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PHENOMENA IN ROCKET ENGINES

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ABSTRACT

As part of an exploratory program of research in the chemical and physical kinetics of rocket exhaust gases, the emission spectra of rocket flames were examined with infrared, visible, and ultraviolet spectrographs of moderate dispersion. A high-speed portable grating spectrograph was constructed for observations in the visible region, and flames from rockets using ten different propellant combinations were photographed. The spectra have been analyzed and the species identified in most instances. A specially constructed infrared spectrograph disclosed a number of emission bands in the spectrum of the flame of a rocket using JP-3 and WFNA, but their identification and interpretation will require further study. Observations of the flames of rockets which will be tested in the future should be made with these instruments as well as with an ultraviolet spectrograph which is now available.

A method for recording the changes in emission spectra along the axis of rocket exhaust flames was devised and tested. The method was shown to be feasible and should be applied to the study of a wide variety of rocket flames. It should be particularly valuable in determining the structure of the exhaust flame and in studying the phenomenon of exhaust flash.

An apparatus was constructed for the examination of rocket flame absorption spectra. Preliminary experiments which were made with the equipment show that the method is promising, but further development will be necessary.

A method for measuring flame temperature was investigated in which the temperature dependence of the slope of an intensity vs wavelength curve is employed. It is recommended that this method be investigated in greater detail and that other methods, which are not dependent on a blackbody distribution, also be studied.

In particular it is recommended that a method which is based on the measurement of the ratio of intensities of two spectral lines emitted by the same flame species be investigated as a possible tool for use in mapping temperature distributions.

FOREWORD

    This report was prepared by the Aerojet Engineering Corporation, Azusa, California, under USAF Contract AF33(038)-18315, Supplemental Agreement S1(52-304). The contract was initiated under the research and development project, identified by Expenditure Order No. 460-35-9 Br-1, and it was administered under the direction of the Aircraft Laboratory, Engineering Division, Air Materiel Command.

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SECTION I

ANALYSIS OF PROBLEM

In principle, spectroscopy can contribute the following kinds of information in the study of combustion in rocket engines: (1) The identities and quantum states of the intermediates of the combustion reactions, (2) their concentrations, and (3) under certain conditions the temperature of the combustion gases.

The ultimate products of combustion are more conveniently determined by conventional methods of chemical analysis, but short-lived intermediates cannot be determined in this way. Not only is it desirable to know their identities in connection with the kinetics of combustion reactions, but it is also necessary to know what species persist in appreciable concentration in the exhaust gas so that the theoretical performance can be calculated.

The magnitude of the lifetimes of these intermediates can be estimated as follows: The number of collisions which a molecule makes per second as given by the kinetic theory for a gas consisting of a single species is:

$$4\pi n\sigma^2 \sqrt{RT/M}$$

where

n is the number of molecules per cubic centimeter

σ is the effective diameter of the molecule

R is the gas constant (8.314×10^7 ergs per degree per mol)

T is the absolute temperature

M is the molecular weight.

The effective diameter of the molecule, σ, is approximately 10^{-8} cm. Assuming a value for M of 30, a molecule thus makes about 10^9 collisions per second at room temperature and atmospheric pressure, or the time between collisions is about 10^{-9} sec. In many reactions not all collisions result in reaction and consequent disappearance of the molecule, so that probability factors of about 10^{-8} are encountered. Taking this extreme value, the lifetime for the molecule is still only approximately 0.1 sec, so that it is evident that analysis for these intermediates by direct chemical methods is not possible.

The presence of a number of these intermediates has been detected by their emission spectra. For example, the presence in flames of the radicals CH, C_2, OH, and CN is easily determined from photographs of visible and ultraviolet emission spectra. These spectra are readily excited, and their observation is further facilitated by the fact that a relatively intense emission spectrum is obtained even though the concentrations of these species are exceedingly low. Other radicals besides those which have been found in emission are undoubtedly present but are not observed because there is no low-energy electronic state to which the molecule can be excited. There may be an upper electronic state which cannot be reached by the molecule with the available excitation energy. These species can nevertheless be studied by the application of absorption techniques. The conditions are favorable for the study of these molecules in absorption since the relative number of molecules in lowest electronic states is high, and they can thus readily undergo the transition to the first allowed excited state with the absorption of a light quantum. Accordingly, the development of equipment for observing absorption spectra has been emphasized in the present work.

These considerations apply to stable molecules, as well as to the short-lived intermediates, but in the case of polyatomic molecules there is little likelihood that more than a few of these, as such, will absorb or emit light in the visible and ultraviolet regions of the spectrum. However, in the near-infrared region of the spectrum, i.e., 1 to 15μ, selective emission is usually molecular in origin, and depends on the vibration and rotation of molecules. For a given vibration-rotation band to appear in emission, the vibration must be accompanied by a change in electric moment, so that no emission is to be expected from homopolar molecules such as O_2 and N_2. Conversely, such polar molecules as H_2O and CO_2 may be expected to be relatively strong emitters. Transition probabilities, and therefore emissivities, are of an entirely different order of magnitude from those for electronic transitions, even for strong infrared emitters, and at present no integrating receiver such as photographic film is available for the infrared. Consequently, only those chemical species which are present in appreciable concentrations will yield detectable emission bands.

Fundamental vibration-rotation bands, i.e., bands which arise from a change of unity in the total vibrational quantum number, occur only in the spectral region beyond 2.5μ, so that all bands below 2.5μ are combination or overtone bands. In absorption the latter are far weaker than the fundamentals, but the energy emitted is proportional to the fourth instead of the first power of the frequency so that in emission, overtones and combination bands are of comparable intensity with the fundamentals. Hence the spectral region 1 to 2.5μ is potentially interesting.

Although the determination of the concentration of an intermediate in a flame is theoretically possible by spectroscopic means, it is very difficult in practice and has not been undertaken in the exploratory program described in this report.

In addition to the possibility of identifying chemical species through the identification of emission or absorption bands, there exists the possibility of using these bands as a basis for flame temperature measurements, provided the bands are thermally excited. Various methods based on band-intensity distribution have been described.[1] If no banded emission is observed from the flame, the temperature can be determined from the slope of the intensity vs wavelength curve of the continuum if the latter has a black-body distribution. Alternately, an emitting substance can be added to the flame, and the intensity ratio of two of the lines in the spectrum of the additive can be used as a basis for measurement of the flame temperature.

In summary, the methods of spectroscopy can be used to advantage in the study of the kinetics of combustion reactions in rocket flames, for the determination of the identity and distribution of intermediates, and for measurements of flame temperature. The following sections describe the work done for this purpose.

SECTION II

EMISSION SPECTRA OF ROCKET EXHAUST FLAMES

IN THE VISIBLE AND ULTRAVIOLET REGIONS

Experimental Details

Observations of the visible spectra of exhaust flames from rocket firings were made with the portable grating spectrograph which is shown in Figure 1 in its present form. Several modifications of the original instrument were made in the course of the program in order to reduce the setup time and facilitate the photographing of the spectra. A long section of tubing between the collimating lens and the camera was removed to permit rapid alignment of the optical system and to increase the light intensity at the camera. For most observations, the slit of the spectrograph was placed approximately 36 in. from the flame. Therefore, with the slit which is 4 in. in length, and the collimating lens which is normally used at an aperture of f/8, the camera views about 15 in. of the flame. In nearly all instances the rocket test-firings were carried out with mixture ratios close to that calculated to give maximum theoretical performance. In order to minimize the effects of afterburning on the spectra of the flames, the region nearest the nozzle of the rocket was chosen for observation. The spectral region covered extends from the limit of transmission of glass at about 3500 A to approximately 6500 A for the Super Panchro-Press, Sports Type, sheet film which was usually used.

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[1] L. Bernath, H. N. Powell, A. G. Robison, F. Weltz, and K. Wohl, Project Squid Technical Report No. 32 (1951); S. S. Penner, Am. J. Phys., 17, 422 (1949); 17, 491 (1949).
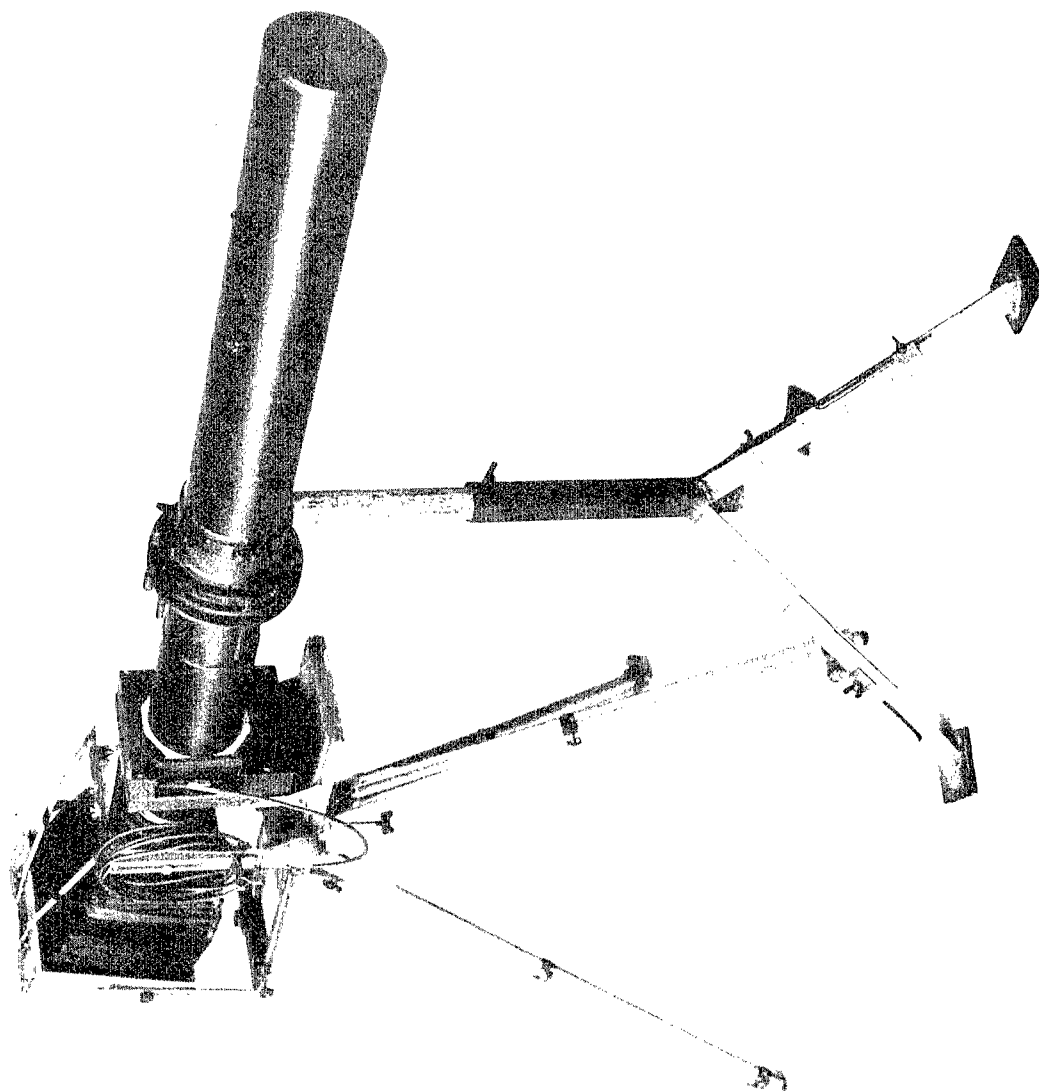
Figure 1. Portable Grating Spectrograph

0352-745

For the ultraviolet region a Hilger Intermediate Quartz spectrograph was used with a spherical condensing lens. This instrument, which was placed about 36 in. from the flame, has an f/7 camera lens and thus views about 5 in. of the flame. The spectral region covered extends from the visible to about 2100 A where the quartz begins to absorb.

Wavelengths of spectral bands and lines were measured from microphotometer traces of the spectra made with a Jarrell-Ash Co. Model 203 Recording Microphotometer. Figure 2 shows a typical spectrogram (enlarged) with the corresponding tracing (reduced).

Spectra of Boron-containing Propellant Systems

1. Experimental Results

Spectrograms were obtained of the exhaust flames of rockets using several boron-containing compounds as fuels. Among these fuels, which were prepared and tested at Aerojet, are aluminum borohydride, dimethylaminodiborane, and a 13% solution of lithium borohydride in hydrazine. The lithium borohydride serves primarily as a freezing point depressant for the hydrazine, but also yields an increase in performance over anhydrous hydrazine.[2] Aluminum borohydride and dimethylaminodiborane have been tested with liquid oxygen and with liquid fluorine as oxidizers. The lithium borohydride and hydrazine solution is currently being tested with liquid oxygen. The tests of aluminum borohydride with liquid oxygen were made prior to the initiation of the experimental work under this contract. The spectrogram[3] shown in Figure 3(a) was taken with a small Littrow quartz spectrograph so that the scale differs widely from those obtained with the grating spectrograph. It has been reproduced in this report in order to show the characteristic features of the flame spectra from boron-containing propellants.

The most prominent feature of the flame spectra from liquid propellants containing boron is the system of boric acid fluctuation bands, which are narrow diffuse bands evenly spaced over the visible region of the spectrum and commonly referred to as "waves." In the negatives, the BO bands recently reported by Singh[4] can be seen superimposed on the bands at 5800 A and 5450 A. These bands are not readily detectable because of the greater intensity of the fluctuation bands, but they are nearly always found along with the latter. The species to which the emission of the fluctuation bands is attributed has not been determined, but it is assumed that it is due to a polyatomic oxide of boron of the type B_xO_y, perhaps B_2O_3.[5] These

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[2] Aerojet Report No. 577 (7 February 1952) p. 6, Confidential.

[3] Aerojet Report No. 490 (22 January 1951) p. 21, Confidential.

[4] N. L. Singh, Proc. Indian Acad. Sci., A29, 424 (1949).

[5] R. W. B. Pearse and A. G. Gaydon, The Identification of Molecular Spectra (John Wiley & Sons, Inc., New York, 1950).
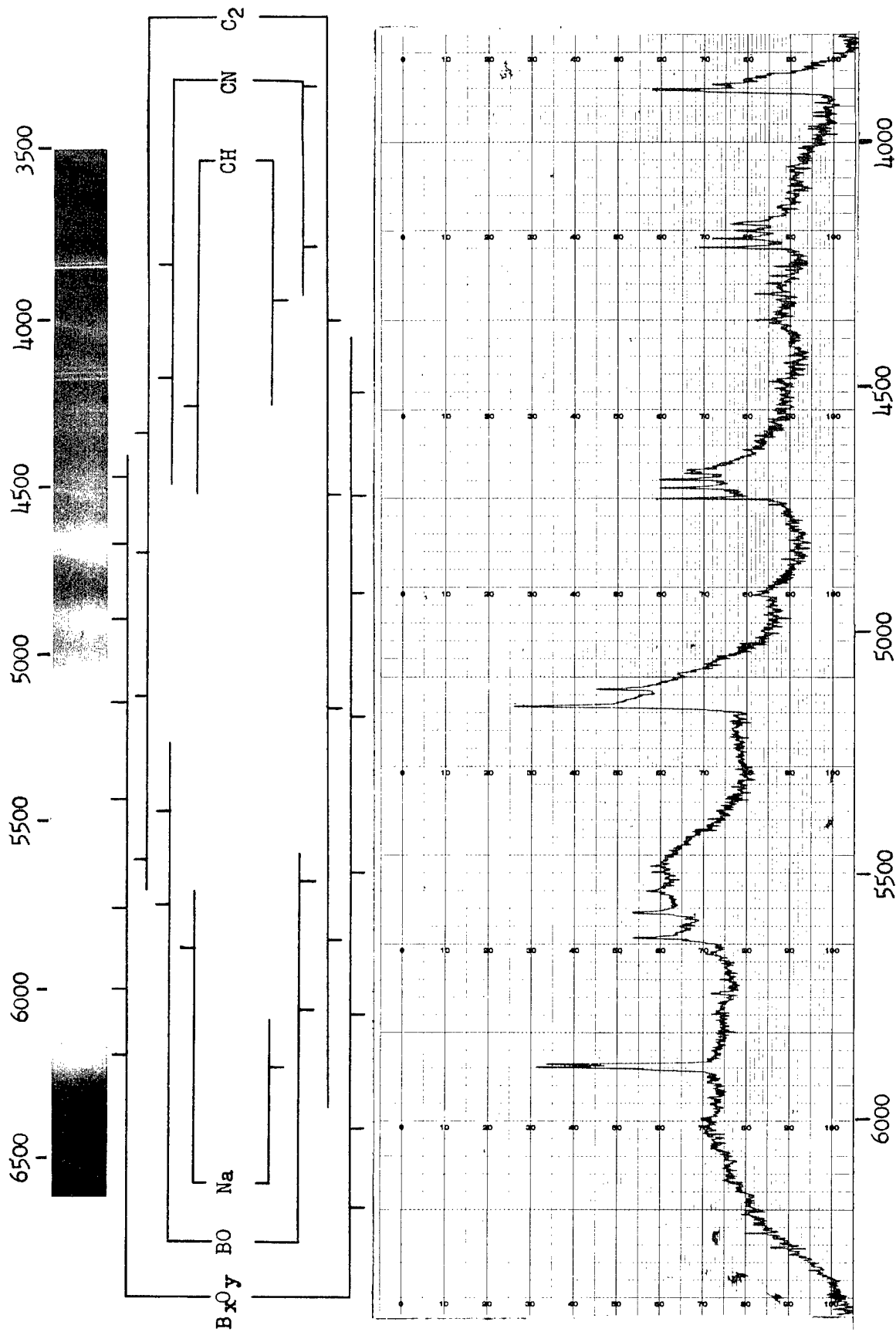
Figure 2. Rocket Exhaust Spectrum (I)

Dimethylaminodiborane with Liquid Fluorine
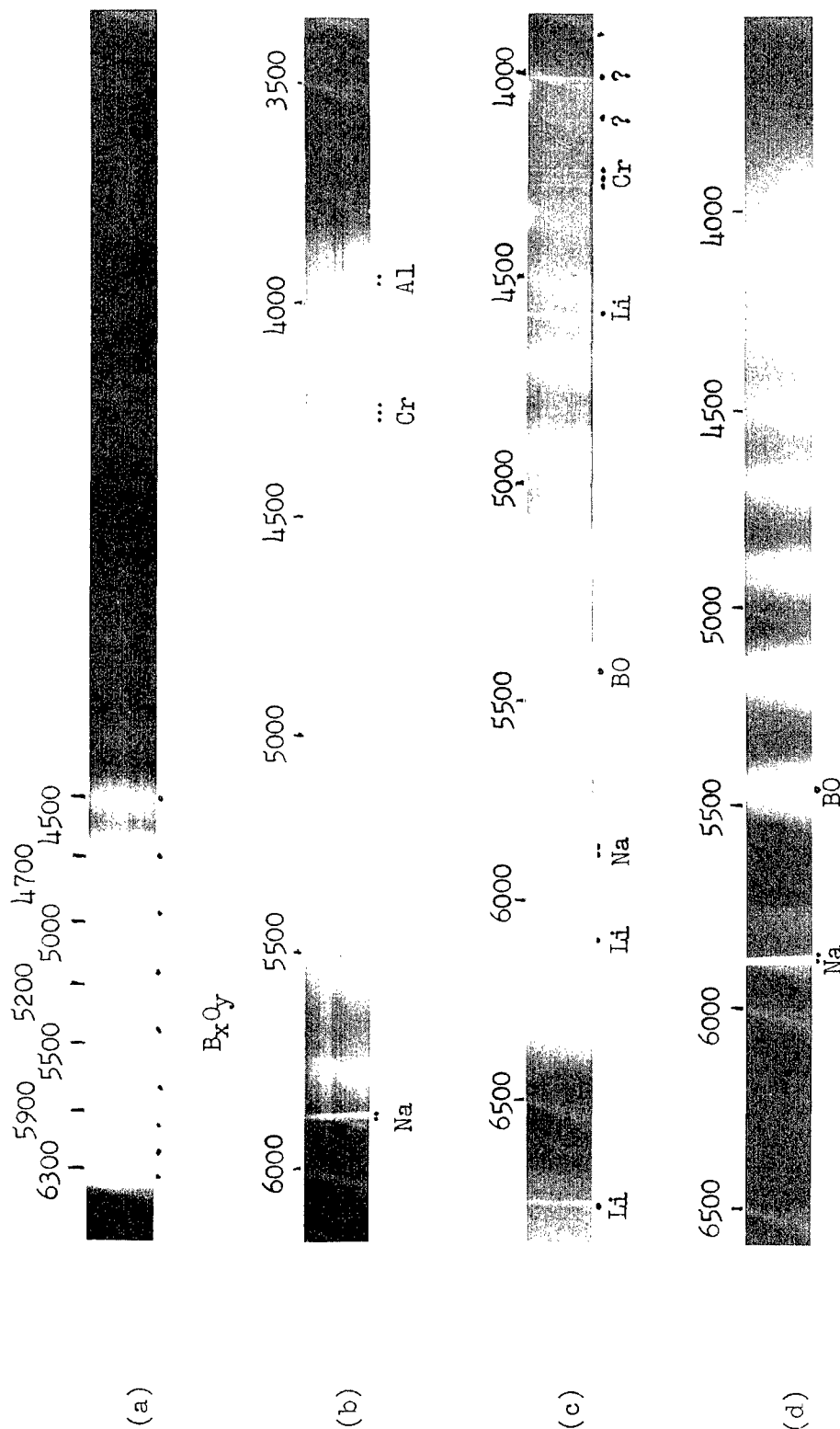
Figure 3. Rocket Exhaust Spectra (II)

(a) Aluminum Borohydride with Liquid Oxygen
(b) Aluminum Borohydride with Liquid Fluorine
(c) 13% Lithium Borohydride in Hydrazine with Liquid Oxygen
(d) Boric Acid in Flame Photometer (for comparison)

bands were also obtained in the laboratory by photographing the spectrum of a saturated solution of boric acid in the Beckmann flame photometer. The spectrum is shown in Figures 3 and 4 for comparison with the spectra of the rocket flames.

a. Aluminum Borohydride. - With liquid oxygen [Figure 3(a)] the boric acid fluctuation bands are by far the most prominent feature of the spectrum of the exhaust flame from this propellant combination. Weak bands due to other species seem to be present, but these were not identifiable from the spectrogram available.

With liquid fluorine [Figure 3(b)] , fluctuation bands are also the most prominent feature. Here the presence of some BO bands of the α system and of Mulliken's combination system can be detected. These are extremely weak and will not be found on the reproductions, but are observable on close visual examination of the original spectrogram. In addition to these are also found the aluminum doublet at 3944 A and 3962 A, the sodium doublet at 5890 and 5896 A, and chromium lines at 4290, 4275, and 4254 A. The aluminum lines are not ordinarily excited in laboratory flames. The requirement of a higher excitation energy is apparently fulfilled by the high temperature of the aluminum borohydride and fluorine flame. The chromium used as a chamber-lining material is responsible for the emission of the chromium lines. Bands appearing at 4360, 4180, 4070, 3860, and 3650 A could not be identified with any species found in the literature, but their appearance indicates strongly that they are an extension of the boric acid fluctuation band system. Although these bands do not appear in the boric acid laboratory flame, the conditions of excitation are considerably milder than those existing in the aluminum borohydride and liquid-fluorine flame. The confirmation of this point requires additional experimental observations.

b. Dimethylaminodiborane. - With liquid oxygen [Figure 4(a)] , this spectrum shows only the boric acid fluctuation bands with the superimposed BO bands of Singh. Some weak bands appear above 6000 A on some of the spectrograms which were subjected to longer exposure. The weakness of these bands made them difficult to measure, but their appearance and visual estimates of their wavelengths suggest that they may be CN bands of the red system. The testing program for this propellant combination was completed before a spectrogram could be taken to confirm this hypothesis.

With liquid fluorine [Figure 4(b)] the boric acid fluctuation bands and the BO bands of Singh are again present with considerable intensity. In addition, the Swan bands of C_2 and the violet bands of CN are quite prominent. They are especially noticeable on spectrograms where the mixture ratio (ratio of weight of oxidizer to weight of fuel, W_o/W_f) is relatively high. The high mixture ratio suppresses the fluctuation bands and permits the C_2 and CN bands to be easily observed. The 4312 A band of CH also appears weakly. The three chromium lines previously described appear on some spectrograms, and the Na doublet is always present.
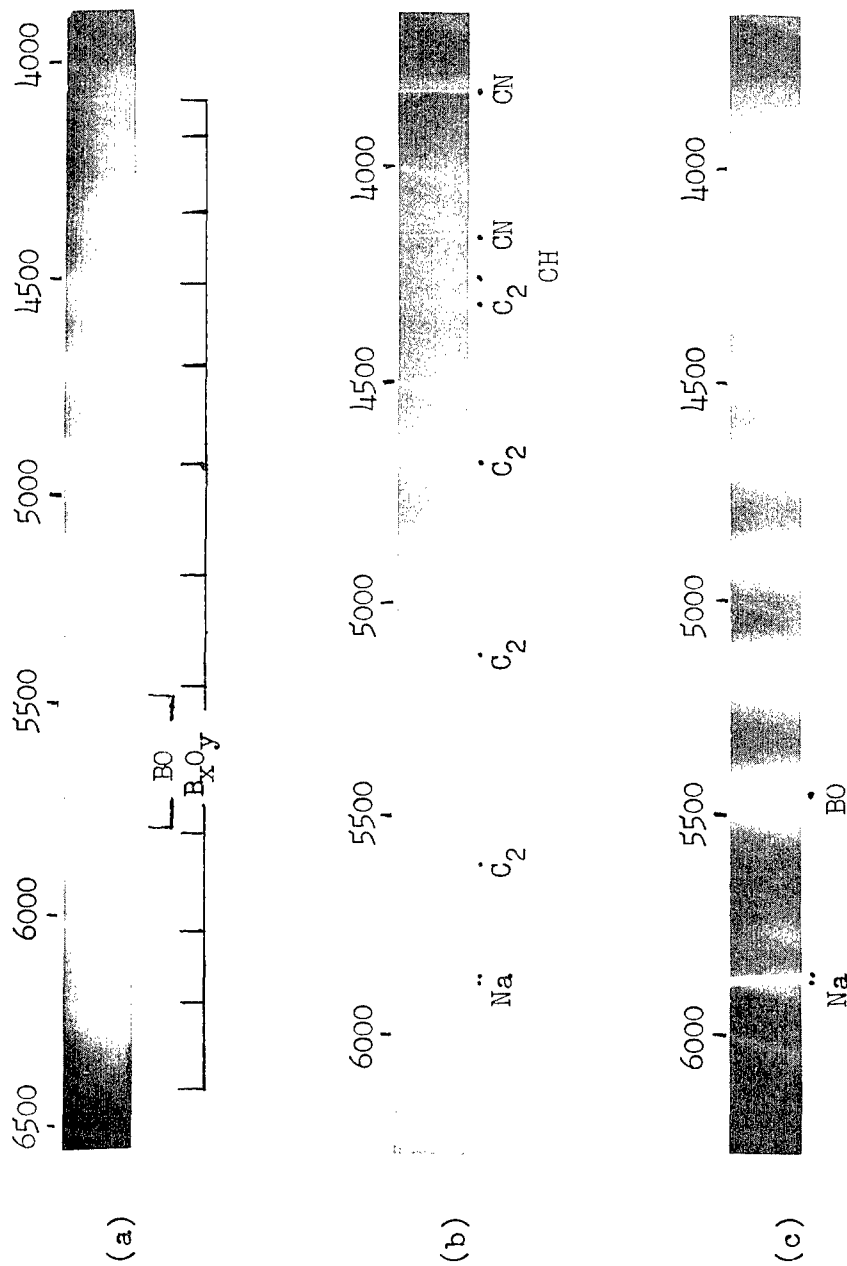
Figure 4. Rocket Exhaust Spectra (III)

(a) Dimethylaminodiborane with Liquid Oxygen
(b) Dimethylaminodiborane with Liquid Fluorine
(c) Boric Acid in Flame Photometer (for comparison)

c.   Lithium Borohydride in Hydrazine. - With 13% lithium boro-
hydride in hydrazine with liquid oxygen [Figure 3(c)] , an exhaust spectrum is
obtained which contains the usual boric acid fluctuation bands and BO bands of
Singh. Atomic lines of lithium appear at 6707.8, 6103.6, and 4603.0 A. The
Na doublet and the three chromium lines are also present. Several other
lines have been found at wavelengths of 4135, 4033, 3933, and 3861 A, but no
conclusions have been reached as to their identity.

d.   Table I summarizes the results of the emission spectro-
graphic studies in the visible and ultraviolet regions.

2.   Discussion of Experimental Results

a.   Some outstanding features are to be noted in the spectra
of flames supported by liquid oxygen and liquid fluorine. The liquid-oxygen-
supported dimethylaminodiborane flame emits with intensity only the fluctua-
tion bands of boric acid. With liquid fluorine the same bands occur, but the
presence of C_2, CH, and CN bands is marked. In addition, no fluorine-con-
taining emitter is detected. Durie[6] observed only C_2 and CH bands in a
variety of fluorine-supported organic flames. Since the corresponding
oxygen-supported flames also exhibited characteristic C_2 and CH emission,
Durie suggested that the mechanisms of burning in the two types of flames are
similar. The absence of these emitters from the dimethylaminodiborane and
oxygen flame is rather surprising. Sufficient data are not available at
present for a reliable explanation, but indicate that the parallelism in
the mechanisms of burning in oxygen- and fluorine-supported flames is not
clearly drawn.

b.   Since the fluctuation bands appear in exhaust flames of
boron-containing fuels supported by fluorine, polyatomic oxides of boron
must be formed by reaction of molecules such as BF and BF_3 with atmospheric
water or oxygen outside the rocket chamber.

c.   The presence of C_2 bands in the dimethylaminodiborane and
fluorine flame requires a polymerization reaction since no C - C bond is
present in the dimethylaminodiborane molecule. Durie reported that C_2
emission is present in flames of CH_4-F_2 as well as CH_4-O_2 and suggested that
the fluorine forms free hydrocarbon radicals which can lead to C_2 formation
and carbon deposition. The fact that in the present experiments relatively
little of the latter is found is interpreted to indicate that polymers com-
posed of relatively short chains are formed. It was observed that an in-
crease in mixture ratio causes an increase of the C_2 and CH emission. This
result could be obtained if either the radical concentration or the tempera-
ture increased. The accompanying decrease in relative intensity of the
fluctuation bands is difficult to explain. Perhaps the increase in mixture
ratio results in more of the conversion of fluorides to oxides occurring
further downstream from the nozzle.

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[6] R. A. Durie, Proc. Roy. Soc. A211, 110 (1952).

TABLE I

SPECTRA OF ROCKET EXHAUST FLAMES

Bands Observed, Wavelengths in Å

1. Aluminum borohydride and liq. fluorine

B_xO_y	B_xO_y (Fluctuation bands)	BO (Singh)	BO (Comb.)	BO (α System)	Al	Na	Cr
4360	6200	5789.5	Wavelengths not meas.	Wavelengths not meas.	3961.5	5895.9	4289.7
4180	6030	5781.0			3944.0	5890.0	4274.8
4070	5800	5777.1					4254.3
3860	5450	5478.5					
3650	5180	5395.2					
	4930	5361.2					
	4710						
	4520						

2. Dimethylaminodiborane and LOX

B_xO_y	BO (Singh)	CN (Red)
(Fluctuation bands) Same as in 1.	Same as in 1.	Not meas.

3. Dimethylaminodiborane and liq. fluorine

B_xO_y	BO (Singh)	C_2 (Swan)	CN (Violet)	CH	Cr	Na
(Fluctuation bands) Same as in 1.	Same as in 1.	6191.2	4216.0	4312.5	4289.7	5895.9
		5635.5	3883.4		4274.8	5890.0
		5165.2			4254.3	
		4737.1				
		4382.5				

(cont.)

TABLE I (cont.)

Bands Observed, Wavelengths in A

Type of Rocket Flame		
4. 13% Sol'n Lithium Borohydride in Hydrazine with LOX	B_xO_y (Fluctuation bands) Same as in 1. BO (Singh) Same as in 1.	Li 6707.9, 6103.6, 4603.0 Cr 4289.7, 4274.8, 4254.3 Na 5895.9, 5890.0 Unidentified 4135, 4033, 3933, 3861
5. JP-3 and LOX	Cont. spectrum	
6. JP-3 and WFNA	Mainly cont. with:	CH 4312.5 CN 3883.4 C₂ 5165.2, 4365.2 Na 5895.9, 5890.0 CH₂(?) 4054.8, 4043.3
7. JP-3 and WFNA	Bands between 6500 A and 5000 A Wavelengths not meas.	Na 5895.9, 5890.0
8. Aniline and Furfuryl Alcohol with WFNA	Cont. spectrum	Na 5895.9, 5890.0
9. Metal-Oxidizer	AlO 5424.3, 5079.3, 4842.1, 4648.2 K (emission) 5782.6, 5802.0, 5812.5, 5832.1 K (absorption) 4047.2, 4044.1 Pb (absorption) 4057.8	Na (absorption) 5895.9, 5890.0 Al (emission) 3961.5, 3944.0 Unidentified 5326, 5344, 5364
10. AN-525J	HCHO(?) See page 17	

d.   Additional bands are observed in the spectra of the rocket exhaust flames obtained with aluminum borohydride and liquid fluorine, dimethylaminodiborane and liquid oxygen, and dimethylamino-diborane and liquid fluorine. The shapes of these bands are very similar to those of the boric acid fluctuation band system, and their positions are such as to make them appear to be a short-wavelength extension of that band system. The fact that they were not previously reported is easily accounted for. These bands were originally found in the boric acid flame spectrum. In the boric acid flame the conditions of excitation are somewhat less severe, and the spectra accompanying the weaker transitions do not appear. The fluctuation bands are also produced in the arc with boric acid, but under these conditions the α and β bands of BO are so much more strongly excited that they would obscure any of the weaker fluctuation bands which might appear in this region. Figure 8(a) is an enlarged spectrogram of the dimethylaminodiborane and liquid-oxygen flame, showing these bands.

Spectra of Other Propellant Systems

    1.   Experimental Results

        In addition to observations of firings of rockets with boron-containing fuels, spectrographic observations of exhaust flames from test-firings with more conventional propellant systems have been made in the past year. These observations were made during firings of standard JATOs as well as during many special types of rocket firings under a variety of test conditions. The results of these observations are presented below.

        a.   JP-3. – With liquid oxygen [Figure 5(b)], the spectrum is entirely continuous, with no suggestion of structure throughout the visible region (6500 to 3700 A).

        With WFNA [Figure 5(a)], the spectrum is essentially continuous with a few bands superimposed. The CH band at 4312 A and the CN band at 3883 A are always present. In some cases of long exposure the Swan bands of C_2 at 5165 A and 4365 A show weakly. The 4737 A, C_2 band does not appear under these conditions.

        Spectrograms were made of the flame inside the chamber of a two-dimensional, transparent Plexiglas motor,[7] using JP-3 and WFNA, during four separate test-firings. On three of these spectrograms, bands were observed beginning at about 6500 A and extending to shorter wavelengths [Figure 5(c)]. On the fourth spectrogram the spectrum was entirely continuous throughout this region. Still another spectrogram was taken of the flame through a Plexiglas chamber section of a 5000-lb-thrust unit using JP-3 and WFNA. This spectrum was also entirely continuous. However, in this test a hypergolic slug start of furfuryl alcohol and triethylamine was used. This results in a heavy carbon deposit on the

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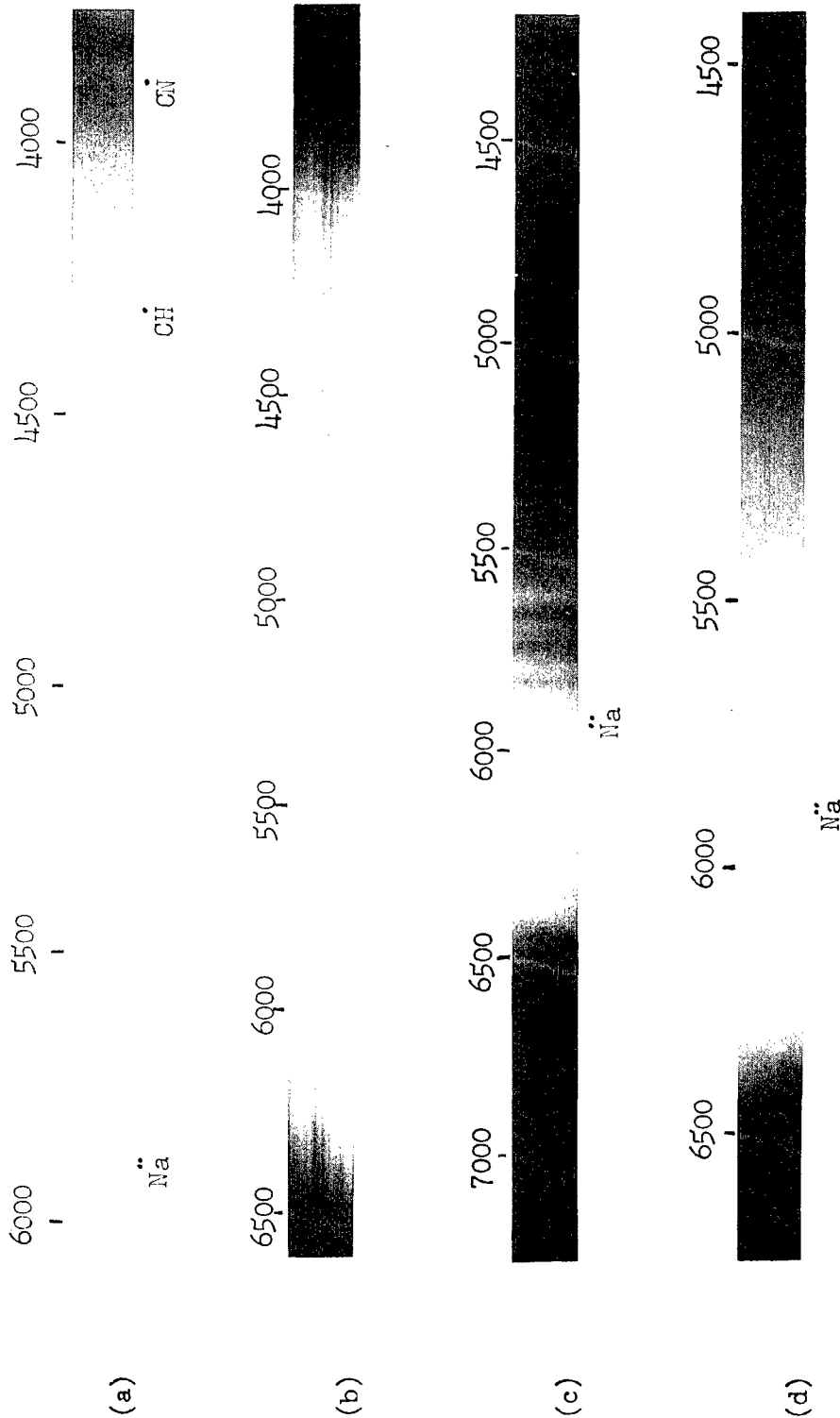[7] J. H. Altseimer, J. Am. Rocket Soc. 22, 86 (1952).

Figure 5. Rocket Exhaust Spectra (IV)

(a)   JP-3 with WFNA
(b)   JP-3 with Liquid Oxygen
(c)   JP-3 with WFNA, 2-Dimensional Motor
(d)   Aniline with WFNA

chamber wall, and it is likely that the continuous spectrum in this case is actually caused by radiation from the glowing carbon. The two-dimensional motor runs use a hydrazine and oxygen start, and in these cases there is little carbon formation. Thus, the one observation in which a continuum was obtained with the two-dimensional motor is anomalous. Unfortunately, it was not possible to clarify this point since further motor tests were not made. The identification of the bands could not be made since they are extremely weak and difficult to measure accurately.

b. Aniline and Furfuryl Alcohol with WFNA. - The spectrum of this rocket flame appears to be continuous in the visible region, though weak bands which are obscured by the spectrum of scattered daylight radiation may be present [Figure 5(d)].

c. Metal-Oxidizer Engine[8]. - A spectrogram was made of the exhaust flame of a rocket engine which uses a propellant consisting of an oxidizer and aluminum with water [Figure 6(a)]. The spectrum of the very intense flame shows a considerable number of bands. In addition, lines are found in both emission and absorption. Most of the bands can be attributed to AlO. Four bands of AlO were positively identified. In emission were found K (I) lines at 5782, 5802, 5813, and 5832 A. In absorption the following lines were found: Na 5890, 5896 A, Pb 4057.8 A, and K 4047, 4044 A.

d. Solid Propellant AN-525J. - Bands are found in the region 4000 to 5000 A in rocket firings from both the 5KS-4500 and 15KS-1000 JATO units. As previously stated (Report No. 1056-4), the bands had been observed only in the flame from the 5KS-4500 unit which contains resonance rods fabricated from Micarta (a phenol-formaldehyde laminate). A more detailed examination of the spectrum shows that these bands are also present but in low intensity in the flame spectrum from the 15KS-1000 unit which contains no Micarta. The spectrogram shown in Figure 6(b) is from the 5KS-4500 unit, and that in Figure 6(c) is from the 15KS-1000 unit. The flame spectrum of a burning AN-525J propellant strand shows no apparent structure in the visible region examined. The identity of these bands has not been established, although the wavelength measurement suggests that some of them might be formaldehyde. The accuracy of the wavelength measurements is poor because the spectrogram from which these were made was not a good one. However, the correspondence and separation of the intensity maxima indicate that some of the bands may be HCHO bands of the Eméleus cool-flame spectrum, identical with the formaldehyde fluorescence bands. Visual estimates of the band intensities are also in general agreement with that of the HCHO band system. No conclusions concerning the identity of the other bands have been made. The correspondence is shown below:

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[8] Aerojet Report No. 579 (7 February 1952), Confidential.
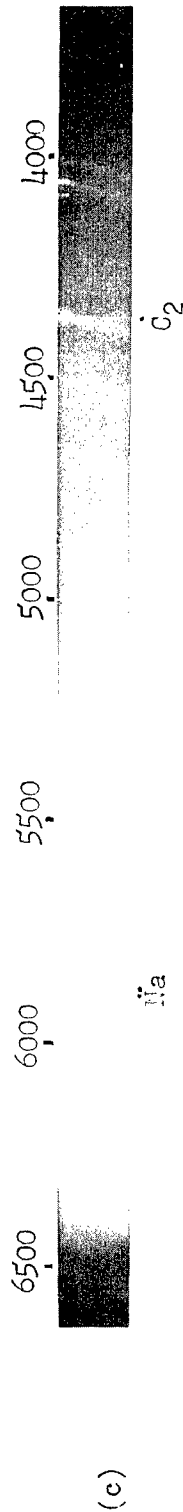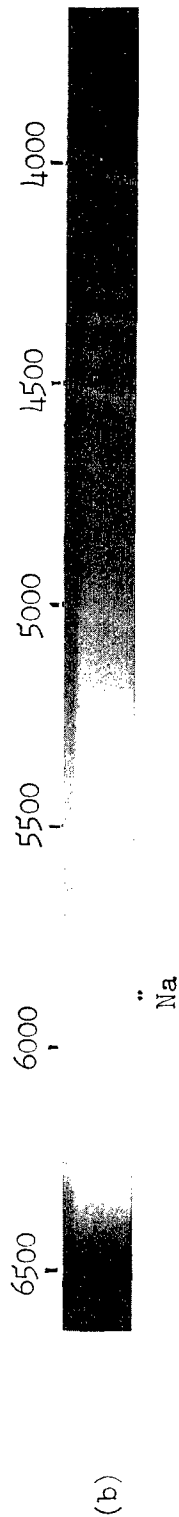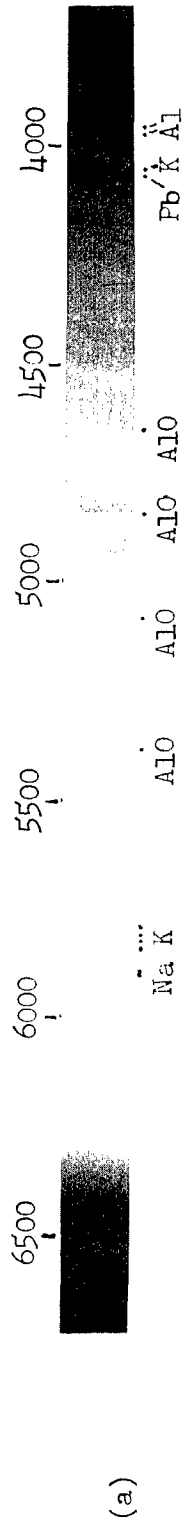
Figure 6. Rocket Exhaust Spectra (V)

(a) **Aluminum with Oxidizer**
(b) AN-525J in 5KS-4500 JATO
(c) AN-525J in 15KS-1000 JATO

λ Measured	λ for HCHO[9]
4997.7	
4965.1	4942
4886.9	
4856.9	4821
	4707
4582.9	4566.8
4533.4	
4496.4	
4443.5	4447.6
4414.6	
4356.6	4359.9
4333.6	
4293.0	
4264.1	4242.8
4133.0	4129.2

[9] R. W. B. Pearse, and A. G. Gaydon, The Identification of Molecular Spectra (John Wiley & Sons, Inc., New York, 1950).

e.   Other rocket flames which were observed but which did not give spectra of interest were the following: Hydrazine with liquid oxygen - Only Na emission could be detected with the grating spectrograph. A faster instrument would be required, or, alternately, a longer test run could be made. Sodium + H_2O - Na emission and some weak bands which could not be measured were observed. Lithium + H_2O - The tests were run with an extremely high mixture ratio, and there was practically no luminous flame.

f.   Observations were made of laboratory and rocket flames with the Hilger intermediate quartz spectrograph. The instrument was received late in the contract period and opportunity for only a few observations on rocket flames was available. Figure 7(a) is the spectrogram obtained from the exhaust flame from a rocket using the 13% solution of lithium borohydride in hydrazine with liquid oxygen. It was necessary to use a 0.1-mm slit in order to obtain sufficient intensity. The spectrum extends to about 2800 A and appears to be continuous below 3500 A. The long-wavelength end of the spectrum is limited by the falling off of the emulsion sensitivity of the Kodak 33 plates used. The use of a wide slit resulted in the presence of a noticeable amount of scattered daylight radiation on the spectrogram, in spite of the fact that it was taken on an overcast day. The spectrum of a natural gas and oxygen laboratory flame taken with a 30μ slit and showing the characteristic OH band system, is reproduced in Figure 7(b).

2.   Discussion of Experimental Results

a.   The band at 4051.5 and 4043.5 is sometimes found in the JP-3 and WFNA flame. It seems to correspond to the 4050 A comet-head group which has been attributed to CH_2. There has been some discussion about this assignment. Durie finds these bands in some organic fluorine flames but disagrees with its assignment to CH_2. He suggests that this is due to C_3 or C_2H rather than CH_2, and points out that in fluorine flames the band appears simultaneously with C_2, whereas it is weak when the CH emission is also weak. Figure 8(b) is any enlarged spectrogram showing this band in the JP-3 and WFNA flame.

b.   Bands occurring in the spectrum of the exhaust from the firing of the 15KS-1000 and 5KS-4500 JATOs are tentatively identified as belonging to HCHO. The available spectrograms do not permit an accurate analysis of the bands. The presence of HCHO bands in the 5KS-4500 flame spectrum can be partially accounted for by the presence in this unit of resonance rods made of Micarta, which is a laminated phenol-formaldehyde plastic. However, this cannot be the complete explanation, since the 15KS-1000 unit does not have these Micarta rods, yet these same bands appear, although with much lower intensity. The flame from AN-525J propellant strands, burned at atmospheric pressure, does not show these bands. Further investigation would be required to confirm this tentative assignment.

Figure 7. Ultraviolet Spectra (VI)

(a) 13% Lithium Borohydride in Hydrazine with Liquid Oxygen
(b) Natural Gas and Oxygen Flame

Figure 8. Rocket Exhaust Spectra (VII)

(a) Dimethylaminodiborane with Liquid Oxygen showing New Bands
(b) JP-3 with WFNA showing 4050 Å Comet-Head Band

c.   The spectrum of the chamber gases of the transparent engine using JP-3 and WFNA exhibits a banded emission which has a complex structure. The origin of these bands has not been established. The fact that some test runs give continuous spectra only is puzzling, but in one case, this can probably be directly attributed to the emission from the carbon deposited on the chamber wall as a result of the use of a triethyl-amine and furfuryl alcohol hypergolic start.

Conclusions and Recommendations

From these studies it is evident that visible emission spectra of rocket exhaust flames usually consist of an intense, continuous spectrum, together with superimposed discrete spectra, which are produced by only a small number of species in the flame. Observations of the spectra of rocket chamber flames were limited in number, but apparently these spectra can be described similarly. Analysis of the visible emission spectra obtained in this work has consisted in the successful identification of most of the species producing the discrete emission, and the association and dissociation reactions, or other processes to which the continuous spectra are to be attributed, have not been identified. Examination of these analyses indicates that generally only a limited amount of information can be obtained from the visible spectrum observed at only one position in a rocket flame.

Because studies of rocket exhaust flames of boron-containing propellant systems which contain no oxygen have demonstrated the presence of one or more oxides of boron, it is evident that oxygen from the air enters the flame as a result of diffusion, convection, and turbulence. Accordingly, care must be exercised in the interpretation of the spectrograms of exhaust flames, but it may be possible to apply this effect to the study of the extent to which oxygen from the air mixes with various parts of the exhaust. An investigation of this type would be pertinent to the study of the mechanism of flash in rocket exhaust flames.

Future work should be directed toward the observation of ultraviolet emission spectra (by use of equipment which is already available) in order to determine the types of information obtainable. For propellant systems which have not previously been photographed successfully in the visible region it will be necessary also to obtain spectrograms in the visible for comparison with those in the ultraviolet region. Although most of these observations will be confined to rocket exhaust flames, the spectra of rocket chamber flames should be observed whenever possible. Other recommendations for future work involving visible and ultraviolet emission spectra are described in Sections IV and VI.

SECTION III

EMISSION SPECTRA OF ROCKET EXHAUST FLAMES IN THE INFRARED REGION

Experimental Details

1.   Infrared Spectrograph

a.   During the past year an infrared spectrograph has been constructed and shown to be suitable for taking infrared emission spectra of rocket exhaust flames. The infrared spectrograph, shown in its present form in Figure 9, consists essentially of a Beckman IR-2 monochromator, shock-mounted on a rigid frame and provided with detecting, amplifying, and automatic recording systems, and a prism drive for producing radiation of various wavelengths. Light from the source under study is "chopped" at 100 cycles per second before entering the monochromator, and the resulting a-c signal from the Golay cell, which serves as detector, is amplified and then recorded on a G. E. oscillograph. About 26 seconds is required to scan the spectral region from 1 to 15μ by use of a rock salt monochromator, or from 1 to 6.3μ by use of a lithium fluoride monochromator.

b.   As originally constructed, the spectrograph incorporated a Beckman IR-2 rock salt monochromator on loan from the Navy, but as soon as the design was shown to be practical, a Beckman lithium fluoride monochromator was purchased and installed shortly before the termination of the contract. The increased resolution which is given by lithium fluoride, as compared with rock salt, is apparent in Figures 10 and 11. The fact that it was possible to use the same slit widths with both monochromators, in spite of the difference in dispersion, showed that either the rock salt monochromator was badly out of alignment or the prism was fogged.

c.   Selected oscillograph records are shown in Figure 10 to illustrate the results obtainable with the spectrograph in its present state of development. In the succeeding figures, the smoothed trace of the oscillograph record for the spectra was obtained by comparison of at least three scans.

2.   Procedure for Observation of Rocket Exhaust Flames

Light from the rocket exhaust gases is picked up by a plane back-surface mirror and is condensed on the slit of the spectrograph by a parabolic front-surface mirror which has a focal length of 43 in. The alignment is checked by placing a small tungsten lamp at the slit and then observing the lamp from the position of a rocket exhaust. The flame is sufficiently large that the errors inherent in this method are not serious. This is demonstrated by the fact that slits have been used with widths comparable to those which were used in observing laboratory flames in spite of the increased distance (nearly 50 ft as compared with less than 3 ft in the laboratory) and the impossibility of adjusting the setup for maximum signal before recording a spectrum. A front-surface pickup mirror would be obtained for any future work.
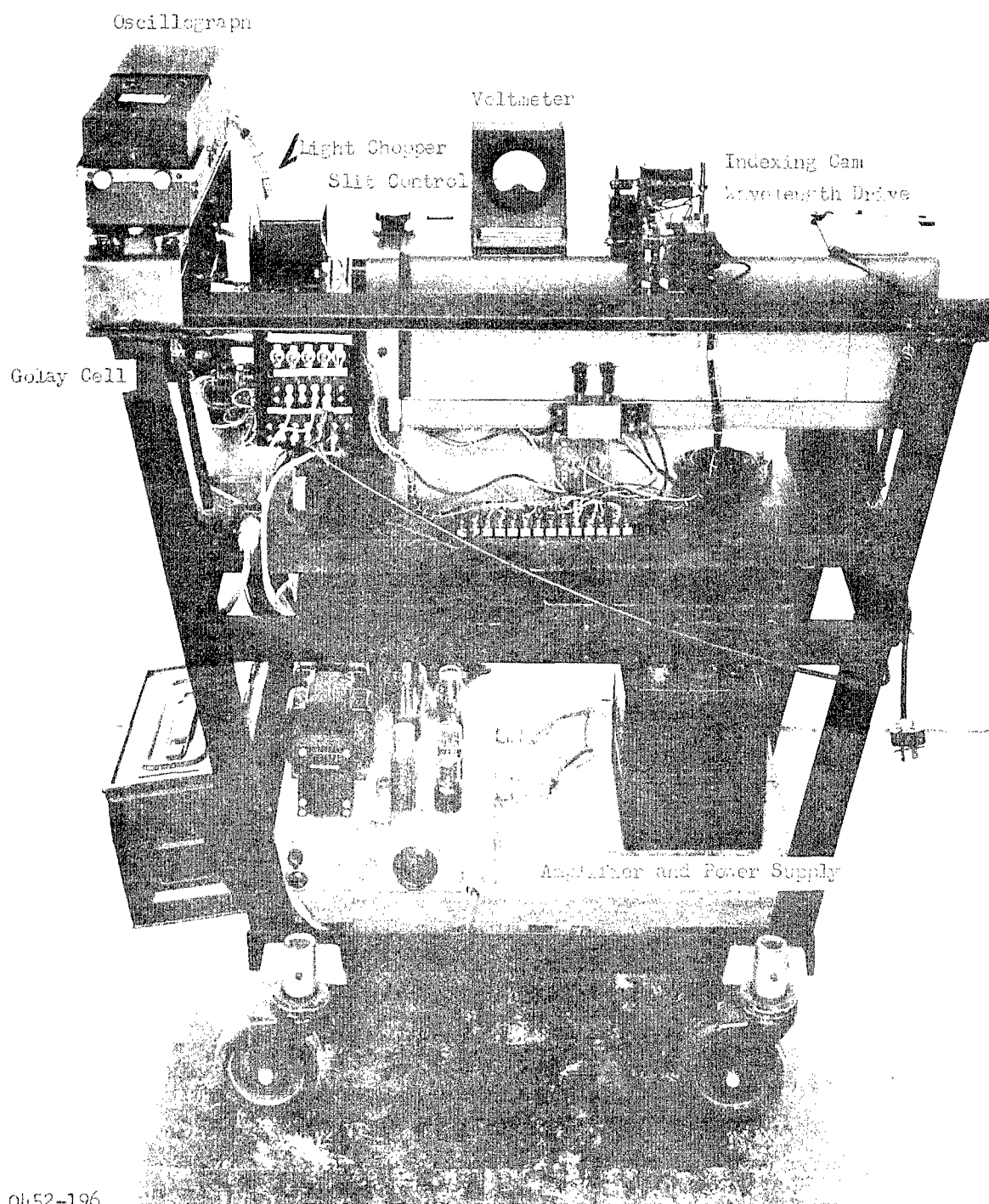
Figure 9. Infrared Spectrograph

Wavelengths in Microns

.08 1.27 1.67 2.35 3.22 4.00 4.68 5.22

Figure 10 (A) Natural gas-O₂ Flame
NaCl Prism
Slit - 0.3 mm
High Gain

Wavelengths in Microns

3.60 3.71 3.22 3.93 4.04 4.14 4.25 4.36 4.46

Figure 10 (B) Natural gas – Air Flame
LiF Prism
Slit - 0.5 mm
Medium Gain

Figure 10 (A) and (B). Oscillograph Records of Infrared Emission Spectra

Wavelengths in Microns

1.30   1.55   1.78   1.99   2.18   2.36   2.53   2.70   2.86   3.03   3.18   4.2.   4.35   4.4.5   4.56   4.65   4.76

Figure 10 (C)   Natural gas – O_2 Flame
LiF Prism
Slit – 1.0 mm
Low Gain

Wavelengths in Microns

1.30   1.55   1.78   1.99   2.18   2.36   2.53   2.70   2.86   3.03   3.18   3.33   3.47   3.59   3.71   3.82   3.93   4.04   4.14   4.24   4.35   4.45   4.55

Figure 10 (D)   Rocket Exhaust Flame – JP–3 and WFNA
LiF Prism
Slit 0.5 mm
High Gain
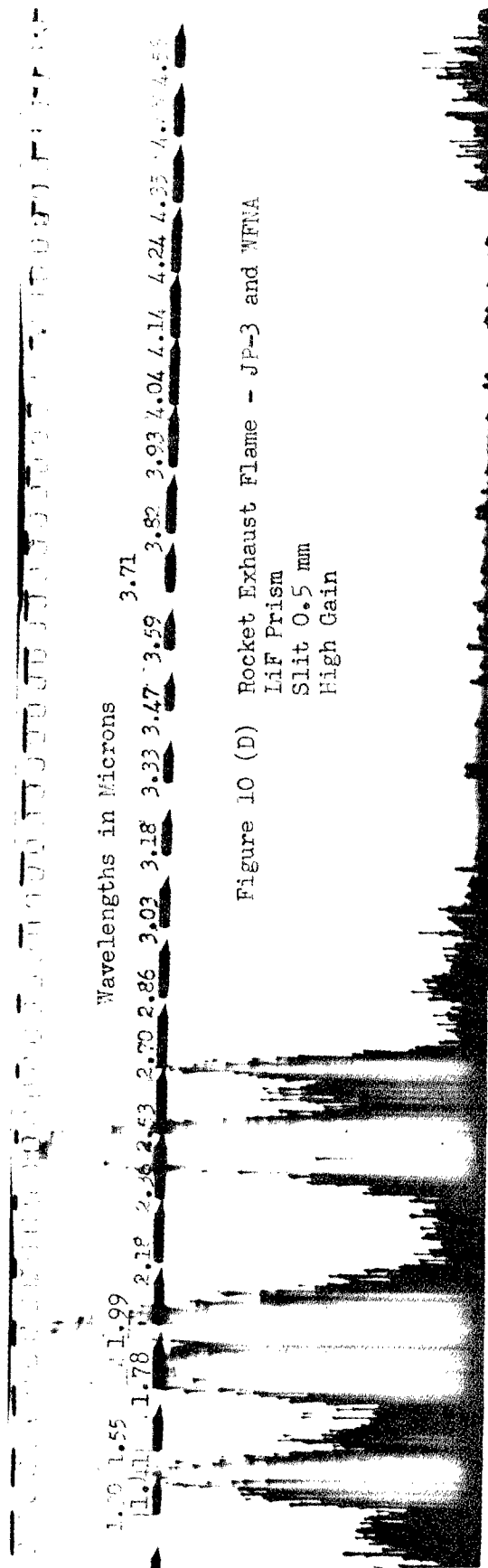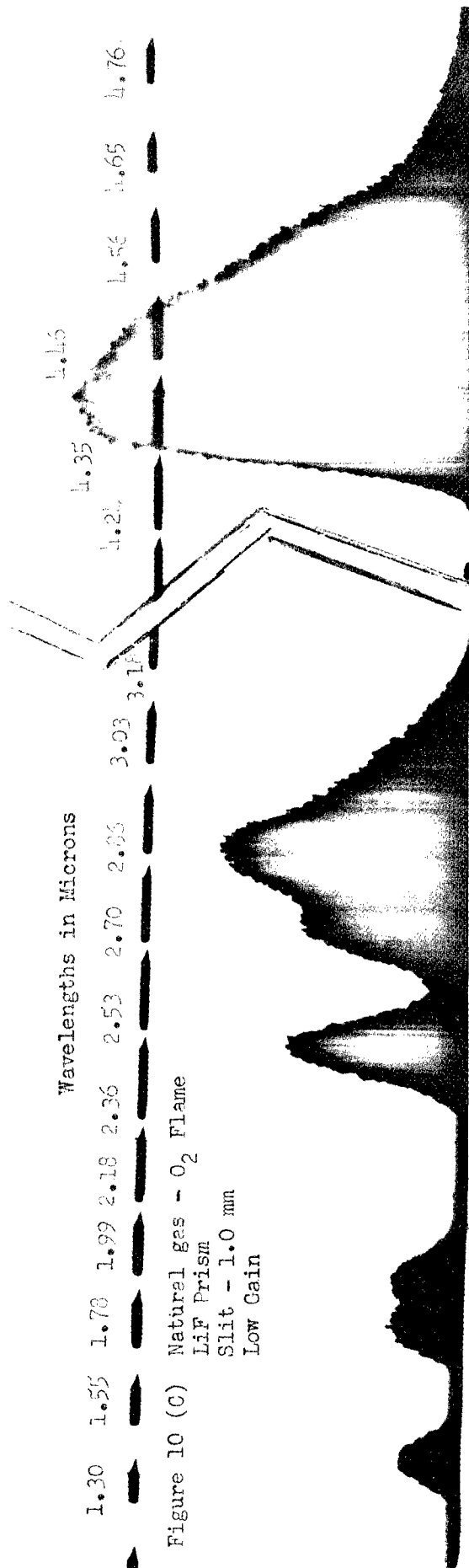
Figure 10 (C) and (D). Oscillograph Records of Infrared Emission Spectra

A. 1.0 mm slit, low sensitivity

B. ———·—— 0.2 mm slit
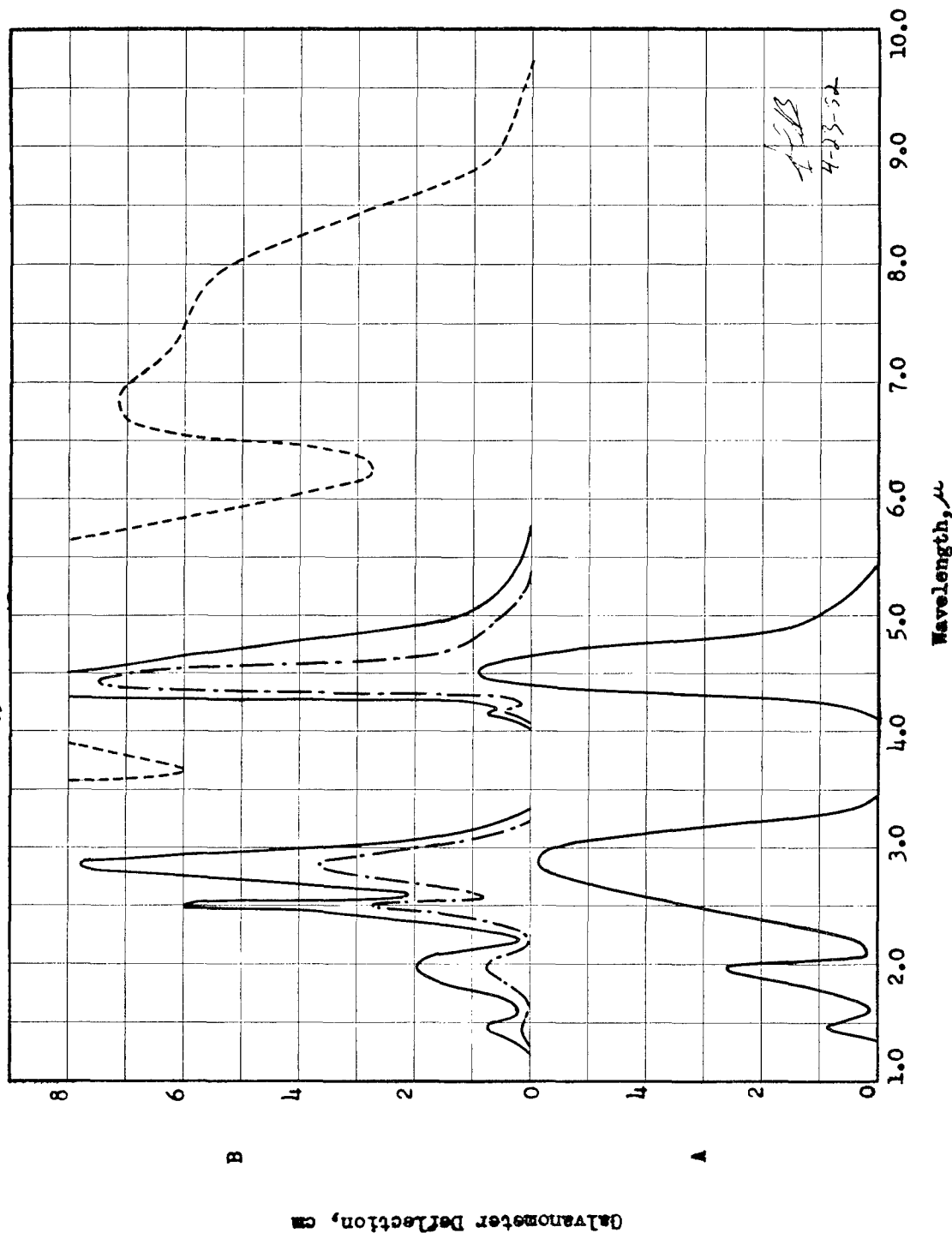   ————— 0.3 mm slit
   ----- 1.5 mm slit

Figure 11. Smoothed Infrared Emission Spectra of Natural Gas – O_2 Flames Obtained by use of NaCl Prism

Experimental Results

Spectra were obtained from two firings of a rocket engine, using JP-3 WFNA, one by use of the rock salt monochromator, and the other by use of the lithium fluoride monochromator. Smoothed spectra are shown in Figure 13, and a sample portion of an oscillograph record is shown in Figure 10. The apparent low intensity of the emission bands beyond 2.7μ arises in part from the use of a back-surface mirror in the optical train. Glass begins to absorb strongly near this wavelength and does not show high reflectivity until much longer wavelengths are reached. It is noteworthy that the chief emitters in the infrared are not greatly different for the JP-3 and WFNA rocket exhaust flame and the natural-gas oxygen flame.

Numerous records of the emission spectra of laboratory flames were taken during the development of the spectrograph. Three of the records are shown in Figure 10 and selected smoothed traces of the oscillograph records for the spectra are shown in Figures 11 and 12.

Emission bands are found at the following wavelengths in microns in each spectrum obtained by use of the lithium fluoride monochromator: 1.44, 1.85, 1.99, 2.49, 2.71, 2.86, and 4.4μ. Wavelengths are given only to the nearest 0.01μ because the wavelength scale on the monochromator has not yet been calibrated. The actual position of the maximum of the 4.4μ band is not clear, partly because of self-absorption and partly because of the width and unsymmetrical shape of the band; hence its position is given only to the nearest 0.1μ.

Approximate positions of bands as found in emission spectra obtained by use of the rock salt monochromator are as follows: 1.5, 2.0, 2.5, 2.9, 4.4, 6.9, and 7.5μ. The 2.9μ band does not show up in the rocket exhaust-flame spectra because of the use of a back-surface pickup mirror.

The genuineness of the band shown at 2.64μ in the rocket exhaust-flame spectra is not established. Although each of the five scans of this region by use of the lithium fluoride monochromator with a 0.3-mm slit appears to show this band, a low-speed scan of this spectral region should be made before it can be accepted as real.

Discussion

1. Resolution

a. The infrared emission spectra of laboratory flames have been examined previously by numerous investigators with resolution comparable with that which was obtained with the rock salt monochromator,[10] and Wohl

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[10] See particularly A. G. Gaydon, Spectroscopy and Combustion Theory (Chapman and Hall, Ltd., London, 1948) Chap. XI for discussion and references.

A. Natural gas – O_2 flame emission, 0.5 mm slit.

B. Natural gas – air flame emission, 0.5 mm slit.
C. Carbon arc emission, showing atmospheric absorption bands, slit widths as shown
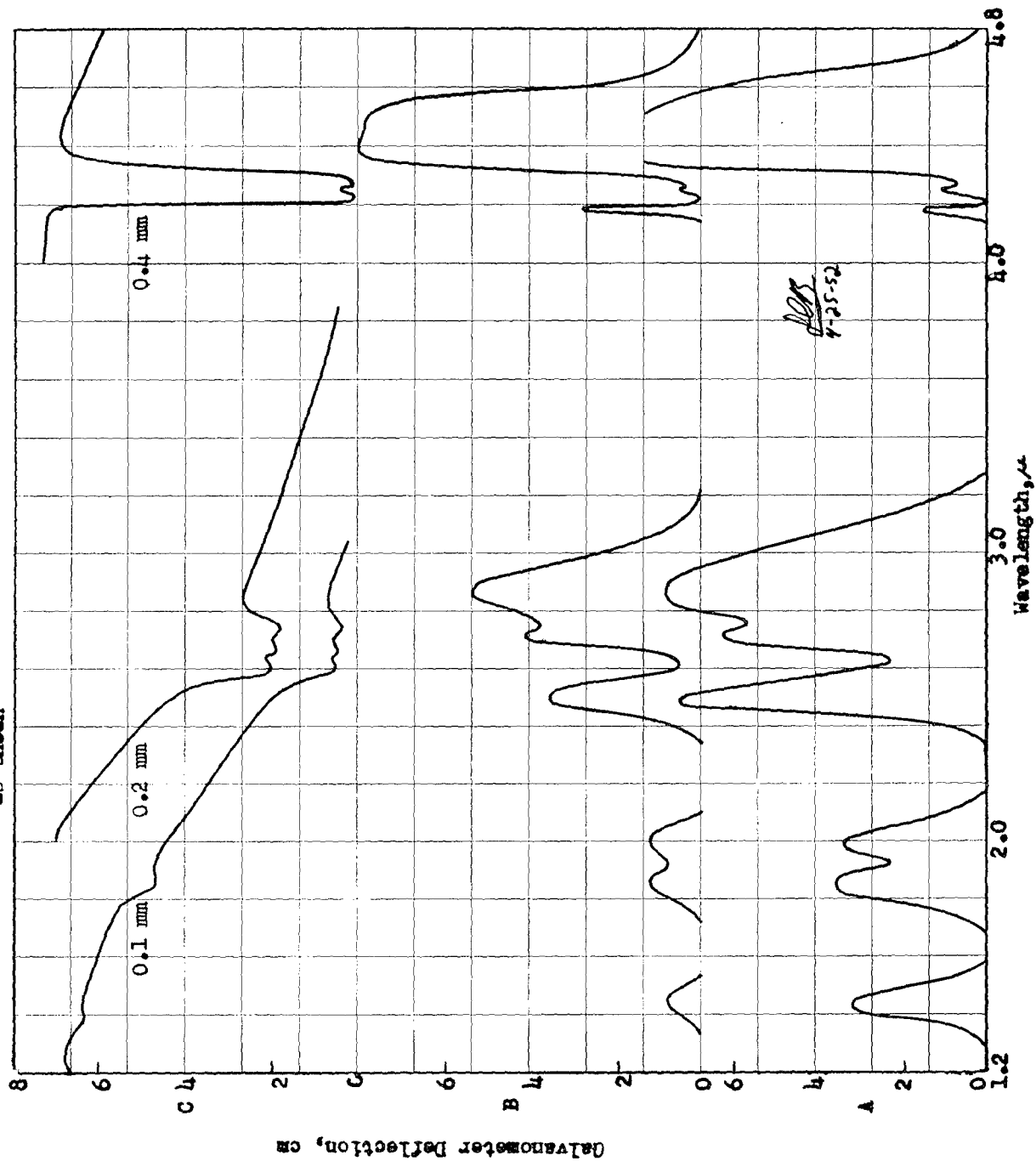
Figure 12. Smoothed Infrared Spectra Obtained by use of Lithium Fluoride Prism

A. NaCl prism ———— 0.2 mm slit
           —·—·— 0.3 mm slit

B. LiF prism ———— 0.3 mm slit
           ———— 0.5 mm slit
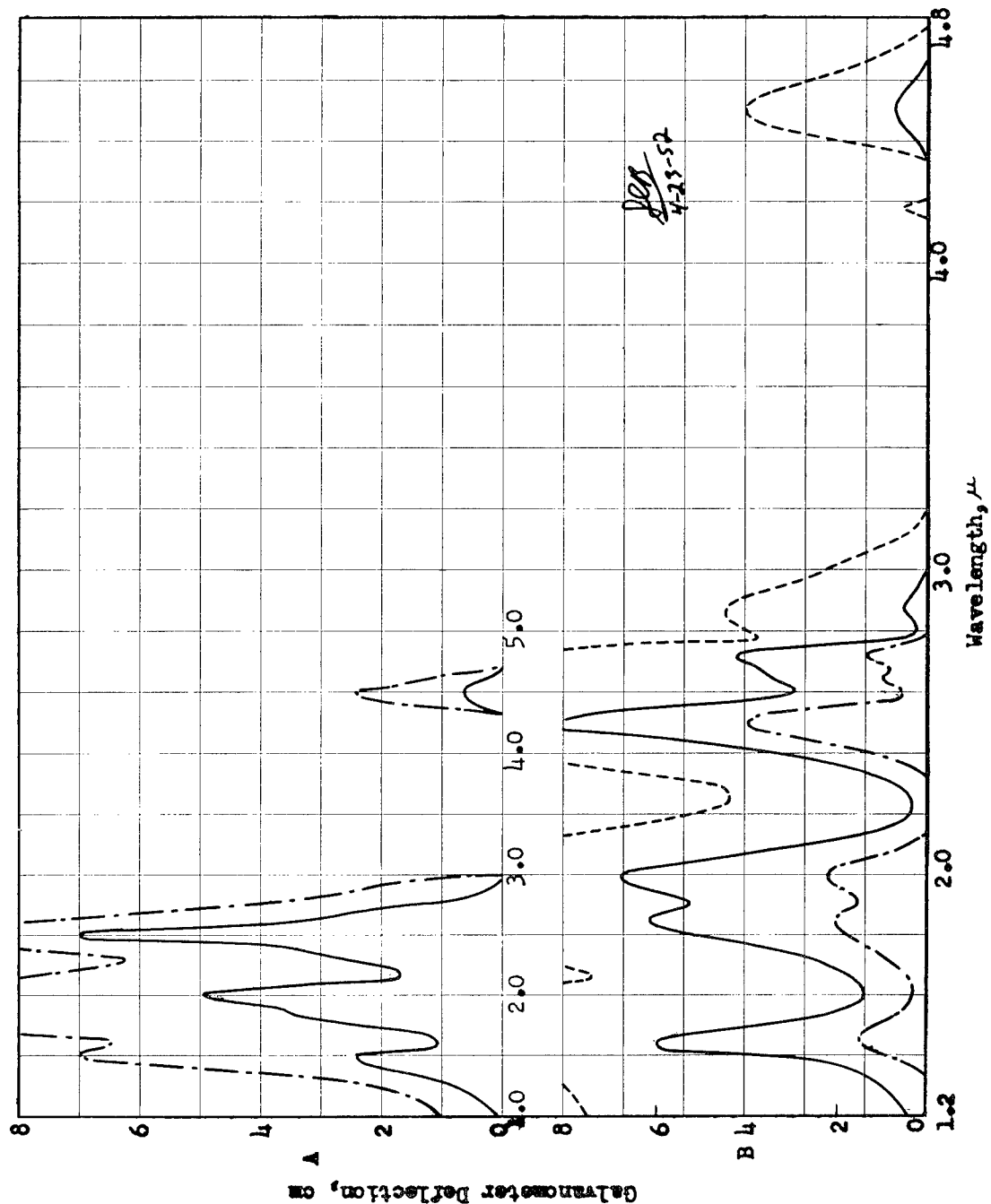   ----- 1.0 mm slit

Figure 13. Smoothed Infrared Emission Spectra of Rocket Exhaust Flames (JP-3 and WFNA)

and co-workers[11] have presented a butane--air flame spectrum, which shows somewhat higher resolution than has thus far been reached with the Aerojet lithium fluoride monochromator. The latter was obtained by use of a Perkin-Elmer lithium fluoride spectrophotometer in conjunction with a lead sulfide photoconductive cell. The resolution shown by the Aerojet spectra is very gratifying in view of the relatively high speed of scan and wide slits which were used. The resolution could probably be significantly improved by lowering the "chopping" speed, which would increase the sensitivity of the Golay cell and thus permit the use of narrower slits. The resulting decrease in the number of galvanometer swings per micron could be partially compensated by using full-wave instead of half-wave rectification. For some runs it should also be possible to decrease the scanning speed.

b.   If subsequent work shows more resolution to be desirable, some additional improvement could probably be obtained in the spectral region 1 to 2.8μ by substituting a lead sulfide photoconductive cell for the Golay cell. Some modification of the optical system following the exit slit would be required. High resolution grating studies of emission spectra are in progress in various laboratories, particularly the National Bureau of Standards,[12] but little has been published as yet. Such studies may be expected to provide both positive identification of emitters and the experimental basis for a theoretical study of the dependence of band shape on chemical excitation.

2.   Identification and Interpretation of Bands

a.   Discussions in the literature of the infrared emission spectra of flames have been based on low resolution work with rock salt prisms. Bailey and Lih,[13] for example, do not resolve the three bands near 2.7μ, but report them as a band at 2.84μ with a shoulder at 2.60μ. Also, the pair of bands near 2μ is uniformly reported as a single band.[14] Hence, earlier discussions must be regarded as incomplete, and must be reconsidered in the light of new data. Wohl and co-workers show the 2μ band as resolved into three components, and the 1.4μ band as resolved into two, but they do not discuss the identity of the bands other than to say that the bands at 1.35μ, 1.82μ, and 2.51μ are also found in the hydrogen-air flame and are presumably due to H_2O alone. A high-speed scan of an ammonia--oxygen flame by use of a vacuum grating spectrograph[15] shows a close resemblance to the butane--air spectrum published by Wohl. The inference is that the bands

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[11] L. Bernath, H. N. Powell, A. G. Robison, F. Weltz, and K. Wohl, Project Squid Technical Report No. 32, 1951.

[12] E. K. Plyler, W. L. Benedict, and S. Silverman, J. Chem. Phys. 20, 175 (1952).

[13] C. R. Bailey and K. H. Lih, Trans. Faraday Soc. 25, 29 and 32 (1928).

[14] Gaydon, op. cit.

[15] Private communication from Roger Newman, California Institute of Technology.

below 2.8μ arise from H_2O emission alone, unless OH can be shown to contribute. Carbon dioxide appears to be the chief emitter at 4.4μ and is reported by Gaydon (op. cit.) to be responsible for much of the emission at 2.86μ. However, the 2.86μ band under high resolution shows the same lines and relative intensities in both ammonia--oxygen and natural gas--air flames, which indicates that more work remains to be done before this band is positively identified.

b.   The band at 1.44μ, which Wohl resolves into two components, is undoubtedly partly due to the combination band of water, $\nu_1 + \nu_3$, and perhaps partly to the first overtone of the band at 2.86μ. Gaydon's suggestion that the latter may arise from OH appears to bear further investigation.

c.   Part of the emission near 2μ no doubt arises from the water combination band, $\nu_2 + \nu_3$, but the source of the remaining emission in this spectral region is very obscure at this time. Emission might be expected in this region from the carbon dioxide combination bands $2\nu_2 + \nu_3$, and $\nu_1 + \nu_3$, but the unchanged appearance of this emission in the ammonia--oxygen flame spectrum, as compared with butane-air or natural gas and air flame spectra is not consistent with such an assignment.

d.   The 2.5 and 2.7μ bands probably arise from H_2O emission, but a careful theoretical study of self-absorption, known energy levels,[16] and transition probabilities,[17] and their effects on band shapes would be desirable. A similar study would be helpful at 1.4 and 2μ also. A thorough understanding of the transitions involved in the emission bands of a flame, beyond the simple identification of the emitter, may be expected to throw light on the mechanism of combustion when the emission is at least partly chemiluminescent.

e.   The work of Daly and Sutherland[18] on the emission of hot carbon dioxide (700°K) near 4μ indicates that the positions of the intensity maxima in this spectral region, which are shown in Figures 15 and 16, are determined solely by the 1→0 transition of ν_3, after allowance is made for the fact that a much longer absorbing path of carbon dioxide was present than Daly and Sutherland used. The emission on the long wavelength side of the 4.4μ maximum is undoubtedly strengthened by transitions involving higher excited states, but a careful study would be required to determine whether the intensity distribution corresponds solely to thermal excitation or whether it also requires some chemiluminescence.

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[16] W. S. Benedict and E. K. Plyler, J. Research Nat. Bu. Standards 46, 246 (1951).

[17] P. C. Cross, R. M. Haines, and G. W. King, J. Chem. Phys. 12, 210 (1944).

[18] E. F. Daly and G. B. B. M. Sutherland, Third Symposium on Combustion, Flame and Explosion Phenomena (The Williams and Wilkins Company, Baltimore, Md. 1949), p. 530.

Conclusions and Recommendations

    1.   The preceding studies demonstrate that the infrared spectrograph can be applied to rocket exhaust flames and indicate the direction to be followed in future work.

    2.   Certain modifications which will improve the performance of the spectrograph are recommended below and the types of investigation to which the instrument should be applied are outlined.

        a.   The design of the infrared spectrograph should be further refined by making the following improvements:

            (1)   The "chopping" rate should be decreased to 40 cps and the cascode amplifier should be modified to reach its peak at this frequency.

            (2)   A means should be provided to scan the spectrum at both a reduced and an increased rate, as desired. This may be achieved by means of a planetary reduction gear which can be controlled by a brake band.

            (3)   The speed of the sweep motor should be adjustable in order to permit small portions of the spectrum to be scanned at lower speeds, thus increasing the resolution at critical portions of the spectrum.

            (4)   The lead sulfide cell should be developed further, together with the accompanying optical components, choppers, and pre-amplifiers.

            (5)   A more satisfactory recording oscillograph could make a vast improvement in recording and presentation of the data.

            (6)   Full-wave rectification of the final signal would double the electrical resolution.

        b.   Infrared emission spectra should be obtained from a large variety of rocket exhaust flames and, if possible, from rocket chamber flames. Complete analysis of these spectra will require a careful theoretical study of the effects of self-absorption and strong thermal excitation on the shapes and positions of maxima of the vibration—rotation bands shown by H_2O, CO_2, and any other strong infrared emitters that might be encountered in rocket exhaust flames. In addition, it will probably be necessary to supplement these theoretical studies with experimental studies of the thermal emission of pure gases in the infrared. In order to apply the theoretical analysis, the absolute absorption intensities of vibration—rotation bands of chemical species which might be found in rocket exhaust flames should be determined in order to calculate emissivities in a manner similar to that described by Penner.[19] The complexity of this program

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[19] Progress Report No. 9-37, Jet Propulsion Laboratory, California Institute of Technology, May 31, 1949.

necessitates a long-term effort and division into two phases is recommended. The first phase should consist of the observation of the spectra of rocket flames and of hot, pure gases, and the second phase should consist of the theoretical analysis and the evaluation of the parameters necessary to the application of the results of the analysis to the spectral data. The first phase should be initiated immediately.

SECTION IV

SPATIAL RESOLUTION OF EMISSION SPECTRA OF ROCKET EXHAUST FLAMES

In studies of combustion it is desirable to know the species present at various positions in the flame. Techniques in which samples are withdrawn from specific portions of the flame and analyzed chemically have the serious disadvantage that chemical reactions may occur in the sample during the interval between its collection and the analysis. This is especially true if the sample contains chemically reactive species, or if the sampling device exerts a catalytic effect on reactions in the sample. If the molecule in the flame has characteristic emission bands, the analysis can be made spectroscopically, thereby avoiding the limitations of a sampling method.

Two spectroscopic methods have been considered: one involves photographing the flame with nearly monochromatic light and another produces a spectrum of the entire flame. The first method made use of narrow band-pass optical filters.[20] The principle of the method was to isolate by means of narrow band-pass optical filters the radiation corresponding to the emission of one of the active species, e.g., CH, C_2, CN, etc. If photographs of the flame were taken through appropriate filters they would indicate the source of the emission of that species in the flame. A Stereotach was adapted so that two photographs through different filters could be made simultaneously. In principle, this should permit emission of the various species to be localized as to the zone in which it occurs. In practice, however, this did not prove possible because the emission of discrete bands is accompanied by strong, continuous emission in most rocket flames. Since the banded emission is weaker than the continuum, it is not possible to observe any significant difference in the intensity of the radiation through the filters. When this became apparent; the work was discontinued and the emphasis was placed on the development of the long-slit technique described in the following paragraphs.

The second method tested involved isolating a portion of the flame as was done, for example, by Penner,[21] by the use of defining slits, and

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[20] Aerojet Report No. 1056-2 and -3.

[21] S. S. Penner, M. Gilbert, and D. Weber, J. Chem. Phys., 20, 522 (1951).

Gaydon and Wolfhard.[22] However, these methods require many exposures in order to cover the entire flame. In principle, it should be possible to construct a large stigmatic spectrograph with a slit which could be adjusted in length to correspond to the extension of the region of the flame which is being studied. Each point on the image obtained on the spectrogram would then correspond to a given point in the flame. In practice this can be done by placing a large slit near the flame. The length of the slit will be determined by the size of the flame, and the width of the slit can be made as narrow as practicable. A grating and a camera can be set up at a sufficient distance from the flame so that the light reaching the grating will be nearly parallel. Of course, the intervening space between the slit and the grating must be dark. The arrangement is shown schematically in Figure 14. The feasibility of this arrangement was demonstrated first in the laboratory, and then an observation was made on the exhaust flame of a rocket. For the laboratory test, a gas discharge tube approximately 3/8 in. in diameter and about 30 in. long was used. This discharge tube containing a mixture of gases at low pressure was set up at one end of the laboratory and served as a luminous slit. The front section of the portable grating spectrograph, containing the slit and the collimating lens, was removed. The grating and camera assembly of the spectrograph was then set up 30 ft away at the opposite end of the darkened room, and a 1-minute exposure was made of the glow discharge. The spectrogram obtained, which is shown in Figure 15, clearly defines the variation in the spectra of the discharge at different points along the tube. The narrow horizontal line near the bottom of the spectrogram is an indicator mark which was placed on the tube. The broad line across the upper part of the spectrogram was caused by a clamp which was used to support the tube. The central image is shown at the extreme right.

The apparatus was then set up for the observation of the flame from the firing of a liquid-propellant rocket. A slit was made of sheet iron by mounting two pieces of 1/2-in. plate, 8 ft long x 3 ft wide, on a suitable frame with a 3/8-in. space between them to form the slit opening (see Figure 14). This turned out to be wider than necessary; however, for this preliminary test this width was chosen arbitrarily to ensure sufficient intensity to produce a spectrogram. The camera and grating assembly was placed about 60 ft from the slit. The camera was focused with the aid of a mercury arc lamp which was placed alternately at the two extremes of the slit while the camera was adjusted so that the spectra of the lamp in the two positions defined a zone approximately in the center of the focal plane of the camera. Also, the camera back was adjusted to give sharply focused spectral lines. A test-firing of a rocket using JP-3 and WFNA was made after sundown in order to minimize the effects of stray light entering the camera. Figure 16 is a reproduction of the spectrogram obtained. Super Panchro-Press, Sports Type, film was exposed for 7 sec. The horizontal lines are index marks spaced at 12-inch intervals to show the location of the spectra in relation to the distance from the nozzle of the motor. The central image is shown at the right. Although this rocket flame does not show

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[22] A. G. Gaydon and H. G. Wolfhard, Proc. Roy. Soc. (London) A194, 169 (1948); A199, 89 (1949); A201, 561 (1950); A201, 570 (1950); A202, 118 (1951).
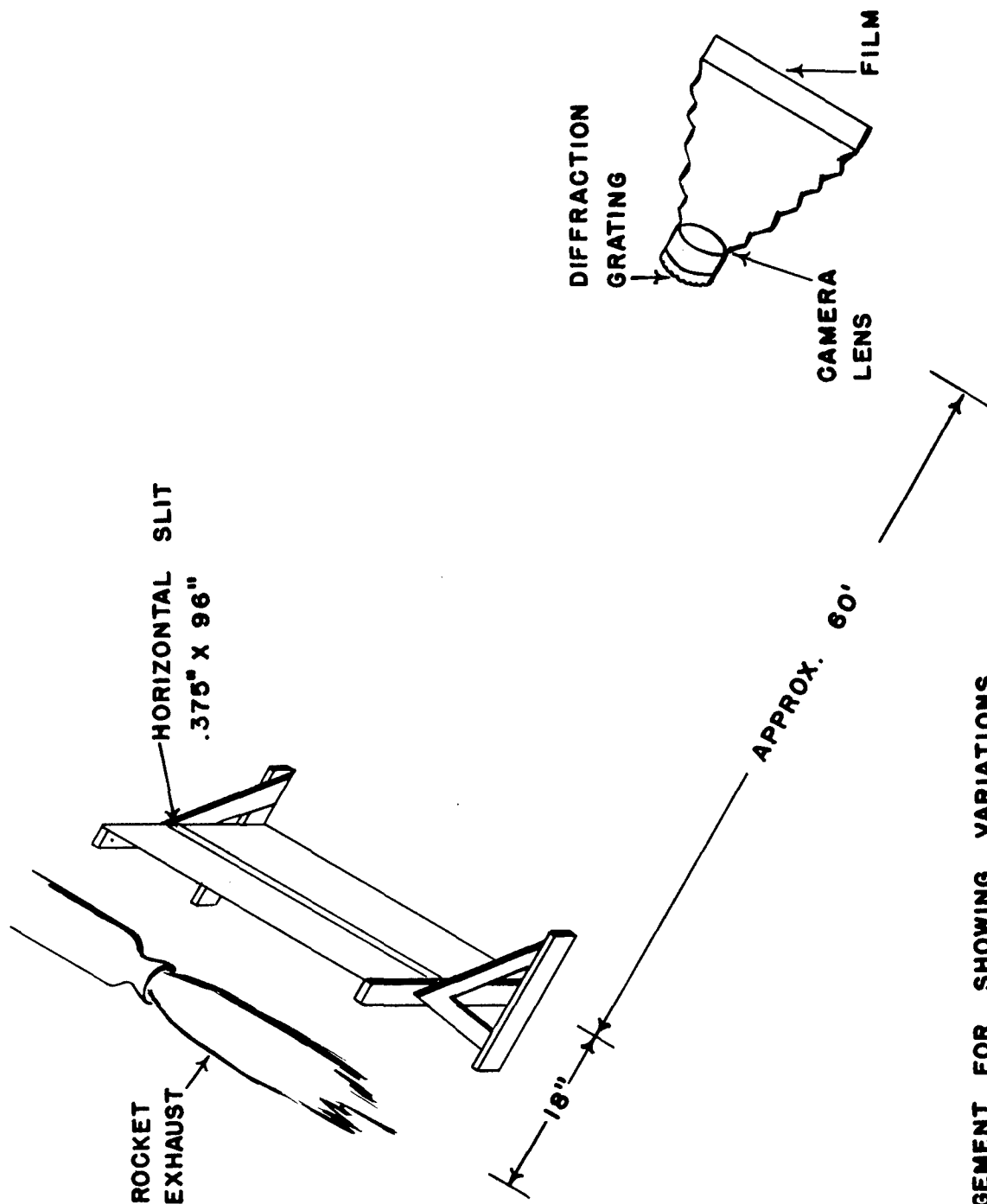
Figure 14. OPTICAL ARRANGEMENT FOR SHOWING VARIATIONS IN SPECTRAL DISTRIBUTION ALONG FLAME AXIS
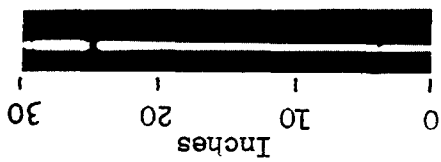
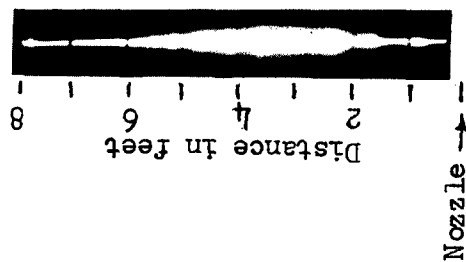Figure 15. Spectrogram of Long Gaseous Discharge Tube

Figure 16. Spectrogram of JP-3 and WFNA Motor with 8 Foot Slit

an abundance of emission bands, the test nevertheless demonstrates the
applicability and feasibility of the apparatus for observations of rocket
firings, and suggests means by which the apparatus can be improved for
future firings. Some overlapping of spectra was encountered on the spectro-
gram since the light from the flame illuminated the walls of the test in-
stallation, and reflections from these walls entered the spectrograph. This
is a problem in shielding and can be remedied with little difficulty.

The results of the preliminary tests with the long-slit apparatus for
obtaining spatial resolution of the spectra of rocket flames are encouraging.
Spectrograms which show the change in the character of the emission from the
flame as a function of the distance from the nozzle of the motor give in-
formation concerning the course of the reaction outside the chamber. One
of the problems which could be conveniently investigated by means of this
technique is the question of the structure of a rocket exhaust flame.
Although the detailed processes which occur in a rocket exhaust flame are
important in determining the intensity of flash and afterburning, no
systematic spectroscopic investigation of the structure of exhaust flames
has been made. Spectroscopic studies on the structure of diffusion flames[23]
have led to conclusions concerning the mechanism of burning in these flames.
In particular, the significance of C_2 emission and carbon formation have
received considerable attention. With the apparatus described above, this
sort of study could be made on a rocket exhaust flame. It is recommended,
therefore, that this aspect of work be continued, and that the apparatus
already developed be applied to the study of other rocket flames.

SECTION V

AN APPARATUS FOR STUDY OF THE ABSORPTION SPECTRA OF ROCKET FLAMES

Many chemical species exist in a rocket exhaust flame that have not
been detected by means of emission spectrography, either because of low
concentration, low transition probabilities, or both. Some of these species
that are weak emitters might be detected by increasing the exposure time if
it were not for the obscuring effect of other relatively strong emitters
near the same regions of the spectrum. Absorption spectrography appears to
offer important advantages at this point in that (1) both excited and un-
excited species absorb, (2) spectrograms may be obtained of exhaust-flame
phenomena of very short duration, and (3) the absorption intensity may be
increased by many traversals by a beam of light through a small exhaust
flame to provide a relatively long absorbing path.

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[23] See H. G. Wolfhard and W. G. Parker, Proc. Roy. Soc., A385, 2 (1952).

From several methods of obtaining a long optical path the method described by Kratz and Mack[24] was adopted for work on absorption spectrography because of its relative simplicity. The apparatus consists essentially of a source of continuous radiation, a right-angle prism, a concave, spherical mirror, a spectrograph, and a rigid bench for securing the components in proper alignment. An over-all view is shown in Figure 17. The source may be an ordinary filament lamp, a carbon arc, a photoflash bulb, or another convenient source providing a continuum in the desired spectral region. The prism is an isosceles right-angle prism with one truncation at the 90° angle, and another at one of the 45° angles. Widths of these truncations impose limits on the number of reflections possible with a given prism. The aluminized spherical concave mirror is mounted on a gimbal ring with adjusting screws to allow for proper orientation with respect to the prism. A Bausch & Lomb spectrometer with camera attachment is used with this apparatus, although any spectrograph of conventional design may be used.

Figure 18 is a schematic view of the optical system. A beam of continuous radiation is introduced through the truncated face at the 90° corner of the prism and is reflected a number of times between the prism and the concave mirror. Adjustment of the mirror is such that internal reflections in the prism are progressively shifted away from the center of the prism toward the 45° corners. After several reflections, the beam is brought to a point opposite and perpendicular to the truncated face at the 45° corner. It then emerges from the prism and falls on the entrance slit of the spectrograph. If an absorbing medium such as a liquid, gas, or rocket exhaust flame is interposed between the prism and mirror, all light reaching the spectrograph traverses this absorbing medium several times. The absorption path is then equivalent to the thickness of the medium times the number of traversals. The apparatus was adjusted for 8 traversals, which is the maximum number possible with the prism now available.

Preliminary experiments were made in the laboratory with this apparatus using various materials which absorb in the visible region. Some representative absorption spectrograms obtained during these tests are shown in Figure 19. Three exposures were made of rocket exhausts. Because of fogging of the spectrographic plates, the results of these exposures could not be evaluated. Delays in completion of the apparatus left insufficient time for some modifications which appeared desirable after field tests.

It is thought that the study of the absorption spectra of the flames will disclose the presence of molecular species which cannot be observed in emission. These studies should be continued in the visible region and extended to include the infrared and ultraviolet regions of the spectrum for which the apparatus is already available. In future work, however, the following improvements are suggested:

1. A more intense source, which will permit a shorter exposure time, will minimize interference by radiation from emitters in the rocket exhaust. In the tests made, a considerable amount of emitted light

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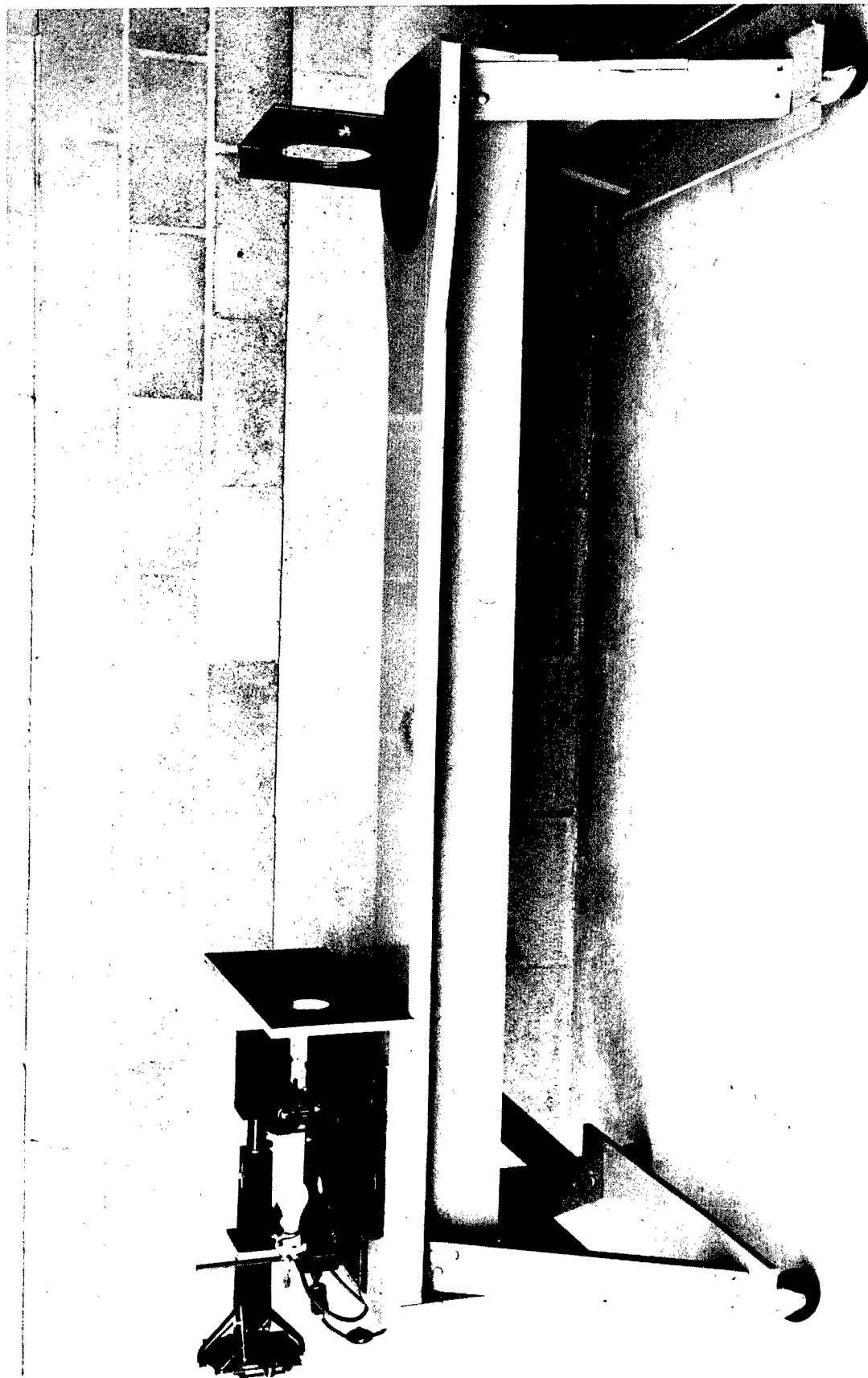[24] H. R. Kratz and J. E. Mack, J. Optical Soc. Am., 32 457 (1942).

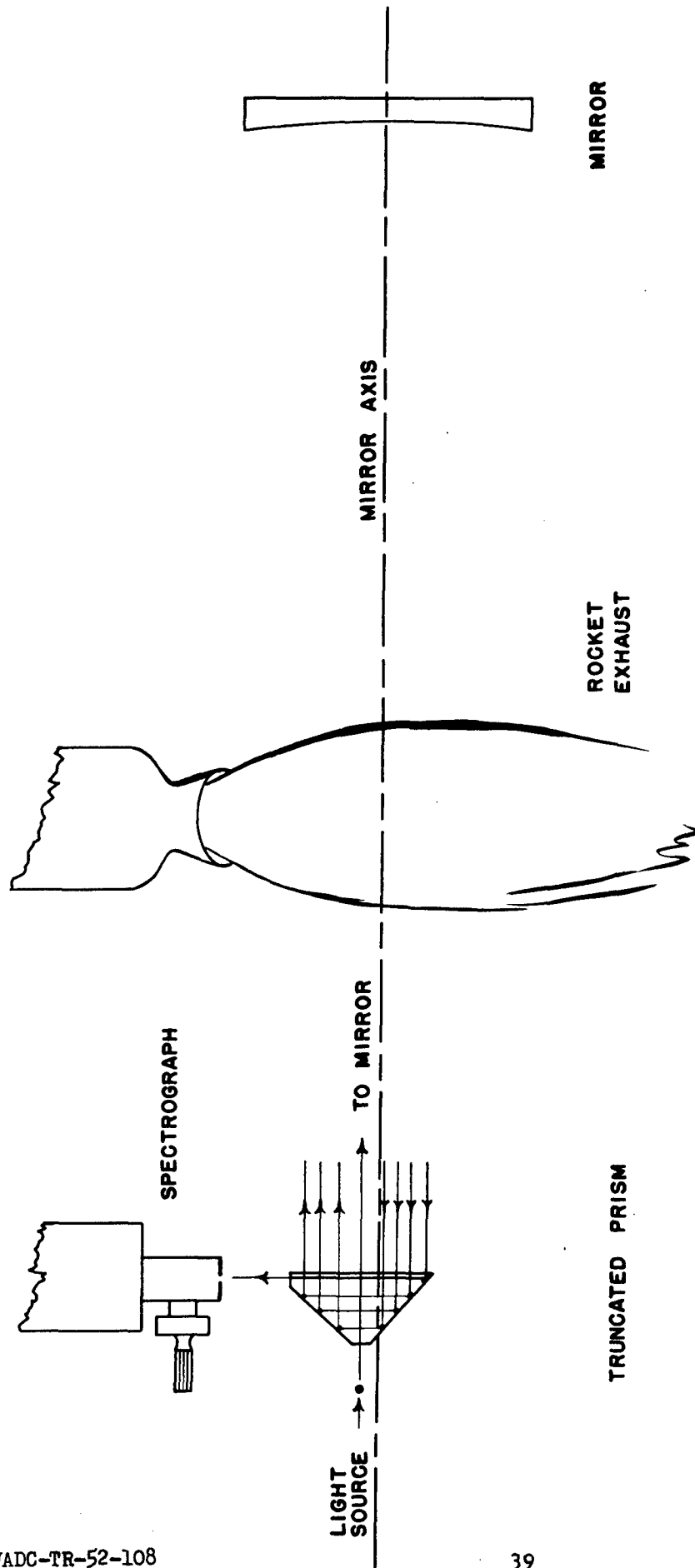Figure 17. Absorption Spectrograph

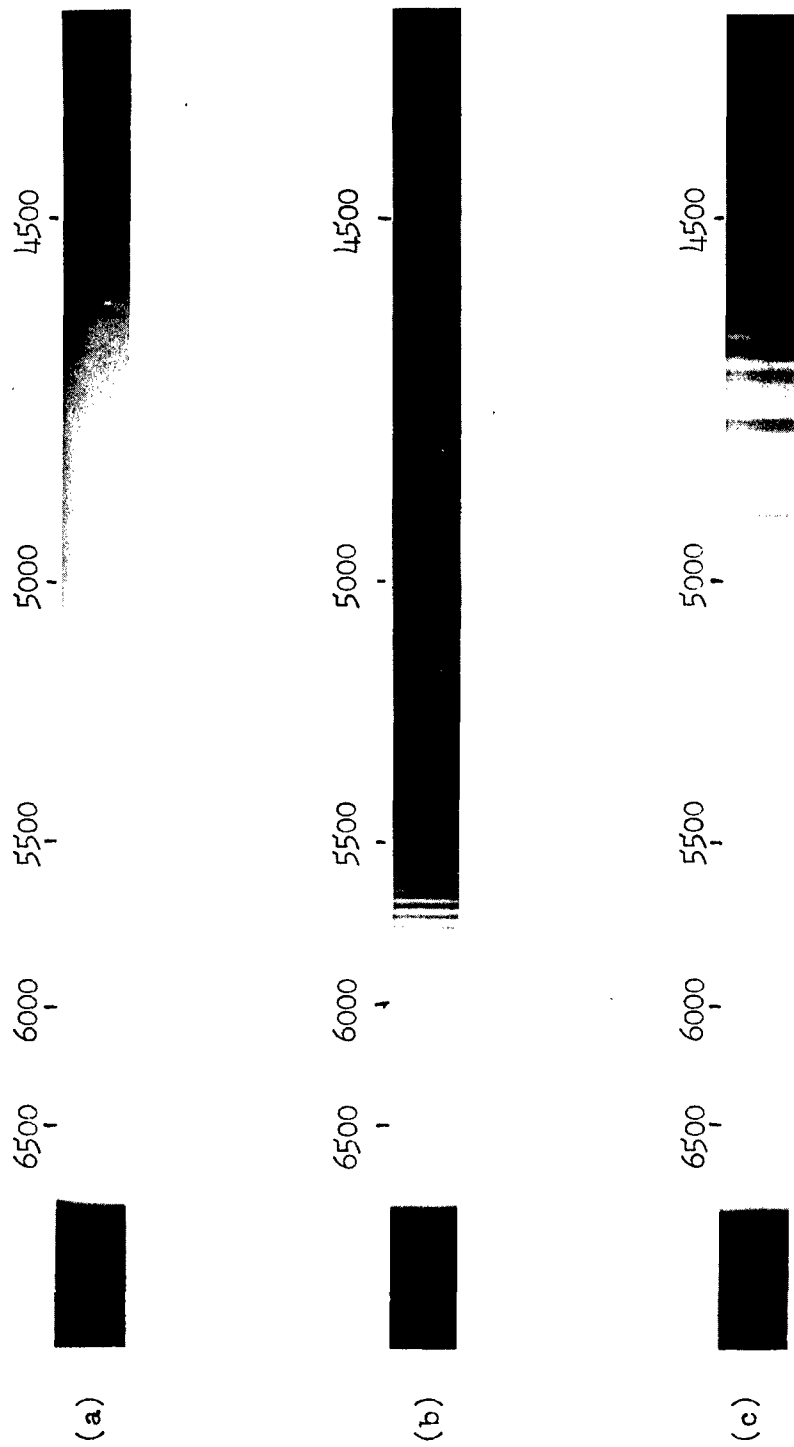FIG. 18   SCHEMATIC DIAGRAM OF OPTICAL SYSTEM
OF ABSORPTION APPARATUS

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Figure 19. Typical Spectra Obtained with Absorption Apparatus

(a) Light source
(b) Iodine vapor
(c) NO_2

reached the spectrograph. Possibly this light may obscure some of the absorption bands.

2. A different prism with very narrow truncated faces will permit a greater number of traversals and hence increase the length of the absorption path.

3. The use of quartz as the prism material along with the incorporation of a quartz spectrograph will increase the spectral range to include the ultraviolet region. Quartz with its low expansion coefficient is also desirable because the prism is heated by the intense light beam source and the rocket exhaust flames.

4. Since the diameter of the cross section of some of the rocket exhaust flames is relatively small, it is desirable to locate the rocket exhaust as near as possible to the prism where the various reflected beams are close together. If the exhaust is placed too far from the prism, some of these beams may pass between the prism and mirror without traversing the rocket exhaust.

SECTION VI

FLAME TEMPERATURE STUDIES

Introduction

In any study of reaction rates, the temperature at which the reaction occurs must be known, or determined. Various methods have been described in the literature[25] for the measurement of flame temperatures, but there is frequently some question as to the significance of the measured temperature, as well as to the reliability of the result. In general, it is best to arrive at a value by comparison of the results obtained from several determinations by independent methods. It is therefore advantageous to have available a variety of methods from which those most convenient for a given experimental condition can be chosen. In the following paragraphs, a method for determining the temperature of a rocket-exhaust flame having a black-body distribution of radiation is described.

A Method for Measuring Flame Temperatures

1. Theoretical Basis

The radiation emitted from a black body at temperature T is distributed among the various wavelengths, λ, in accordance with Planck's radiation equation, i.e.,

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[25] For discussion of optical methods, see S. S. Penner, Am. J. Phys., 17, 491 (1949).

$$E_\lambda d\lambda = \frac{hc^2}{\lambda^5}\left(\frac{1}{e^{hc/KT\lambda}-1}\right)d\lambda \qquad (1)$$

where E_λ is the intensity of radiation of wavelength, λ, h is Planck's constant, k is Boltzmann's constant, and c is the velocity of light. When the spectrum of the radiation from a black body is photographed, the blackening of the photographic film, quantitatively expressed in terms of the photographic density, D, is a measure of the relative intensity of this radiation. This relation can be represented by the following equation over a considerable range of photographic exposure

$$D = a \log_{10}(\text{Exposure}) \qquad (2)$$

where a is a constant for a given emulsion. Under conditions where the reciprocity law[26] is valid the exposure can be expressed as a product of intensity and time, i.e.,

$$\text{Exposure} = Et \qquad (3)$$

where E is the intensity and t is the time. Thus D is related to the intensity through the equation

$$D = a \log_{10} E + a \log_{10} t \qquad (4)$$

and on a spectrogram, at wavelength λ,

$$D_\lambda = a_\lambda \log_{10} E_\lambda + a_\lambda \log_{10} t_\lambda \qquad (5)$$

where a_λ is a function of wavelength.

For the spectrogram of a black body, the slope at a given wavelength of the experimental D vs λ curve would be given by the derivative of the equation given above, i.e.,

$$\frac{dD_\lambda}{d\lambda} = a_\lambda \frac{d}{d\lambda}(\log_{10} E_\lambda) + a_\lambda \frac{d}{d\lambda}(\log_{10} t_\lambda) \qquad (6)$$

For a particular spectrogram, t is the same for all λ, and the second term on the right is zero. E_λ is a function of the two variables λ and T, and for a given λ is a function of T only, i.e.,

$$\log_{10} E_\lambda = \log_{10} hc^2 - 5\log_{10}\lambda - \log_{10}(e^{hc/kT\lambda}-1) \qquad (7)$$

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[26] See C. E. K. Mees, The Theory of the Photographic Process (The Macmillan Co., New York, 1942) Ch. VI.

so that Equation (6) becomes

$$\frac{dD_\lambda}{d\lambda} = -a_\lambda \frac{d}{d\lambda}(5\log_{10}\lambda) - a_\lambda \frac{d}{d\lambda}\log_{10}\left(e^{hc/kT\lambda} - 1\right)$$

$$= -\frac{5a_\lambda}{\ln 10}\frac{d}{d\lambda}\ln\lambda - \frac{a_\lambda}{\ln 10}\frac{d}{d\lambda}\ln\left(e^{hc/kT\lambda} - 1\right)$$

$$= -\frac{5a_\lambda}{\lambda\ln 10} + \frac{a_\lambda}{\ln 10}\frac{hc}{kT\lambda^2}\frac{e^{hc/kT\lambda}}{e^{hc/kT\lambda} - 1} \qquad (9)$$

In the temperature and wavelength ranges at which the measurements are being made, i.e.,

$$T \cong 2500^\circ K \text{ and } \lambda \cong 5000A$$

$$hc/kT\lambda \cong 11.5$$

and

$$e^{hc/kT\lambda} - 1 \cong e^{hc/kT\lambda}$$

Therefore, Equation (9) simplifies to

$$\frac{dD_\lambda}{d\lambda} = -\frac{5a_\lambda}{\lambda\ln 10} + \frac{a_\lambda}{\ln 10}\frac{hc}{kT\lambda^2}$$

Hence, if $\frac{dD}{d\lambda}$ is measured at a particular λ for a black body at a series of temperatures T, a calibration plot of $\frac{dD_\lambda}{d\lambda}$ vs $\frac{1}{T}$ should be a straight line with slope equal to $\frac{a_\lambda hc}{k\lambda^2 \ln 10}$ and intercept equal to $-\frac{5a_\lambda}{\lambda\ln 10}$. From this plot the temperature of a black body can be determined by measuring $\left(\frac{dD}{d\lambda}\right)_\lambda$.

2. Experimental Procedure and Results

      A series of exposures on the same film were made with the grating spectrograph using a tungsten ribbon lamp at a series of known temperatures ranging from 1885 to 2135°K as the source. Super Panchro-Press, Sports Type film was used. The tungsten lamp was calibrated by means of a Leeds and Northrup optical pyrometer which had been checked against a tungsten lamp standardized at the General Electric laboratories. The exposure times were adjusted so that approximately equal maximum densities were obtained on the film for all temperatures. After exposure, the film was developed for 5 min in fresh Kodak DK-60a developer and fixed

in an appropriate fixer. Microphotometer traces of the spectra were then made. This gave the D vs λ curves. A convenient λ was arbitrarily chosen for measurement of slopes. This was usually chosen to be that λ at which the inflection was greatest. The slopes were then plotted vs the reciprocal temperature. Typical plots are shown in Figure 20. From this graph the temperature of a black-body source within this temperature range can be determined by measurement of the slope of the D vs λ curve at the same λ. On the assumption that the straight lines drawn through the points in Figure 20 represent the correct slope vs 1/T relationships, the estimated standard error was 24°K for the measurements at 5322 A, 35°K at 5430 A, and 41°K at 5591 A.

   3.   Discussion of the Method

        a.   The preliminary data obtained for the calibration of a tungsten ribbon lamp indicate that the black-body curve slope method is feasible for the measurement of temperatures of black-body radiators. A plot of the slope of the microphotometer trace at an appropriate wavelength vs the temperature of the source for a series of known temperatures serves as the working curve.

        b.   The principal experimental difficulty in the method is in estimating the correct exposure time for the various lamp temperatures and for the rocket flame. This difficulty was overcome to some extent by the discovery that there appears to be a linear dependence of the logarithm of the exposure time on the lamp temperature. The correct exposure time for the rocket flame can only be obtained by experimentation, but this may be reduced by introducing a neutral-density step filter at the slit of the spectrograph to give a series of exposures. The filter must be of fairly small dimensions so that the effects of possible nonuniformity in illumination of the slit would be avoided. When this is done, however, the height of the steps becomes small and may lead to errors in measurement of densities.

Conclusions and Recommendations

        1.   The studies described in the present report indicate that the temperature of a rocket exhaust flame which emits radiation characteristic of a black body can be measured by the black-body curve slope method. The feasibility of the method has been demonstrated, and there remains further developmental work to reduce the operational difficulties. However, the applicability of the method is limited by the fact that it can only be used to measure temperatures of flames which have a black-body radiation distribution. Furthermore, the temperatures measured by this method represent an average over the region of the flame photographed. It is therefore recommended that, in addition to the completion of the development of the black-body curve slope method, further work be initiated to develop a method which does not depend on a black-body distribution in the flame, and which can measure temperatures at a specified location in the flame.
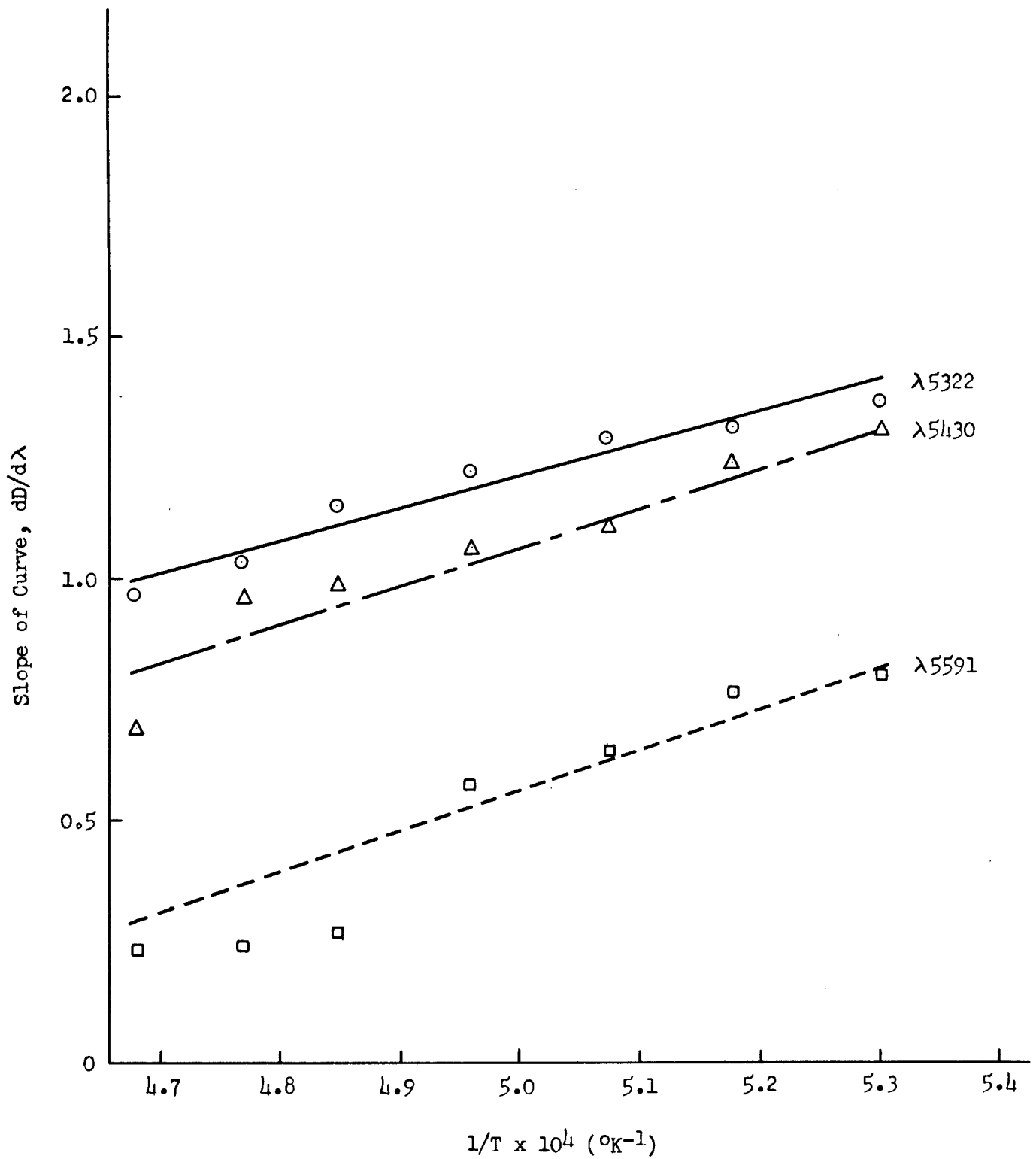
Figure 20.   Calibration Curve for Flame Temperature Measurement

2.   A method for flame temperature measurement which has not been applied to rocket chambers is that of Smit and Ornstein,[27] whereby a substance is added to a flame and the ratio of the intensities of two of the emitted spectral lines is used to calculate the flame temperature. It will be necessary to solve problems which arise as a result of self-absorption of the spectral line and perhaps also as a result of catalysis of the flame reactions by the additive. If these problems can be overcome, the method will afford a means by which the temperature distribution in the chamber and exhaust of a liquid rocket can be mapped. The value of a tool of this type justifies the investigation of the feasibility of the method as applied to rocket flames. For this purpose a high-resolution grating spectrograph should be constructed to obtain the details of the spectra in the visible and ultraviolet regions. A 1.5-meter concave grating which is ruled 30,000 lines/in., available on the present contract, should be used to construct a high-dispersion instrument for measuring quantitatively the intensity distribution of molecular emission bands as well as atomic emission lines. The instrument should be applied to laboratory flames to which the additive is added in controlled amounts at carefully controlled positions. With the solution of the fundamental problems in the laboratory, the method should then be applied to rocket firings.

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[27] J. A. Smit, Physica 2, 683-700 (1946).

ATI-155 638

Aerojet Engineering Corp., Azusa, Calif.
CHEMICAL KINETICS PHENOMENA IN ROCKET
ENGINES, by S.C. Burket, G. Moe, and J.L.
Nicholson. June '52, 66 pp. incl. photos, table, diagrs,
graphs.   UNCLASSIFIED

As part of an exploratory program of research in the
chemical and physical kinetics of rocket exhaust
gases, the emission spectra of rocket flames were
examined with infrared, visible, and ultraviolet
spectrographs of moderate dispersion. A method of
recording the changes in emission spectra along the
axis of rocket exhaust flames was devised and tested.
(over)

1. Engines, Rocket -
   Combustion
2. Flames, Exhaust
3. Flames - Spectroanalysis
4. Reactions, Chemical -
   Kinetics
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II. Moe, G.
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The method was shown to be feasible and should be applied to the study of a wide variety of rocket flames. An apparatus was constructed for the examination of rocket flame absorption spectra. Preliminary experiments which were made with the equipment show that the method is promising, but further development will be necessary. It is recommended that a method which is based on the measurement of the ratio of intensities of two spectral lines emitted by the same flame species be investigated as a possible tool for use in mapping temperature distribution.