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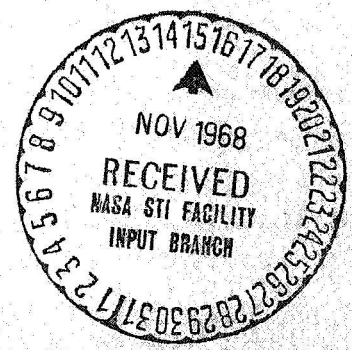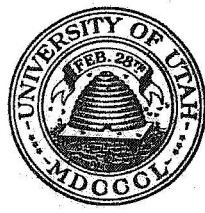
# University of Utah

# Department of Chemical Engineering

Technical Report

on

Ammonium-Perchlorate Diffusion Flames -
A Spectrographic Investigation

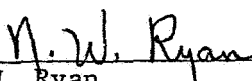July 1, 1968

## Salt Lake City, Utah

University of Utah
Department of Chemical Engineering

Technical Report

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Ammonium-Perchlorate Diffusion Flames
A Spectrographic Investigation

July 1, 1968

Report approved by

N. W. Ryan
Principal Investigator

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# ABSTRACT

Diffusion flames between a body of ammonium perchlorate (AP) and various fuel sources--solid polybutadiene-acrylic-acid copolymer or gaseous methane or hydrogen--were investigated spectroscopically over a wavelength range of 0.3 to 5.5μ with a Warner-Swasey Model 501 Millisecond Scanning Spectrometer.

With gaseous fuels, the flame was approximately in the center of the gap between the fuel source and the surface of the AP. An AP-*vs.* AP flame was produced, but it was totally nonvisible to the eye. The polymer flames were very close to the fuel surface. Spectrograms are published for the hydrogen-*vs.*-AP, methane-*vs.*-AP, AP-*vs.*-AP, and polymer-*vs.*-AP flames in the 1.9-to-4.7μ range.

For the methane-*vs.*-AP flame, temperatures of about 2400°K were measured by a sodium-D-line-height-comparison technique as a subsidiary study. No significant variation in the temperature across the gap was revealed by this technique.

$CO_2$, $H_2O$, HCl, $CH_4$, and probably $N_2O$ were detected in the flames. No evidence of CO was found. HCl emission was observed as near the surface of the polymer as it was possible to observe; however, it was not detected near the AP surface. Similar results were obtained in the gaseous-fuel flames. It is concluded that HCl was not a primary product of the gasification of AP.

Since $CO_2$ emission was observed as near the surfaces of the fuel sources as could be observed, there must be reactive oxidizer species

which survive the flame and diffuse to this location to react with the fuel. The $CO_2$- and HCl-emission distributions across the gap are explained by postulating that a chlorine-oxygen compound, perhaps ClO or $ClO_2$, was a product of the gasification of AP and that a portion of it diffused to the fuel surface, where it oxidized the gasified fuel. In the polymer-*vs*.-AP flame, this compound may have participated in the degradation of the fuel.

# CHAPTER I.  INTRODUCTION.

Engineers have had remarkable success in designing solid-propellant rocket engines by sophisticated equivalents of cut-and-try methods, including full-scale firings.  However, these methods are costly and slow.  Research is necessary to provide knowledge of the combustion mechanism so that propellants may be tailored to meet precisely defined mission requirements.

The objective of such rocket-propellant research is to develop equations or other relationships from which one can calculate the thrust-time curve for a motor, given the important variables; such as, propellant composition, significant features of the rocket-case shape and grain design, nozzle parameters, initial temperature and pressure, etc.  At the present time, work toward this objective has not progressed even far enough to have identified all of the important variables.  Characterizing the combustion of the propellant is one of the more important stages in attaining the ultimate objective.

This Utopian goal is beyond immediate attainment.  However, research on combustion mechanisms will lead to means of providing the designer with more reliable and accurate information for design purposes; such as, rational bases for choosing between alternative propellant systems and development of standardized small-scale experiments which would permit choice of an optimum system.

However, despite the apparent conceptual, manufacturing, and operational simplicity of solid-rocket engines and their propellants,

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a comprehensive description of their ignition and burning phenomena is very difficult. One encounters not only the complicated kinetics and the steep concentration and temperature gradients usually associated with flames but also the possibility (or, in our case, the probability, since we deal with composite propellants) of time-dependent combustion-zone heterogeneity, induced by the nature of the propellant. Of paramount importance is identification of the rate-controlling process or processes. Hall and Pearson [16] discuss several theoretical treatments of these phenomena and reference many others.

This research project was initiated in order to aid in dispelling the controversy and confusion over the proper analytical treatment of propellant combustion. A diffusion flame between large bodies of the two major components of one type of rocket propellant was investigated. To this arrangement of spatially separated components with a flame located between them, we give the descriptive name, "chemical arc."

In this investigation, the diffusion flame was produced between a body of ammonium perchlorate (AP) and a fuel source. The latter consisted of either a body of solid polybutadiene-acrylic-acid copolymer (PBAA) or a stainless-steel fritted disk, through which flowed hydrogen or methane. In some runs, copper chromite, which is a burning-rate and ignition catalyst, was added to the ammonium perchlorate or to the polymer.

The goals of this project were (1) to identify reactive species, (2) to discover their spatial distribution and the rates of gasification of the initial components, and (3) to determine whether hetero-geneous pyrolysis of the individual components in this chemical arc is possible; that is, whether the pyrolysis of one component may be

influenced by chemical species originating from the other component.

The major pieces of equipment obtained to accomplish these tasks are a Warner-Swasey Model 501 Millisecond Scanning Spectrometer with a radiation source unit [29]; a Precision Instrument 60-ips single-extended-range FM tape recorder, a Tektronix 564 oscilloscope; and a Honeywell 906A Visicorder. Also, a test burner and a traversing mechanism were constructed.

In each experiment, approximately 180 spectral scans were taken with this equipment in successive positions across the gap between the AP pellet and the fuel source. The scans taken were recorded on tape for every traverse in each run. Spatial resolution was about 0.1 inch; and spectral resolution was about $0.03\mu$ in the middle IR region (1.9 to $4.7\mu$), which was the most useful region.

# CHAPTER II.  REVIEW OF PREVIOUS WORK
## ON AMMONIUM-PERCHLORATE-SUPPORTED COMBUSTION.

"The key role of AP [ammonium perchlorate] in the combustion
process has been apparent for some years.  This is illustrated by
the fact that AP alone exhibits a number of the burning properties
of composite propellants based upon it" [16].  However, "despite
technological interest in ammonium perchlorate because of its extensive
use in solid-propellant rockets, the mechanism of the decomposition is
not well understood at the present time" [21].

While in this work our attention is focused mainly on AP reac-
tions, we do not, in general, assume that the fuel necessarily plays
a minor role.  For example, we consider the work of Cheng [6] on
oxidative decomposition of PBAA (polybutadiene-acrylic-acid copolymer)
very significant.  He found that a very important reaction, probably
heterogeneous, occurs between AP or its decomposition products and the
polymer or its decomposition products.  He observed a significant
reduction in polymer decomposition temperature when AP was added.
Cheng also found that copper chromite expedited the decomposition but
not to the extent obtained with AP.  Clearly, the work of Cheng and
others on the polymeric fuels is important, especially, for example,
as it pertains to an underoxidized propellant to be decomposed as a
fuel source in a staged combustion system.  On the other hand, Cheng
also implies that AP should be assigned a dominant role in the ignition
and burning of fully oxidized propellants and thereby encourages us, at

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least for limited purposes, to concentrate on AP reactions.

## A. SUBLIMATION AND THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE

Differential thermal analysis of AP yields an endotherm at 240°C and two exotherms at 300°C and 440°C, respectively [16]. The endotherm accompanies a crystal transition from orthorhombic to cubic [3,16], and the exotherms are attributed to the "low"- and "high"-temperature thermal decomposition of AP [16]. The low-temperature thermal decomposition is thought to begin at centers in the crystal [13,22] and to develop in an anisotropic manner. Raevskii [42] offers confirmation; he etched crystals and noted the similarity between the patterns he obtained and those obtained in AP decomposition.

*In vacuo* sublimation combined with decomposition has been found [16] to start at 130°C. This process, however, was not complete, the amount sublimed increasing monotonically from 4.4% at 226°C to 86% at 331°C. Recrystalization from water of the residual material resulted in a material whose fraction of decomposition was the same as that of fresh material [3].

Bircumshaw and Newman [3,4] first reported that decomposition in an inert-gas stream or *in vacuo* proceeds only to 28 to 30% consumption of the solid in the temperature range of 220 to 280°C. After being exposed to water vapor or being ground up, the residue decomposed again to about the same extent as fresh material. They attributed this to the formation of a new crystalline lattice, free from voids amounting to about 30%.

In support of Raevskii's thesis and in contradiction to a rival suggestion [13] that the 30% decomposed material began as interstitial

material, Kraeutle [22] reports that single large crystals exhibit the same partial decomposition behavior.

Osada and Kakinouchi [31] report that the crystal structure of AP affects its decomposition velocity. The more regular the crystal structure, the higher the velocity.

The complexity of AP decomposition is manifest. Depending on the experimental conditions they imposed, investigators have apparently found at least three modes of decomposition; and there is no agreement as to whether sublimation is a necessary part of any of them. The following summary of past work illustrates the situation.

For the low-temperature (below 300°C) decomposition, Bircumshaw and Newman [3] report the following overall reaction:

$$4NH_4ClO_4 \rightarrow 2Cl_2 + 3O_2 + 8H_2O + 2N_2O.$$
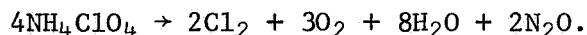
Several experimenters [3,16] have noted that the high-temperature (above 300°C) decomposition proceeds to completion, does not exhibit an induction period, and is described by the following overall reaction:

$$2NH_4ClO_4 \rightarrow 4H_2O + Cl_2 + O_2 + 2NO.$$

At temperatures in or above the range 440 to 450°C, however, ammonium perchlorate will explode after an induction period [16].

From their studies, Heath and Majer [17] concluded that AP decomposition does not occur in the gas phase after sublimation but, rather, occurs at the surface. This was indicated by the appearance of NO, $NO_2$, $O_2$, and $Cl_2$ under very low pressure conditions in a mass spectrometer. They also concluded that "ammonium perchlorate sublimes by dissociation over the range 120-500°C, corresponding to a vapour pressure range of $3.7 \times 10^{-6}$ to 760 mm Hg and is thus similar in behaviour to the ammonium halides."

In his mass-spectrographic investigation of AP which had been flash pyrolyzed with laser light, Pellett [33] reported that proton-transfer dissociation of AP into $NH_3$ and $HClO_4$ appeared to be the first step and that $ClO_2$ and $HCl$ were major products. $HOCl$ was formed by a slower secondary process. Pellet concluded that $ClO_2$ is an important reactive intermediate in the heterogeneous decomposition of $HClO_4$ at high temperatures and postulated that it might be one of the reactive chlorine oxides sought by Pearson and Sutton [32] in order to explain the role of $HClO_4$ vapor in solid-propellant ignition. (See section on perchloric-acid-supported flames, page 12.)

Rejecting the idea that several grossly different decomposition mechanisms need be invoked, Jacobs [21] presents a unified mechanism of proton transfer for both high- and low-temperature decomposition and for sublimation:

$$
\begin{array}{c}
NH_3(ads) + R(g) \xrightarrow{\text{I}} P(g) \\
| \qquad\qquad \uparrow \\
NH_4^+ClO_4^-(c) \rightleftharpoons NH_3(ads) + HClO_4(ads) \\
\downarrow \qquad\qquad \downarrow \\
Sublimate \xleftarrow{\text{III}} NH_3(g) + HClO_4(g) \\
| \qquad\qquad \downarrow \\
NH_3(g) + R(g) \xrightarrow{\text{II}} P(g),
\end{array}
$$
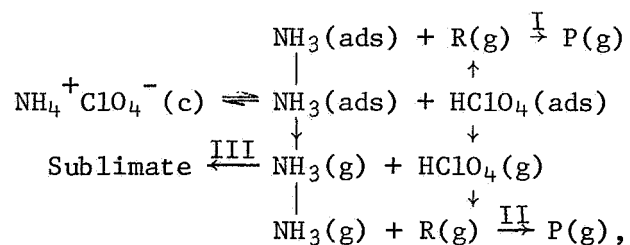
where R and P represent radical intermediates and products, respectively. Path I is the low-temperature mechanism, II is the high-temperature mechanism, and III is the sublimation process. Surface accumulation of the adsorbed ammonia is suggested as the reason why the low-temperature process stops at 30% consumption of reactant. If the temperature is raised, the ammonia desorbs; and the high-temperature reaction proceeds to completion. The sublimation process (which is significant only at low pressure) is just the reassociation of the ammonia and perchloric acid.

This proton-transfer mechanism and the subsequent alternative processes seem to fit the experimental observations better than any other. However, work on slow thermal decomposition only provides a background for deflagration which is more nearly related to the process studied in this work. The relevance of Jacobs' explanation of thermal decomposition to the faster deflagration process is still to be shown, but the assumption that it does apply is a good first working hypothesis.

## B.   DEFLAGRATION OF AMMONIUM PERCHLORATE

Under certain conditions, AP will support a deflagration flame. Arden $et$ $al.$ [1] found that the products of deflagration were $H_2O$, $O_2$, NO, HCl, $N_2$, $Cl_2$, $N_2O$, $CO_2$, and CO. Such species as NOCl, ClO, $ClO_2$, and HClO may be present as intermediates too short-lived to identify. Flame zones are extremely thin, and the temperature gradient may be thousands of degrees per millimeter [40]. The burning rate has been found [16] to increase with the density of the AP; but, in the absence of additives such as $Na^+$ or $MnO_4^=$ or of high pressures, deflagration occurs without attendant melting.

Ammonium perchlorate by itself will not support a deflagration flame under normal conditions (STP); a source of additional energy or a reduction in heat losses is required. Higher pressure, preheating of the original material, radiative heating of the burning surface, addition of various catalysts or small amounts of fuel to the AP matrix, and placing AP in a fuel atmosphere have proven efficacious in supplying this energy. Levy and Friedman [25] found that AP, pure and unheated, will support a decomposition flame if the pressure is above

22 atm. Reports of an upper pressure limit [25], based on experiments with small strands, are apparently mistaken; for strands of sufficient size, no limit has been found up to 1000 atm [16,25]. AP will sustain combustion at atmospheric pressure, however, if sufficient energy is supplied to raise the flame temperature to a minimum of about 930°C [1,16]. For example, Powling and Smith [40] observed spontaneous ignition of AP in a stream of hot air at 360°C; and Horton [20] noted that extremely small amounts of fuel were sufficient to sustain combustion at pressures below those at which pure AP will not deflagrate. For ammonium perchlorate to burn at atmospheric pressure, at which considerable quantities of the endothermic nitric oxide are formed, the addition of about 107 cal/g of extra heat, in the form of a volatile fuel, is required, while, at high pressures, the extra heat available if oxides of nitrogen are not present in the products is about 124 cal/g [1]. The only effect of the catalyst was to reduce the $N_2O$ [25]. Friedman *et al.* [12,25] found that a radiant-energy flux of 10 cal/$cm^2$ sec (equal to 102 cal/g) was required to support combustion. The deflagration rate was essentially linear in radiation flux.

Flame-zone structure in a methane atmosphere appears to be

> . . . an oxidizer decomposition flame within a few microns of each ammonium perchlorate pellet, into which a small fraction of the fuel might diffuse and react, followed by the final flame a few hundred microns from the surface, which is sustained by reaction between the oxidizer decomposition products and the large remaining fraction of the fuel vapors [27].

Arden *et al.* [1] said that the limiting flame temperature, 930°C, is not significantly influenced by the chemical nature of the fuel, especially in the case of fuels which are reasonably volatile. Para-formaldehyde, metaldehyde, and polystyrene all fall on the same curve

of burning rate *vs.* flame temperature; however, for preheated AP (without fuel), the curve is much steeper. The starting points of the burning-rate, temperature curves are very close at about 0.023 cm/sec and 930°C. " . . . The heat generated by the ammonium perchlorate surface decomposition flame, slightly augmented by a very small quantity of fuel, is the principal source of energy fed back to the surface to produce deflagration of the ammonium perchlorate burner" [27], but "the limiting rates of burning at atmospheric pressure are all within the range 0.02 to 0.03 cm/sec, irrespective of the manner in which the heat is added" [1]. High pressures (1000 psi) increase the flame temperature about 80°C by reducing the formation of NO [1,16], while catalysts work by reducing the $N_2O$ [16].

It seems plausible that small amounts of fuel promote AP deflagration by raising the reaction temperature and, therefore, the energy feedback; however, the interpretations of the effects of pressure and catalyst must be taken as educated speculation at best. Any change that causes a net increase in the reaction rate relative to the heat-loss rate acts in the direction of producing a stable flame.

Barrère *et al.* [2], in working with pressed AP spheres, found that the exponent in the rate equation changed for some fuels. They ascribed this effect to different diffusivities of the fuels.

Using, as fuels, paraformaldehyde, stearic acid, paraformaldehyde and $NH_4Cl$, polystyrene, benzoic acid, and nil (AP preheated), Arden *et al.* [1] obtained surface temperatures of 450 ± 30°C for all fuels and compositions examined (only lean fuel ratios were used) and burning rates between 3 and 10 cm/sec. In their experiments at atmospheric pressure with pure AP (preheated), AP in hydrogen-nitrogen ratios of

0.36/1 and 1/0, AP in $CH_4$, and AP with 11% $(CH_2)_n$, Powling and Smith [40] found that the surface temperature of AP was close to 490°C and did not increase significantly with the rate of burning, which they hypothesized to be governed by the temperature gradient established by the gas-phase flame reaction. This hypothesis indicates that heat feedback is rate controlling. They also found that such catalysts as copper chromite affected only the burning rate. Surface temperatures were not only unaffected by the addition of catalyst but also differed only slightly when practical composite propellants were used in place of weak fuel-AP mixtures.

Powling and Smith [41] also observed that fuel concentration, at any given pressure (25 to 760 mm Hg), had little effect on surface temperature, concluding from their observations that "thermodynamic equilibrium between solid ammonium perchlorate and its dissociation products, ammonia and perchloric acid, exists at the burning surface." The surface temperature was found, however, to increase with pressure; and, for weak mixtures of fuel and AP, the pressure exponent of the burning rate fell suddenly at about 1000 psi, which Powling and Smith hypothesized to be the result of a change of the location of the rate-controlling process reactions from the gas phase to the solid surface. From their work, they concluded that the "surface temperature of the ammonium perchlorate . . . is only of incidental importance at moderate pressures." The possible temperature range in these experiments, 420 to 480°C, would, with an activation energy of 30 kcal/mole, produce a ratio of burning rates of over six to one, which is above the range of burning rates Powling [39] investigated. Thus, Powling's experiment apparently seems to lack sufficient precision to justify

his conclusions.

Powling [39], after first espousing it, now rejects the concept of dissociation equilibrium at the surface. He suggests that experimental data on the gasification process, for AP burning over a wide variety of conditions, indicate that dissociation is generally better represented by a kinetic decomposition law having an activation energy of about 30 kcal/mole.

## C. PERCHLORIC-ACID-SUPPORTED FLAMES

Since work with AP decomposition indicates that the ammonia separates from the perchlorate in some manner, flame investigations in which perchloric acid serves as the oxidizer have been conducted. Heath and Pearson [19] investigated premixed methane-perchloric-acid flames, finding that chlorine was formed in the reaction zone but decayed to HCl downstream. In all chlorine-in-acid-flame analyses, the chlorine was found to be in excess of the equilibrium value. Their results indicated that "the burning velocity of methane-acid flames is about three times that of an oxygen flame at the same flame temperature" and that, in methane-rich acid flames, "only two molecules of methane are consumed per molecule of acid, excess methane acting as a diluent."

In his studies, Levy [24] found that perchloric acid decomposed on a hot wire goes to $0.5 H_2O + 0.5 Cl_2 + 1.75 O_2$ at 200°C. At low (ca. 10 mm) pressure, perchloric-acid vapor explosions were noted at 170 to 250°C. A first-order reaction rate was reported.

Cummings and Hall [7] found that the addition of oxygen or air to a low-pressure, fuel-rich methane-acid flame caused the formation of a second luminous zone downstream of the one associated with the acid.

The first zone gave the acid-flame spectrum, while the second gave the oxygen-flame spectrum. Relative to methane-oxygen flames of a similar temperature, methane - perchloric-acid flames have an increased rate of $CO_2$ formation early in the flame; and consumption of methane in the reaction zone is enhanced [18]. These phenomena have been ascribed to oxidizer species from $HClO_4$, which are more reactive than those from $O_2$. Heath and Pearson [18] then proposed a mechanism which would utilize ClO radicals.

While Heath and Pearson stated that "perchloric acid does not act in flames simply as a source of oxygen," Cummings and Hall [7] concluded that "perchloric acid or its decomposition products are more reactive oxidizers than molecular oxygen." In their study, Cummings and Hall noted that all the flames were colored blue--though a white-blue in the cases of methane and ethane--at atmospheric pressure, whereas pink, green, and blue flames were noted at low pressures. They found that, for a stoichiometric methane-perchloric-acid flame which had been diluted with three moles of nitrogen, OH-line reversal produced a temperature of 2350 ± 20°K. From their results, they concluded that acid-molecule dissociation is not the rate-determining step.

Studying perchloric acid and its reactions or essentially pure ammonium perchlorate as a means of learning about the combustion of AP-oxidized propellants is a reasonable scientific gamble. However, it does not seem to be a route to inspire great expectations. For example, compared with perchloric-acid-methane flames, complicated as they are, the AP-polymer-fuel reactions are vastly more complex. This work has striven to make a lesser departure from the full complexity

of propellant combustion by concentrating on AP as the oxidizer. It

has concentrated largely on gaseous fuels but has also devoted some

attention to a typical fuel polymer--polybutadiene-acrylic-acid

copolymer.

# CHAPTER III.  EXPERIMENTATION.

## A.  APPARATUS

The experimental objective was to establish a diffusion flame, the chemical arc, between a plane surface of AP and a planar source of fuel, then spectroscopically to traverse the zone between the two reactant sources.  Accordingly, the essentials of the equipment were the spectrometer with its radiant source, a windowed chamber for containing and displaying the combustion process, and provision for the beam of the spectrometer system to traverse the reaction zone.  Figure 1 is a schematic of the apparatus.

### 1.  Spectrometer and Auxiliary Equipment

A Warner-Swasey Millisecond Scanning Spectrometer, Model 501 S/N 1004, with a synchronized source unit [29] was used to analyze the radiation from the flame zone.  Radiation from the source in the source unit passes through a vertical slit and leaves the unit through a casagranian condenser, which was adjusted to focus the beam at a distance of 30 inches from the unit.  The diverging beam is gathered by a matched casagranian objective and passed through an adjustable vertical slit into the spectrometer.

In the work reported here, the source unit and the spectrometer were separated by 60 inches.  The effective entrance aperture of the casagranian was 4.5 inches.  Thus, the angle of convergence of the beam was 8.5 degrees.

With a flame thickness of 1.5 inches, the beam width at the edge of the flame due to the divergence of the beam was 0.28 cm (0.11 inch). The width of the spectrometer entrance slit, 0.5 mm, projected to the flame would be additive with the above beam width; but its contribution was insignificant.

The spectrometer is a modified Czerny-Turner monochromator, in which a scan wheel carrying corner mirrors is mounted such that the mirrors pass through the focus zone and perform the scanning function. Due to the symmetry of the corner mirror arrangement, two monochromatic beams are reflected and pass out two exit slits into two detectors selected for the wavelength band scanned. Thus, the instrument scans two wavelength regions simultaneously. The speed of the scan wheel can be varied incrementally such that one- to one-hundred-millisecond scan times (800 to 8 scans per second) may be obtained.

In this study, the spectrometer was used at a scan time of ten msec in four spectral ranges: 0.3 to 0.65μ, 0.65 to 1.9μ, 1.9 to 4.7μ, and 3.1 to 5.5μ. In the first range, a 258.03-line/mm grating and two photomultipliers (IP28 and 4473) were used at a slit width of 0.5 mm. In the second range, an 86.01-line/mm grating and 1-mm slits were used with a 7102 photomultiplier and a $N_2(\ell)$-cooled InAs IR detector. In the third range, a 35-line/mm grating was used with $N_2(\ell)$-cooled InAs, InSb IR detectors, and 0.5-mm slits. In the fourth range, $N_2(\ell)$-cooled InSb detectors were used with 0.2-mm slits and a 11.58-line/mm grating.

A chopper in the source unit, synchronized with the scan wheel, blocked the beam during alternate spectral scans. Thus, absorption and emission spectra were taken alternately. Only the emission spectra

contained useful information, due to the low pressure-path-length product in the burner.

The output from the spectrometer was in the form of three electronic signals, two of which contained the spectra, while the other was a timing signal used to trigger the oscilloscope. The signals from the spectrometer were displayed on an oscilloscope screen and were, thus, continuously monitored. Use of the memory feature of the scope or a camera permitted recording a single spectral scan or the envelope of the traces. In addition, the signals were recorded at 60 IPS by a Precision Instrument PI 2100 FM tape recorder so that the spectra could be reproduced at convenience and analyzed in detail. A specially designed triggering device for the oscilloscope allowed a successive pair of absorption and emission traces for each of the pair of spectral intervals to be recorded on each photo. Sequences of photographs of the spectra were taken as the gap between the AP and the frit was traversed. For a limited number of runs, the tape recorder was played back at a speed of 7.5 inches per second; and the spectra were recorded by a Visicorder oscillograph. Due to excessive noise in the oscillograph, this procedure did not prove to be very useful.

## 2. Combustion Chamber

The combustion chamber was machined from an aluminum block, with provision made for mounting viewing windows and for inserting and locating an AP pellet and either a corresponding polymer pellet or a frit for the introduction of a gaseous fuel. The exhaust was vented to the atmosphere (12.5 psia in Salt Lake City) vertically out the top and bottom. Figure 2 is an exploded-view sketch of the test section.

The gap between the AP and the frit or the polymer surface was one-half inch. The flame was ignited by an electrically heated coil of nichrome wire, which touched the AP at its upper edge. This coil was placed out of the view of the spectroscope in order that its thermal radiation would not complicate the flame spectra.

As discussed in Chapter I, AP will not burn by itself at low pressure unless additional energy is supplied. This characteristic made ignition difficult. For example, in a polymer-AP run at 0.5-inch gap, even burning of a slug of propellant which filled the gap would not ignite a self-sustained chemical arc. Preheating of the test section was the method found efficacious as an ignition aid. The body of the test section was heated by electrical heating cartridges to 320°C, as measured in the body of the chamber. The final temperature of the AP was just under the crystal transition temperature of 240°C. Thus, at ignition, the AP, which was preheated, was being subjected to radiant and convective heat fluxes. Depending on the wavelength range of interest, either Irtran-3 or fused-quartz windows, purged by a flow of nitrogen, were provided for passing radiation through or from the combustion zone.

## 3. Traversing Mechanism

The sheer bulk of the spectrometer system, combined with its very sensitive optical alignment, ruled out the possibility of moving it to cause the beam to traverse the combustion zone. Instead, the combustion chamber was moved back and forth, presenting different positions in the combustion zone to the spectrometer view as the chamber moved.

The chamber was driven by a screw which was powered through a gear

train by a three-phase synchronous electric motor. At the end of its travel, the chamber tripped a microswitch, which activated relays to reverse the rotation of the motor and, thus, to reverse the direction of travel. These events were repeated at the other extreme of chamber travel. Two traverses were thus made during each cycle of chamber motion.

The time required for one traverse of the gap was 2.5 seconds, and the speed of the chamber during the effective time of spectral scanning was 0.51 cm per sec (.2 IPS). During a single scan (0.01 sec), therefore, the chamber moved 0.0051 cm, or 0.02 times the beam width. The linear displacement in the combustion chamber of the beam was 0.006 cm (0.0025 inch) between a given absorption spectrum and the successive emission spectrum. Thus, the displacement of the test section during a spectral scan and between scans was negligible compared with both the gap width and the spectroscope beam width. While the chamber motion was slow enough that it was not a factor in space resolution, it yielded about 90 spectra of each kind in each of the many traverses made during an experiment. The indistinguishability of successive emission (or absorption) spectra indicated a reproducibility that permitted selection of five to ten scans, spaced across the gap, for detailed analysis.

## B.  FUELS AND AMMONIUM PERCHLORATE

The gaseous fuels were delivered via pressure regulators and Dwyer rotameters from cylinders. The methane was Matheson technical grade, free from mercaptan.

The liquid polybutadiene-acrylic-acid copolymer was supplied by

the Thiokol Chemical Corporation. It was mixed thoroughly by stirring with twenty percent by weight of Shell Epon 828 resin, cast as a film and cured seven days at 80°C. The cured film, 5-mm (0.2 inch) thick, was cut into discs 38 mm (1.5 inches) in diameter.

Some polymer samples contained one percent by weight of copper chromite, Harshaw Cu-0202 P, by analysis supplied, approximately 82 percent CuO and 17 percent $Cr_2O_3$. Weight average particle size was 3.7μ.

The top sieve fraction (-48 mesh, 400+ μ) of ammonium perchlorate, supplied by the American Potash and Chemical Company, was formed into 20-gram pellets (9 × 39.3 mm) in a die whose internal pressure was taken up to 17.5 tons per square inch. The density of the pellets was 19.3 g/cc, or 99% of that of the crystal. Catalyzed AP pellets were made by mechanically mixing copper chromite with the granular AP prior to pressing.

## C.  EXPERIMENTAL PROCEDURE

While the spectrometer was running and with the test-section temperature at about 200°C, the AP-pellet holder (and polymer holder, if applicable) was loaded into the burner. Just before the ignition temperature was reached, the tape recorder was started; and, as the potentiometer indicated 320°C, the ignition current and the fuel flow were turned on.

Ignition phenomena were similar in all cases observed. A short time after the ignition current (and fuel flow, if applicable) was turned on, ignition commenced suddenly at the point where the ignition coil touched the AP pellet. (It was found that ignition was easiest if

the coil was in contact with the AP.) The flame then spread over the AP surface and moved away from it, stabilizing at its final position after less than ten seconds. The difficulty in ignition varied greatly. The flames involving polymer fuels were the most difficult, methane and hydrogen being much easier and similar to each other. Catalyst (copper chromite, 0.1%) in the AP pellet made ignition much easier, but in the polymer (1.0%) it had little noticeable effect.

# CHAPTER IV.  RESULTS.

## A.  METHANE-VS.-AMMONIUM-PERCHLORATE FLAME

### 1.  Description of Flame

Figure 3 shows a sequence of three photographs of an experiment in which the AP pellet was opposed by a stainless-steel frit, through which methane was introduced.  Photograph (a) shows the back-lighted chamber before ignition, AP disc on the left, frit on the right.  Photos (b) and (c) are illuminated by the flame itself.

Photograph (b) shows the diffuse, irregular flame shortly after the ignition process was complete.  Photograph (c) shows the edge-on view of the very sharp, steady flame with its diffuse halo that was observed during most of the firing.  To the left of the flame, reflecting light from it, can be seen the AP surface.  In color and brightness, the flame resembled a candle or other hydrocarbon-air diffusion flames.  However, spectral measurements indicate that the visible radiation is due almost entirely to sodium-D-line emission.  Traces of sodium contaminant in the AP provide the color, rather than carbon-particle continuum, as in a candle flame.

In the test depicted in Figure 3, for which the linear burning rate of the AP was .01 cm/sec, 0.145 mole of $CH_4$ was introduced into the chamber and 0.17 mole of AP was consumed--a $CH_4$/AP mole ratio of 0.85.  If, for the sake of reference, we assume reaction to the products $CO_2$, $H_2O$, $N_2$, $Cl_2$, we see that stoichiometric products call for a ratio of 0.50, the minimum value consistent with absence of $O_2$ or oxides of nitrogen in the products.  It is interesting to note that

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the ratio required to produce exclusively CO, $H_2O$, $N_2$, and HCl is 0.83, a value equal, within errors of measurement, to that observed. For reasons given below, this agreement is regarded as sheer coincidence. The stoichiometric ratio for a reaction yielding $CO_2$, $N_2$, $H_2O$, and HCl, products observed spectroscopically, would be 0.625, compared with the observed value of 0.85. If 25% of the $CH_4$ bypassed the flame, the observed ratio is compatible with the products observed. It is presumed that the $CH_4$ flow required to sustain and stabilize the flame was in excess of reaction needs, the excess escaping virtually unreacted.

Meaningful overall material balances cannot be made for the reaction carried out here, where geometry is dictated by the spectrometer. The self-regulating stoichiometry of the flame zone itself is of great significance but, as yet, is beyond our power to determine it.

## 2. Flame Temperature

The AP-disc-frit gap was traversed in an experiment in which a grating (258.03 lines/mm) and detectors suitable for the visible range were employed, and the AP contained 0.1 weight percent $NaClO_4$. Temperatures were computed from peak-height measurements by the sodium-D-line-comparison method, as described in Appendix A. Figure 4 displays the results. All experimental conditions were the same as those for the experiment photographed (Figure 3).

The fact that there was no great difference in these temperatures is of significance in the interpretation of the spectra obtained from this flame.

## 3. The Spectra

Photographs and flame-temperature measurements are interesting prelim-
inary studies, but the heart of this investigation was the spectroscopic
findings. To sum up the experimentation, the vertically oriented beam of
the spectrometer, in effect, traversed the 0.5-inch gap between the face of
the AP pellet and the frit from which the methane evolved. The spectra of
interest were in the 1.9-to-4.7μ region, where a 35-line/mm grating and
0.5-mm slits were used. The region was scanned in two ranges, 1.9 to 3.0
and 3.0 to 4.7μ, simultaneously. A detailed consideration of the spectra
in this region, based on previous work, and a complete analysis of a typi-
cal spectral scan are to be found in Appendix B. Because of the low
temperature of the radiation source, lower than the flame temperature,
absorption measurements yielded no significant information.

In Figure 5, numbered zero through six, are spectrograms obtained in
one traverse of the gap at a methane rate of 2.5 liters/minute (STP). Spec-
trogram 0 is a calibration trace taken through the loaded burner prior to
firing. The absorption spectra observed are due to atmospheric $CO_2$ and $H_2O$
in the optical path external to the burner. Of course, there was no emission
spectrum.

In each of Spectrograms 1 through 6, we find at 1.9, 2.5, 2.7, and 2.9μ
the peaks of four emissions, which are primarily $H_2O$. At 4.4μ is the peak of
an emission predominantly due to $CO_2$. At 3.3μ in Spectrograms 1 and 2, super-
imposed on the upper wing of the 2.9μ water spectrum can be seen an emission
due to $CH_4$. A corresponding absorption can also be seen. It should be noted
in Spectrogram 1, as close to the methane frit as could be observed with
the spectrometer, that HCl emission around 3.8μ is clearly indicated. At an
equal distance from the AP face (see Spectrogram 6), HCl emission could
not be seen. It might be supposed that, whatever the HCl distribution

might have been, a higher temperature near the methane frit could have accounted for the emission of HCl there but not near the AP. However, measurements by the sodium-D-line-comparison technique showed no great difference in the temperatures at the two locations, as can be seen in Figure 4. It is especially interesting that chlorine species, which must originate with the AP, diffused so far (0.5 cm, approximately) beyond the flame and also that HCl does not seem to be a primary product of AP gasification.

In view of the discussion of stoichiometry in Section A1 of this chapter, it is of interest to seek evidence of the presence of CO. It is particularly active at 4.5μ, but very strong $CO_2$ emission in this region would mask CO emission. In parts of the flame, Spectrograms 5 and 6, in which $CO_2$ emission was absent, a faint emission peak appears at about 4.5 to 4.6μ. These parts of the flame are those in which any carbon present should be fully oxidized. As will be discussed later, emission at that wavelength and of about the same intensity is present also when carbon is absent—in the $H_2$-$vs$.-AP and the AP-$vs$.-AP flames. Near 2.3μ, a region clear of other radiation, CO emission has been reported [37,43]. No activity was observed at this wavelength in this study, even under conditions which, for these flames, would be the most favorable for formation of CO. The 2.3μ emission of CO is relatively weak, however; so some CO could have been present without being detected. It is concluded that CO is probably not an important species.

Figure 6 is comprised of a set of plots of the 4.4μ $CO_2$ and 2.9μ $H_2O$ peak heights and of the ratio of the peak heights measured from spectrograms of the $CH_4$-AP flame. All plots are corrected for differences in detector sensitivity and electronic gain for the two spectral

ranges. The flame photos show that the visible flame corresponds approximately to the maximum in the plots of emission-peak heights. The value of plotting the ratio is due to the similarity of the variations with temperature of the emissions from each species. In the ratio, the temperature effect is canceled out. In the plots of emission-peak heights, the temperature effect can obscure the concentration effect.

The plots of the ratio of $4.4\mu$ $CO_2$ to $2.9\mu$ $H_2O$ peak heights are interpreted as follows: The ratio increases with the distance from the surface of the methane frit, going through a maximum and then falling. This maximum must be due to formation of $CO_2$ by reaction between freshly supplied methane and counterdiffusing oxygen-carrying species; the $H_2O$ concentration remains more nearly constant. The converse effect--*i.e.*, a minimum in $CO_2/H_2O$ ratio--is found at the AP side of the gap, where the $H_2O$ was principally a decomposition product of AP, little $CO_2$ having diffused close to the AP surface.

## B.  METHANE (6.1 LITERS/MINUTE)-VS.-AMMONIUM-PERCHLORATE FLAME

The visual appearance of the flame was, as expected, very similar to that of the 2.5-liters/minute methane-*vs*.-AP flame. The flame was closer to the AP face, just half way across the gap. It would be expected at first glance that the larger quantity of methane would favor the formation of CO; however, it was not detected. This fact may be due to the self-regulating nature of the stoichiometry of the flame; *i.e.*, the manner in which an increase in the methane flow results in an increase in the consumption rate of the AP. Also, the fraction of the methane which did not react in the flame was undoubtedly larger.

The spectrograms were very similar to those of the 2.5-liters/ minute methane flame. The methane absorption was much more pronounced near the frit, probably because of the lower temperature there than in the other experiment. The maxima of the $2.9\mu$ $H_2O$ and $4.4\mu$ $CO_2$ emissions moved nearer the AP. Figure 7 displays the $4.4\mu$-$CO_2$-to-$2.9\mu$-$H_2O$ peak-height ratio and corresponds to Figure 6 for the lower methane flow rate. There is little difference between the plots that can be attributed to the difference in methane flow rates.

## C. METHANE (2.5 LITERS/MINUTE)-VS.-AMMONIUM-PERCHLORATE (0.1% COPPER CHROMITE) FLAME

The catalyzed-AP-with-methane flame was the most vigorous of the flames studied. The flame region was more diffuse than that of the uncatalyzed flame and did not exhibit the well-defined inner flame sheet.

The general features of the spectra are virtually the same as those of the uncatalyzed flame, with the exception of the fact that methane absorption was not observed, due probably to higher temperatures near the frit.

The maximum of the plot of the $2.9\mu$ $H_2O$ peak heights moved closer to the fuel side of the gap, but the $4.4\mu$ $CO_2$ maximum moved the other way. This resulted in a $CO_2/H_2O$ ratio which exhibited less extreme variations and had its maximum and minimum closer together. See Figure 8.

## D.  HYDROGEN-VS.-AMMONIUM-PERCHLORATE FLAME

The hydrogen (2 liters/minute)-*vs*.-AP flame closely resembles the methane-*vs*.-AP flame, the only distinguishing feature being slightly fainter intensity.

The spectra obtained from this flame, Figure 9, did not, of course, exhibit any $CO_2$ emission at 4.4µ.  At 4.5 to 4.6µ, the emission noted in the $CH_4$-AP flame is seen in Spectrogram 4.  Its existence in this carbon-free flame is the basis for attributing it to species other than CO.  The other spectral features of this flame are much the same as those of the methane flame.

## E.  AMMONIUM-PERCHLORATE-VS.-AMMONIUM-PERCHLORATE FLAME

The AP-*vs*.-AP flame was totally nonvisible to the eye.  The only way to tell that deflagration was occurring was to note that the AP was disappearing.  The surface of the AP visually resembled that of dry ice when it vaporizes.

In the spectrograms of Figure 10, the 4.5-to-4.6µ peak (see discussions of $CH_4$-*vs*.-AP flame, page 25, and $H_2$-*vs*.-AP flame, above) is quite large, especially in comparison with the other peaks.  It is large also compared with the corresponding emission peaks in the spectrograms for the $CH_4$-AP and $H_2$-AP flames (Figures 8 and 9) even though the low temperature of this flame, 800 to 900°C, would lead one to expect reduced emission levels.  In addition to the observation that this emission could not be CO, we note further that it is not due to a product of combustion involving a fuel.  Obviously, it is a product of AP decomposition.  $N_2O$ has a very strong absorption line at 4.5µ, while $NO_2$ has a very weak one at the same point [35].  Other probable products--

such as, $ClO_2$, $Cl_2O$, and $NOCl$--had no absorption lines which corresponded to the unidentified emission peak.

## F.  POLYMER-VS.-AMMONIUM-PERCHLORATE FLAME

The polymer-*vs*.-AP flame was quite different in character from the others.  It was bright yellow in color but was opaque to the source beam and very close to the face of the polymer rather than being in the middle of the gap, as were the gaseous-fuel flames.  The emission trace, Figure 11, approached the absorption trace as the beam approached the polymer face.  Spectrograms of the flame region in the visible range showed both the sodium-D emission and a continuum.  The continuum and the flame opacity can both be explained by the presence of incandescent carbon particles.

A rather large amount of background (continuum) radiation is present in all of the spectrograms relative to the flames with gaseous fuels.  The HCl emission is detected in Spectrograph 3, which is as near the polymer face as spectra can be seen due to the interference of the flame.  Even in this flame, with glowing carbon particles present, no hint of CO is detected at $2.3\mu$.

Plots of the peak heights would not be expected to be like those for the gaseous-fuel flames because the flame is very near the polymer and the fuel side of the flame cannot be scanned.  The $4.4\mu$-$CO_2$-to-$2.9\mu$-$H_2O$ peak-height-ratio plot fulfills expectations, being low and not exhibiting extrema, as observed in the $CH_4$-AP flame.  However, both the $CO_2$ and $H_2O$ peak heights, plotted separately in Figures 12 and 13, exhibit maxima in the middle of the gap.  These maxima are probably due to attenuation of the beam as the beam approached the flame and are not

believed to indicate a maximum in either temperature or concentration.


## G.  POLYMER (1% COPPER CHROMITE)-VS.-AMMONIUM-PERCHLORATE FLAME

Addition of 1% copper-chromite catalyst to the polymer did not change the characteristics of the flame in any observed way.  Ignition phenomena, visual appearance, and plots of peak heights are quite similar.


## H.  POLYMER-VS.-AMMONIUM-PERCHLORATE (0.1% COPPER CHROMITE) FLAME

This flame was much like the uncatalyzed flame.  It was opaque and very close to the polymer but was visibly much more vigorous than the uncatalyzed flame.  As in the other polymer flames, the $CO_2$ and $H_2O$ plots have maxima in the middle of the gap.

# CHAPTER V.   CONCLUSIONS.

The chemical arc offers an approximately one-dimensional, quasi-steady, space-distributed combustion system convenient for spectroscopic study.  It has certain limitations, however; such as, it is impossible to vary independently all of the stoichiometric variables that can usually be varied in propellant combustion studies.  This is due to the fact that the AP consumption rate adjusts itself automatically to accommodate a change in the gaseous-fuel flow rate.  Burning rate can still be adjusted by an increase in the fuel flow rate.  When a solid fuel is used, control of this variable is lost also.  The arc is a departure from the physical situation found in propellant.  There, the polymer and AP are in contact or have, at most, a very small gap between them.  Also, the flow patterns are not simple, nor are they easily discerned.

There are certain advantages to analyzing this phenomenon.  The sources of reactants and the zone of intense reaction are separated in space; thus, the chemistry of the flame is conveniently distributed in a region large compared with the spectrometer view.

In this work, the absorption spectra were of little value, a disappointment because absorption is generally preferred.  Most molecules are in the ground state and respond to absorption, whereas emission is associated with the small fraction of excited molecules and may be misleading as an index of concentration.  The reason why absorption measurements were not of much use is, basically, that the path-length-

pressure product was not great enough. Another problem was that the radiation source was not hot enough. Its temperature, about 1100°C, was actually much less than that of the flame, above 2000°C.

Spatial resolution was marginal, of the order of 0.1 inch, which is large compared with the thickness of the flame. If intermediates form and react again in a narrow band, they would have to be in high concentration to make their presence known. A probe could be used to withdraw samples, thus reducing the spatial resolution significantly; but the species have time to react after being withdrawn. This procedure would be questionable in this situation. It would, however, yield interesting supplementary data.

Even with these limitations and disadvantages, use of the spectrometer yielded several interesting results.

Probably the most interesting result bearing on chemical mechanisms is the distribution of HCl, to which the saw-tooth structure near 3.8μ is attributed. In both the $CH_4$-AP and the $H_2$-AP systems, this spectrographic feature was observed near the fuel source of the diffusion flame but not close to the AP. Since sodium-D-line comparison indicated nearly the same temperatures on the two sides, we cannot explain large differences in HCl emission by invoking a temperature effect. We conclude that HCl is not a primary product of AP gasification, whatever that process may be, and that the chlorine flows and diffuses to the flame in another molecular form, probably combined with oxygen. Strong indications of $CO_2$ very near the frit ($CH_4$-AP system) suggest that some reactive oxidizing species survive the flame and find their way close to the fuel source.

Another very interesting result is that CO was not detected, even

on the fuel side of the $CH_4$-AP flame, although $CO_2$ appeared to be abundant there. If CO is present in significant concentrations, it is present in a zone very narrow compared with the spatial resolution of the spectrometer. (Emission in the spectral region where CO is to be sought, 4.5 to 4.6μ, is tentatively attributed to $N_2O$.) The inference is that, if CO is an intermediate in the combustion process, it is short-lived, as one would expect of Cl-O compounds are present to oxidize it.

The presence of carbon particles in the gas phase made spectroscopic observations very near the polymer impossible. This difficulty was anticipated at the initiation of the study. However, the expectation that parts of the distributed flame zone would be free of solid particles justified investigation. In these zones, some interesting results were noted.

In this system, as in the gaseous-fuel flames, HCl was not detected near the ammonium perchlorate but was detected as near the polymer as could be seen. Again, it is surmised that HCl is not a primary gasification product but is formed in a secondary reaction in the gas phase, probably from a chlorine-oxygen compound such as ClO or $ClO_2$. Risking unsupported extrapolation, we suggest that some of these powerfully oxidizing species may survive the flame and reach the polymer surface to participate in polymer decomposition in the oxidative pyrolysis process discussed by Cheng [6].

If we extend speculation to composite-propellant combustion, we would postulate that there, too, the AP gasifies, not in the decomposition flame to the ultimate products reported by some investigators

(see Chapter II) but, rather, to intermediates, including Cl-O compounds. Some of these species attack the polymer surface to gasify the fuel. Final reactions then occur in the gas phase. These findings, based on the HCl distribution, represent the attainment of one of the major objectives of this investigation.

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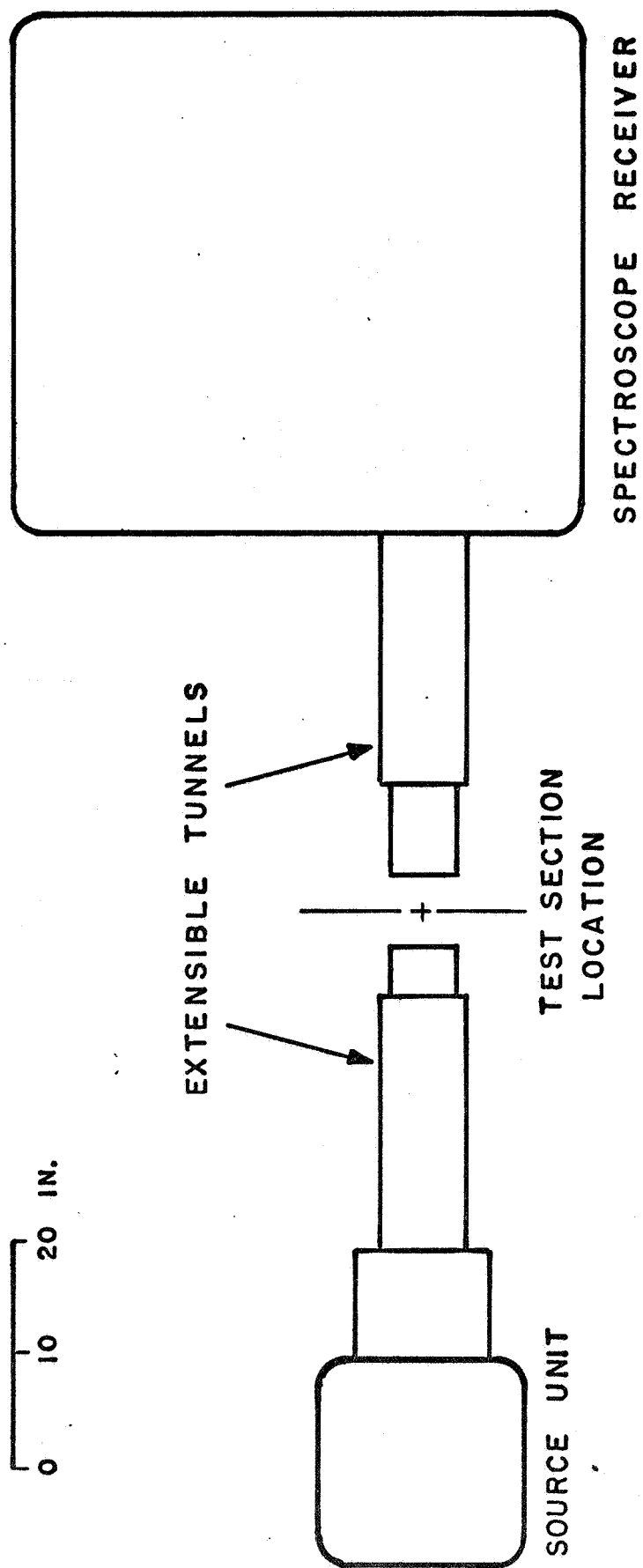
FIGURES

SPECTROSCOPE RECEIVER

EXTENSIBLE TUNNELS

TEST SECTION LOCATION

EXTENSIBLE TUNNELS

SOURCE UNIT

0    10    20    IN.

FIG. 1    SCHEMATIC DIAGRAM OF APPARATUS

IGNITER LEADS

EXHAUST VENT

WINDOW

AP PELLET

FUEL INLET

INCHES

0  1  2  3  4

FUEL FRIT (MAY BE
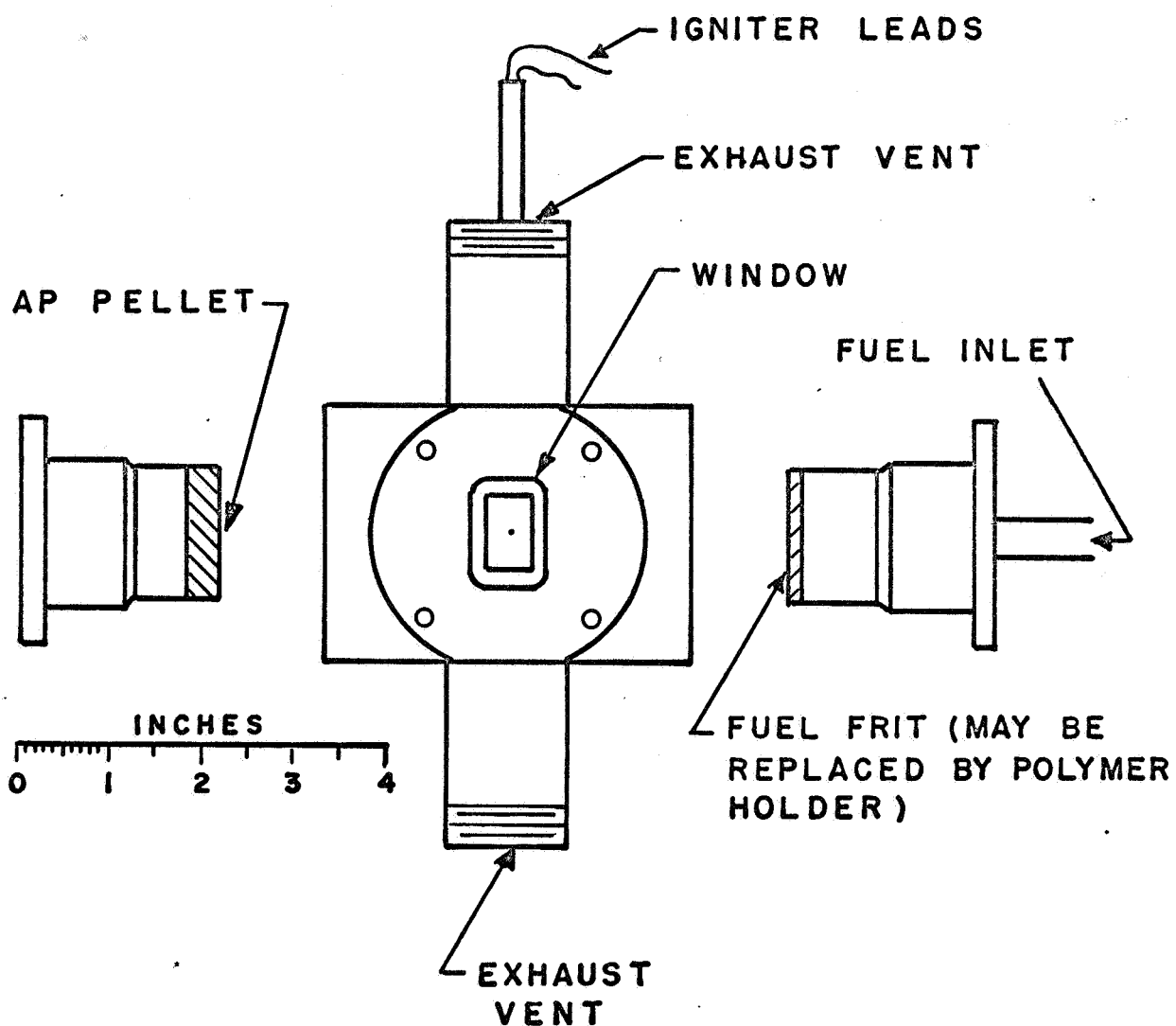REPLACED BY POLYMER
HOLDER)

EXHAUST
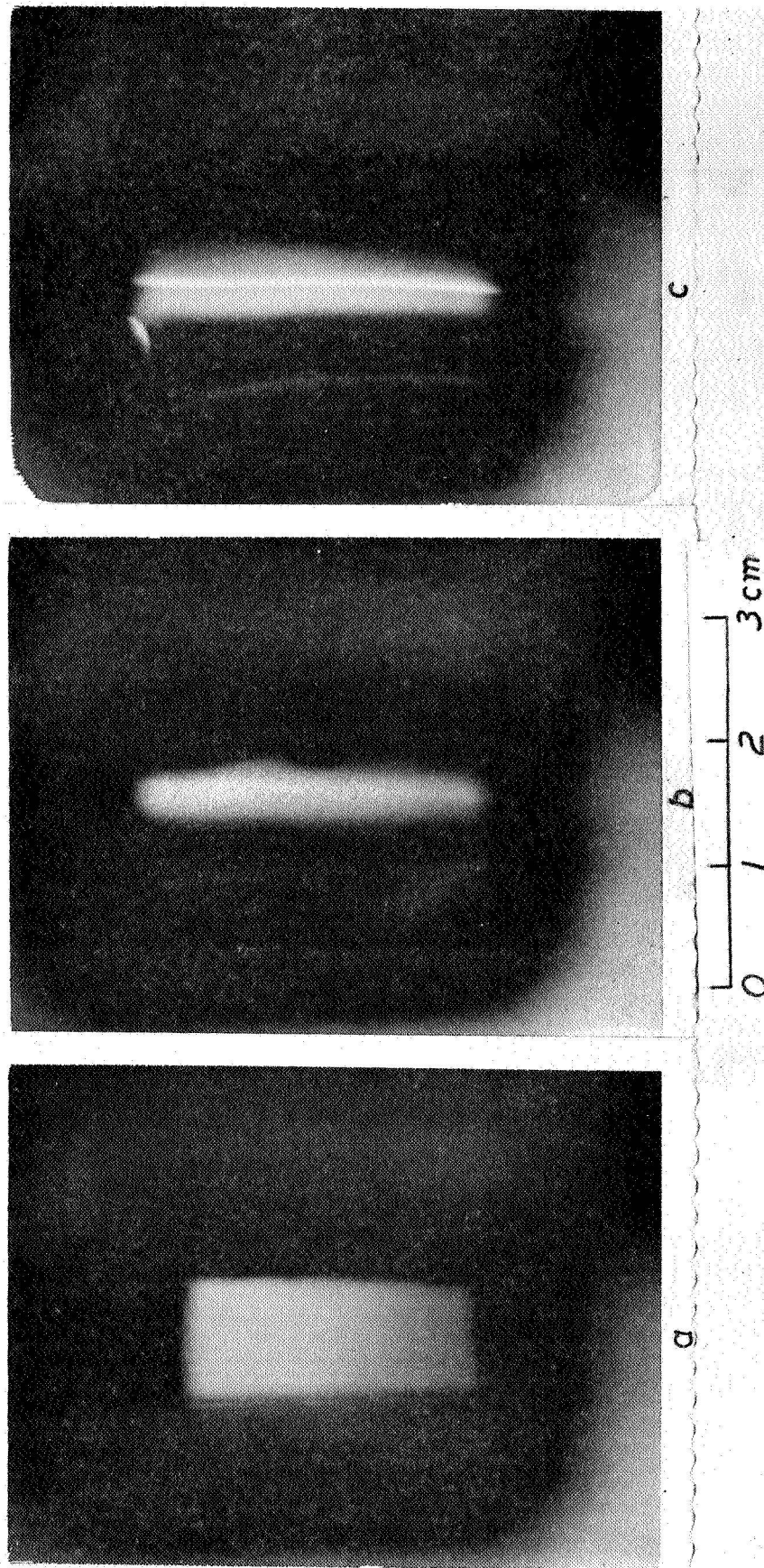VENT

FIG. 2     SKETCH OF BURNER

Figure 3.   PHOTOGRAPHS OF METHANE *vs* AMMONIUM PERCHLORATE FLAME

The methane flow rate was 2.5 lit/min and a 20 gm AP pellet was consumed in 1.3 minutes. The window holder, out of focus, can be seen around the combustion chamber. It furnishes a reference frame for the combustion zone. Photograph (a) shows the back-lighted chamber prior to ignition. Photograph (b) shows the flame shortly after ignition was complete. Photograph (c) shows an edge on view of the steady-state flame with its sharp flame sheet and diffuse halo. In (b) and (c), the chamber was not back-lighted.
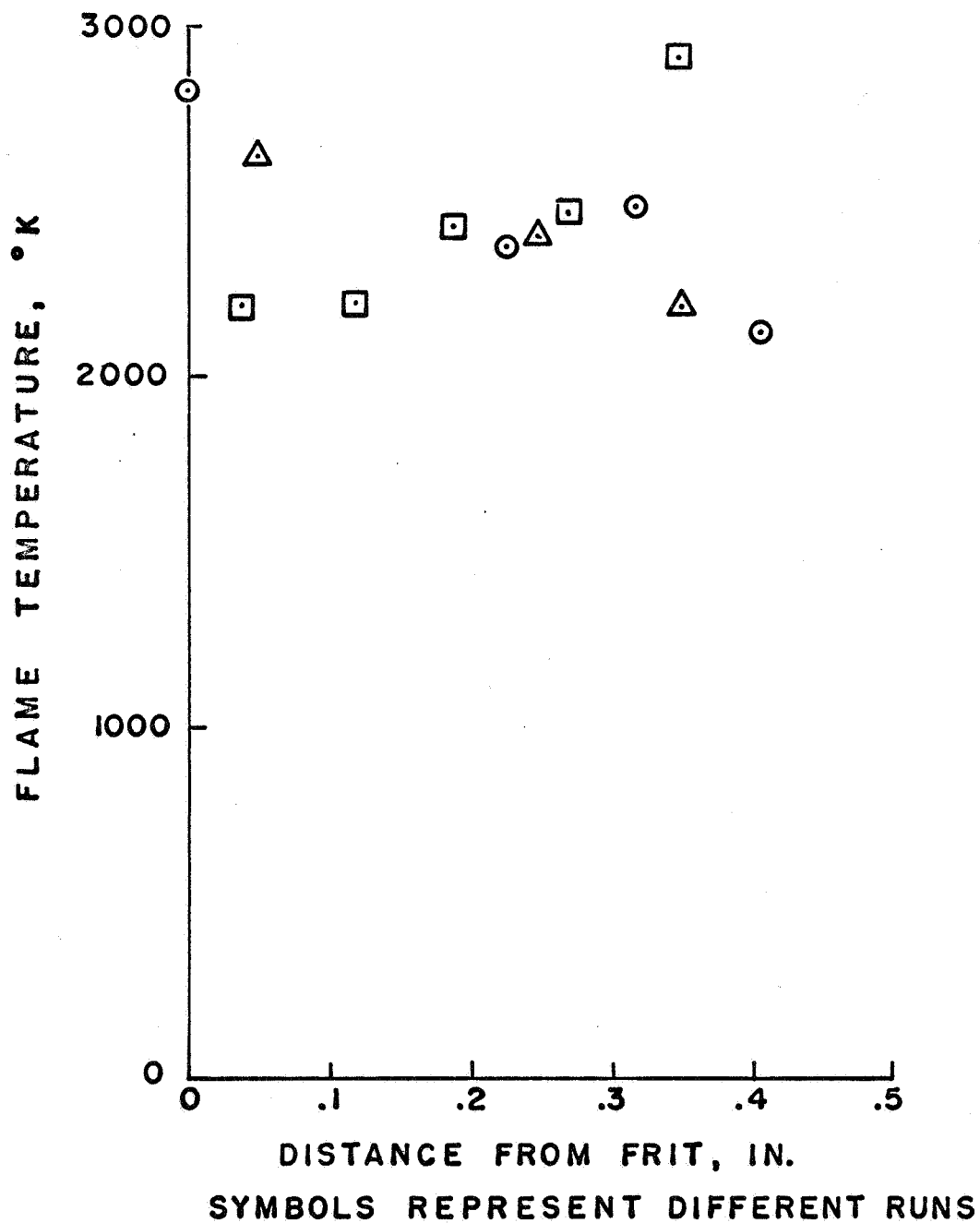
FIG. 4          FLAME TEMPERATURES
CH$_4$ (2.5 LPM) vs AP

WAVELENGTH, μ

WAVELENGTH, μ
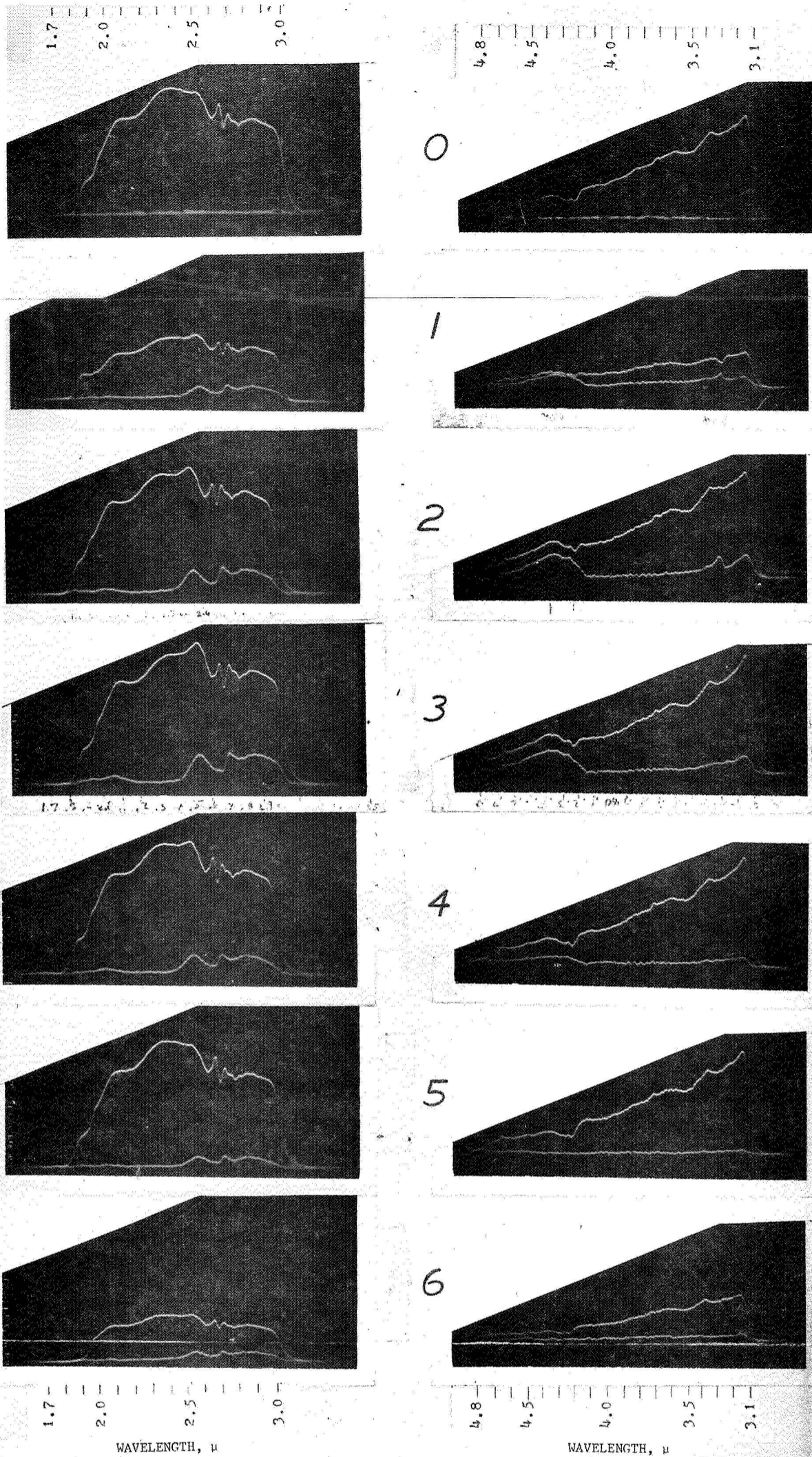
Figure 5. SPECTROGRAMS OF METHANE (2.5 lit/min)
vs AMMONIUM PERCHLORATE FLAME

Methane issued from a stainless steel frit.
A pellet of AP opposed this frit across a
0.5-inch gap. The diagram at left illus-
trates the positions of the spectrograms
in the gap. Spectrogram 0 is a calibra-
tion trace taken prior to ignition.
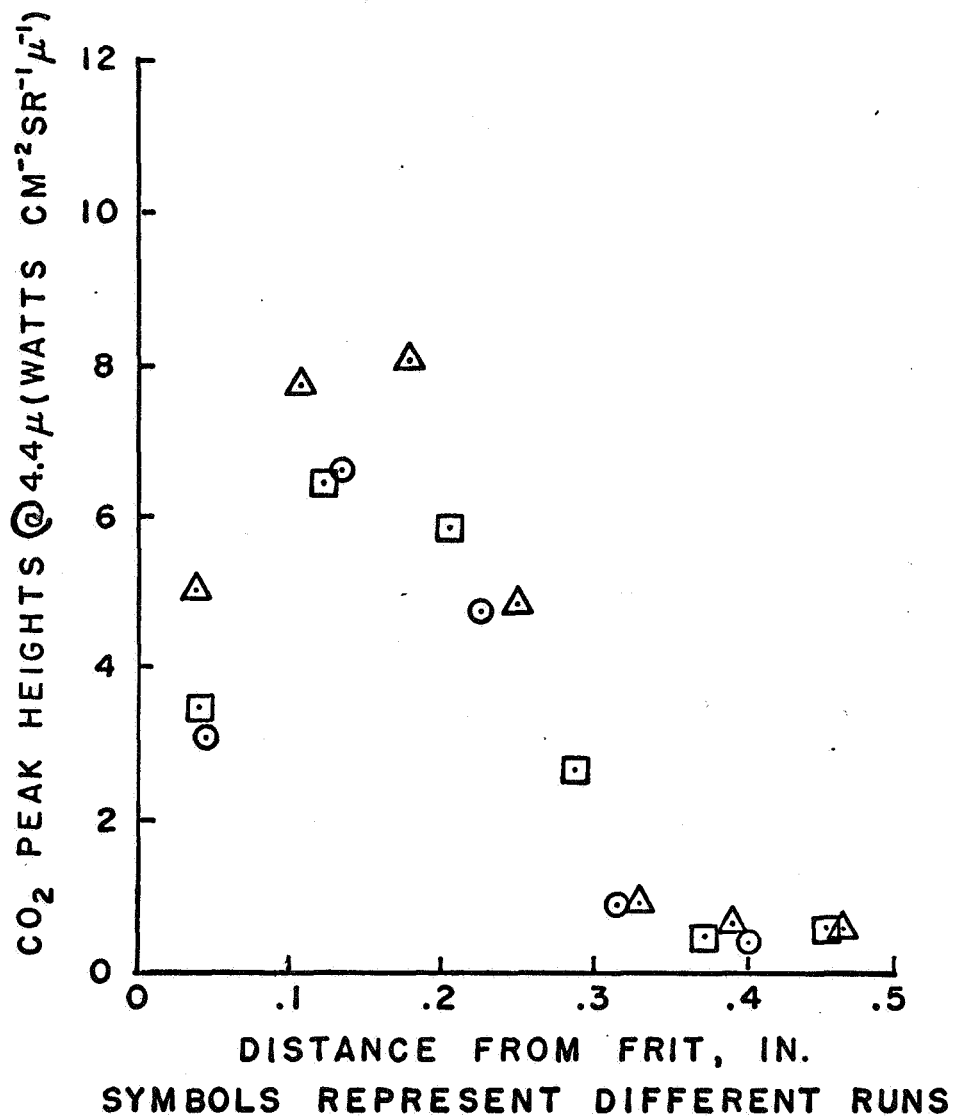
FIG. 6a    CO$_2$  PEAK  HEIGHTS

CH$_4$ ( 2.5 LPM ) vs AP
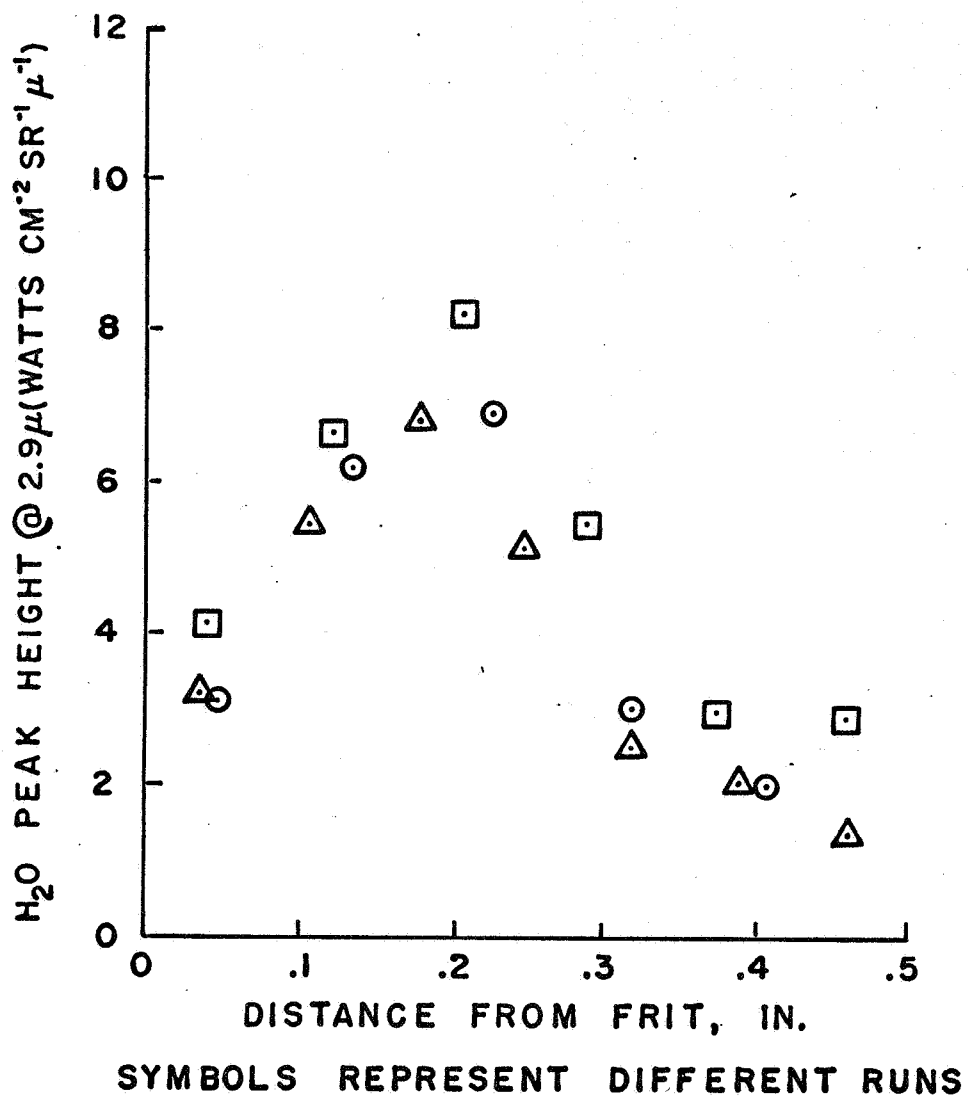
FIG. 6 b     H₂O    PEAK   HEIGHTS

CH₄ (2.5 LPM) vs AP
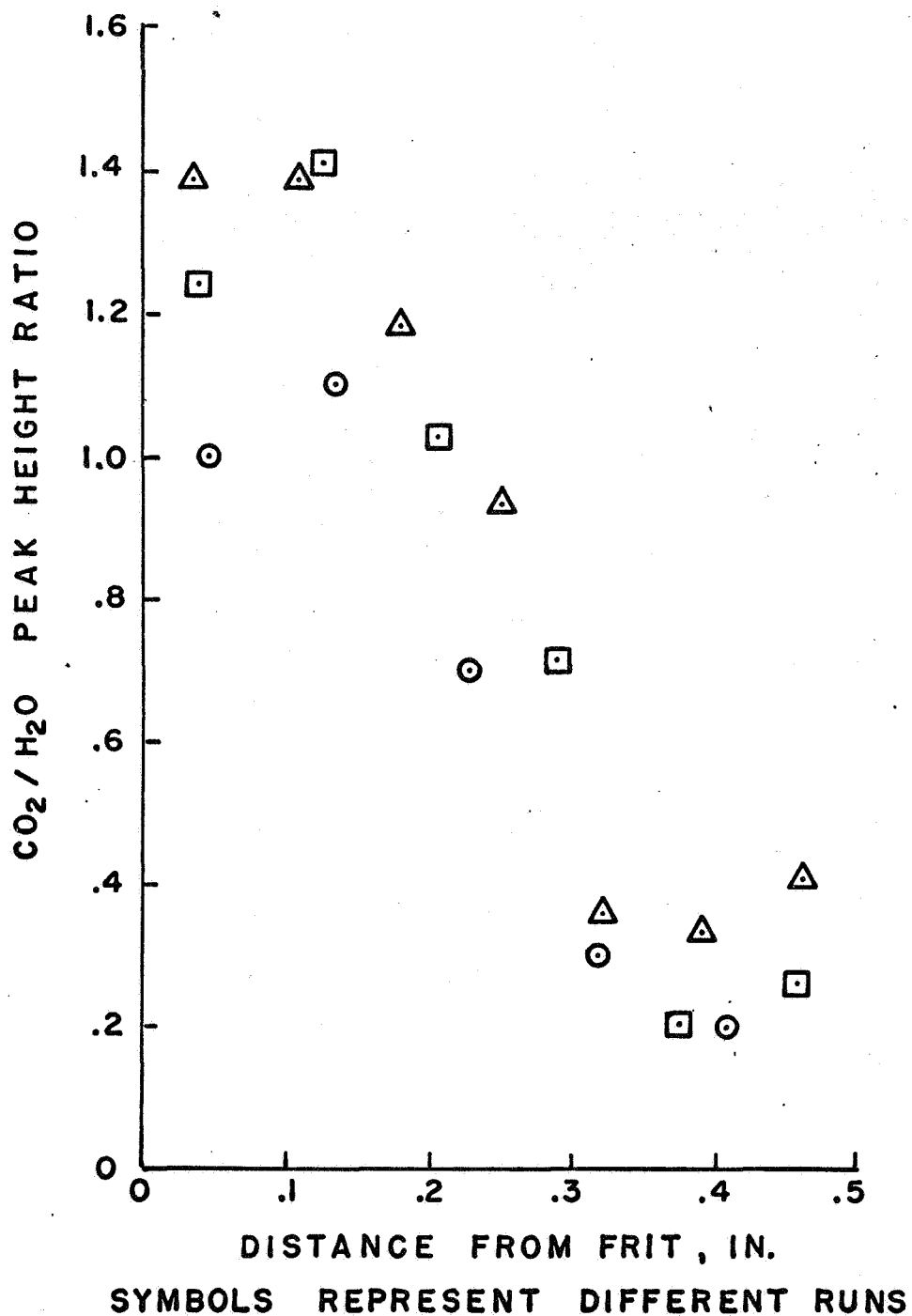
FIG. 6c        $CO_2/H_2O$ PEAK-HEIGHT RATIOS
              $CH_4$ (2.5 LPM) vs AP
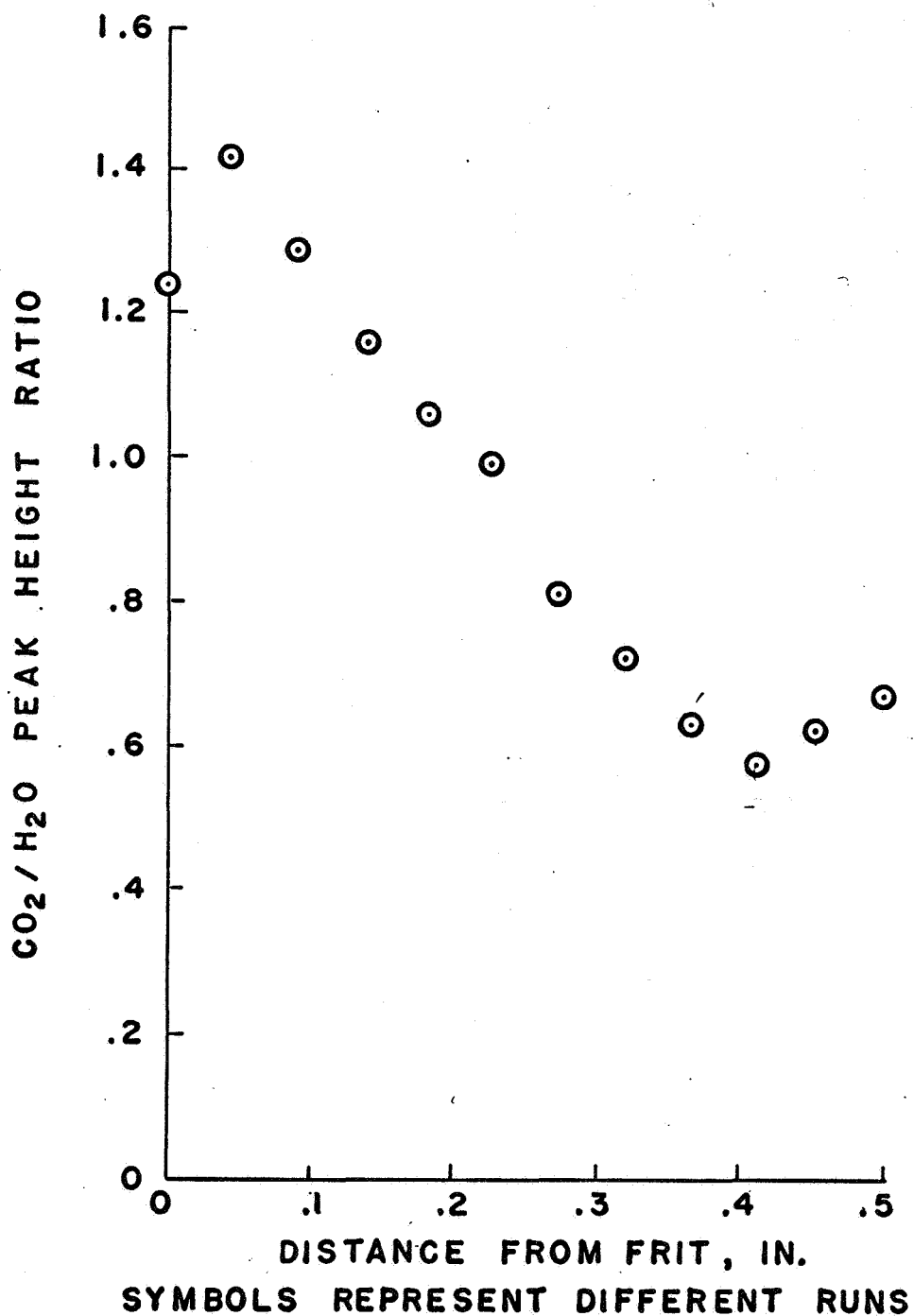
FIG. 7    $CO_2/H_2O$ PEAK - HEIGHT RATIOS
$CH_4$ (6.1 LPM) vs AP
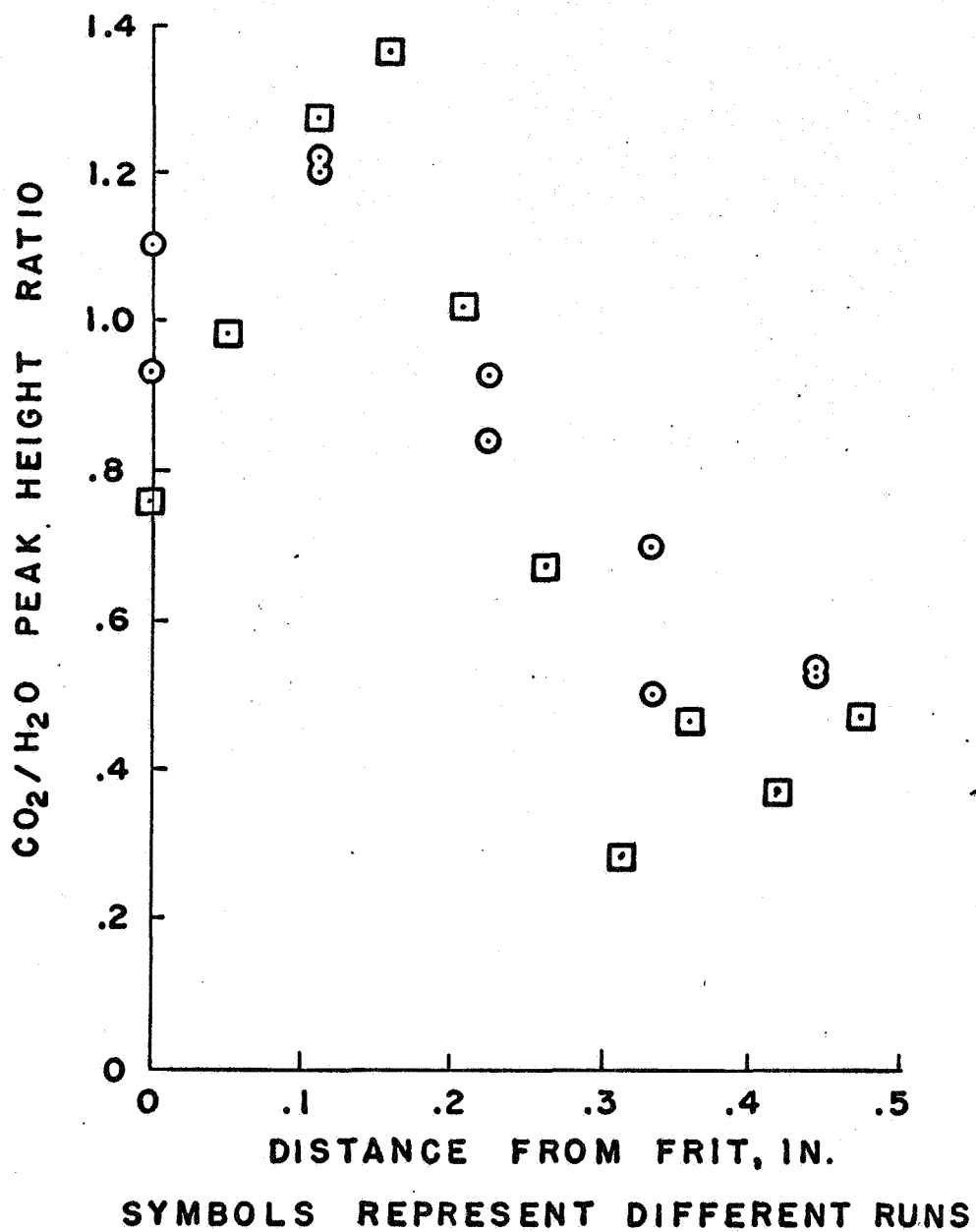
FIG. 8    $CO_2/H_2O$ PEAK HEIGHT RATIOS

$CH_4$ (2.5 LPM) vs AP(+CAT.)
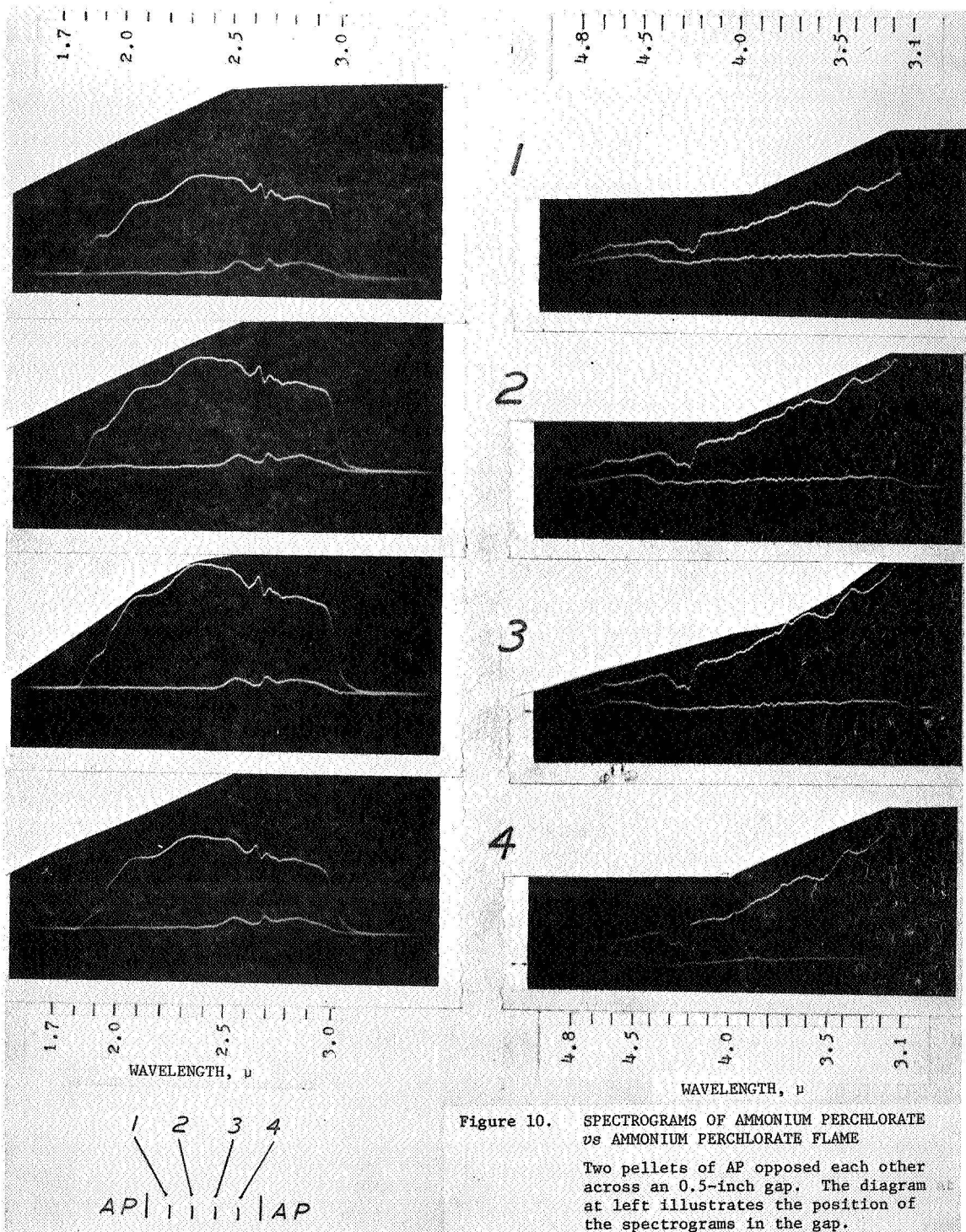
Figure 10.   SPECTROGRAMS OF AMMONIUM PERCHLORATE
*vs* AMMONIUM PERCHLORATE FLAME

Two pellets of AP opposed each other
across an 0.5-inch gap.  The diagram
at left illustrates the position of
the spectrograms in the gap.

Figure 9. SPECTROGRAMS OF HYDROGEN vs AMMONIUM PERCHLORATE FLAME

Hydrogen issued from a stainless steel frit. A pellet of AP opposed this frit across an 0.5-inch gap. The diagram at left illustrates the positions of the spectrograms in the gap.

WAVELENGTH, μ

WAVELENGTH, μ
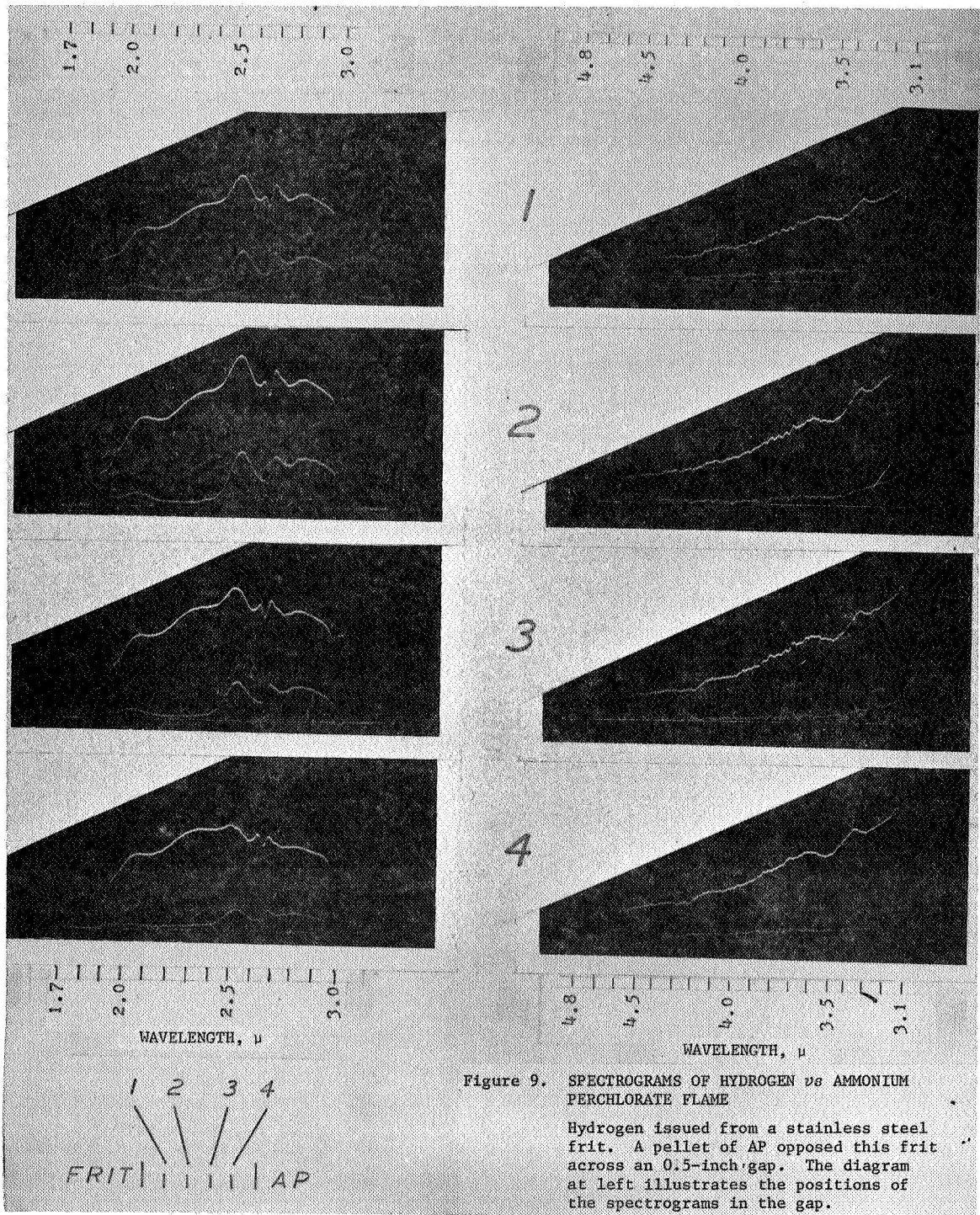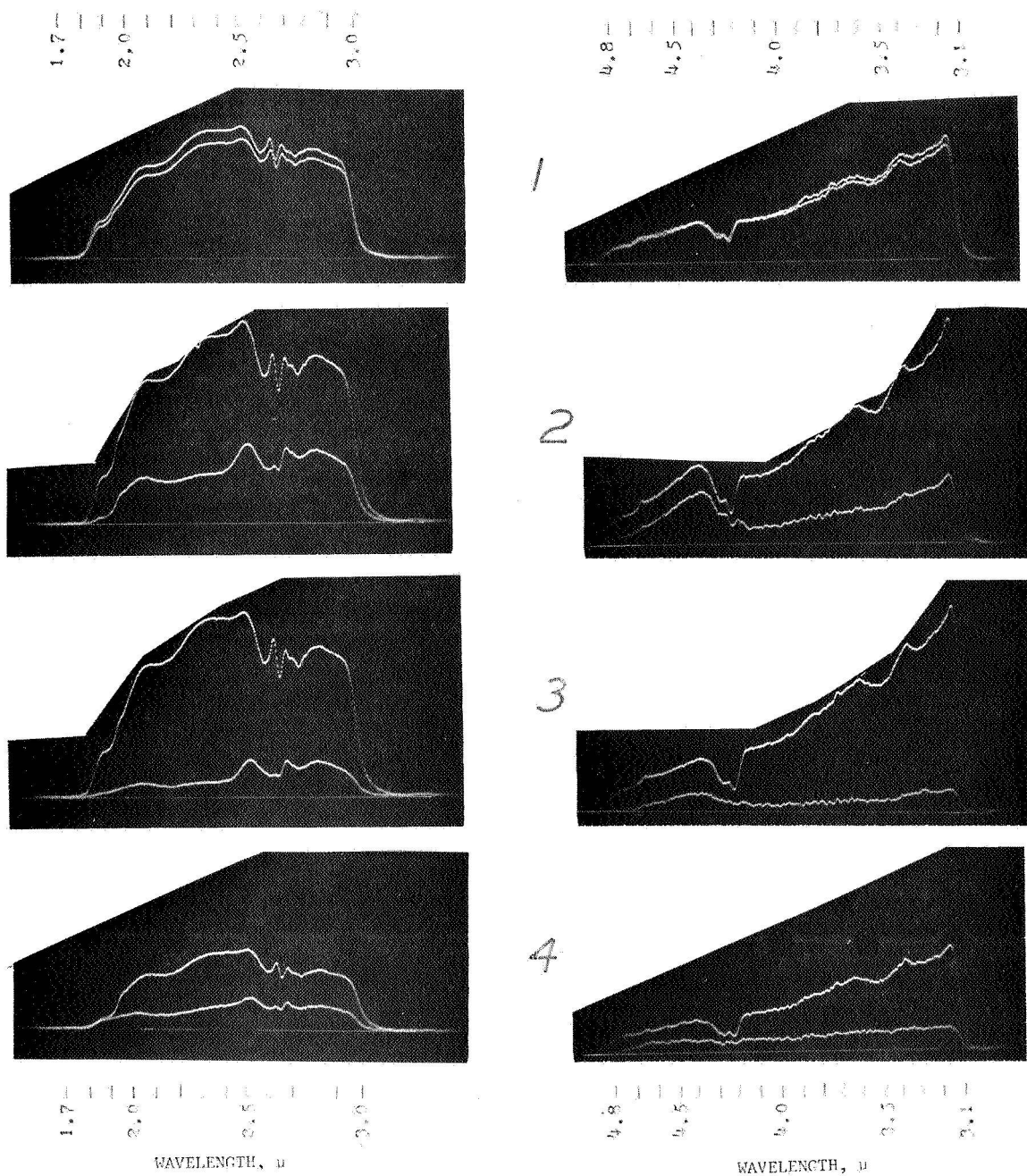
Figure 11. SPECTROGRAMS OF POLYMER *vs* AMMONIUM PERCHLORATE FLAME

A pellet of polybutadiene-acrylic-acid copolymer opposed a pellet of AP across an 0.5-inch gap. The diagram at left illustrates the positions of the spectrograms in the gap.
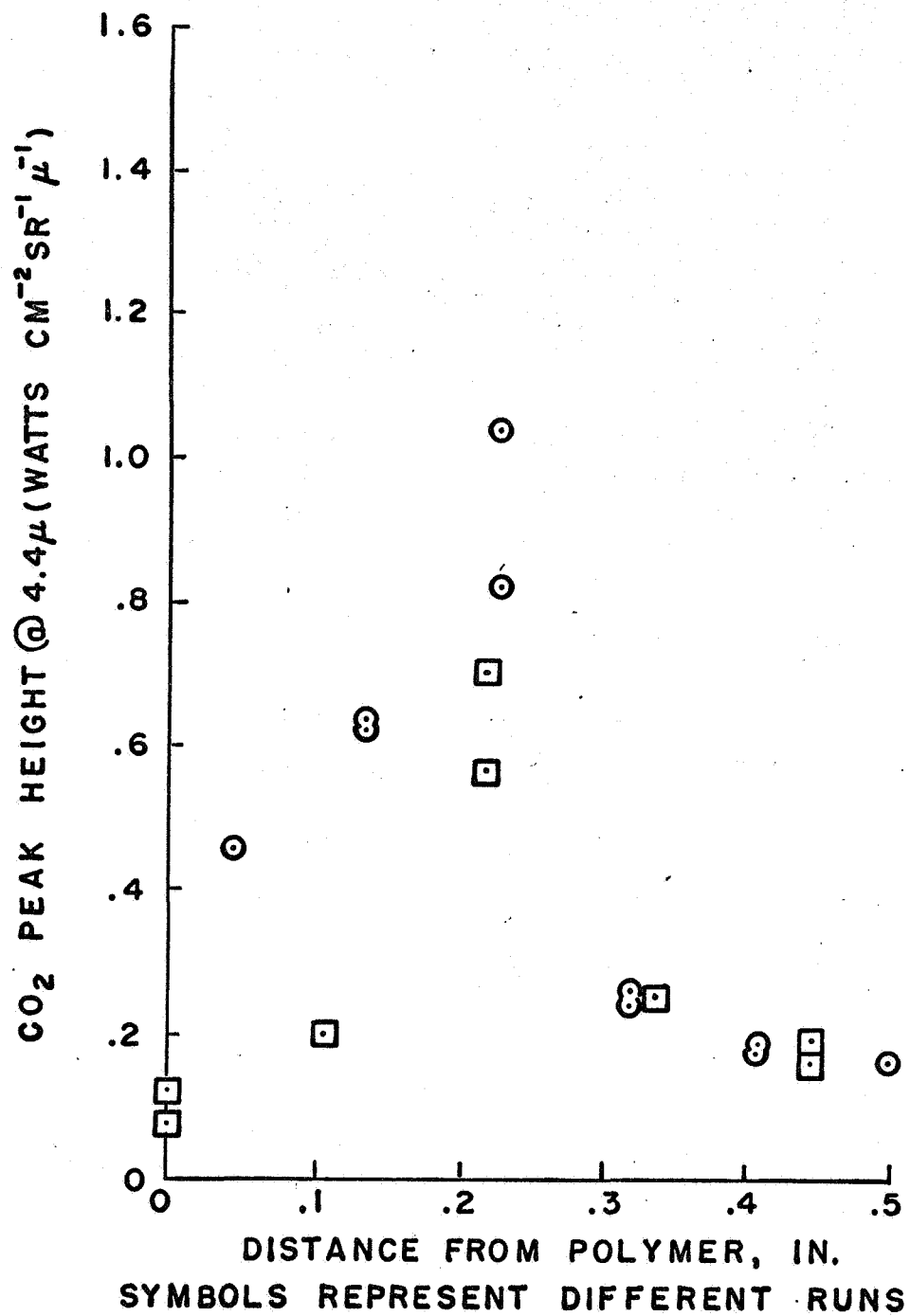
FIG. 12        CO$_2$ PEAK HEIGHTS
POLYMER vs AP
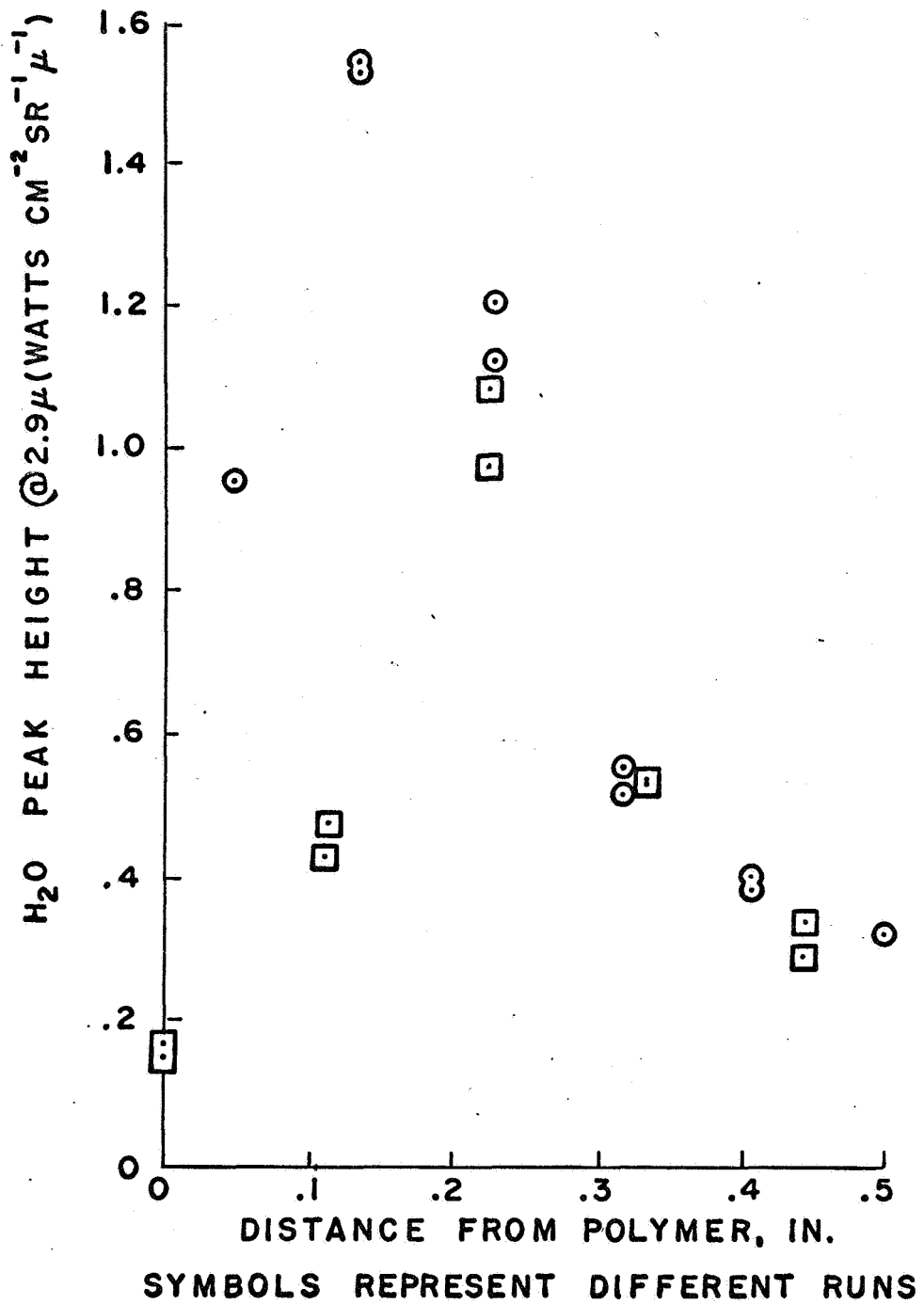
FIG. 13              H₂O  PEAK  HEIGHTS
                         POLYMER vs AP

TABLES

TABLE 1.  PEAK-HEIGHT DATA FOR METHANE (2.5 LITERS/MINUTE)

*VS*. AMMONIUM PERCHLORATE.

| Distance from Frit, inches | $CO_2$ Peak Height $(4.4\mu)$ watts $cm^{-2}$ $sr^{-1}$ $\mu^{-1}$ | $H_2O$ Peak Height $(2.9\mu)$ watts $cm^{-2}$ $sr^{-1}$ $\mu^{-1}$ | $CO_2/H_2O$ |
|---|---|---|---|
| Run 1/31/1 | | | |
| .41 | 0.4 | 2.0 | 0.20 |
| .32 | 0.9 | 3.0 | 0.30 |
| .23 | 4.8 | 6.9 | 0.70 |
| .14 | 6.6 | 6.2 | 1.1 |
| .05 | 3.1 | 3.1 | 1.0 |
| Run 2/12/1 | | | |
| .04 | 3.47 | 4.08 | 1.24 |
| .13 | 6.43 | 6.63 | 1.41 |
| .21 | 5.81 | 8.16 | 1.03 |
| .29 | 2.65 | 5.41 | .71 |
| .38 | .41 | 2.96 | .2 |
| .46 | .51 | 2.86 | .26 |
| Run 2/12/2 | | | |
| .04 | 5.40 | 3.22 | 1.39 |
| .11 | 7.73 | 5.47 | 1.39 |
| .18 | 8.06 | 6.83 | 1.18 |
| .25 | 4.82 | 5.15 | .93 |
| .32 | .90 | 2.49 | .36 |
| .39 | .67 | 2.01 | .33 |
| .46 | .56 | 1.37 | .40 |

TABLE 2. PEAK-HEIGHT DATA FOR METHANE (6.1 LITERS/MINUTE)

VS. AMMONIUM PERCHLORATE.

| Run 2/12/4 | | | |
|---|---|---|---|
| Distance from Frit, inches | $CO_2$ Peak Height (4.4$\mu$) watts cm$^{-2}$ sr$^{-1}$ $\mu^{-1}$ | $H_2O$ Peak Height (2.9$\mu$) watts cm$^{-2}$ sr$^{-1}$ $\mu^{-1}$ | $CO_2/H_2O$ |
| .5 | 1.36 | 2.03 | .67 |
| .41 | 1.57 | 2.76 | .57 |
| .32 | 3.87 | 5.30 | .72 |
| .23 | 9.0 | 9.1 | .99 |
| .14 | 6.27 | 5.4 | 1.16 |
| .05 | 3.24 | 2.36 | 1.42 |
| | 2.3 | 1.79 | 1.29 |
| .00 | 2.2 | 1.79 | 1.24 |
| .09 | 5.85 | 4.47 | 1.29 |
| .18 | 9.4 | 8.93 | 1.06 |
| .27 | 5.44 | 6.66 | .81 |
| .36 | 1.99 | 3.17 | .63 |
| .45 | 1.36 | 2.19 | .62 |

TABLE 3.  PEAK-HEIGHT DATA FOR METHANE (2.5 LITERS/MINUTE)
VS. AMMONIUM PERCHLORATE (0.1% COPPER CHROMITE).

| Distance from Frit, inches | $CO_2$ Peak Height (4.4μ) watts $cm^{-2}$ $sr^{-1}$ $\mu^{-1}$ | $H_2O$ Peak Height (2.9μ) watts $cm^{-2}$ $sr^{-1}$ $\mu^{-1}$ | $CO_2/H_2O$ |
|---|---|---|---|
| Run 2/23/3 | | | |
| .00 | 3.6 | 3.2 | 1.1 |
| .11 | 6.2 | 5.1 | 1.22 |
| .22 | 5.1 | 6.1 | .84 |
| .33 | 2.8 | 5.5 | .50 |
| .44 | 2.2 | 4.18 | .53 |
| .44 | 1.9 | 3.5 | .54 |
| .33 | 4.29 | 6.12 | .70 |
| .22 | 5.0 | 5.4 | .93 |
| .11 | 6.9 | 5.7 | 1.20 |
| .00 | 2.8 | 3.0 | .93 |
| Run 2/23/4 | | | |
| .42 | 1.02 | 2.8 | .37 |
| .32 | .93 | 2.3 | .28 |
| .21 | .60 | 5.8 | 1.02 |
| .11 | 6.1 | 4.9 | 1.27 |
| .00 | 1.2 | 1.6 | .76 |
| .05 | 2.7 | 2.7 | .98 |
| .16 | 8.2 | 6.1 | 1.36 |
| .26 | 3.2 | 4.7 | .67 |
| .37 | 1.5 | 3.2 | 1.46 |
| .47 | 1.3 | 2.8 | .47 |
| | 1.0 | 1.9 | .53 |

TABLE 4. PEAK-HEIGHT DATA FOR POLYMER *VS.* AMMONIUM PERCHLORATE.

| Distance from Frit, inches | $CO_2$ Peak Height $(4.4\mu)$ watts $cm^{-2}$ $sr^{-1}$ $\mu^{-1}$ | $H_2O$ Peak Height $(2.9\mu)$ watts $cm^{-2}$ $sr^{-1}$ $\mu^{-1}$ | $CO_2/H_2O$ |
|---|---|---|---|
| | | Run 2/27/1 | |
| .14 | 6.26 | 15.45 | .402 |
| .23 | 10.41 | 12.16 | .85 |
| .32 | 2.41 | 5.2 | .46 |
| .41 | 1.96 | 4.03 | .201 |
| .50 | 1.66 | 3.2 | .50 |
| .41 | 1.89 | 3.81 | .49 |
| .32 | 2.64 | 5.57 | .47 |
| .23 | 8.22 | 11.28 | .73 |
| .14 | 6.33 | 15.31 | .41 |
| .05 | 4.6 | 9.59 | .48 |
| | | Run 2/28/2 | |
| .44 | 1.66 | 2.84 | .59 |
| .33 | 2.56 | 5.29 | .48 |
| .22 | 5.62 | 9.7 | .57 |
| .11 | 2.04 | 4.02 | .51 |
| .00 | .77 | 1.47 | .52 |
| .00 | 1.28 | 1.66 | .77 |
| .11 | 2.04 | 4.7 | .13 |
| .22 | 7.03 | 10.87 | .65 |
| .33 | 2.56 | 5.39 | .47 |
| .44 | 1.92 | 3.33 | .57 |

# APPENDIX A: LINE-HEIGHT-COMPARISON TECHNIQUE
## FOR MEASUREMENT OF FLAME TEMPERATURES.

The method utilizes measurements, at the wavelength chosen, of the line height, $h_\varepsilon$, of the flame-emission-trace record above the baseline and measurements of the line height, $h_a$, of the absorption trace (flame plus source lamp) above the height of the trace for the source lamp alone. The first, $h_\varepsilon$, is proportional to energy emitted by the flame; and the second, $h_a$, to flame emission plus transmitted energy from the source lamp less source-lamp energy:

$$h_\varepsilon \propto B_{F_\lambda},$$

$$h_a \propto B_{F_\lambda} + B_{R_\lambda} \left( \pi_{F_\lambda} - 1 \right).$$

Here $\pi_{F_\lambda}$ is the transmissivity of the flame. If the flame neither reflects nor scatters the source-lamp beam [26],

$$\pi_{F_\lambda} = 1 - \alpha_{F_\lambda}.$$

Kirchoff's law is used to equate the flame's absorptivity, $\alpha_{F_\lambda}$, to its emissivity, $\varepsilon_{F_\lambda}$. The above relationships can then be combined as

$$\frac{h_a}{h_\varepsilon} = 1 - \frac{B_{R_\lambda} \varepsilon_{F_\lambda}}{B_{F_\lambda}} . \tag{A-1}$$

The energy rates can be expressed by Wien's law, which applies here:

$$B_{R_\lambda} = C_1 \lambda^{-5} e^{-\left( C_2 / \lambda T_{be} \right)}, \qquad B_{F_\lambda} = \varepsilon_{F_\lambda} C_1 \lambda^{-5} e^{-\left( C_2 / \lambda T_F \right)},$$

where $T_{be}$ and $T_F$ are the source and flame temperatures, respectively. If these two expressions are substituted into Equation (A-1), rearrangement produces

$$\frac{h_a}{h_\varepsilon} = 1 - \exp\left(-\frac{C_2}{\lambda\,T_{be}} + \frac{C_2}{\lambda\,T_F}\right),$$

$$\frac{1}{T_F} = \frac{1}{T_{be}} + \frac{\lambda}{C_2}\,\ell n\left(1 - \frac{h_a}{h_\varepsilon}\right). \tag{A-2}$$

If a variable-temperature source were used, $T_{be}$ could be adjusted such that $h_a = 0$; thus,

$$T_F = T_{be}.$$

This is known as the line-reversal temperature-measurement technique.

The use of Equation (A-2) requires knowledge of the effective black-body source temperature, $T_{be}$. A source temperature, $T_p$, was measured at $\lambda_p = 0.653\mu$ with a Leeds and Northrup Model 8632-C optical pyrometer. If $T_R$ is the source temperature, Wien's law gives

$$C_1\,\lambda_p^{-5}\,e^{-\left(C_2/\lambda_p\,T_p\right)} = \varepsilon_p\,C_1\,\lambda_p^{-5}\,e^{-\left(C_2/\lambda_p\,T_R\right)},$$

thus defining $\varepsilon_p$, source emissivity, at $\lambda_p$. Similarly, at $\lambda_D$,

$$C_1\,\lambda_D^{-5}\,e^{-\left(C_2/\lambda_D\,T_{be}\right)} = \varepsilon_D\,C_1\,\lambda_D^{-5}\,e^{-\left(C_2/\lambda_D\,T_R\right)}.$$

Dividing one equation by the other gives

$$\frac{1}{T_{be}} = \frac{1}{T_p} + \frac{\lambda_p}{C_2}\,\ell n\,\varepsilon_p - \frac{\lambda_D}{C_2}\,\ell n\,\varepsilon_D. \tag{A-3}$$

Forsythe and Worthing [11] have published emissivities for tungsten.

Combining Equations (A-2) and (A-3) yields

$$\frac{1}{T_F} = \frac{\lambda_D}{C_2}\,\ell n\left(1 - \frac{h_a}{h_\varepsilon}\right) + \frac{1}{T_p} + \frac{\lambda_p}{C_2}\,\ell n\,\varepsilon_p - \frac{\lambda_D}{C_2}\,\ell n\,\varepsilon_D.$$

Substituting the values,

$$\lambda_D = 0.589 \ ,$$

$$\lambda_p = 0.653 \ ,$$

$$\varepsilon_D = 0.44 \ ,$$

$$\varepsilon_p = 0.43 \ ,$$

$$C_2 = 1.439 \ \text{cm K}° ,$$

for all calculations gives the working equation:

$$\frac{1}{T_F} = 0.4093 \cdot 10^{-4} \ \text{K}^{°-1} \ \ell n \left(1 - \frac{h_a}{h_\varepsilon}\right) + \frac{1}{T_p} + 0.49 \cdot 10^{-5} \ \text{K}^{°-1}.$$

For a sample calculation, we use the data from an experimental point in the center of the gap,

$$T_p = 1720°C = 1993°K,$$

$$h_a = 2.96,$$

$$h_\varepsilon = 3.32,$$

to obtain

$$T_F = 2404°K.$$

## NOMENCLATURE

$B_{F_\lambda}$     brightness of flame (emission trace) at $\lambda$

$B_{R_\lambda}$     brightness of radiation source at $\lambda$

$C_1$     $3.740 \times 10^{-12}$ joules cm /sec

$C_2$     $1.439$ cm K°

$h_a$     line height above source trace

$h_\varepsilon$        emission line height above baseline

$T_{be}$        equivalent black-body temperature of the radiation source at $\lambda_D$

$T_F$        temperature of the flame

$T_p$        temperature indicated by pyrometer

$T_R$        temperature of radiation source

$\alpha_{F_\lambda}$        absorptivity of flame at $\lambda$

$\varepsilon_D$        emissivity of pyrometer filament at $\lambda_D$

$\varepsilon_{F_\lambda}$        emissivity of flame at $\lambda$

$\varepsilon_p$        emissivity of pyrometer filament [11]

$\lambda$        wavelength

$\lambda_D$        wavelength of sodium-D lines, $0.589\mu$

$\lambda_p$        wavelength at which pyrometer operates [30], $0.653\mu$

$\mu$        microns

$\pi_{F_\lambda}$        permeability of flame at $\lambda$

# APPENDIX B. IDENTIFICATION OF SPECTRA.

The only useful spectral features lay in the $1.7$-to-$4.7\mu$ region. Therefore, the following discussion will be limited to the spectra in this zone, with a few exceptions.

The first peak in this region is at about $1.9\mu$. This has been reported [36] to be an overlapping of water and $CO_2$ peaks, with water being the major contributor [37,38]. Ellis [9] reports the water peak to be at $1.8\mu$ and the $CO_2$ peak to be at $2.0\mu$. Rossman and Wood [43] found a CO emission at $2.4\mu$ and identified it as the first overtone of the $4.5\mu$ fundamental. This line was also identified by Plyler and Humphreys [37] in an acetylene-oxygen flame but at a wavelength of $2.3\mu$. Ferriso [10] has published spectra of rocket-nozzle gases which show an emission at $2.3\mu$ which is presumed to be CO, but he did not identify it.

Water exhibits rotational branch spectra, with the R branch at $2.5\mu$, O at $2.7\mu$, and P at $2.9\mu$[9,15,36,38]. Plyler and Humphreys [37] noted a possible contribution due to CO at $2.5\mu$. Though $CO_2$ [9,10,36] and, perhaps, NO [5] or OH [36] might contribute to the $2.7\mu$ peak, it is nearly all water [38]. The $2.9\mu$ peak is broad, extending as far as $3.6\mu$. Under high resolution, fine structure, including some OH rotation lines, may be seen [37]. Emission from CH ($CH_2$, $CH_3$, $CH_4$) at about $3.32\mu$ was observed [36] to be superimposed on the water emission. Spectra centered at about $3.7\mu$ are reported [28] to be due to HCl. A band peaking at $4.4\mu$ has been reported [9,36,37] to be due to $CO_2$, while, in the absence of $CO_2$, a band peaking at $4.6\mu$ and due to CO is

observed [43]. An NO peak at $5.3\mu$ was noted by Breeze and Ferriso [5].
Though numerous $C_2$-band, CN-band, and other emission spectra have been
reported [8,14] in the visible range, none were observed in this experi-
ment. A strong water emission is reported [36] at $6.7\mu$, but this is
beyond the range of the spectroscope used.

Spectra taken in a rocket nozzle have been published [28,44], and
the identification of peaks agrees with those above.