A BASIC STUDY ON THE IGNITION OF HYPERGOLIC LIQUID PROPELLANTS

INTERIM (12 MONTH) FINAL REPORT SN-80-MOD 3-F

NAS 7-438

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L. B. ZUNG, E. A. TKACHENCKO, AND B. P. BREEN

DYNAMIC SCIENCE A DIVISION
OF MARSHALL INDUSTRIES
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FOREWORD

This interim (12 month) report documents the work performed at the Dynamic Science Division of Marshall Industries under NASA Contract NAS7-438, Dynamic Science Number SN-80 Mod 3-F, for the period 5 May 1967 to 5 May 1968.

All phases of this contract were monitored by Dr. Raymond Kushida of Jet Propulsion Laboratories. At Dynamic Science, Dr. L. B. Zung was the program manager assisted by Dr. E. A. Tkachenko. Dr. B. P. Breen was the Director of Combustion Research and approved all phases of the work.

Thanks are expressed to Mr. B. R. Lawver for his help in designing and building the experimental model. The Quantitative Analysis of Reaction Products was performed by Aerojet-General Analytical Laboratories, under the direction of Mr. D. L. Quick, Chief Investigator.

CONTENTS

SUMMARY

A brief critical review of the ignition mechanism of the hypergolic propellant system hydrazine/nitrogen dioxide* is presented.

Quantitative analysis of the distribution of products due to gas phase reactions of hydrazine/nitrogen dioxide at low concentrations ($\approx$ 1-6 mole %) and low temperatures ($0^{o}C$ and $25^{o}C$) gives N_2O, NO, N_2, and H_2O as the main gaseous products. With an excess of hydrazine, hydrazinium nitrate is observed as the predominant solid intermediate. With excess nitrogen dioxide, ammonium nitrate is found to be the main solid intermediate. Any hydrazinium nitrate formed as an intermediate may be presumed to react with the excess nitrogen dioxide to yield ammonium nitrate.

Ignition studies are conducted using a burner based on the principle of stagnation flow field. By introducing nitrogen dioxide-nitrogen gas mixture to flow over liquid hydrazine, in a direction normal to the liquid surface, minimum concentrations of nitrogen dioxide that induce ignition are measured as a function of hydrazine temperature. Effects of flow Reynolds number, burner pressure, oxidizer temperature and hydrazine water content are being evaluated. For a 30% increase in flow velocity, it is observed that the threshold concentration of nitrogen dioxide increases by about 20%.

It is found that for hydrazine temperature under approximately $310^{o}K$, the vapor pressure of hydrazine is not high enough to sustain a vapor phase ignition. Reactions between nitrogen dioxide and liquid hydrazine are significant as evidenced by foaming and bubbling observed on the liquid surface. Heat release associated with these reactions gradually raise the hydrazine temperature which in turn leads to a vapor phase ignition. Measurements also show that for hydrazine temperatures below $310^{o}K$, the threshold nitrogen dioxide concentration assumes a constant value. This can be partly explained by the fact that the rate of diffusion of nitrogen dioxide plays a more dominant factor in the vapor-liquid phase reaction. Foaming and bubbling on the liquid surface are less significant at higher temperatures. For hydrazine near its boiling point, it is observed that ignition can take place before the introduction of nitrogen dioxide mixture. It is presumed that hydrazine at these temperatures can react with oxygen in the burner leading to ignition.

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*In the text, nitrogen tetroxide or nitrogen dioxide represents the equilibrium mixture of nitrogen tetroxide and nitrogen dioxide.

INTRODUCTION

Reliable starting and restarting at space conditions of rocket engines employing hypergolic propellants is essential for the success of present and future space missions.

Present experience with vacuum ignition of hypergolic bipropellants, nitrogen tetroxide/hydrazine and nitrogen tetroxide/hydrazine-derivatives, shows that damaging, high amplitude pressure waves develop, on occasion, during space starts. A sufficient understanding of the ignition process for these propellant combinations must be gained in order to eliminate or suppress space start problems.

Research work concerning preignition stoichiometry and the ignition threshold (in the presence of a fuel liquid surface) for the nitrogen tetroxide/hydrazine system has been carried out. Gas phase reactions at low temperature and low concentrations (diluted with helium so as to produce an isothermal environment) clarify whether explosive solid intermediates such as NH_4NO_3 and $N_2H_5NO_3$ are formed. Further by monitoring the N_2H_4-NO_2 reactions, it helps to resolve the question as under what conditions the NH_4NO_3 or $N_2H_5NO_3$ is the predominant solid intermediate. Quantitative results from these preignition chemistry studies can be used as inputs to certain mathematical space start model (Ref. 1). The reason for this is, that any clarification of the paths of formation of detonable and sensitizing substances, together with the associated preignition heat release and gas formation, will help predict chamber pressurization and the chemical species present in the chamber at ignition.

Ignition of N_2H_4(liquid)-N_2O_4(vapor) system presents complications which do not often exist in the gas phase reactions. When the hydrazine vapor concentration, given off by the liquid, is not high enough to sustain a vapor phase ignition, reactions can occur between nitrogen tetroxide and liquid hydrazine. The dissolved solid products produced by the preignition reactions contaminate the liquid fuel to the extent of changing its ignition characteristics significantly from that of a "clean" fuel. Determining the range of pressure and temperature conditions within which the vapor/liquid or vapor/vapor reactions predominate are important.

In summary, results of practical significance gained from these studies will indicate potential space start problems and thus help in formulating design and operational criteria for the propellant systems.

CRITICAL EVALUATION OF IGNITION MECHANISM

Hypergolic propellant ignition involves a complex interrelationship of chemical and physical phenomena. During rocket engine ignition the rates of preignition reactions, the chemical nature of preignition products, and the associated heat release are closely coupled with physical transport properties such as heat and mass transfer. In order to help unravel the relative significance of these basic processes on hypergolic ignition, it becomes necessary to isolate, and study separately and under controlled conditions, important chemical and physical factors. Some such studies have been already carried out for the N_2O_4/N_2H_4 propellant combination and have been reported in the literature, and presented at an informal meeting on hypergolic ignition(Ref.2). As a background to the discussion of the research performed in this investigation, a brief and critical review of important work concerning the ignition mechanism for the N_2O_4/N_2H_4 system, will be presented. Reference will be made to the open literature, as well as to subject matter presented at conferences, although still unpublished.

The chemistry of the system N_2O_4/N_2H_4 is undoubtedly complex both from the standpoint of kinetics and of the diversity of reaction products. In addition, the reaction rates in the gaseous or liquid phase are very rapid (ignition delay times of the order of microseconds (Ref. 3) to milliseconds (Ref. 4) depending on the method of measurement), and the overall reaction is highly exothermic. Preignition reactions in the vapor phase yield gaseous as well as condensed reaction products (Ref. 5). For these reasons, and because it was believed that mere identification of reaction product species already could help to better understand rocket engine vacuum start problems, most investigations to date have been qualitative studies. More recently, as in the present study, emphasis is placed on the quantitative determination of the preignition chemistry. Quantitative data concerning preignition stoichiometry, is highly useful for the calculation of preignition heat release as well as for obtaining the actual mass of explosive substances formed during the preignition period.

Although relatively extensive literature reviews concerning hypergolic propellant ignition, in general, have been performed (Ref. 6) a critical evaluation of studies dealing with chemical aspects of the ignition mechanism is presently not available. In the following, the most pertinent work treating N_2O_4/N_2H_4 ignition will be discussed in brief.

Gaseous reaction products of the argon N_2O_4/N_2H_4 vapor reaction have been analyzed (Ref. 5). The mass spectrometric, infrared, gas chromatographic methods, or combinations of these techniques for gas analysis yielded N_2, NO, N_2O, NH_3, and H_2 as detectable products. No attempts were made to determine H_2O or any condensed species. The reactants were always introduced at equal molar quantities ranging from 2 mole % each to 6 mole % each, the remainder being argon. Thus, the effect of N_2O_4 or N_2H_4 excess on the nature or relative quantities of reaction products was not investigated. In order to explain the formation of the detected gaseous reaction products eighteen known, and possible sub- or side reactions for the N_2O_4/N_2H_4 system were considered. Most of these reactions occur at high temperature ($T > 770^{\circ}K$) and as such are not directly useful to explain the low temperature preignition mechanism. The only cited reaction indicated as taking place at room temperature is

$$N_2H_4(\ell) + 2NO_2(g) \rightarrow N_2O(g) + NH_4NO_3(s). \qquad (1)$$

This equation accounts only partly for the chemical species detected at low reactant concentrations (and therefore low temperature rise). The formation of ammonium nitrate was found to occur when a hydrazine droplet is exposed to nitrogen tetroxide (2.0 mole %) argon gas mixtures. It must be borne in mind, however, that the droplet experiment does not provide controlled, or well defined, reactant concentrations, since the influences of convection, diffusion, and heat transfer are difficult to evaluate.

To sum up, Skinner, Hedley, and Snyder's work concerning the N_2O_4/N_2H_4 system indicates that the ignition process proceeds by a thermal, rather than a free radical mechanism. The cited possible and known subreactions apply mainly to higher temperature levels than encountered in vacuum start preignition reactions.

Perlee, Christos, and Miron (Ref. 7) carried out ignition experiments with N_2O_4/N_2H_4 in a two-dimensional, plastic combustion chamber, studying both physical and chemical aspects of hypergolic ignition. Of considerable interest from the chemical standpoint is the fact that, during the ignition transient, residue accumulates on the chamber wall in sufficient quantity to make possible chemical analysis. By means of the infrared method, the engine residue was analyzed, and this spectrum was compared to the spectrum of laboratory prepared hydrazinium nitrate. These two spectra are nearly indistinguishable, indicating that at the end of the plastic engine experiment, the same material is present on the engine walls as was prepared in the laboratory by reacting a hydrazine/water solution with nitric acid and then removing the water by freeze-drying methods.

An additional experimental fact, namely the presence of water solutions of hydrazinium nitrate on the chamber wall after the termination of the ignition experiment, raises the question whether (1) a hydrazine film deposits on the engine walls and subsequently reacts with nitrogen tetroxide vapor to form hydrazinium nitrate, or (2) the reaction occurs in the gas and liquid phases in the reactor space, and the mixed reaction products ($N_2H_5NO_3$ and H_2O) accumulate on the walls. Although bringing up these questions, Perlee, Christos, and Miron do not pursue further the possible predominance of either mechanism. In general, the experimental apparatus and procedure employed in the cited study tend to simulate actual rocket engine ignition at near vacuum conditions, and as such do not attempt to isolate the chemical from the physical transient processes.

Since the research effort reported in Reference 7, Perlee and coworkers have continued with additional work on the N_2O_4/N_2H_4 system. In particular, at the "Pressure Spike Symposium" held on 15 November 1967 at NASA, Houston, Perlee described modifications of the two-dimensional plastic rocket engine, such as a "freeze plug" and high response pressure measuring devices, designed to resolve better details of the hypergolic propellant start transient at vacuum conditions.

At the same Symposium, Ray, Koehler, Salser, and Dauerman presented a paper (unpublished) concerning chemical intermediates possibly responsible for pressure spikes in engines using N_2O_4/N_2H_4. On the basis of their experimental results, these investigators propose that hydrazoic acid and azides are responsible for the space start spiking problem. Employing rapid-scanning infrared and rapid-scanning mass spectroscopy, hydrazoic acid and azides were identified. Attention should be called to the fact that these reaction products were formed after mixtures of N_2O_4 condensed (at liquid N_2 temperatures) onto N_2H_4 and were allowed to warm up slowly. Similar experiments were performed condensing N_2H_4 onto N_2O_4. The effects of N_2H_4 excess, and N_2O_4 excess, were investigated. Although the formation of azide at the cited experimental conditions has been demonstrated, we must bear in mind that the temperatures prevalent in this work are far below those to be expected at rocket engine space start conditions (Ref. 8). Without discussing in detail the literature and their own experimental basis for the reaction scheme proposed by Dauerman and coworkers, their overall mechanism is stated as follows:

$$6N_2H_4 + 5N_2O_4 = 5NH_4NO_3 + 3N_2O + 3N_2 + 2H_2O \tag{2}$$

$$2H_2O + 2N_2O_4 = 2HNO_3 + 2NHO_2 \tag{3}$$

$$2N_2H_4 + 2HNO_3 = 2N_2H_5NO_3 \tag{4}$$

$$2N_2H_5NO_3 + 2HNO_2 = 2HN_3 + 2HNO_3 + 4H_2O \tag{5}$$

$$2HN_3 + 2N_2H_4 = 2N_2H_5N_3 \tag{6}$$

$$2HNO_3 + 2N_2H_4 = 2N_2H_5NO_3 \tag{7}$$

$$12N_2H_4 + 7N_2O_4 = 5NH_4NO_3 + 2N_2H_5NO_3 + 2N_2H_5N_3 + 3N_2O + 3N_2 + 4H_2O$$

Compared to Skinner and coworkers' results concerning gaseous reaction products, the above overall stoichiometry neglects to account for the presence of NO and NH_3. An additional comparison of Dauerman and coworkers' infrared spectra can be made with those of Weiss (Ref. 9). Carrying out experiments at similar temperature conditions, the infrared spectra of Weiss indicate absorption at 4.9μ, confirming the presence of N_3^- (the vibrational frequencies of NH_4NO_3 for example are $1345cm^{-1}$, $652cm^{-1}$, and $2030cm^{-1}$, of which $1345cm^{-1}$ is not infrared active, and $652cm^{-1}$ is beyond the recorded wavelength range).

In summary, Dauerman and coworkers' qualitative instrumental analytical study at low temperatures of the N_2O_4/N_2H_4 reaction indicates the formation of azides in addition to previously identified species.

Ignition delay measurements were made on the liquid hydrazine and liquid nitrogen tetroxide system (Ref. 4). Modification of ignition delay times due to the effect of additives were observed. A total of twenty four additives were used on hydrazine and in one case iodine was added to nitrogen tetroxide. The measured ignition delay time of 2.9 milliseconds was reported. With additives, the delay time varies from 1.2 milliseconds for triethylborane to 3.9 milliseconds with solid ethylbromide dissolved in hydrazine. Delay times were shortened with surfactant FC-126 and Santomerse 85, two surface active agents, indicates that solubility of the two reactants is a factor in the delay times. The authors suggested that preignition reactions might be proceeded by a chain branching mechanism. Although based on modifications of delay time due to additives it does not conclusively support this view. Ignition studies with additives have also been conducted by Skinner, et al (Ref. 5). Gas mixtures containing 15 mole % nitrogen tetroxide, 80% argon and 5% inhibitor were tested. None of the twenty seven gaseous inhibitors tested prevented ignition under these conditions. Similar gas mixtures containing vaporized liquid inhibitors were also tested. Eight liquid inhibitors among the twenty eight appeared effective. Ignition delay measurements were not reported. In view of the fact that failure to find any highly effective inhibitors out of fifty five candidates tried, the authors suggest that a thermal reaction mechanism is operative. Based on these works, there are disagreements on the governing ignition mechanisms. It is noteworthy that there are only four out of the fifty-five additives used by Skinner et al (Ref. 5,) were tested in the delay measurements (Ref. 4). Of these four water and ethyl iodide reported ineffective by Skinner et al, shortened the delay time by 0.3 millisecond and 0.2 milliseconds respectively; benzene and diethylether reported as effective shortened the delay time by approximately 1.2 milliseconds.

Ignition studies at low pressure simulating space environmental conditions have been conducted, (Ref. 10, 11, and 12). Results are mostly qualitative. Minimum ignition pressures have been measured. These data appeared to depend on the experimental apparatus and above all, on the method used in admitting the propellants to the reaction chamber. Three reaction chambers of various sizes were used by Wilber, et al (Ref. 11 and 12). With respect to the gas phase reactions in the ten liter system with initial gas temperature close to 280° K spontaneous ignition occurred at total pressures between 0.41 torr and 0.04 torr. (Fuel to oxidizer ratio was not specified). Ignition pressures decrease by a two order of magnitude between the 0.1 liter vessel and the 1600 liter vessel. Based on these data, the ignition pressure of approximately 0.1 torr was extrapolated to a reaction chamber of volume-to-area ratio of sixty inches. Based on an entirely different injection system, Wasko (Ref. 10) obtained ignition pressure of an order of magnitude larger.

Flammability characteristics of hydrazine fuels in nitrogen tetroxide atmospheres have been studied using a modified ASTM autoignition temperature apparatus (Ref. 13). At ambient temperature (298° K) and pressure, liquid hydrazine ignite spontaneously in nitrogen tetroxide-air mixtures containing 14% of nitrogen tetroxide by volume. Spontaneous ignition temperature was found to increase with decreasing hydrazine temperature. This certainly appears to be reasonable when thermal ignition is operative since an increase in the fuel vapor concentration due to higher liquid temperatures increase the reaction rate at any specified oxidant temperature and concentration and thereby lowers the spontaneous ignition temperature. But a closer examination of the experimental data presented (Fig. 1, Fig. 2 of Ref. 13) appears to indicate that spontaneous ignition temperature for liquid hydrazine at 298° K is lower than that at 309°K.

Ignition of a hydrazine droplet fell into a pool of nitrogen tetroxide has been studied (Ref. 14). Qualitative results have been obtained. Probability of explosions seem to depend on the impact velocity. Ignition studies by impinging two streams of liquid hydrazine and liquid nitrogen tetroxide is presently being carried out at Dynamic Science (Ref. 3). Ignition at the point of impact of the two streams plays a dominate role in the stream separation phenomena. Stream separation characteristics have been defined in terms of first Damkohler number. It appears that for large Damkohler number (greater than one), ignition appears to occur at the point of impact.

To summarize, we observe that explosive solid intermediates such as NH_4NO_3, $N_2H_5NO_3$ and azide were formed depending on various experimental conditions. The temperatures range, in which azide formation has been demonstrated, are far below those expected in rocket conditions. The possibility of pressure spikes due to azides in engines using N_2H_4/N_2O_4 is subject to considerable question. Questions regarding various processes in which $N_2H_5NO_3$ is formed have been raised (Ref. 7), but no attempts were made to resolve these questions and to relate to the conditions in which NH_4NO_3 is formed (Ref. 5). In fact, part of the present work as discussed in Quantitative Analysis of Reaction Products of this report is to define conditions in which $N_2H_5NO_3$ or NH_4NO_3 is formed.

It appears that governing ignition mechanisms for vapor phase and liquid phase reactions are quite different. Vapor phase ignition studies with additives have been conducted by Skinner, et al (Ref. 5) where the authors suggest that a thermal reaction mechanism is operative. Based on ignition delay measurements made on liquid hydrazine and liquid nitrogen dioxide (Ref. 4), Gerstein, et al suggested that preignition reaction might be preceded by a chain branching mechanism.

Useful data on ignition have been obtained at simulating space environmental conditions (Ref. 10, 11, 12, 13). Results are mostly qualitative and appeared to depend on the experimental techniques being employed. To help resolve some of these questions, part of the present study, which is described in the section on Ignition Studies of this report, is to determine ignition thresholds as functions of Reynolds number, total pressure and fuel temperature.

QUANTITATIVE ANALYSIS OF VAPOR PHASE REACTION PRODUCTS OR HYDRAZINE AND NITROGEN TETROXIDE

Statement of Problem

The complexity of hypergolic propellant ignition in general, and that of the nitrogen tetroxide/hydrazine (hydrazine derivative) system in particular, necessitates the study of the nature and stoichiometry of preignition products of such a system. In order to examine products formed under preignition conditions, dilute mixtures of N_2H_4 and N_2O_4 were introduced into a batch reactor. Main reason for dilution is to keep temperature rise small and hence obtain nearly isothermal reaction. The reactor and sampling system were designed and built to provide the following features: (a) inert surfaces, (b) rapid mixing of reactants, and (c) easy removal of gas, liquid, or solids reaction products. Reactions of hydrazine and nitrogen tetroxide, at varied mole ratios, were carried out at 0°C and 25°C.

Experimental Apparatus

Reaction and Sampling System. - A Pyrex glass system was used in preference to metal because of the known catalytic decomposition effects of certain metals (e.g., Fe^{+++}, Cr^{+++}, Al^{+++}, Cu^{++}, Ni^{++}) upon hydrazine. All control valves used in the reaction and sampling system were Fischer and Porter 4 mm quick opening Teflon valves(Cat.#795-120-0004). Connections between the reaction chamber, holding bulbs, and trap (Figure 1), were glass/butyl O-ring vacuum connectors. Potential reactive sites such as metals and vacuum grease were excluded from the reaction and trapping zones. The relative volumes of the bulbs and the reaction chamber allowed a 1 to 7 expansion and mixing of the reactants into the reaction chamber.

Procedure. - Known amounts of hydrazine and nitrogen dioxide were blended with helium to 600 mm pressures in separate holding bulbs. Nitrogen dioxide/helium mixtures were blended by a pressure/volume relationship (corrected for $N_2O_4 \rightleftarrows 2NO_2$ dissociation). Hydrazine was measured by a liquid microliter Micro Tek vacuum pipet and cryogenically transferred into a holding bulb for pressurizing with helium. The two holding bulbs were attached to the reaction chamber, allowed to equilibrate at the desired temperature, and surged into the evacuated reaction chamber maintained at the same temperature. At time (t), a gas aliquot (reaction products + helium) and/or the condensables (at -175°C) from the reaction chamber were trapped and transferred to the mass spectrometer for analysis. Solid residues from the reaction were collected after each series of similar reactions (N_2O_4 or N_2H_4 in excess) by solvent extraction with methanol. It is anticipated that at these low temperatures, reactions between solid residues and methanol are not significant. The extracts were submitted for infrared analysis.

Mass Spectrometer. - A CEC 21-130 mass spectrometer was used for all gas analyses. A unique feature of this instrument is a special low volume fractionation and sample introduction system placed in parallel with the conventional sampling system. The special inlet because of its low surface area ($\approx$1/100 that of the conventional system) is invaluable when surface effects, temperature, or minute sample size preclude the conventional approach.

Infrared Spectrometry. - Six methanol extracted residues from the N_2O_4/N_2H_4 reactions were submitted for infrared analysis. The solid residues were prepared as thin films and/or KBr pellets. Selected infrared spectra of the solids are included in the Appendix (Fig. 14 to 25).

Experimental Results

Twenty-nine low pressure nonignition vapor phase reactions of hydrazine and nitrogen tetroxide were carried out. Milligram weights of each reactant were separately diluted with helium, to concentrations of 0.6 to 2.5 mole-%. The partial pressures of the reactants were, accordingly, of the order of about 1 torr. Reactant concentrations and ratios were varied to determine their effects upon the solid or gaseous reaction products. Reactions were carried out at 25 and 0°C. The data are presented in Table I.

Reactions at 25°C. - Run numbers 1, 3, and 4 represent, respectively, approximately equal mole concentrations of N_2H_4 and NO_2, N_2H_4 excess, and NO_2 excess. Run numbers 23 through 28 are with nearly equimolar concentrations of NO_2 and N_2H_4, repeated six times to collect sufficient solids for accurate weighing. Table III lists the four solids obtained from the 25°C reactions of NO_2 and N_2H_4.

The results of the mass spectrometric gas analysis from run numbers 1,

TABLE 1

LOW PRESSURE $N_2O_4^*/N_2H_4$ REACTIONS

Run No.	Reactants (mg)			Reactants as Mole-% of Total Gas Pressure				Reaction Time Min.
	N_2O_4(1)	N_2H_4	H_2O	NO_2(1)	N_2H_4	H_2O	Temp. °C	
1	1.6	1.0	-	0.6	0.7	-	23.3	95
2	2.9	1.0	-	1.4	0.7	-	23.7	40
3	1.6	2.0	-	0.6	1.3	-	24.5	25
4	4.3	1.0	-	2.0	0.7	-	24.5	15
5	1.6	-	-	0.6	-	-	24.0	15
6	-	1.0	-	-	0.7	-	24.0	25
7	-	1.0	-	-	0.7	-	24.0	45
8	-	1.0	-	-	0.7	-	-	-
9	1.7	1.0	-	0.8	0.7	-	24.5	25
10	3.8	1.0	-	1.7	0.7	-	24.5	25
11	5.3	1.0	-	2.5	0.7	-	25.0	15
12	1.7	1.0	-	0.8	0.7	-	24.5	1(2)
13	1.7	2.0	-	0.8	1.3	-	24.5	15(2)
14	1.7	3.0	-	0.8	2.0	-	25.0	15(2)
15	1.7	1.0	1.0	0.8	0.7	0.5	25.0	30
16	3.8	1.0	-	1.7	0.7	-	25.0	-
17	1.7	1.0	-	0.8	0.7	-	0	-
18	1.7	1.0	-	0.8	0.7	-	0	15
19	1.7	2.0	-	0.8	1.3	-	0	15(2)
20	3.8	1.0	-	1.7	0.7	-	0	15
21	3.8	1.0	-	1.7	0.7	-	0	35
22	3.8	1.0	-	1.7	0.7	-	0	15(2)
23	1.1	1.0	-	0.8	0.7	-	24.0	60
24	1.1	1.0	-	0.8	0.7	-	25.0	15
25	1.7	1.0	1.0	0.8	0.7	0.5	25.0	55
26	1.7	1.0	-	0.8	0.7	-	24.0	60
27	1.7	1.0	1.0	0.8	0.7	0.5	24.0	24 hours
28	1.7	1.0	-	0.8	0.7	-	24.0	25
29	3.8	2.0	-	1.7	1.3	-	25.0	2

*(1) Blended by pressure measurement and corrected for $N_2O_4 \rightleftarrows 2\,NO$ dissociation.

(2) Gaseous products introduced into special mass spectrometer (bypasses conventional inlet) and analyzed.

3, and 4 are presented in Table II (run number 2 was discarded because of air contamination). The predominant gaseous species resulting from all the runs are N_2O, and N_2. Hydrogen was not observed in any case. In run numers 1 and 4, lean in terms of N_2H_4 concentration, N_2O, N_2, and NO concentrations are higher than in run number 3, rich in N_2H_4. NH_3, which was not detected in the other two runs, is very prominent in the N_2H_4-rich run number 3. Solids formed and/or losses calculated from material balance data for run numbers 1 and 3 are similar; however, the value for run number 4 is much higher. This larger value (in the absence of sufficient N_2H_4 for complete reaction) may be due to the loss of excess NO_2 by reaction with the mass spectrometer inlet walls. This is, at least qualitatively, indicated by the presence of CO_2 in the reaction gases. The gas reaction products are compared with those of Reference 5 and are shown in Figure 2.

The solids formed successively from run numbers 1 through 4 were collected, and an infrared spectrum was obtained as presented in Figure 14 and 15 of the Appendix. The solid reaction products from run numbers 9 through 11 (NO_2 excess) and 12 through 14 (N_2H_4 excess) are shown in the infrared spectra of Figures 16, 17, 18, and 19 respectively. Inspection of the infrared spectrum (Figures 16 and 17) of solid No. 2 (excess NO_2) shows strong absorbance peaks at 3.2 to 3.3 microns ($\approx 3000\ cm^{-1}$) at 7.0 to 7.5 microns (≈ 1430 to $1340\ cm^{-1}$), 12.0 microns ($\approx 840\ cm^{-1}$), that can be attributed to ammonium nitrate. Minor peaks at 9.4 microns and 10.6 microns indicate a relatively small amount of $N_2H_5{}^+$ion. The presence of other minor peaks also indicates additional compounds not resolved. The formation of an azide ($N_3{}^-$)ion is not indicated because of a lack of absorption at ($2030-2040\ cm^{-1}$), Solid No. 1 shows an absorption spectrum similar but much weaker than that from solid No. 2. The infrared spectrum of solid No. 3(N_2H_4 excess) from run numbers 12 to 14 shows hydrazinium nitrate to be the major solid constituent. Again there is no positive indication of the $N_3{}^-$ion.

Gaseous and solid products from run numbers 23 to 28 are summarized in Table 4. Nearly equimolar concentrations of reactants were introduced into the reaction chamber six times in order to obtain a weighable amounts of solids. Water was added to one of the reactants in run number 25 (added to NO_2) and run number 27 (added to N_2H_4) before the reaction. Effect of water addition increases the N_2O production. The recovered solid reaction product for the six reactions weighed 6.102 mg or a little over one mg per reaction.

TABLE II

GASEOUS PRODUCTS FROM REACTIONS 1, 3, and 4

Components	Run No. 1	Run No. 3	Run No. 4
NO_2	Not detected	0.2 Mole %	Not detected
N_2O	44.3 Mole %	34.0 Mole %	47.1 Mole %
NO	3.3 Mole %	1.2 Mole %	6.0 Mole %
N_2H_4	0.4 Mole %	0.2 Mole %	0.2 Mole %
NH_3	Not detected	24.2 Mole %	Not detected
N_2	13.3 Mole %	7.4 Mole %	16.2 Mole %
O_2	2.0 Mole %	0.7 Mole %	Not detected
H_2O	37.0 Mole %	31.7 Mole %	28.8 Mole %
A	< 0.1 Mole %	Not detected	Not detected
CO_2	Not detected	Not detected	1.6 Mole %*
Reactants			
N_2O_4	1.6 mg	1.6 mg	4.3 mg
N_2H_4	1.0 mg	2.0 mg	1.0 mg
Total mg collected as Gas	1.2 mg	2.3 mg	2.6 mg
Solid + loss	1.4 mg	1.3 mg	2.7 mg

*Reaction of NO_2

TABLE III

SOLID SAMPLES FROM N_2O_4/N_2H_4 REACTIONS

Solid No.	Reaction Series*	
1	Run No. 1	25° C Reactions equimolar
	2	excess NO_2
	3	excess N_2H_4
	4	excess NO_2
2	Run No. 9	25°C Reactions N_2O_4 in excess
	10	
	11	
3	Run No. 12	25°C Reactions N_2H_4 in excess
	13	
	14	
4	Run No. 15	0° C Reactions N_2H_4 in excess
	16	
	17	
	18	
	19	
5	Run No. 20	0°C Reactions N_2O_4 in excess
	21	
	22	
6	Run No. 23	25°C Reactions approx. equimolar concentrations of N_2O_4 and N_2H_4 Solids collected and weighed
	24	
	25	
	26	
	27	
	28	

*Methyl alcohol used to remove solids from reactor after each series of reactions. Solids analyzed by I.R.

TABLE IV

GASEOUS AND SOLID PRODUCTS FROM REACTIONS 23 TO 28

Run Number	23(1)	24	25	26	27	28
Major Reaction Products (mg)						
NO	-	0.2	0.3	<0.1	0.2	<0.1
N_2O	-	0.5	0.7	0.4	1.1	0.3
H_2O	-	0.1	0.6	0.1	1.0	0.1
Reactants (mg)						
N_2H_4	1.0	1.0	1.0	1.0	1.0	1.0
NO_2	1.7	1.7	1.7	1.7	1.7	1.7
H_2O	-	-	1.0	-	1.0	-
Total Gaseous Reaction Products Recovered (calc.)	-	0.9	1.7	0.6	2.5	0.5
Avg. Solid Reaction Product per Reaction (2)	1.0	1.0	1.0	1.0	1.0	1.0
Loss	-	0.8	1.0	1.1	0.3	1.2

(1) Reaction products were not analyzed.

(2) Solid No. 6 collected from Reactions 23 to 28 weight 6.102 mg.

In the chemical equation

$$6\ N_2H_4 + 10\ NO_2 = 5\ NH_4NO_3 + 3\ N_2O + 3\ N_2 + 2\ H_2O \qquad (8)$$

the weight ratios of NH_4NO_3 to N_2O and to H_2O are 1 to 0.33 and 1 to 0.09. In the chemical equation

$$3\ N_2H_4 + 4\ NO_2 = 2\ N_2H_5NO_3 + N_2O + N_2 + H_2O \qquad (9)$$

the weight ratios of $N_2H_5NO_3$ to N_2O and to H_2O are 1 to 0.23 and 1 to 0.09. The weight ratios of solids to N_2O for three of the above reactions (in the absence of added water) were 1 to 0.5, 0.4, and 0.3; for water the ratios were 1 to 0.1 in each case. These data favor Reaction (8) over (9) and are in agreement with the infrared spectrum (Figures 20 and 21) which indicates NH_4NO_3 as the principle solid reaction product. The two reactions containing water produced a substantially higher amount of N_2O.

Products from run numbers 12, 13, 14, 19, and 22 were analyzed by mass spectrometry in a special unheated low volume inlet in an effort to detect reactive and/or thermally unstable reaction products. Low intensity mass spectral peaks at m/e 43 were observed but not confirmed as due to hydrazoic acid. Solids from run number 29 were acidified with HCl and tested for liberated HN_3 from any azides present (ferric chloride changes to red $Fe(N_3)_3$ for a positive test). A negative test was obtained.

It should also be pointed out that a material balance in terms of the actual gaseous and solid products is not carried out as indicated in Table II. The product loss in certain runs can be as high as 25%.

Major gas products of reaction are compared with those of Reference 5 and are shown in Figure 2.

Reactions at 0°C. - The infrared spectrum of Solid No. 4 collected from run numbers 17, 18, and 19 is shown in Figures 22 and 23. The reactions were carried out at 0°C with a slight excess of N_2H_4. The infrared spectrum is poor because of the low solid product yield. Infrared spectrum of Solid No.5 is shown in Figures 24 and 25 and is similar to that of previous NO_2 rich reactions. Solid No. 5 was obtained from run numbers 20, 21, and 22. The principle gaseous reaction products for run numbers 18 and 20 are compared in Table 5.

TABLE V

REACTION PRODUCTS FROM 0°C REACTIONS

Run Number	18	20
Mg recovered		
N_2O	0.46	0.28
NO	0.06	0.96
H_2O*	1.50	0.10
Reactants (mg)		
NO_2	1.7	3.8
N_2H_4	1.0	1.0

*Air leak indicated

Discussion

The nonignition vapor-phase reaction of excess hydrazine with nitrogen dioxide at 25°C produced hydrazinium nitrate as the major solid reaction product. Major gaseous reaction products were N_2O, H_2O, N_2, NO, and NH_3 as indicated by the following equations:

$$N_2H_4 + 2\ NO_2 = NH_4NO_3 + N_2O \tag{10}$$

$$NH_4NO_3 + N_2H_4 = N_2H_5NO_3 + NH_3 \tag{11}$$

$$3N_2H_4 + 4NO_2 = 2N_2H_5NO_3 + N_2O + H_2O + N_2 \tag{12}$$

$$2NO_2 + H_2O = HNO_3 + HNO_2 \tag{13}$$

$$3HNO_2 = HNO_3 + H_2O + 2NO \tag{14}$$

With an excess of nitrogen dioxide, the NO_2/N_2H_4 vapor phase reaction at 25°C produces ammonium nitrate as the predominant solid reaction product, and NH_3 is absent from the gaseous products.

$$N_2H_4 + 2NO_2 = NH_4NO_3 + N_2O \tag{15}$$

$$NH_4NO_3 = N_2O + 2H_2O \tag{16}$$

Any hydrazinium nitrate formed as an intermediate may be presumed to react with the excess NO_2 to yield ammonium nitrate:

$$6N_2H_5NO_3 + 2NO_2 = N_2O + 3N_2 + 6NH_4NO_3 + 3H_2O \tag{17}$$

The quantitative recovery of both solid and gaseous reaction products in a series of reactions containing nearly equal moles of reactants resulted in a weight ratio of $NH_4NO_3/N_2O/H_2O$ similar to Reaction (17). The addition of water to either reactant before the reaction increased the production of N_2O.

Similar but less extensively investigated reactions carried out at 0°C produced comparable products.

Some evidence for the presence of traces of gaseous hydrazoic acid was obtained by mass spectrometry. However, neither hydrazoic acid nor azides were detected in the solids by either infrared or more sensitive chemical tests. This is significant because ammonium azide and, especially, hydrazinium azide are certainly much more sensitive to detonation than the corresponding nitrates. The following equations illustrate possible routes to azide formation:

$$N_2H_4 + HNO_2 = HN_3 + 2H_2O \tag{18}$$

$$N_2H_5NO_3 + HNO_2 = HN_3 + HNO_3 + 2H_2O \tag{19}$$

$$HN_3 + N_2H_4 = N_2H_5N_3 \tag{20}$$

$$HN_3 + NH_3 = NH_4H_3 \tag{21}$$

The presence of water in the reaction system would favor azide formation through production of intermediate HNO_2.

IGNITION STUDIES OF NITROGEN TETROXIDE AND HYDRAZINE

Introduction

Potter and Butler (Ref. 15) were able to investigate the extinguishment of diffusion flames by metering fuel and oxidant flow rates through two opposed jets. In terms of an apparent flame strength, a more detailed study on the flame blow-off for various fuel-oxidant combinations has been carried out by Potter, Heimal, and Butler (Ref. 16) and propane-oxygen flames at low pressures by Anagoston and Potter (Ref. 17). Based on this principle of employing directly opposed flows of reactants, Pandya and Weinberg (Ref. 18) were able to stabilize a one-dimensional diffusion flame. Flow patterns were studied and a one-dimensional temperature distribution was obtained. The thermal structures were analyzed to yield the distribution of the rate of heat release per unit volume. The flame structure was analyzed by Kushida (Ref. 19) who also used such a counter-flow burner to study ethylene oxygen flames.

This experimental technique can also be used to great advantage for studying ignition phenomena. The burner permits experimentation with known conditions in terms of reactant concentrations, gas temperatures, and burner pressures. For fuel-oxidant systems involving two different phases, as ignition of liquid or solid fuels by an oxidizing gas, the burner can be modified by employing a stagnation flow field. The oxidizing gases are led to flow over the fuel in the direction normal to the fuel surfaces. Effects of physical transport properties and quantitative evaluation of thermal reactions leading to ignition can be studied. The ignition of liquid hydrazine by nitrogen tetroxide gas has been studied using a burner based on the principle of stagnation flow.

Experimental Apparatus

Ignition studies are conducted by introducing a stream of nitrogen tetroxide/nitrogen gas mixture to flow over a dish of liquid hydrazine in a direction normal to the liquid surface. Based on this stagnation flow field, a cylindrical ignition burner (Figure 3) is constructed. A schematic of the burner is shown in Figure 4. The hydrazine supply system consists of a stainless steel syringe of 0.75 inches inner diameter. The syringe is connected to a hydrazine storage flask through a "bleed" valve and a "fill" valve. These valves are to facilitate easy refilling of the fuel in the syringe.

By applying a constant pressure on the plunger, liquid fuel is injected into the burner cup which consists of a stainless steel porous disc (7/16 inch diameter) recessed 1/16 of an inch into an aluminum holder (1 1/2 inches dia.). The porous disc serves as a heat sink so as to prevent possible flame propagation towards the hydrazine supply line. A microgauge valve is used to regulate the liquid fuel flow rate. The temperature of the burner cup is controlled by water passages through the holder and also by heating tapes when higher temperatures have to be achieved. An iron-constantan thermocouple, 0.01 inch diameter with a 0.04 inch stainless steel sheath, is imbedded in the porous disc to record hydrazine temperatures.

The nitrogen tetroxide storage tank and the line leading to the mixing tee where nitrogen tetroxide is diluted with nitrogen are maintained at approximately 320°K to prevent nitrogen tetroxide condensation. The flow rates of nitrogen and nitrogen tetroxide are metered by two sonic orifices. The gas mixture is led to two separate lines, one leading into the burner and one to the exhaust. Two sonic orifices are installed along these lines to control the net gas flow rate into the burner. Through a flow straightener (15/16 inch inner diameter) the gas mixture is led to flow over the liquid hydrazine in a direction normal to the liquid surface. The straightener is partly imbedded in an aluminum holder. The open end of the straightener is fitted with a porous disc. By first filling the straightener with stainless steel wools and controlling the temperature of the aluminum holder by water passages and heating tapes, the gas mixture temperature can be easily varied. An iron constantan thermocouple is installed immediately above the porous disc to record the gas mixture temperature. When hydrazine is being introduced into the burner, the known mixture of N_2O_4 and N_2 is led to flow through the solenoid valve leading to the exhaust. After the hydrazine cup is filled, the gas mixture is led to flow through the second solenoid valve leading into vapor straightener as shown in Figure 3. These two solenoid valves are thus used to minimize possible transient flow errors. The gap spacing between the porous disc and the liquid fuel surface is 1/8 inch. The burner is enclosed within a bell jar. The burner pressure is controlled by a two stage air ejector. Pressures of 1/6 atm can be easily achieved. The important parameters that can be varied using this stagnation burner are the fuel and oxidizer temperature, the burner pressure, and the oxidizer concentration and flow velocity.

Using the same oxidizer supply system, a second two dimensional burner with a pyrex glass window is built (Fig. 5). The two dimensional burner is for photographically recording the ignition phenomena.

Method of Study

Mass flow rates of nitrogen and nitrogen tetroxide are calibrated in terms of the upstream pressures of their respective sonic orifices. The pressure ranges from 30 psi to 100 psi . Different nitrogen tetroxide concentrations can be achieved by varying the upstream pressures. The flow rate of the gas mixture into the burner is calibrated in terms of the supply pressure which is the pressure upstream of the third sonic orifice. These values are shown in Table VI for three different supply pressures of 2.5 psi, 5 psi, and 7.5 psi with the burner at 1 atm pressure and 20°C. The notations in Table VI are explained as follows:

Supply Pressure: Pressure upstream of the third orifice leading into the burner.

N_2 Pressure: Nitrogen pressure upstream of the nitrogen orifice.

$\dot{m}_{N_2}$: Calibrated nitrogen mass flow rate corresponding to the nitrogen pressure.

N_2O_4 Pressure: N_2O_4 pressure upstream of the N_2O_4 orifice. All ignition measurements are conducted by maintaining N_2O_4 supply pressure at 50 psi, except for one special case, in order to minimize possible errors due to orifice flow calibration. The N_2O_4 mass flow rate corresponding to 50 psi pressure is 2.55×10^{-4} lb/sec.

$\dot{m}_{total}$: Total mass flow rate which is the sum of $\dot{m}_{N_2}$ and $\dot{m}_{N_2O_4}$.

$\frac{\dot{m}_{N_2O_4}}{\dot{m}_{total}}$: Mass concentration of N_2O_4 in the gas mixture.

$\dot{m}_{N_2}$ to burner: Rate of nitrogen mass flows to the burner recorded by volume displacement and by first condensing the N_2O_4 through cold trap.

TABLE VI - AVERAGE SUPPLY VELOCITY OF N_2O_4-N_2 MIXTURE

Supply Pressure psi	N_2 Pressure psi	$\dot{m}_{N_2}$ lb/sec	N_2O_4 Pressure psi	$\dot{m}_{total}$	$\frac{\dot{m}_{N_2O_4}}{\dot{m}_{total}}$	$\dot{m}_{N_2}$ to burner	$\dot{m}_{total}$ to burner	Mixture Density lb/ft³	Average Velocity ft/sec	Reynolds Number
2.5	20	2.4×10^{-4}	50	4.35×10^{-4}	.515	2.36×10^{-4}	4.87×10^{-4}	.1456	.428	29.0
2.5	30	3.125×10^{-4}	50	5.675×10^{-4}	.450	2.48×10^{-4}	4.51×10^{-4}	.1369	.424	29.2
2.5	40	3.800×10^{-4}	50	6.35×10^{-4}	.402	2.64×10^{-4}	4.42×10^{-4}	.1307	.435	29.4
2.5	50	4.55×10^{-4}	50	7.10×10^{-4}	.359	2.92×10^{-4}	4.56×10^{-4}	.1250	.476	32.0
5.0	35	3.45×10^{-4}	50	6.00×10^{-4}	.425	3.42×10^{-4}	5.95×10^{-4}	.4250	.576	40.2
5.0	40	3.80×10^{-4}	50	6.35×10^{-4}	.402	3.53×10^{-4}	5.89×10^{-4}	.4020	.579	40.2
5.0	45	4.15×10^{-4}	50	6.70×10^{-4}	.381	3.56×10^{-4}	5.74×10^{-4}	.3810	.578	40.0
5.0	50	4.55×10^{-4}	50	7.10×10^{-4}	.359	3.70×10^{-4}	5.77×10^{-4}	.3590	.593	40.8
7.5	45	4.15×10^{-4}	50	6.70×10^{-4}	.381	4.10×10^{-4}	6.70×10^{-4}	.1280	.673	46.0
7.5	50	4.55×10^{-4}	50	7.10×10^{-4}	.359	4.55×10^{-4}	7.10×10^{-4}	.1250	.730	50.5

$\dot{m}_{total}$ to burner:	Based on $\dot{m}_{N_2}$ to burner the rate of mass flow to the burner is calculated and is equal to $\dfrac{\dot{m}_{N_2} \text{ to burner}}{\dot{m}_{N_2}} \times \dot{m}_{total}$
Mixture density:	The density of the gas mixture is calculated based on the N_2O_4 density of 0.209 lb/ft^3 and nitrogen density of 0.078 lb/ft^3 .
Average velocity:	An average exit velocity V is defined in terms of the total mass flux supplied to the burner, the gas mixture density, and the area of the oxidizer supply duct of diameter 15/16 inches.
Reynolds number:	A Reynolds number Re is defined in terms of the kinematic viscosity of pure nitrogen at 1 atm and 20°C and the gap spacing of 1/8".

The calibration shows that the average exit velocity of the gas mixture, within the experimental error, is a function of supply pressure only. V assumes a value of .43 ft/sec, .58 ft/sec and .70 ft/sec respectively of supply pressures of 2.5 psi, 5 psi, and 7.5 psi. For the case when the burner is operating at different pressures than 1 atm, variation of gas density with respect to pressure has to be taken into account.

Minimum mass concentrations of nitrogen tetroxide in a nitrogen tetroxide/nitrogen gas mixture that induces ignition when it is led to flow over liquid hydrazine are measured. In order to evaluate the effects of physical transport properties, the velocities and the temperatures of the gas mixtures are varied. These are conducted for hydrazine temperatures varying from approximately 290°K to 350° K, and also, for hydrazine temperature ranges from its melting point to boiling point. Burner pressures have varied from 1.0 atm to 0.166 atm and water as a diluent has been used in hydrazine to study the changes in ignition properties.

Preliminary studies using flox and hydrazine have also been conducted. Difficulties were encountered during the pacification stages and the experiment was not pursued further.

Based on the two dimensional burner, the entire preignition reactions, from the introduction of oxidizing gas mixture to the formation of the one dimensional flame, have been photographed by a HyCam motion picture camera at 50 frames per second. Similar observations have also been carried out to study the ignition of droplets. A hydrazine droplet is suspended on a metal wire ring of 3/16 inches diameter by its own surface tension. Preignition surface activities were observed. Photographic results are difficult to obtain. As soon as bubbles start to form, surface tension is greatly reduced and the droplet immediately falls off from its support. Based on the motion picture results, the ignition delay time is also estimated.

Experimental Results and Discussions

Figure 6 is a threshold measurement showing points of ignition and no ignition as a function of nitrogen tetroxide mass concentrations. The burner pressure is 1 atm with the gas exit velocity equal to 0.43 ft/sec. The flow Reynolds number, based on the kinematic viscosity of nitrogen gas and the gap spacing is about $Re = 29$. The gas temperature is kept at approximately $310^\circ K$. The solid line divides the region of ignition and no ignition and thus represents the threshold concentration or the minimum mass concentration that induces ignition. For the hydrazine temperatures between its melting and boiling point, the ignition mechanism can be divided into three regions. For hydrazine temperature below $\approx 315^\circ K$, the minimum ignition concentration of nitrogen tetroxide is independent of the hydrazine temperature. For hydrazine temperature ranges between $315^\circ K$ and $365^\circ K$, the nitrogen tetroxide threshold concentration decreases with increasing hydrazine temperature. The logarithm of the threshold concentration appears to decrease linearly with the inverse of the hydrazine temperature. For hydrazine above $365^\circ K$, hydrazine often ignites without the introduction of nitrogen tetroxide. This can be due to reactions of hydrazine vapor with oxygen in the burner. and the nitrogen tetroxide threshold concentration decreases sharply. These regions clearly indicate that different ignition mechanisms might be present. To investigate this problem further, a two-dimensional burner with a pyrex glass window is used. The ignition phenomena is recorded by a high speed motion picture camera. The photographic result shows that a very significant amount of surface activities, with bubbling and foaming appear on the hydrazine surface prior to ignition, (Fig. 7). These surface activities are more pronounced for hydrazine at lower temperatures. For hydrazine temperature above 320°K, this surface phenomena is sometimes not noticeable. Ignition always first appears very close to the liquid surface, leading quickly to a steady state combustion with the flame appearing approximately at the midpoint of the gap. Delay time of the order of one second was observed for hydrazine below 320°K and one tenth of a second for hydrazine at higher temperatures. Ignition delay time was estimated based on the photographic results. Although this data is not conclusive and often difficult to reproduce, it does indicate that the delay time is of an order of magnitude greater for hydrazine in the lower temperature range.

Similar observations on the ignition of liquid droplets have also been conducted. The result is not conclusive because of difficulties encountered in obtaining photographic results as mentioned earlier.

Ignition of liquid hydrazine can thus be divided into three regions. For hydrazine at lower temperatures, below 315° K for the case shown on Figure 6, the vapor pressure of hydrazine is not high enough to sustain a vapor phase ignition. Nitrogen tetroxide mixture diffuses towards liquid surface and preignition reactions mainly occur between nitrogen tetroxide and liquid hydrazine. Reaction products formed and also dissolved in the liquid fuel produce very noticeable foaming and bubbling as evidenced by photographic results. Heat is released and at the same time heat is lost to the surrounding medium. It is noteworthy that because of the convective flow field, heat loss is more significant as compared with ignition studies in a static atmosphere. Heat release associated with these reactions raises the hydrazine temperature which is qualitatively illustrated by the disc temperature as shown on Figure 8. This heating of liquid hydrazine, in turn, gives off more vapor which eventually leads to a vapor phase ignition.

The preignition reaction mechanism between nitrogen tetroxide and liquid hydrazine depends mainly on the net mass flow rate of nitrogen tetroxide towards the liquid surface, and thus does not depend on the liquid temperature. This explains the reason that the minimum concentration of nitrogen tetroxide that induces ignition is independent of the liquid temperature.

For hydrazine temperature above 315° K the vapor pressure of hydrazine appears to be high enough to sustain a vapor phase ignition.

The logarithm of the ignition threshold concentration decreases linearly with the inverse of the hydrazine temperature.

At the hydrazine temperature above 365°K, the minimum ignition threshold concentration of nitrogen tetroxide decreases sharply. The effect of hydrazine decomposition becomes more significant. This coupled with possible catalytic effect of the experimental setup, which is more pronounced at these higher temperatures and possible reactions with oxygen in the burner ignition very often occurs before the introduction of nitrogen tetroxide gas mixture into the burner.

Effects of different flow velocities on ignition have been studied. Flow velocities are important in two respects. For the case when the gas temperature is lower than the liquid temperature, heat is gained by the gas at the expense of the liquid hydrazine. The reverse is true when the liquid hydrazine is hotter than the gas. Increasing the flow velocity increases the convective heat transfer. The residence time of the gas mixture within the burner is proportional to the ratio of the gap distance and the gas velocity. Increasing flow velocities reduces the residence time. Three different flow velocities, corresponding to Reynolds number 29, 40, and 50 respectively are shown on Figure 9. The same basic feature is present namely for hydrazine below a certain critical temperature, ignition threshold concentration of nitrogen tetroxide is a constant. The threshold concentration increases significantly for higher flow velocities due to the convective heat loss and the reduced residence time. A 30% velocity change increases the minimum ignition concentration of nitrogen tetroxide by 20%. The hydrazine temperature, which separates the two regimes of ignition, also increases by about 10°K.

Convective heat transfer between liquid hydrazine and nitrogen tetroxide/nitrogen gas mixture depends also very much on the gas temperature. Also there is a higher concentration of the more reactive nitrogen dioxide at these higher temperatures. Figure 10 shows the ignition measurements for nitrogen tetroxide/nitrogen gas mixtures at 303°K and 322°K. Especially for liquid hydrazine at temperatures lower than 322° K, the ignition threshold concentration differs almost by 80%.

Variation of burner pressure does not seem to change the ignition characteristics. Ignition threshold measurements for burner pressures at 1/2 atm, 1/3 atm, and 1/6 atm are shown in Figures 11, 12, and 13. The effect of pressure on ignition arises principally through the dependence of the chemical reaction rate on pressure. The rate of heat transfer and mass are not appreciably influenced. One is thus inclined to suggest that chemical kinetics is not the governing rate, although based on these measurements alone, it does not conclusively support this view.

Water as an additive has been used. Water concentration to approximately 10% by mass has been added to liquid hydrazine. No significant modifications on ignition characteristics have been observed.

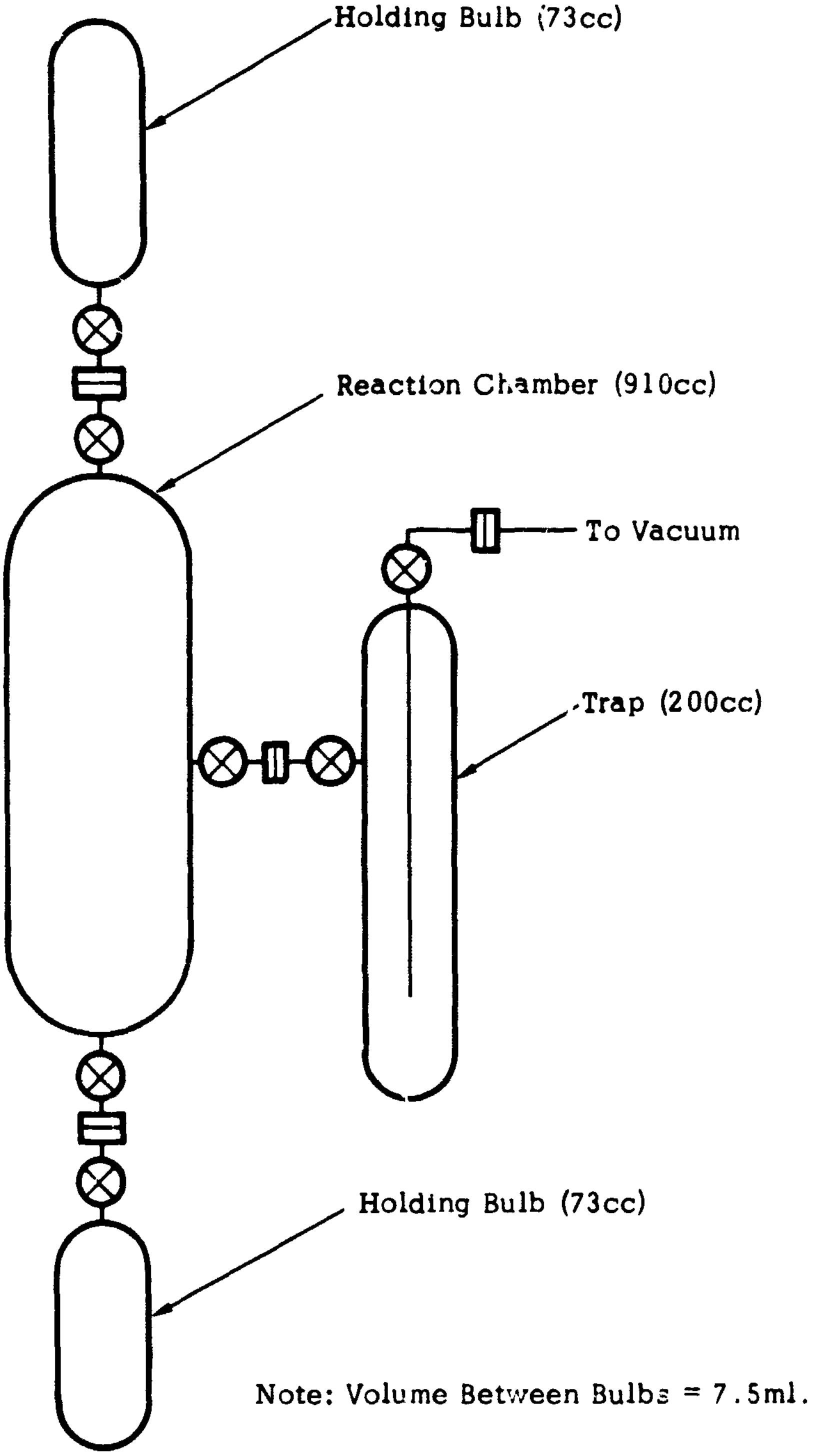

Figure 1. Reactor Assembly

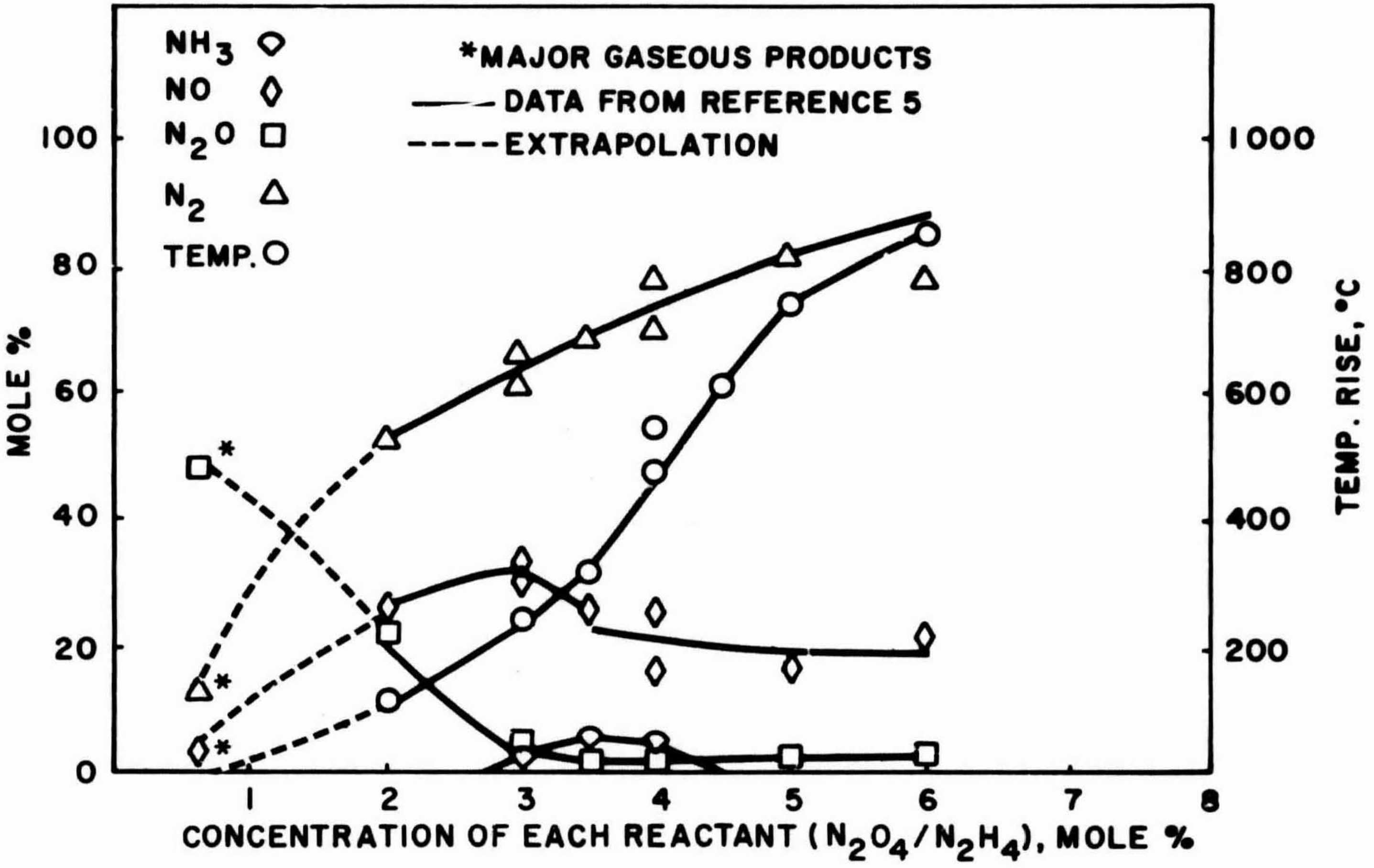

Figure 2. Comparison of N_2O_4/N_2H_4 Gas Reaction Products With Those of Ref. 3

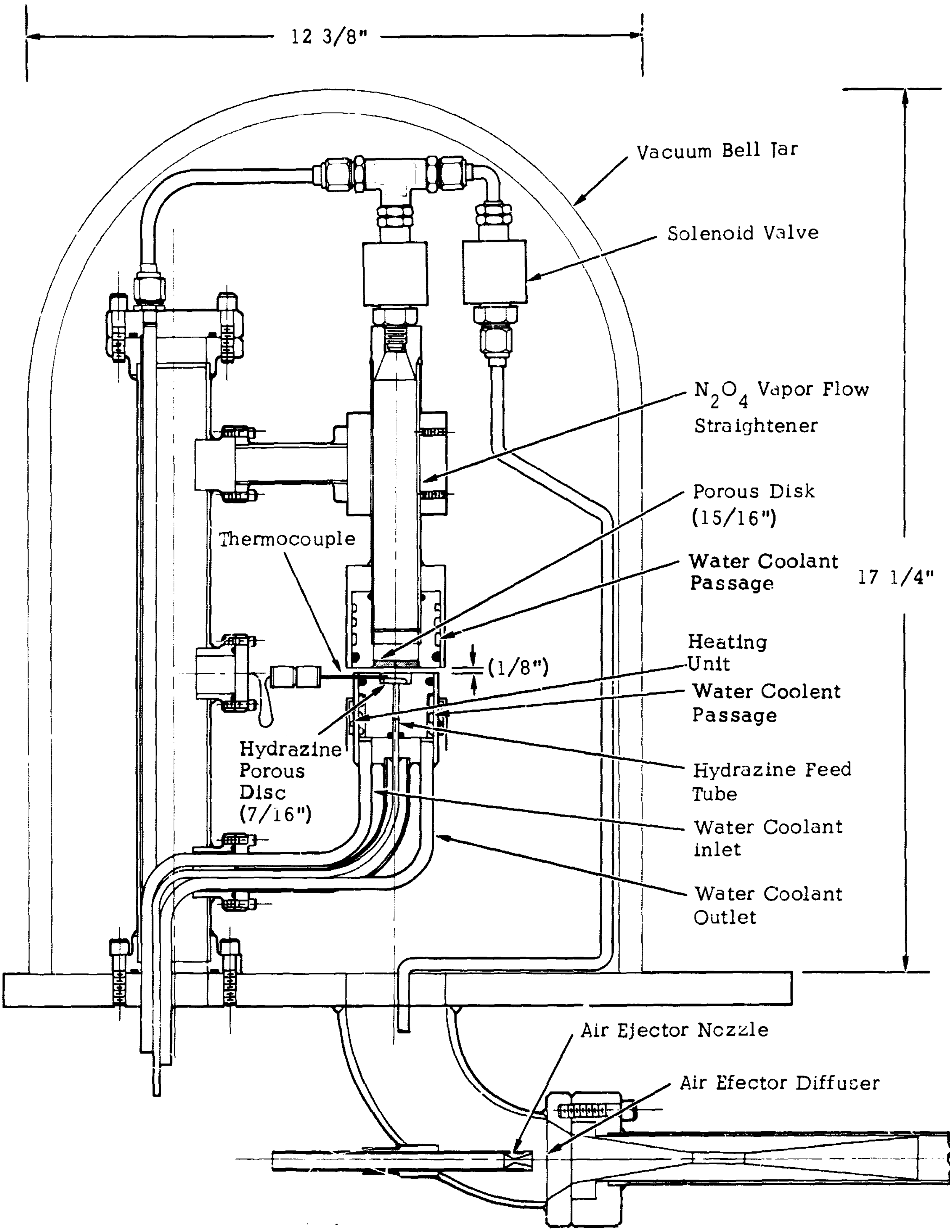

Figure 3. Stagnation Flow Diffusion Flame Burner

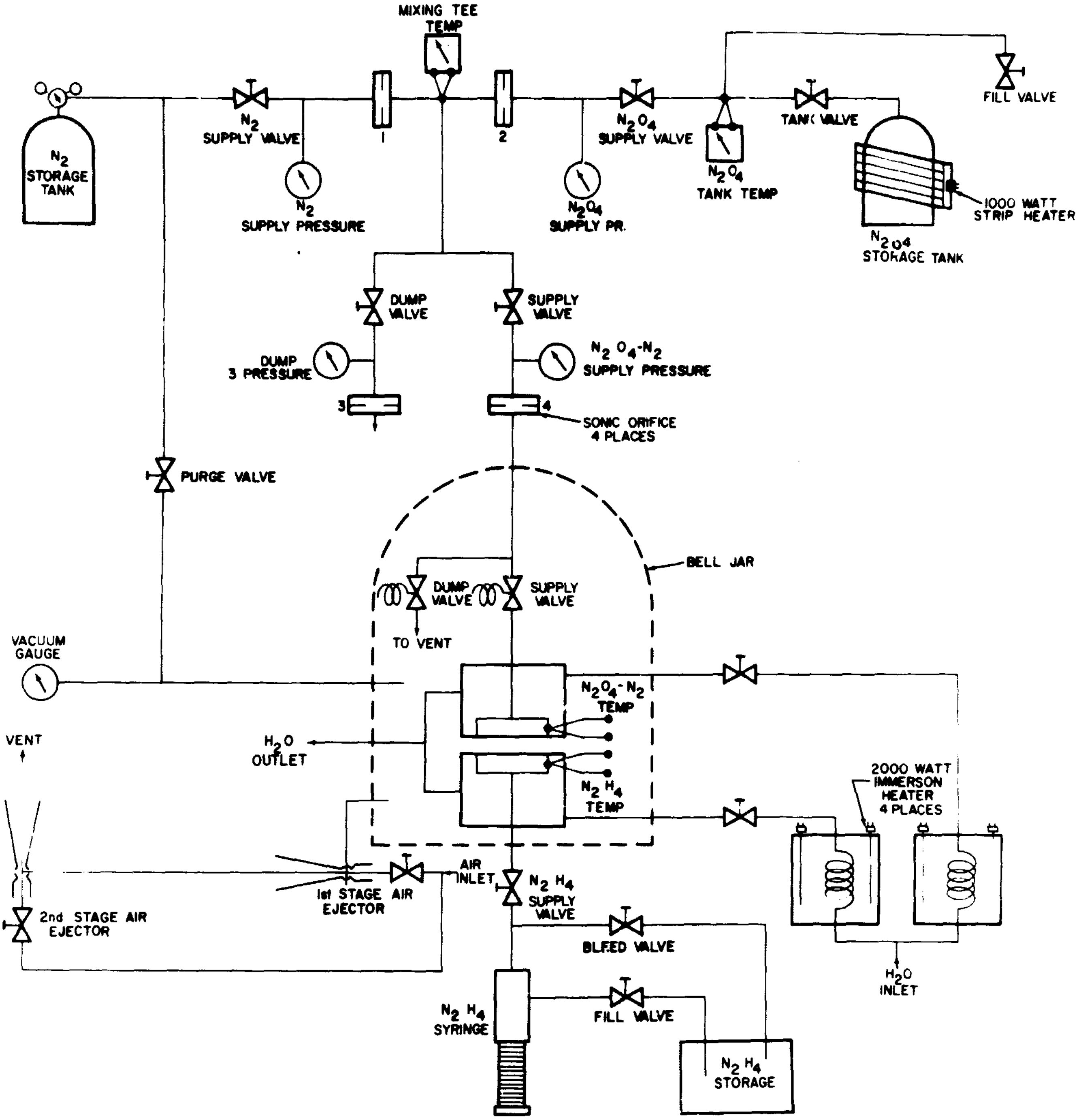

Figure 4. Schematic Diagram of the Burner

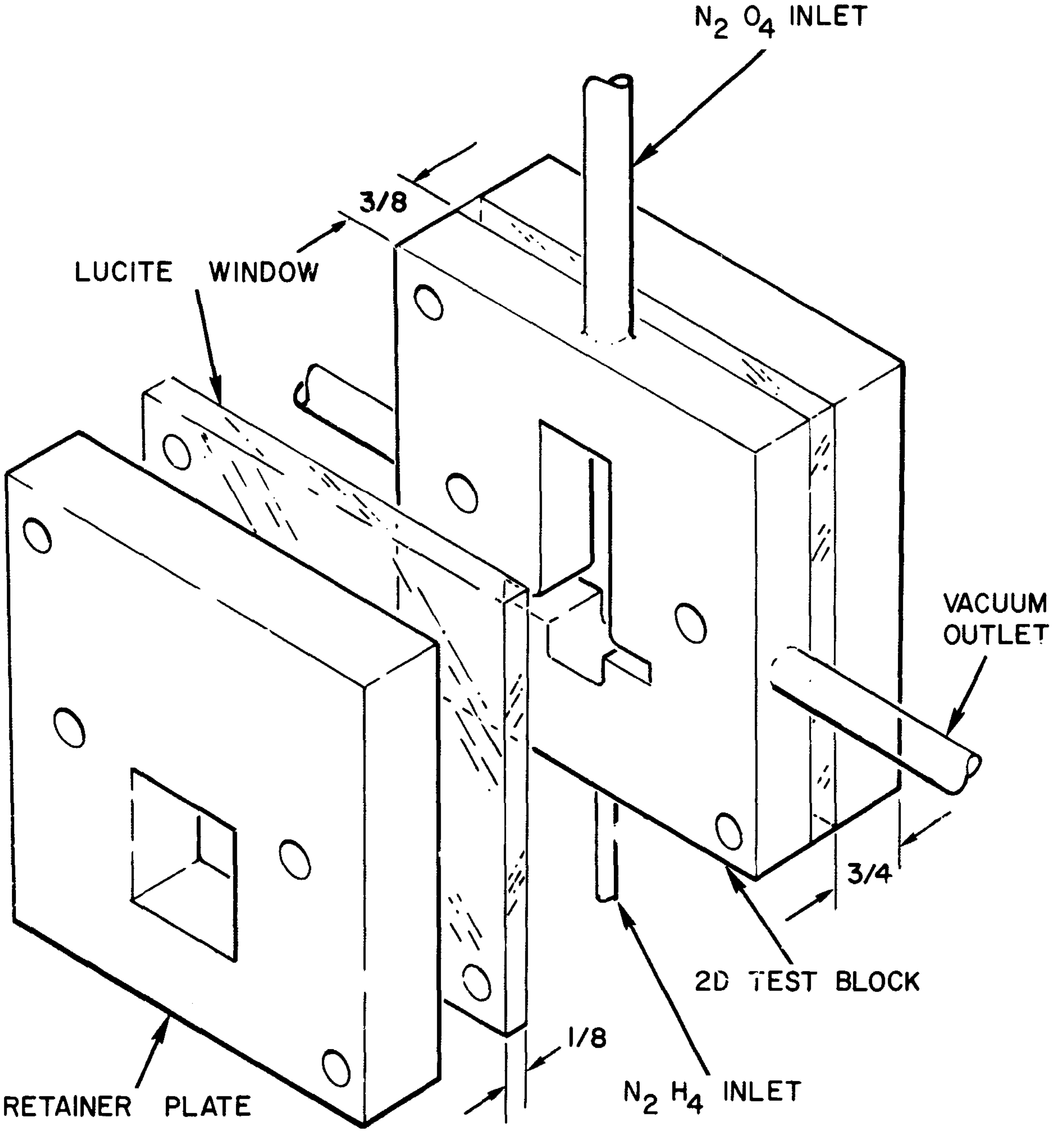

Figure 5. 2-D Stagnation Burner

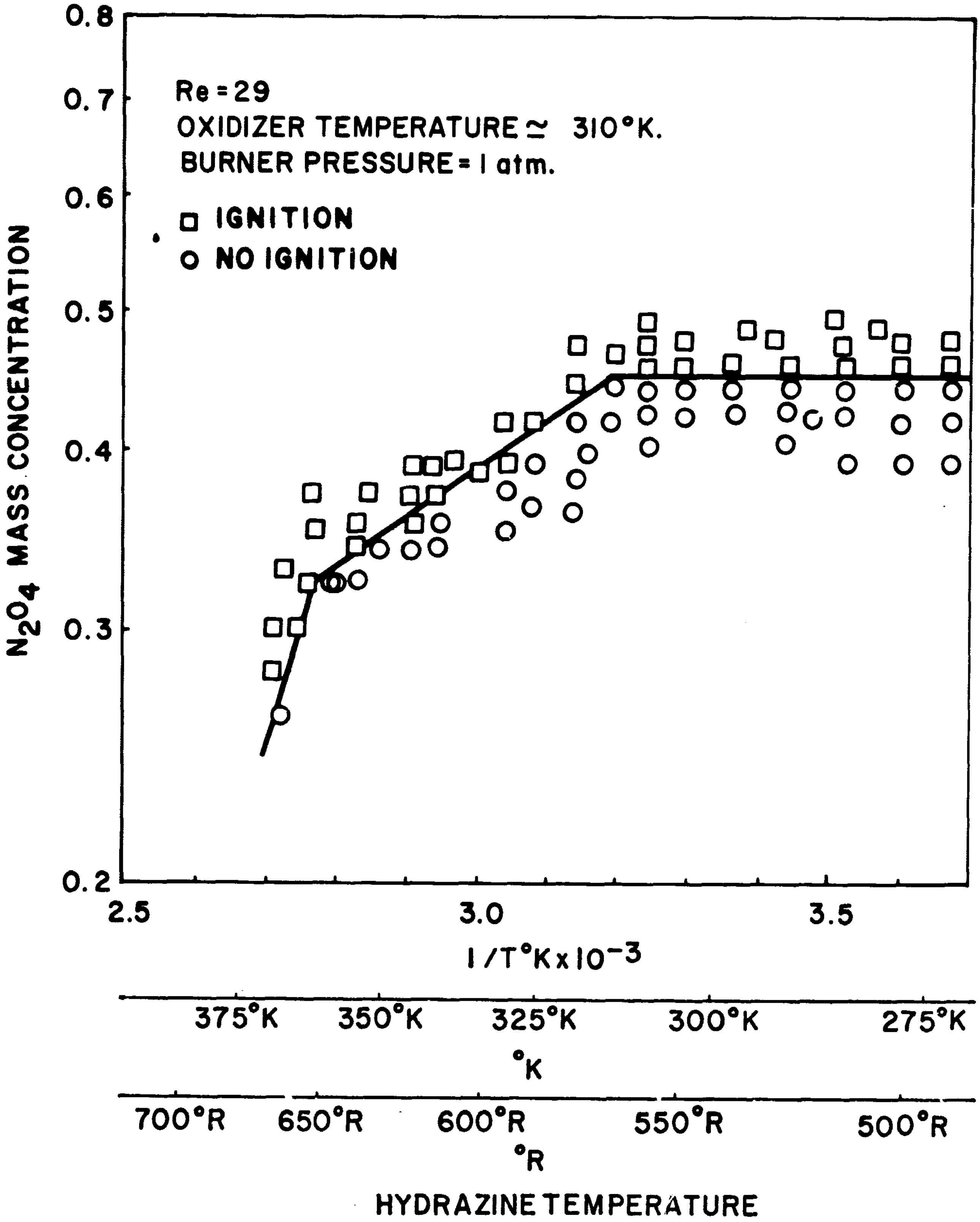

Figure 6. Ignition Threshold

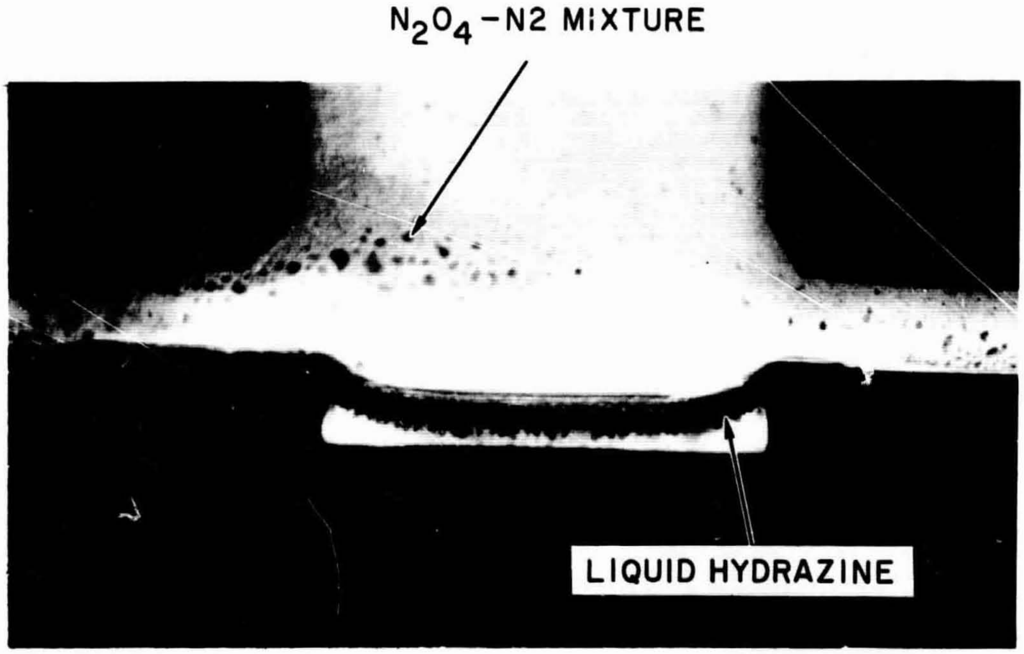

Figure 7. Foaming and Bubbling During Preignition Reactions

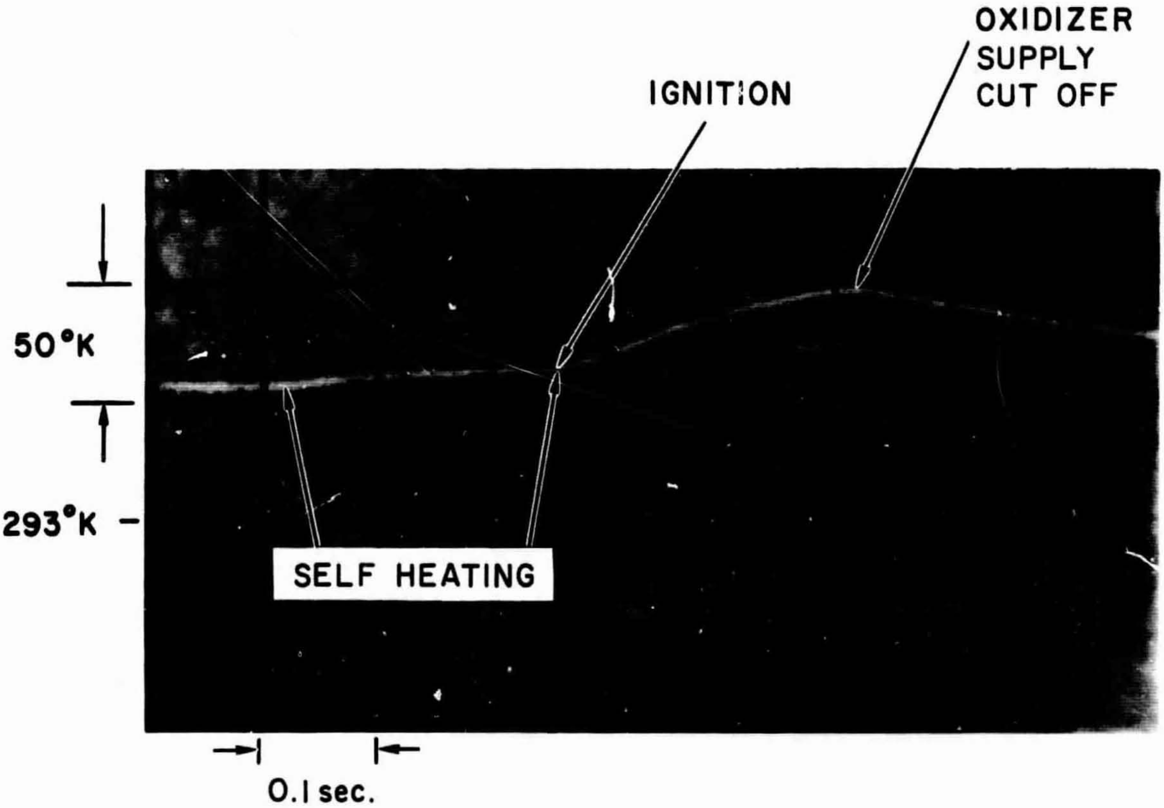

Figure 8. Temperature History of Hydrazine Cup

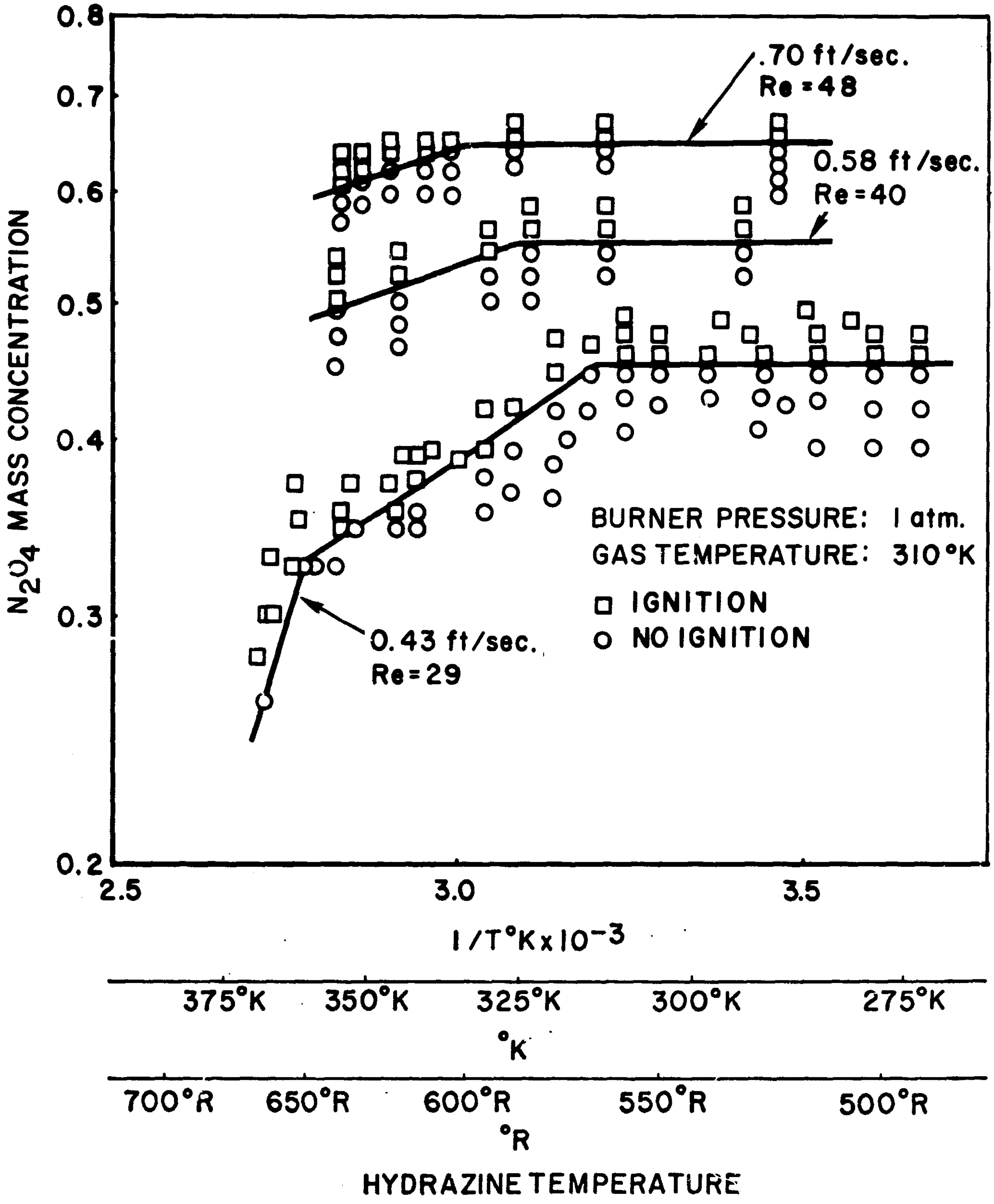

Figure 9. Ignition Threshold

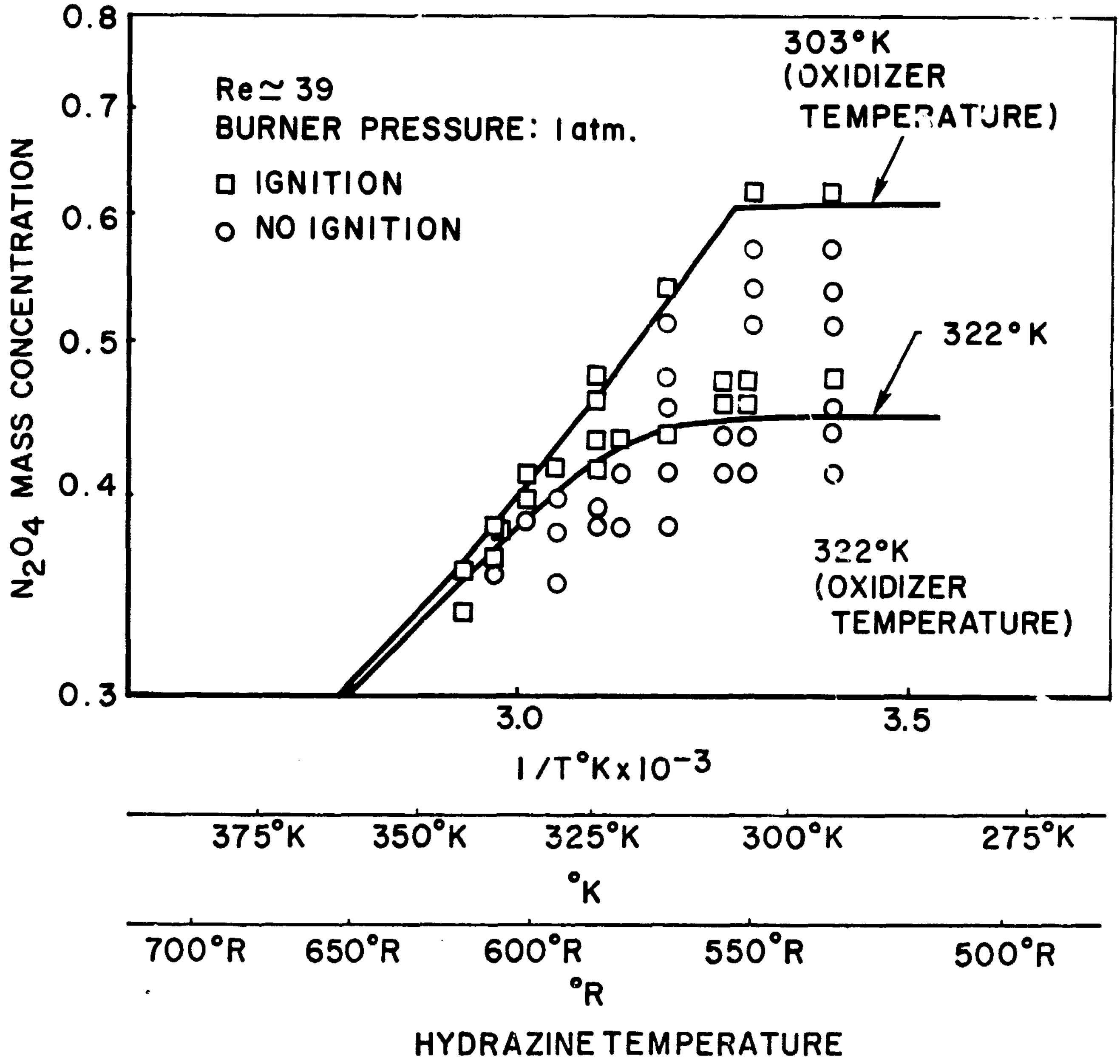

Figure 10. Ignition Threshold

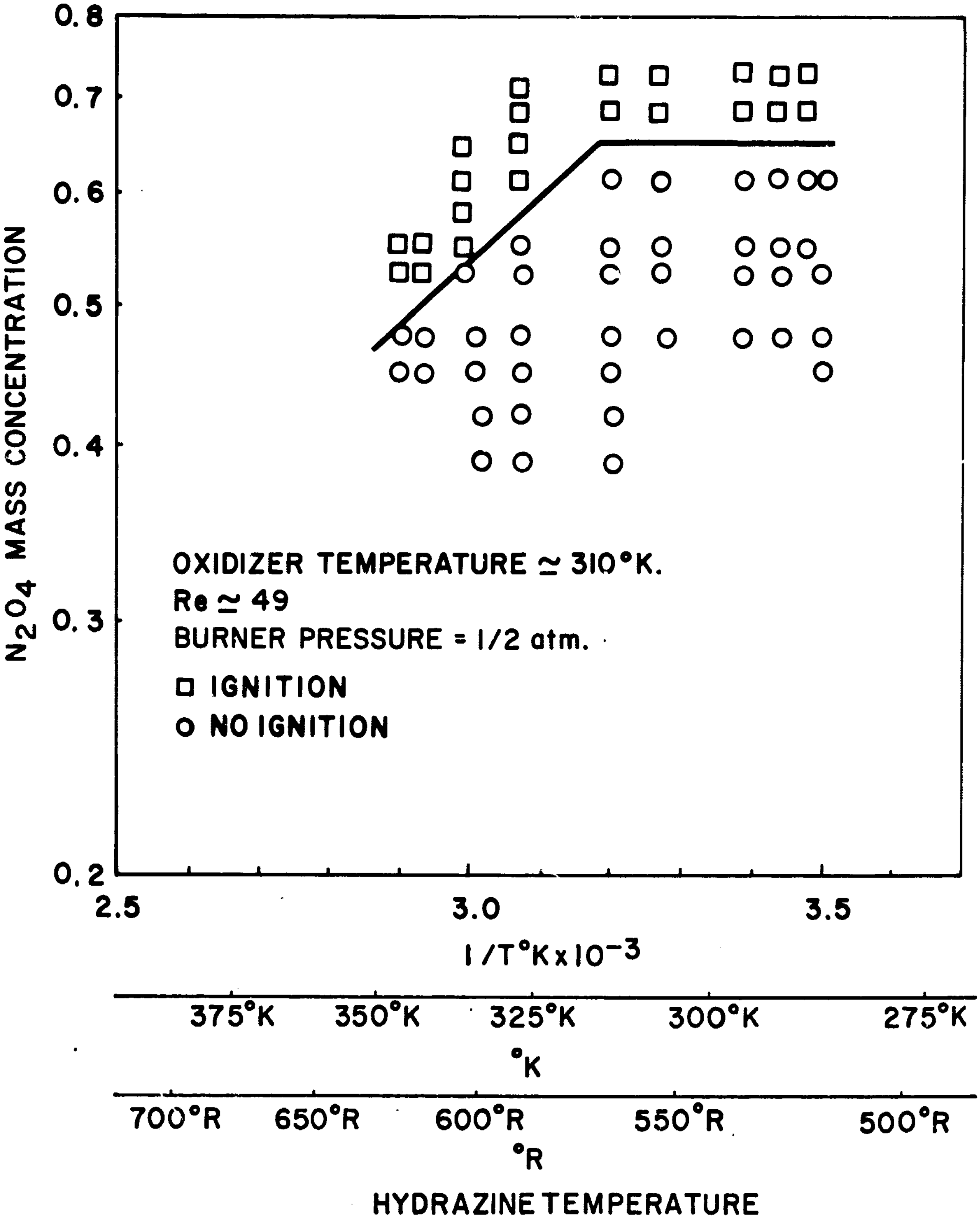

Figure 11. Ignition Threshold

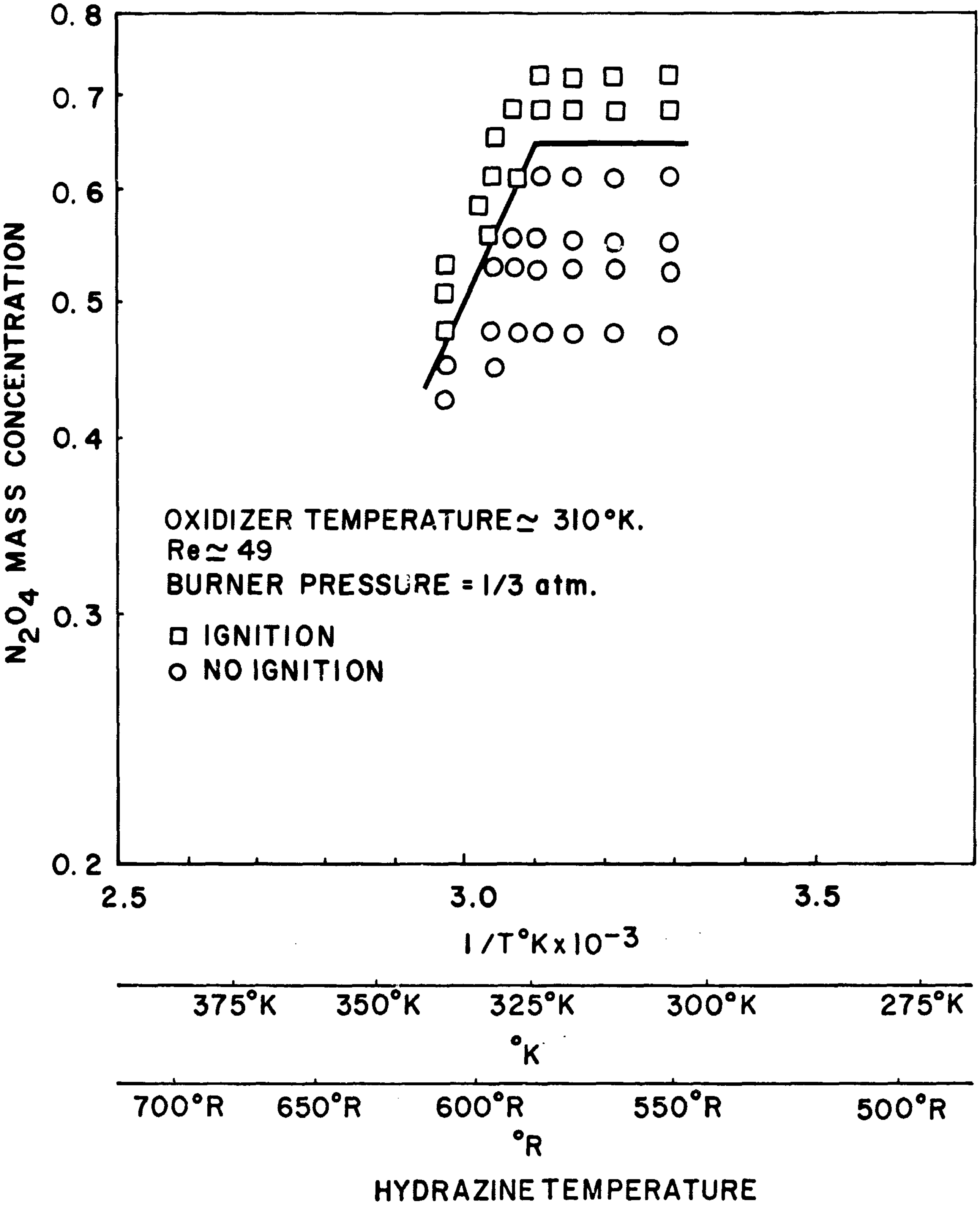

Figure 12. Ignition Threshold

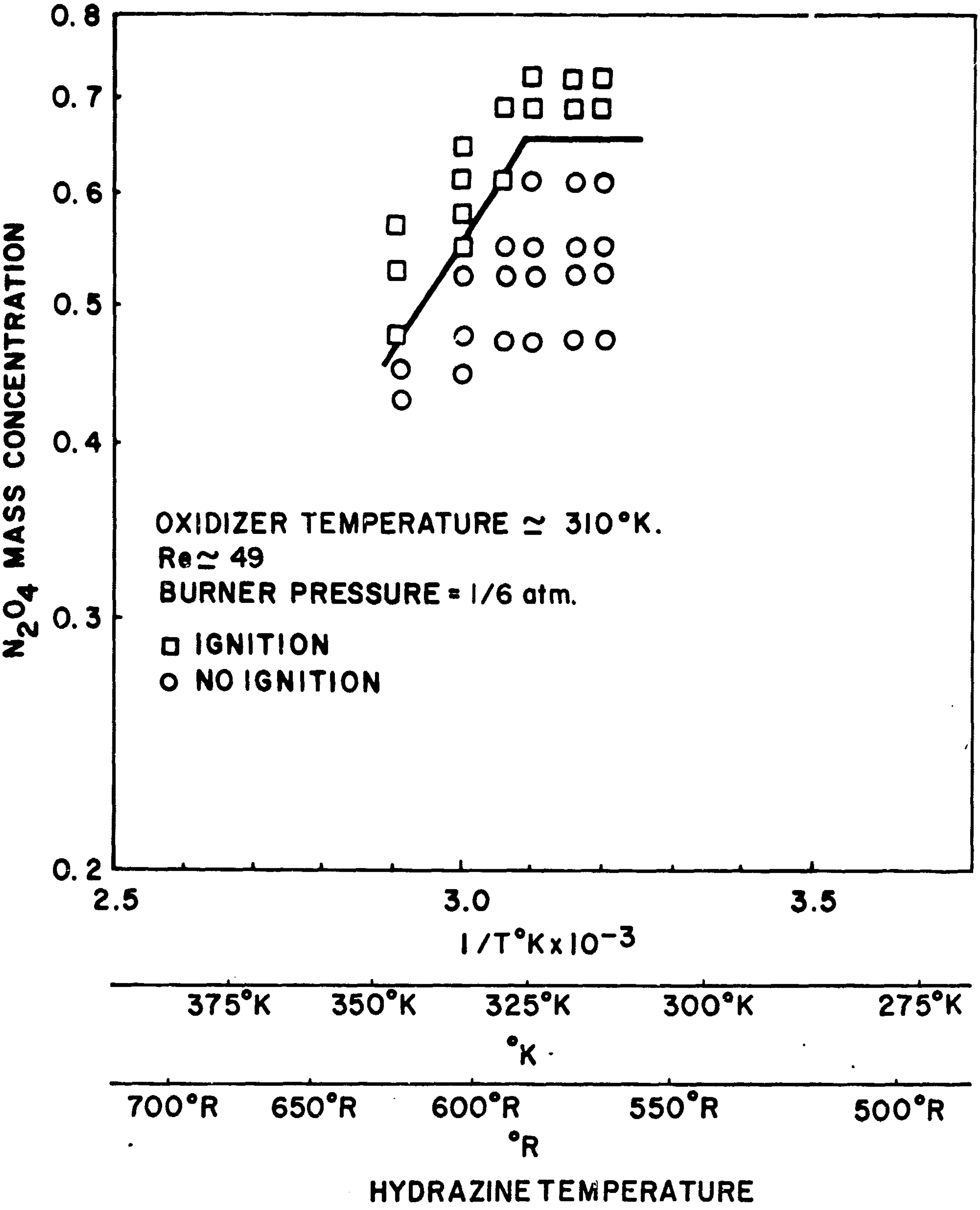

Figure 13. Ignition Threshold

APPENDIX A

INFRARED SPECTRUM

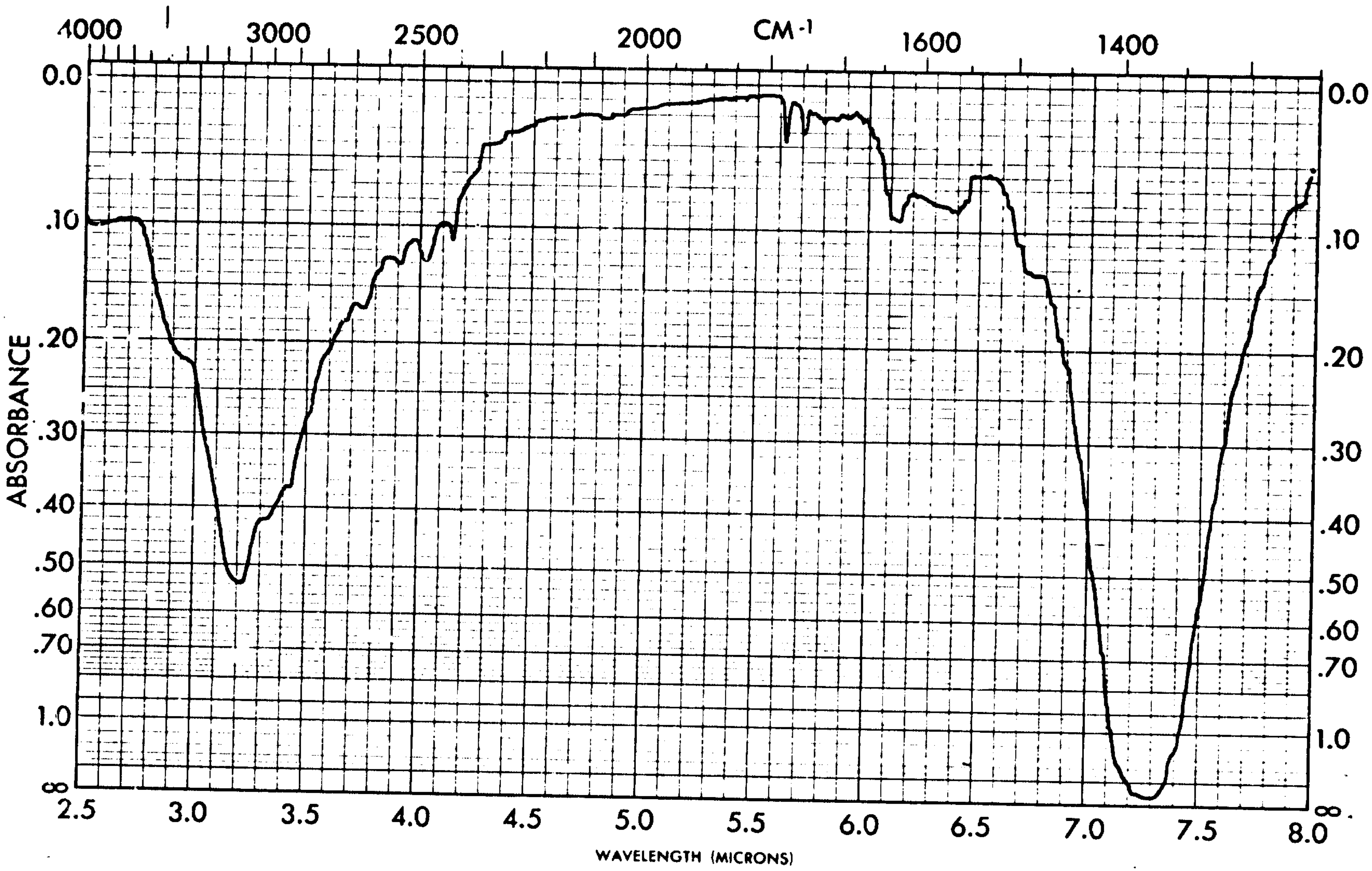

Figure 14. Infrared Spectrum - Solid #1

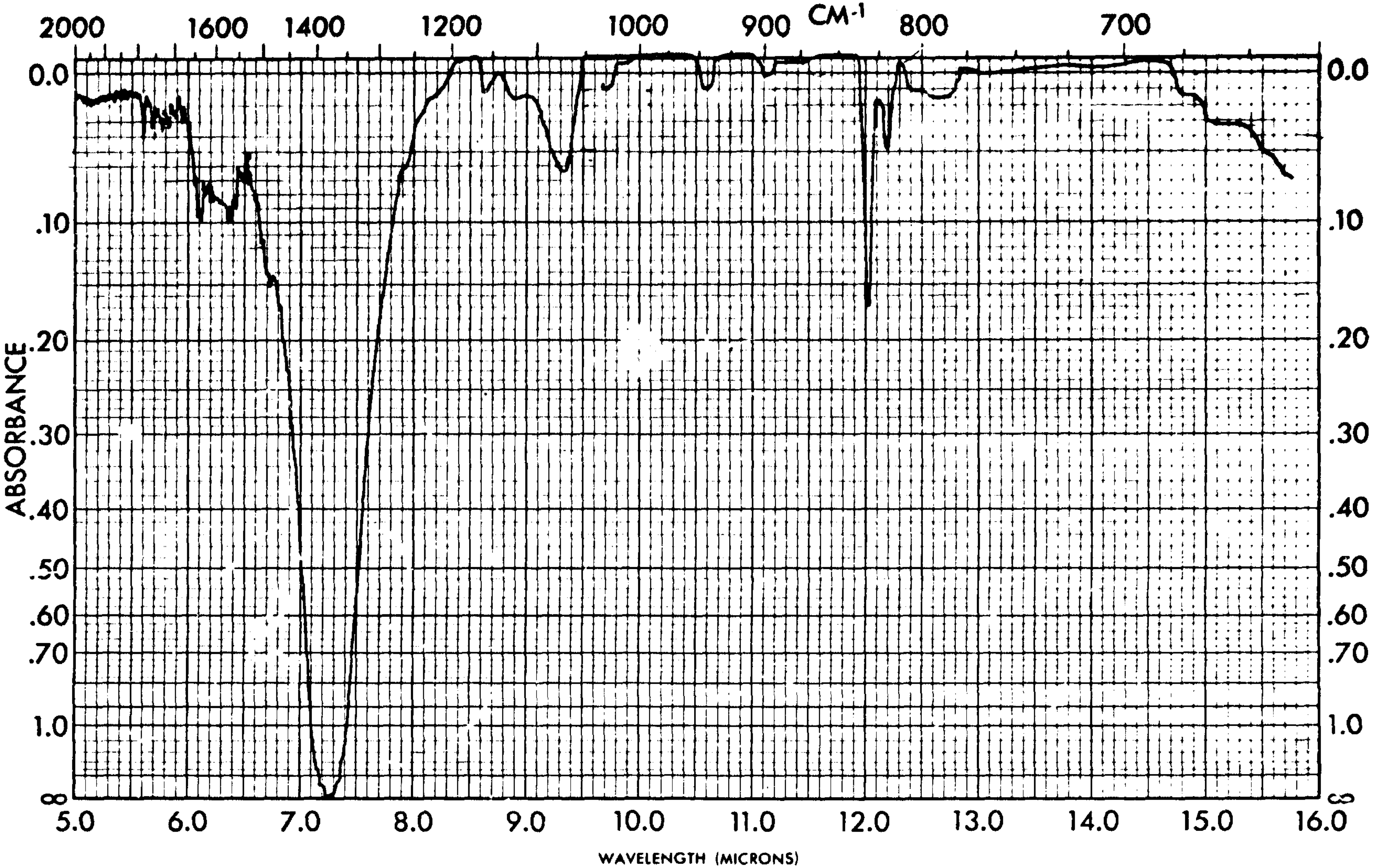

Figure 15. Infrared Spectrum - Solid #1

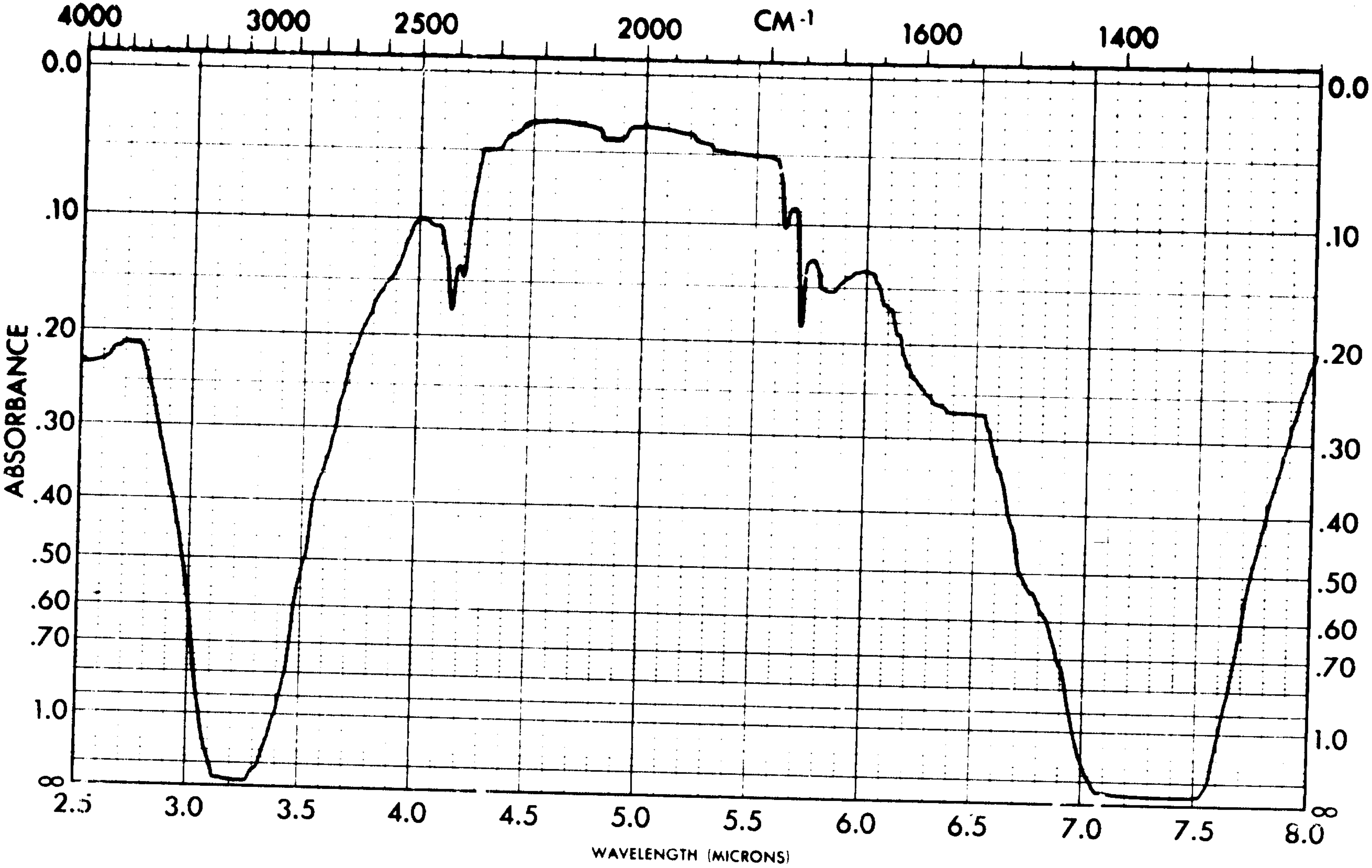

Figure 16. Infrared Spectrum - Solid #2

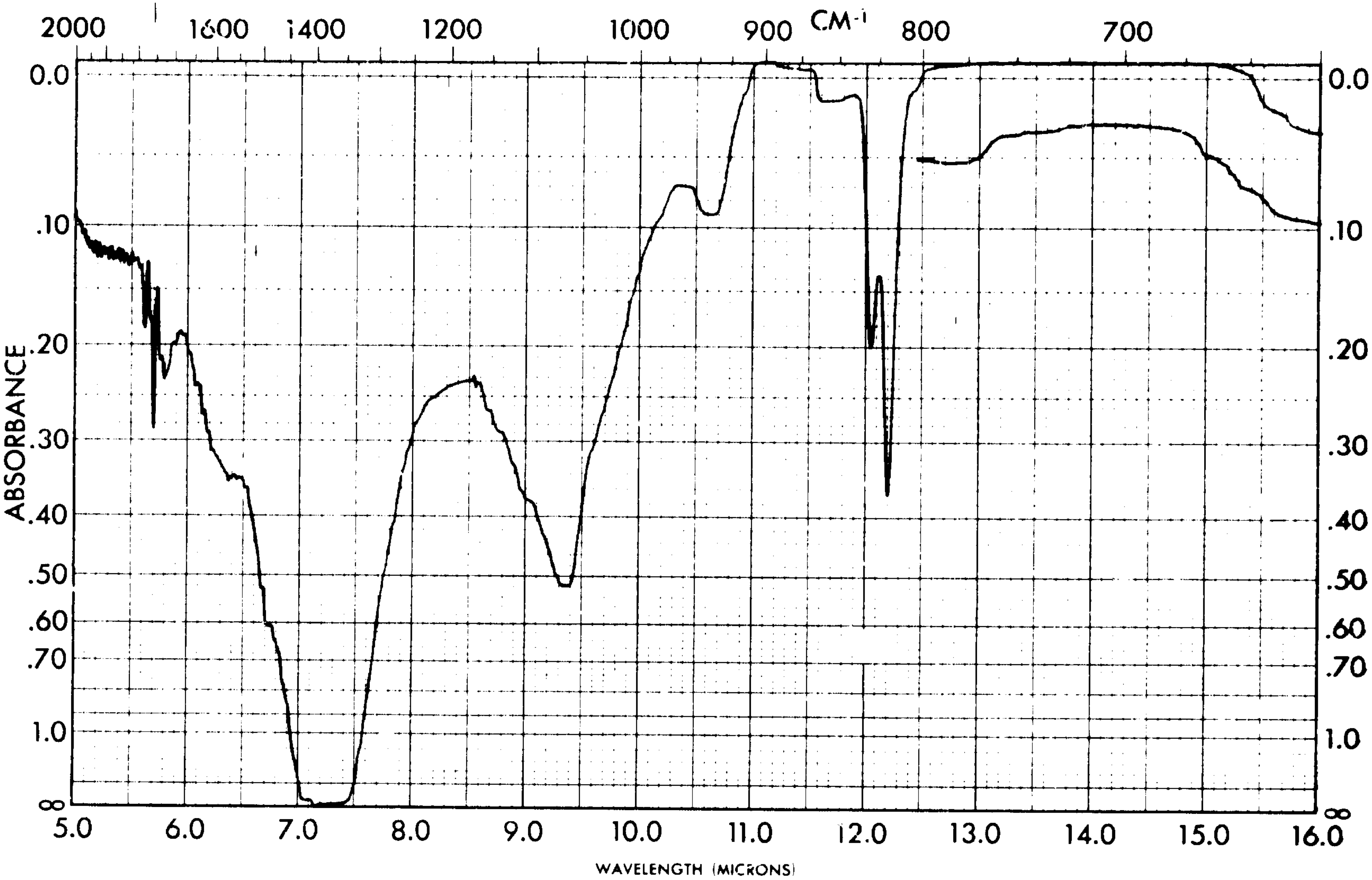

Figure 17 Infrared Spectrum - Solid #2

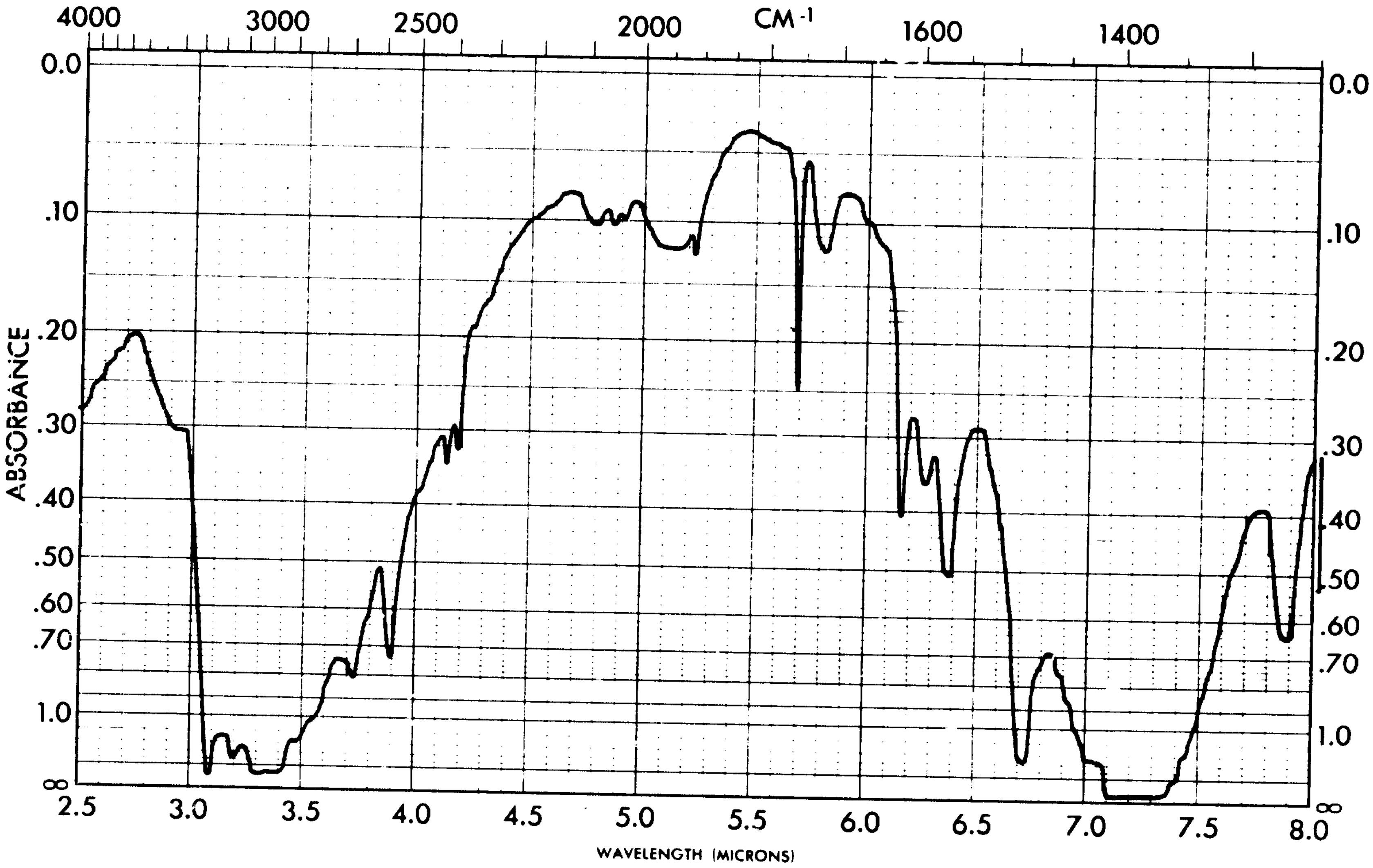

Figure 18. Infrared Spectrum - Solid #3

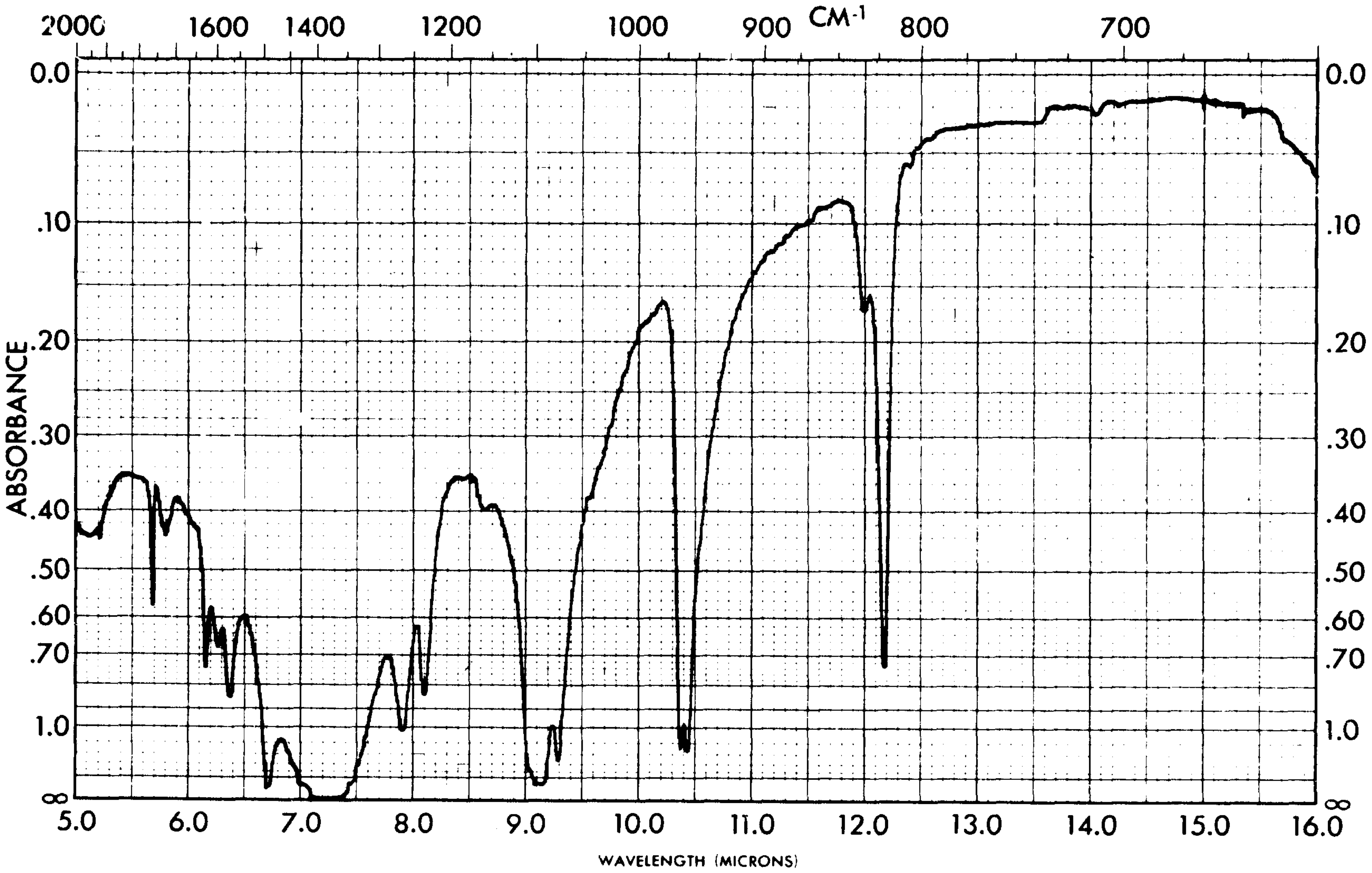

Figure 19. Infrared Spectrum - Solid #3

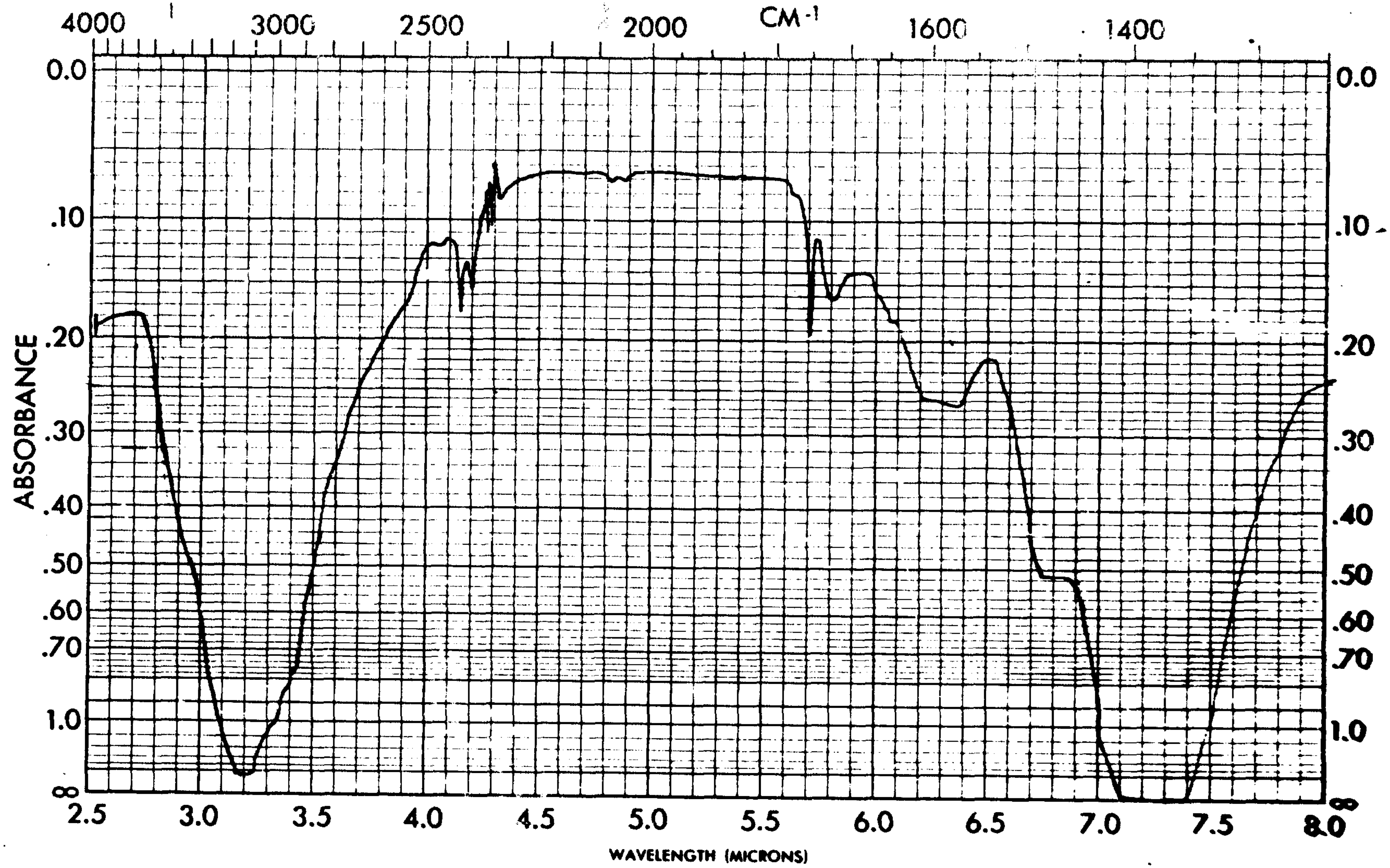

Figure 20. Infrared Spectrum - Solid #6

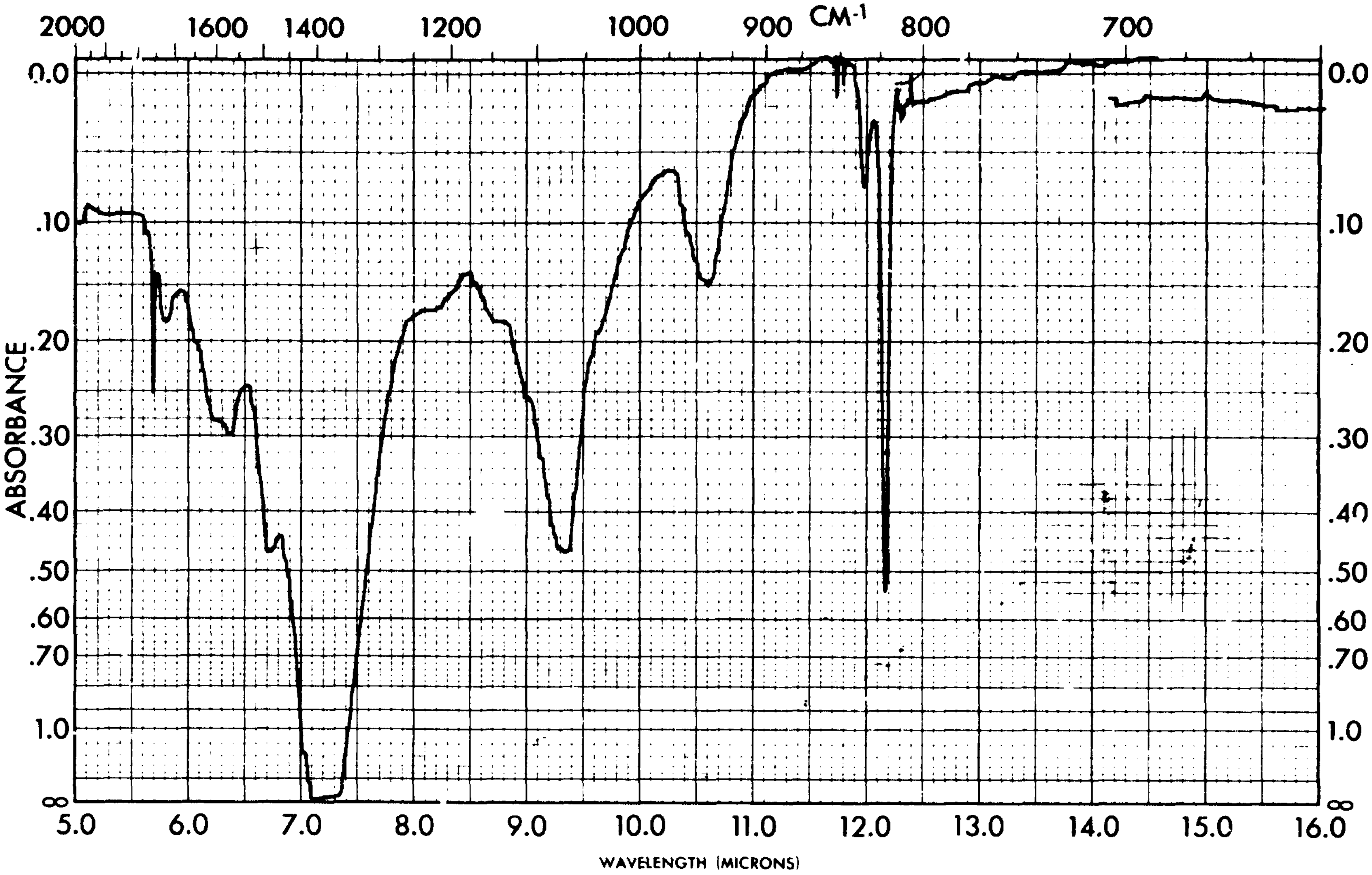

Figure 21. Infrared Spectrum - Solid #6

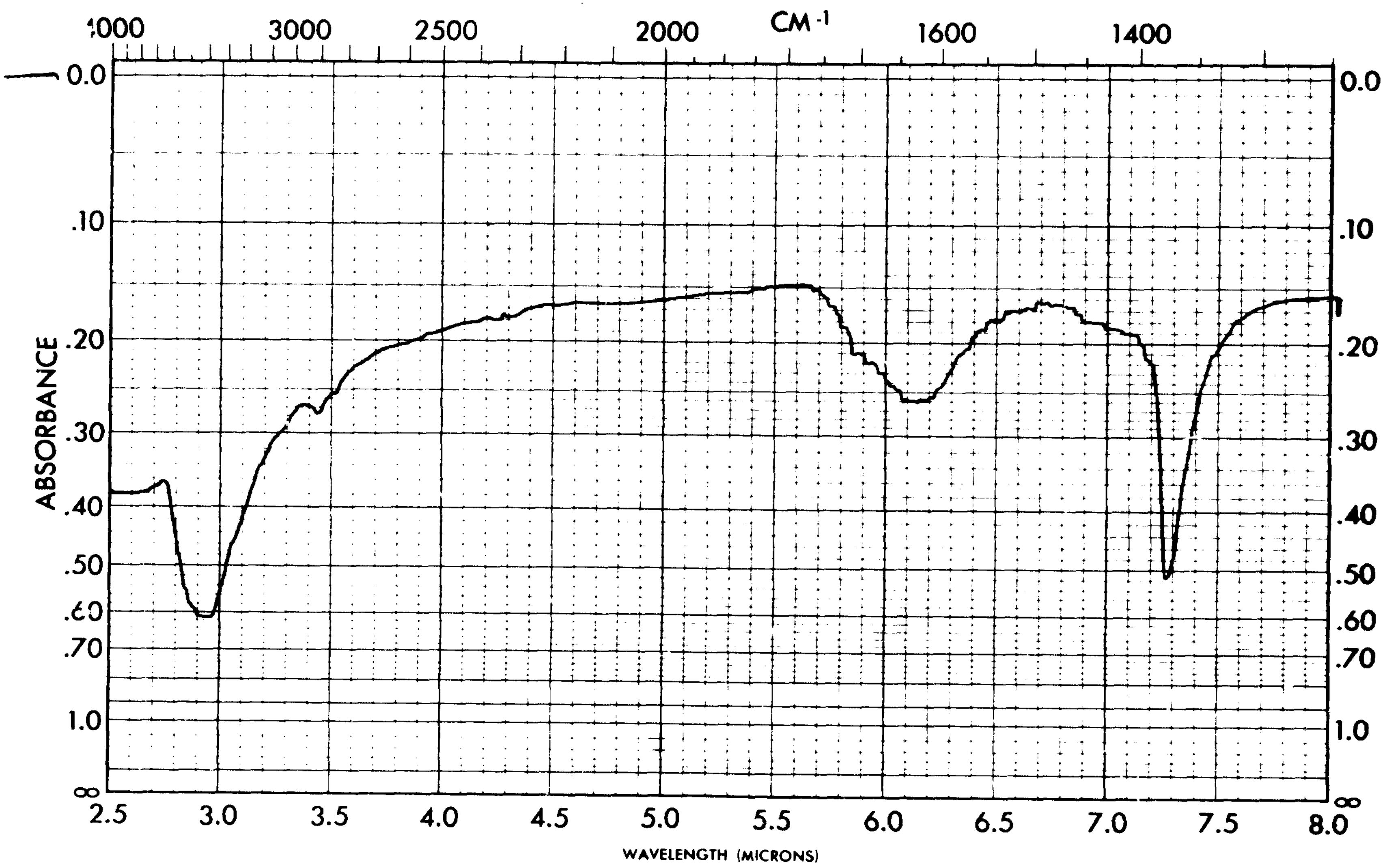

Figure 22. Infrared Spectrum - Solid #4

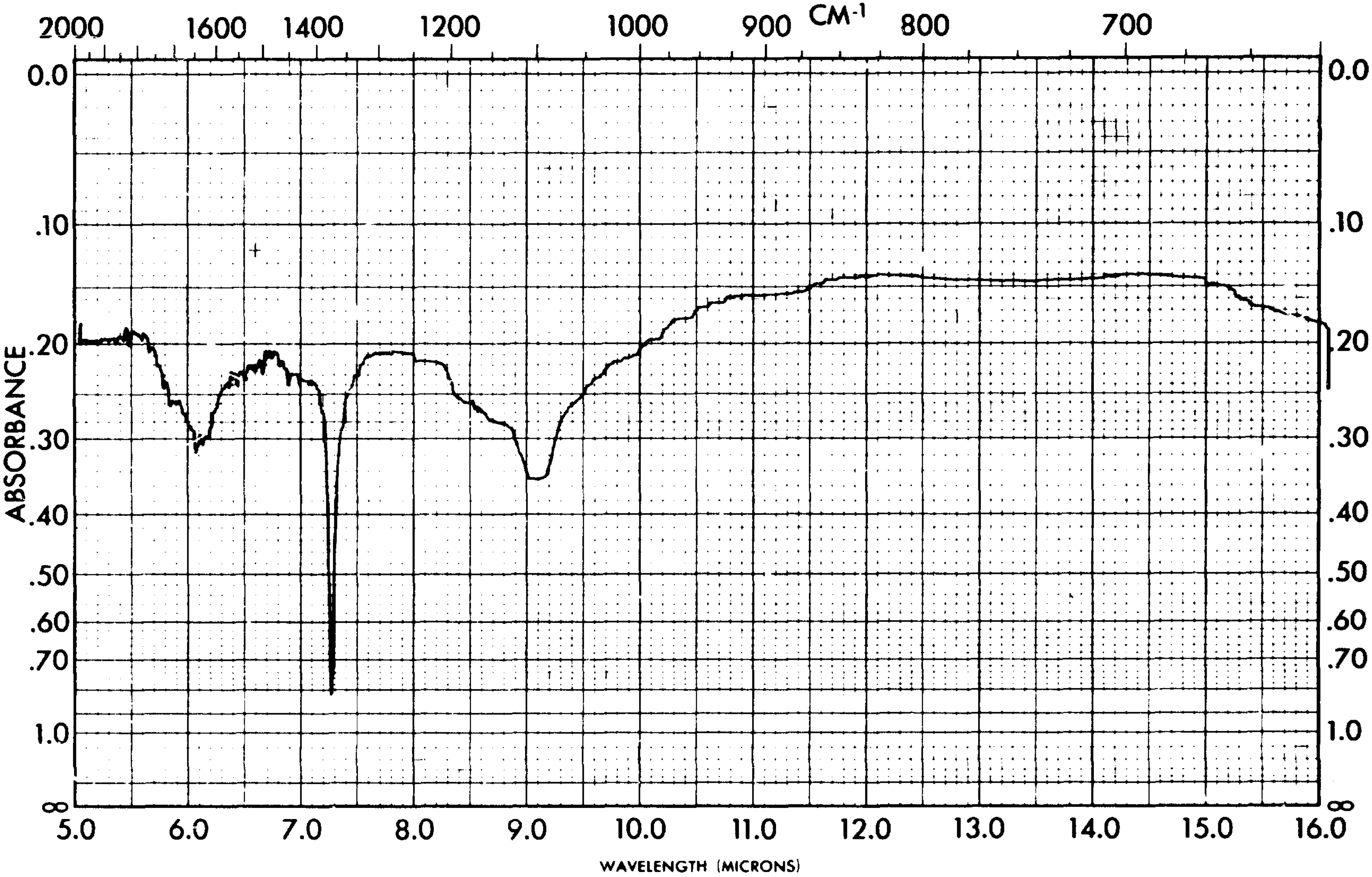

Figure 23. Infrared Spectrum - Solid #4

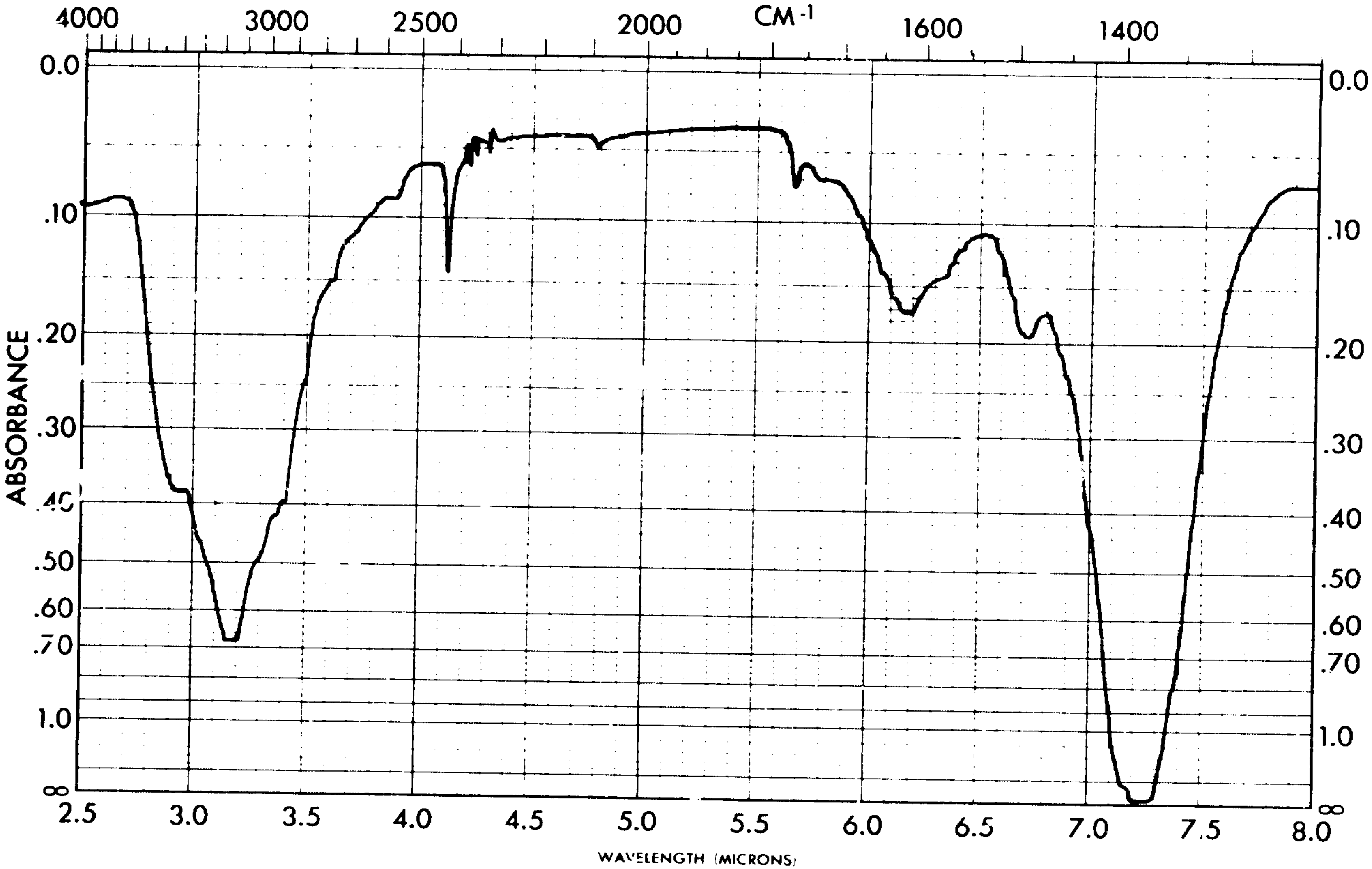

Figure 24. Infrared Spectrum - Solid #5

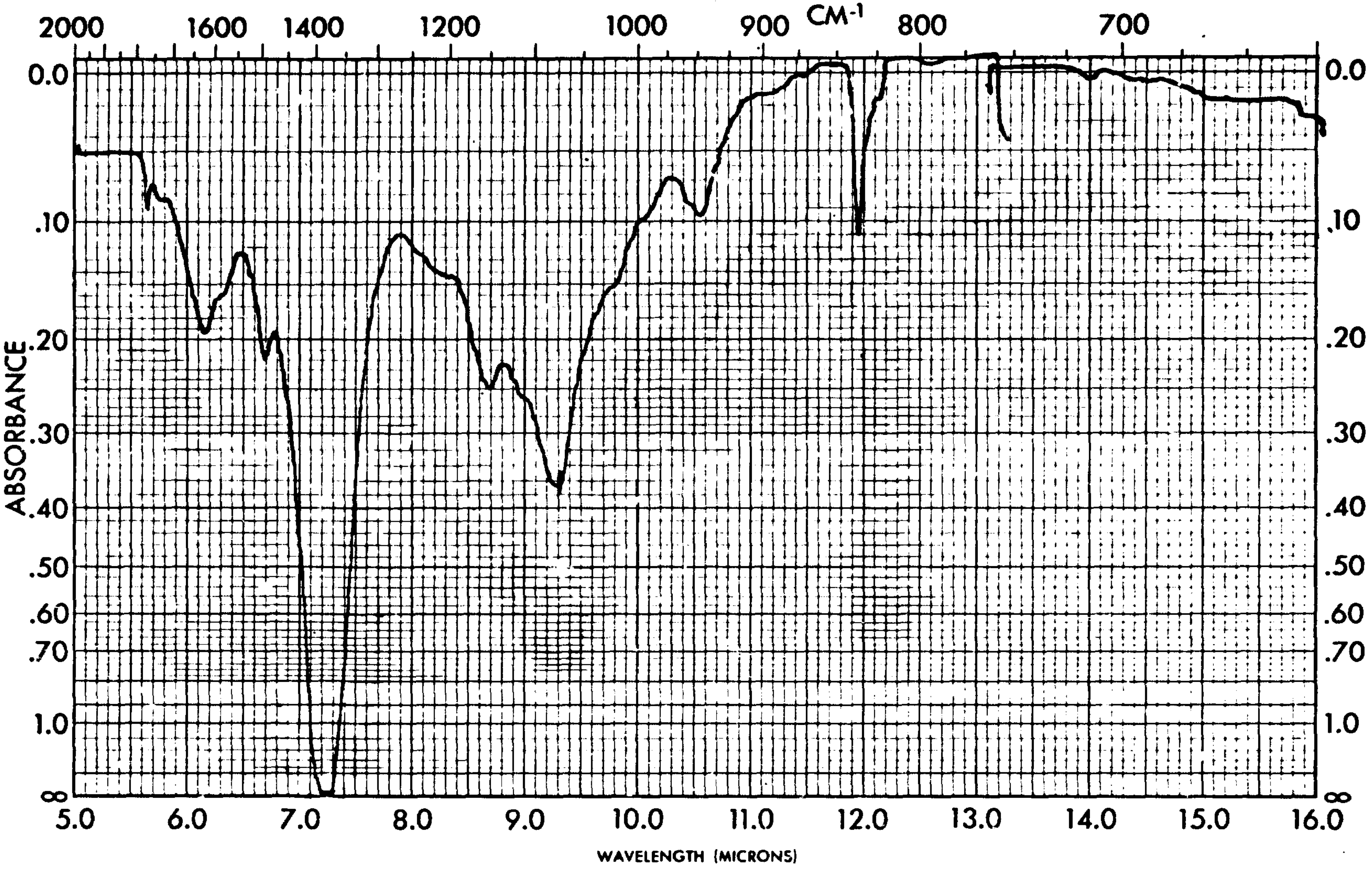

Figure 25. Infrared Spectrum - Solid #5

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