase, all of which promote oxides of nitrogen formation.

Under road-load cruise conditions and during full throttle accelerations, high speeds produce higher concentrations.

During part-throttle accelerations there is no general effect of speed, and high concentrations may be exhausted even at low speeds.

During idling and deceleration, oxides of nitrogen concentrations are so low as to be considered insignificant.

## B. Methods for Control of Contaminants in Automotive Gaseous Emission

### 1. Crankcase Blow-by (L-8)

It has been found that hydrocarbon concentrations in blow-by and crankcase vent gases are about 30 times that of exhaust gas. Blow-by gases consist of a mixture of unburned fuel-air charge and exhaust products blown by the piston rings. Crankcase vent gases are composed of these blow-by gases plus ventilation air.

Since blow-by is due to the pressure differential across the pistons of the automotive internal combustion engine, most of the blow-by must occur during the compression and expansion strokes. At top dead center the direction of the piston travel changes, and at about this time the piston side thrust reversal occurs. Both of these factors would be expected to interfere with the piston ring sealing near the time of maximum cylinder pressure. Accordingly, one would expect maximum blow-by rates to occur near top center.

It has been shown by flame photographs that even at full throttle the charge in the combustion chamber does not burn "completely" until after the piston has reached top center.

One can see that the land clearance between the piston and the cylinder wall is of the order of magnitude of the dead space near the engine wall, so this is an additional factor influencing the hydrocarbon content of blow-by gases.

To control the emission from the automotive crankcase a device was suggested in Ref. (L-8) based on the idea of feeding the crankcase gases back into the induction system of the engine, thereby eliminating the direct emission of crankcase gases.

### 2. Reduction of Exhaust Hydrocarbons during Deceleration (L-6)

This reference describes a device for reducing the hydrocarbon content of automobile exhaust during deceleration. This device, in addition to limiting the manifold-vacuum to reduce exhaust hydrocarbon concentration, uses a retarded engine spark to overcome the serious loss of engine braking.

During normal vehicle operation the system is deactivated. The intake manifold vacuum acts on the spark advance unit to provide normal spark advance. Under these conditions the vacuum diaphragms on the spark-retarding units and the throttle opener units are vented to the atmosphere and are inoperative.

When intake manifold vacuum exceeds 22 inches Hg. during deceleration, the vacuum control valve actuates the system and in this case manifold vacuum is directed to the carburetor throttle-opener units and to the distributor spark retarding units which, in turn, open the throttle and retard the spark timing.

It was found that the device was 82% effective in reducing exhaust hydrocarbon concentration when measured in parts per million but only 53% effective on a weight (lbm. per hour) emission basis.

In order to be most effective in reducing exhaust hydrocarbon emission during deceleration, the device must be properly matched to the operating characteristics of the particular vehicle.

Also one might notice that as the device operates by introducing an additional air-fuel mixture into the intake manifold during deceleration, it obviously must increase fuel consumption during deceleration.

### 3. Reduction of Exhaust Hydrocarbons by Engine Tune-up (L-7)

It was indicated in this reference that exhaust hydrocarbon emissions could be reduced 60% by regular tune ups.

With proper idle adjustments, it was found that emissions of hydrocarbons at idle could be reduced roughly one-third and emissions of carbon monoxide roughly two-thirds, without seriously affecting engine operation.

Carburetor cleaning detergents in the gasoline are very effective in preventing accumulation of deposits of gum and sludge around the throttle plate and elsewhere.

A proposal for anti-smog tune-up was shown which was believed to be a practical method for reducing the hydrocarbon emission by 60% - 80%.

### 4. Manifold Air Oxidation of Exhaust Gas (L-10)

The oxidation of exhaust gas hydrocarbons and carbon monoxide by injection of air into the exhaust manifold was investigated. Homogeneous oxidation of hydrocarbons and carbon monoxide will occur if sufficient oxygen is present and the mixture is held at a high enough temperature for a suitable time. The Man-Air-Ox System was used for injecting air into the engine exhaust.

It was shown that the reduction of hydrocarbon emission ranges from 9-29% and from 12-43% for CO which varies according to the type of system used and to the engine operating conditions.

### 5. Catalytic Oxidation of Exhaust Gases (L-11)

The Oxy-catalyst converter has been designed specifically to oxidize the small amount of hydrocarbons present in exhaust gases. There are two main functional parts of the converter, the air aspirator and the catalyst container.

It was found that the percentage reduction of emission depends on many factors and is around 75% for CO and 90% for hydrocarbons and also 90% for oxides of nitrogen.

The useful life of the catalyst was estimated to be about 12,000 miles.

### 6. Control of Oxides of Nitrogen in Exhaust Gases (L-4)

A significant reduction of oxides of nitrogen was achieved by modifying the carburetor. The principle underlying this practice is to provide rich air-fuel mixtures in the maximum power range at all driving conditions. This reduction is at the expense of fuel economy. It was found that 90% reduction in the oxides of nitrogen would cost the individual car owner about $70 a year.

One can see that by providing rich fuel-air mixtures, the amount of hydrocarbons emitted will be increased, so it was suggested that this method can be used combined with the principle of catalytic oxidation to provide a method for eliminating the hydrocarbons and the nitrogen oxides.

### 7. Carburetor and Gas Tank Losses (L-12)

The exhaust pipe and the crankcase of the automotive engine are not the only sources of hydrocarbon emission, but fuel is also lost through the external front bowl vents of the carburetors and gas tank vents.

A system has been developed Ref. (N-12), for measuring the amount of hydrocarbon loss from the carburetor vent.

It was found that this loss is as high as 7% by weight of the fuel used and is a function of the fuel stability and temperature. To eliminate this loss, an internal vent was used but was found to affect the performance of the car at different running conditions.

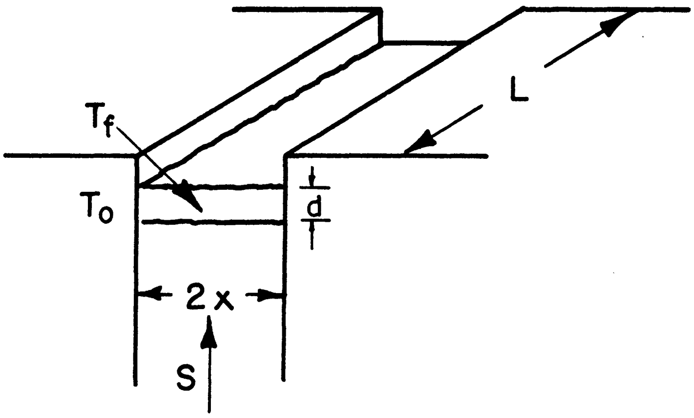

Fig. 1. Flame model of Friedman (A-5).

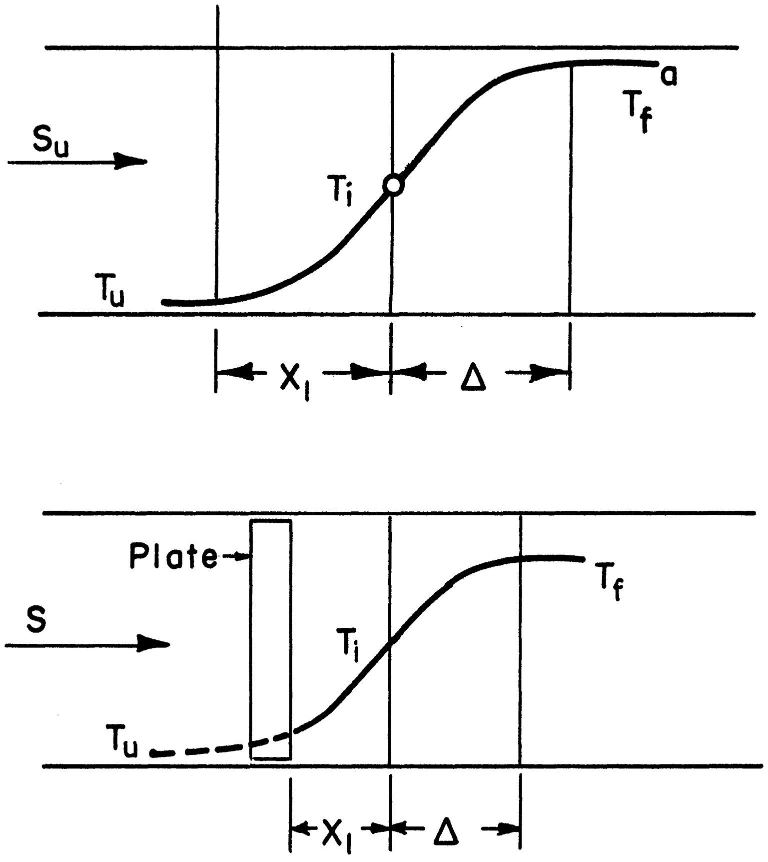

Fig. 2. Flame model of K. Wohl (A-2).

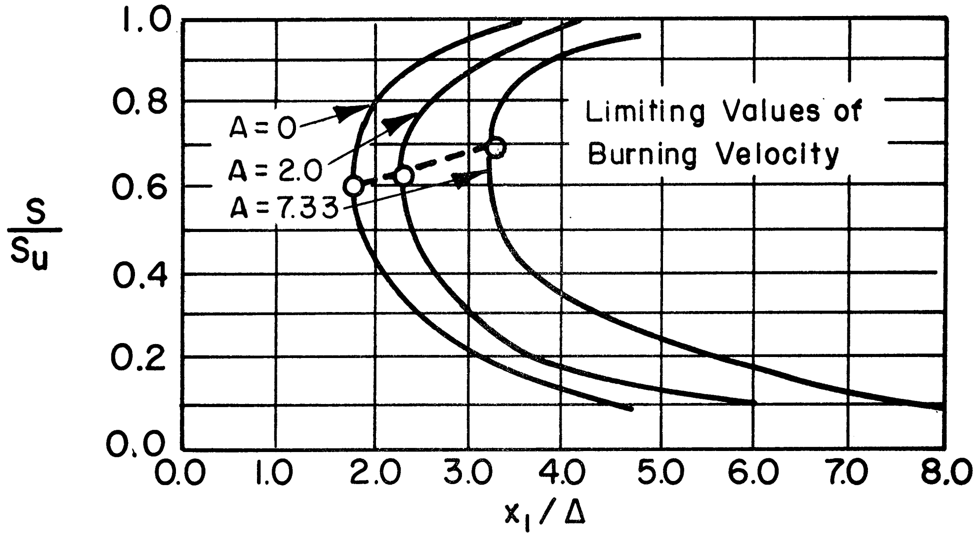

Fig. 3. Plot for determining quench distance from Ref. (A-2).

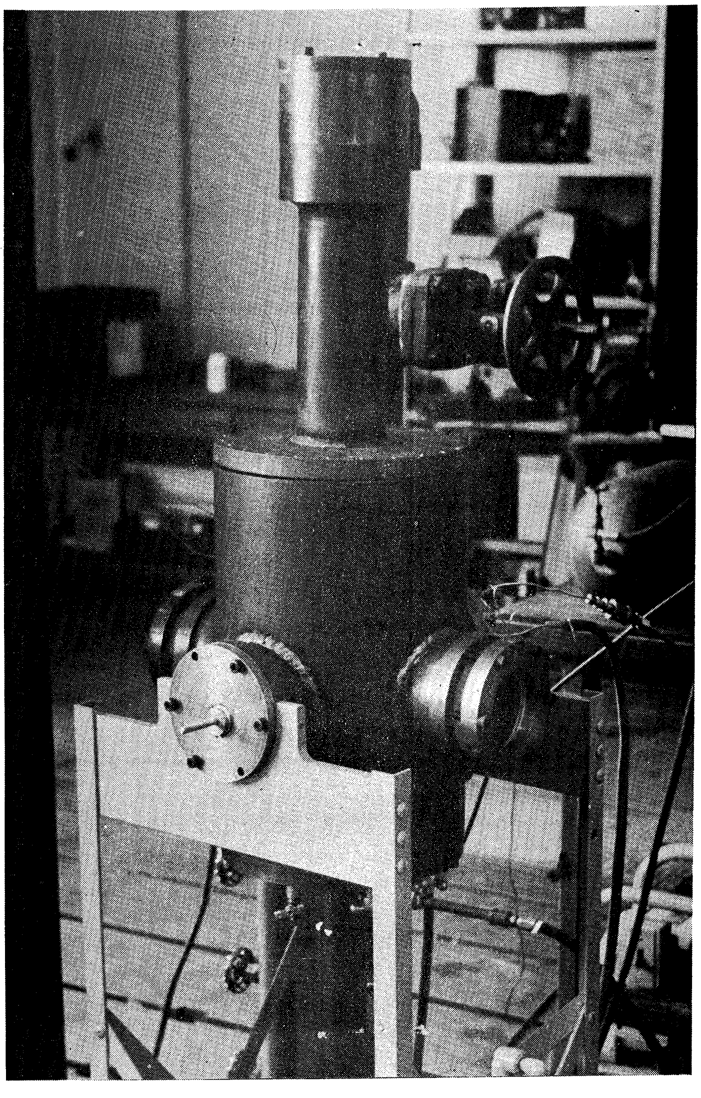

Fig. 4. Housing for steady-state burner.

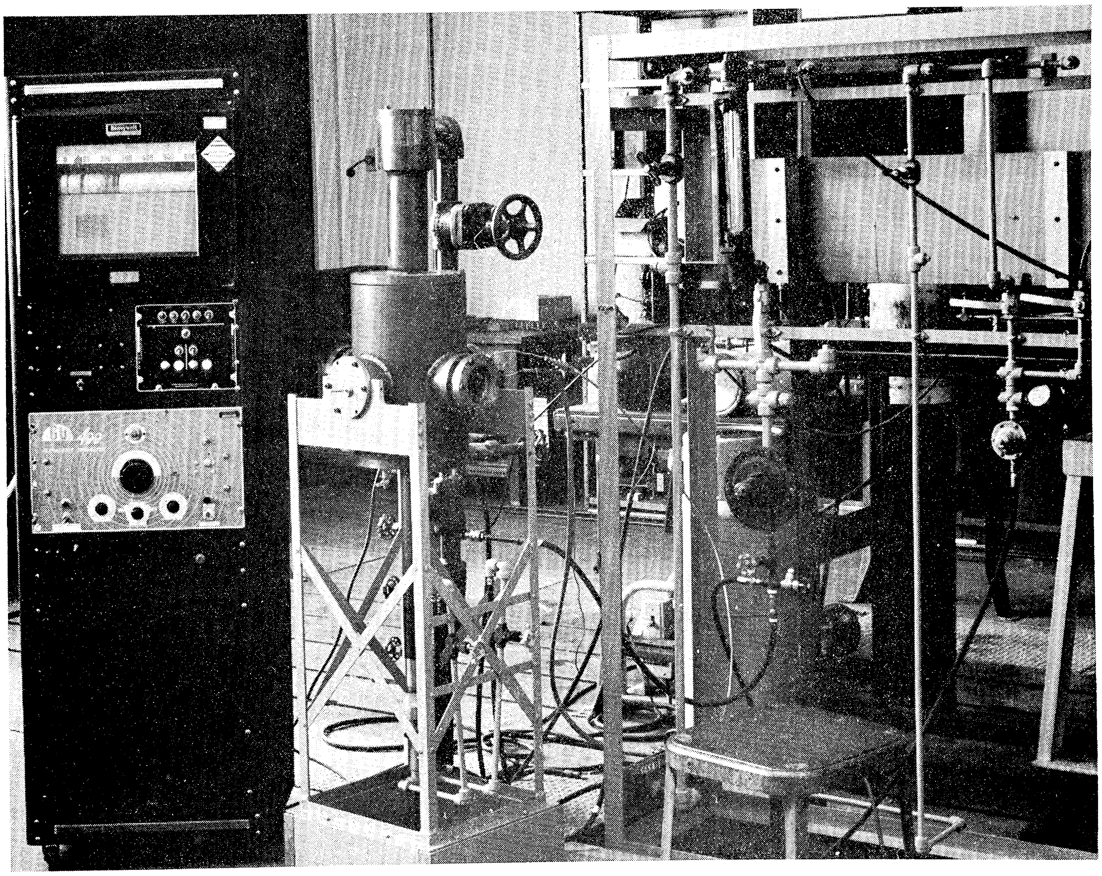

Fig. 5. General view of steady-state burner apparatus.

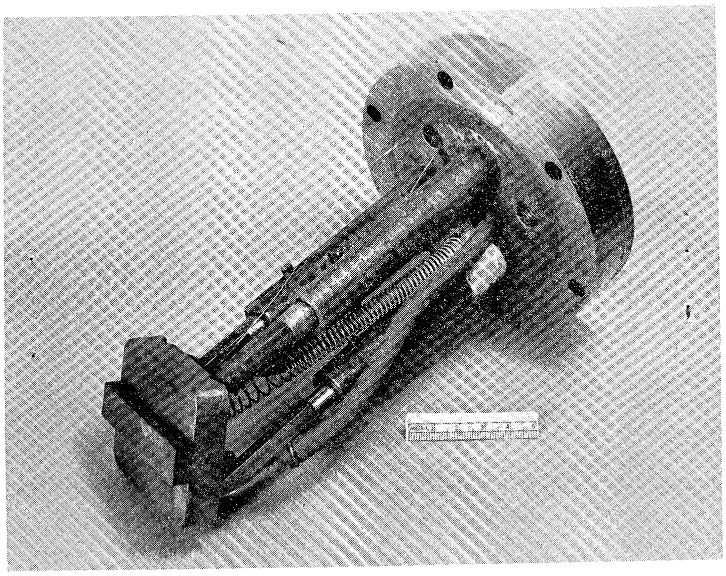

Fig. 6. First model of quench plate.

Fig. 7. Flame configuration with wedge.

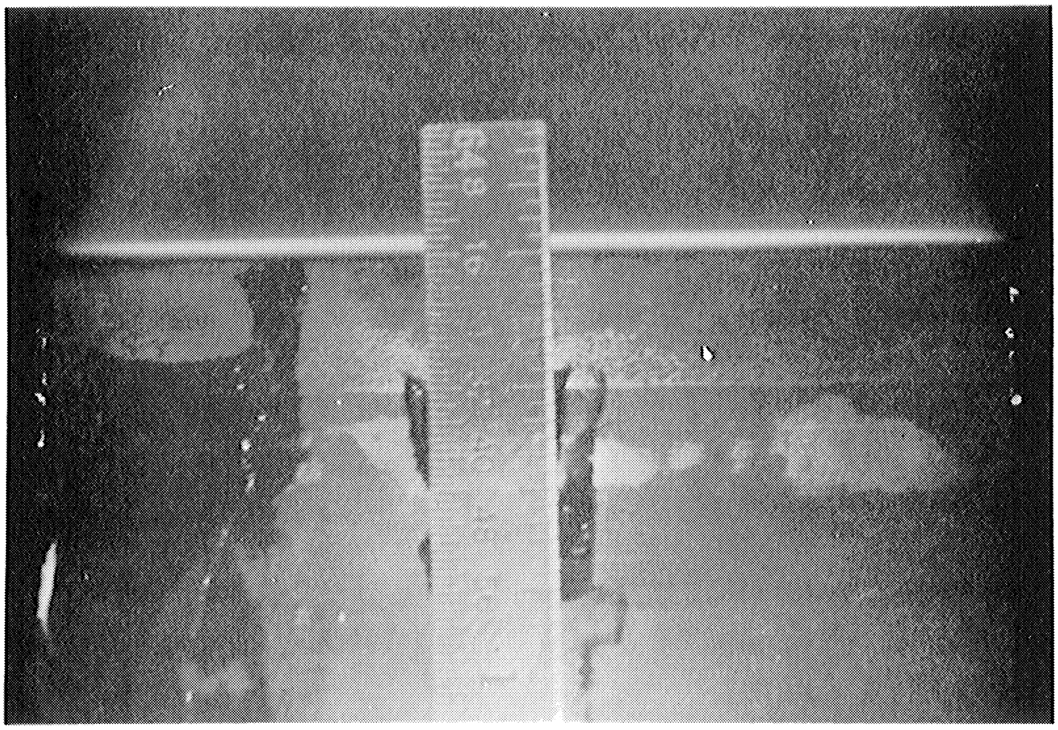

Fig. 8. Flame configuration with porous plate.

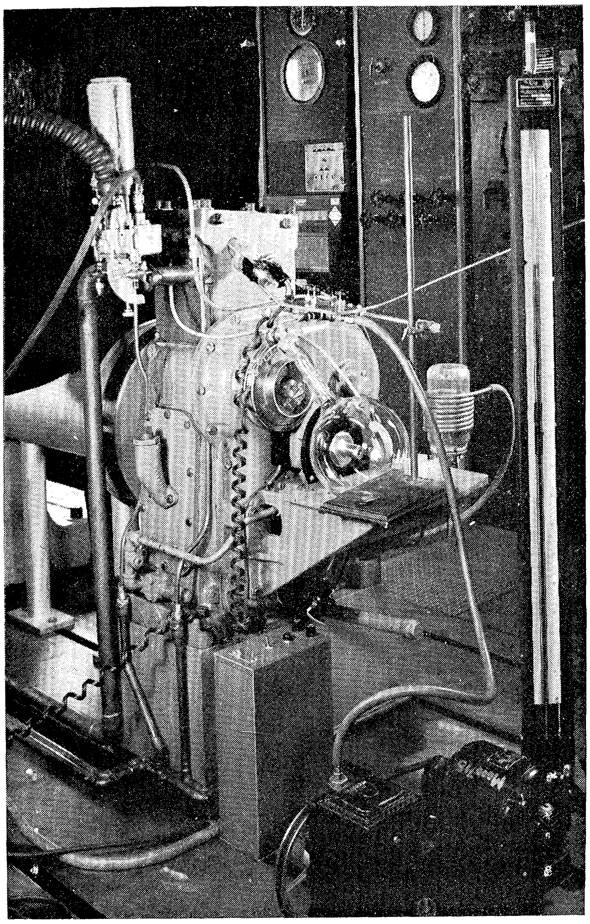

Fig. 9. Single cylinder engine with gas sampling apparatus.

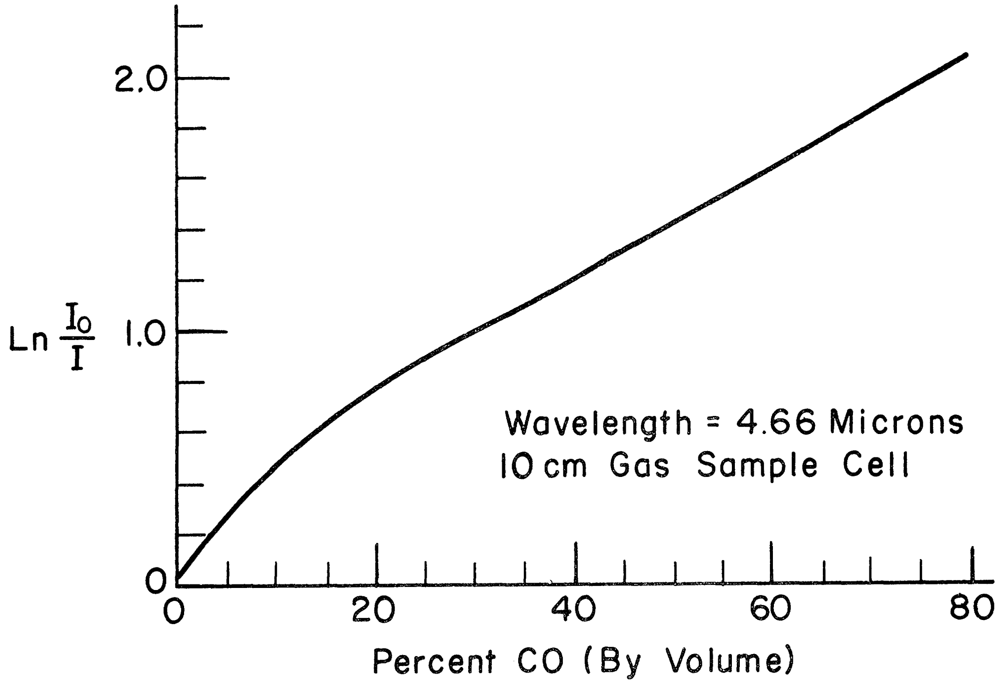

Fig. 10. Spectrometer calibration curve for CO.

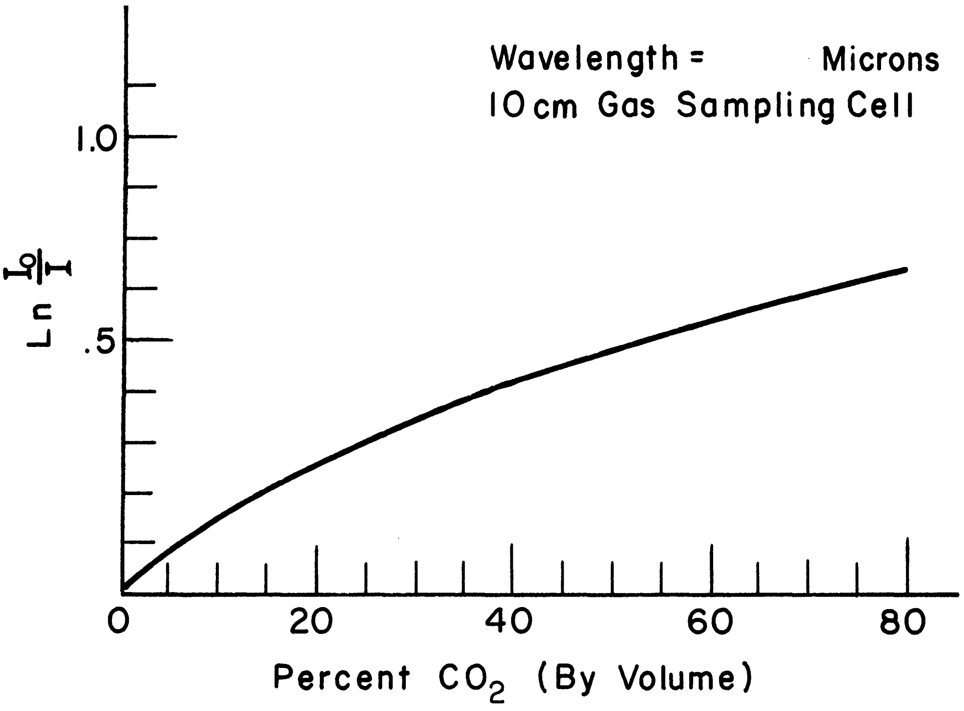

Fig. 11. Spectrometer calibration curve for $CO_2$.

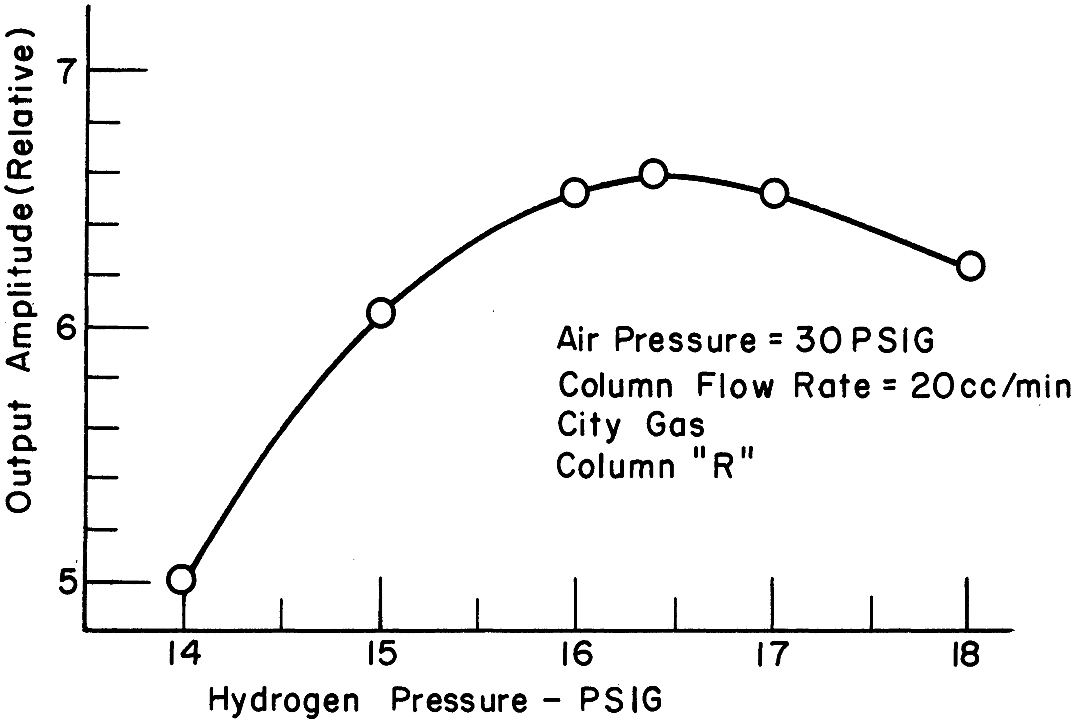

Fig. 12. Variation of flame ionization detector sensitivity with hydrogen pressure.

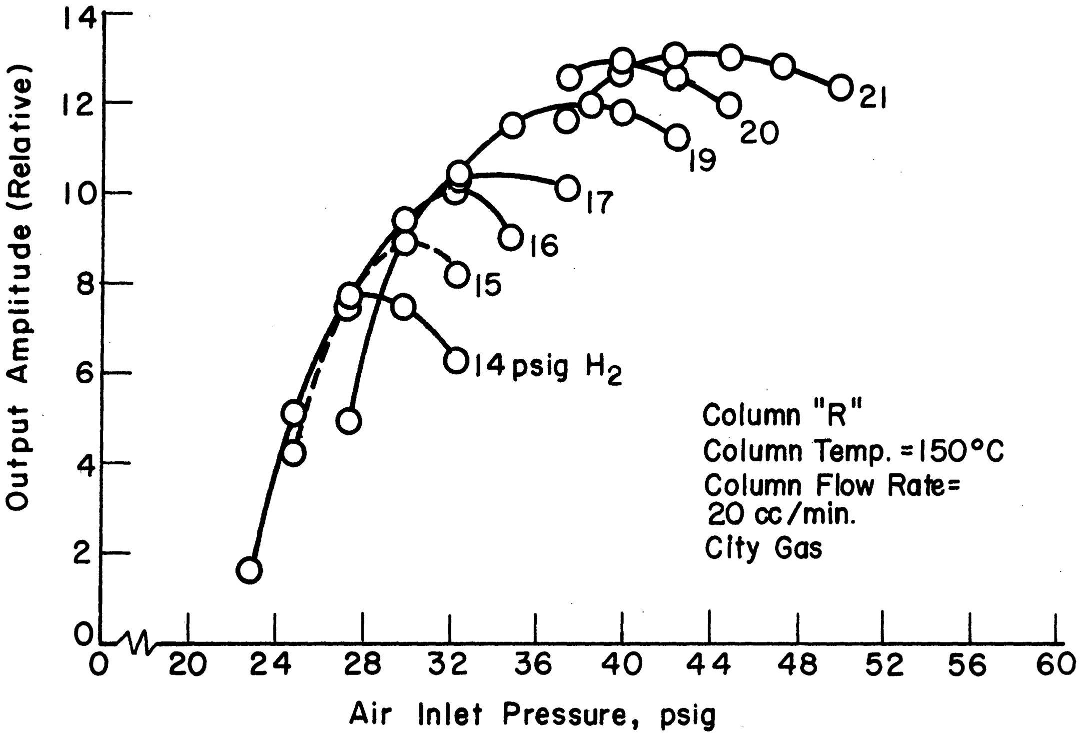

Fig. 13. Variation of flame-ionization detector sensitivity with hydrogen pressure and air pressure.

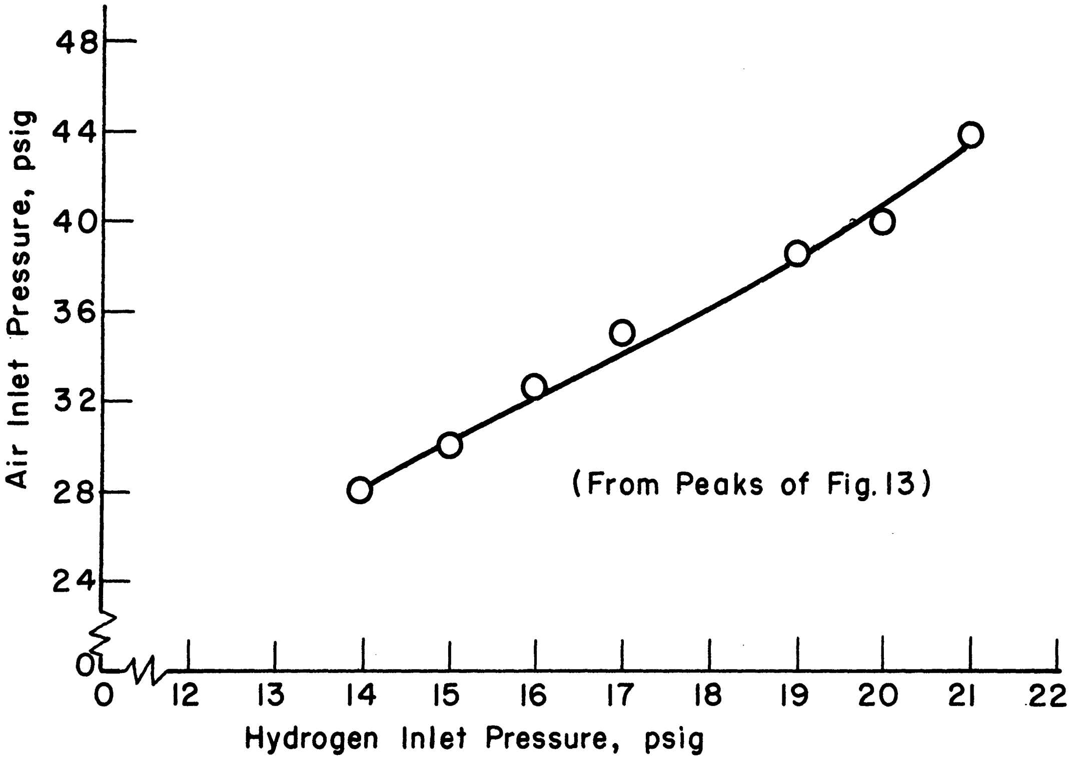

Fig. 14. Best combination of $H_2$-air pressure for maximum selector sensitivity.

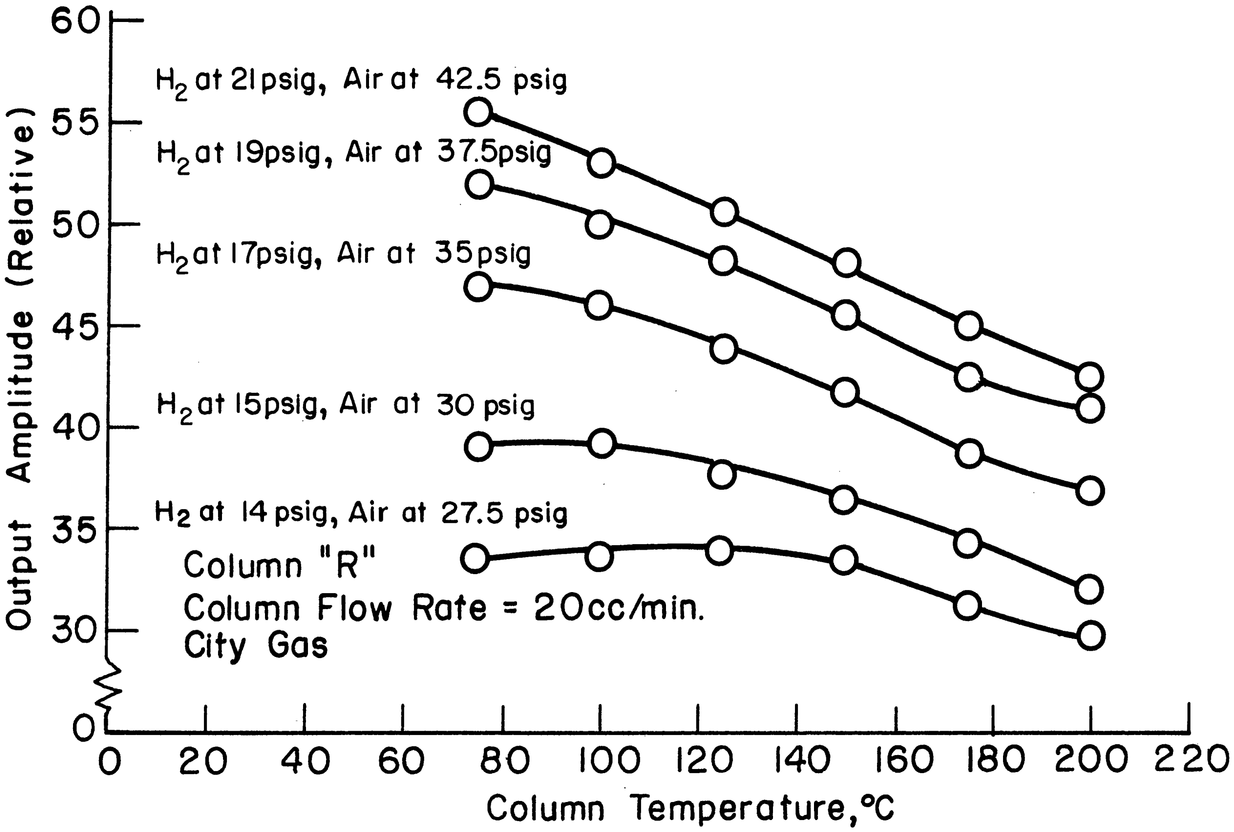

Fig. 15. Variation of detector sensitivity with column temperature.

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