UNCLASSIFIED

AD NUMBER
AD497917
CLASSIFICATION CHANGES
TO: unclassified
FROM: confidential
LIMITATION CHANGES
TO: Approved for public release, distribution unlimited
FROM: Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 28 MAR 1951. Other requests shall be referred to Department of the Navy, Attn: Public Affairs Office, Washington, DC 20350.
AUTHORITY
28 Feb 1963, DoDD 5200.10; Navy, per DTIC Form 55

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NAVY DEPARTMENT
BUREAU OF AERONAUTICS
WASHINGTON, D.C.

1 February 1951
Report No. 493
(Final)
Copy No. A-80

FILE COPY

RESEARCH ON NITROMETHANE

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FEB 25 1971
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Contract NOa(s) 10365

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AEROJET ENGINEERING CORP., AZUSA, CALIF.

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Final Report No. (14) 493

(6) RESEARCH ON NITROMETHANE.

(15) ~~Contract~~ NOa s -10365

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The bulk of this material is Restricted; however, 3 pages are Confidential and 3 are Unclassified; they are marked accordingly.

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(12) No. of Pages: 63 p.

(9) ~~Period Covered:~~ Final rept.
24 Jun[redacted]49 [redacted] 24 Dec[redacted]50

This d[redacted]ins information affect[redacted]he natio[redacted]efense[redacted]States[redacted]thin t meani[redacted]of the Es[redacted]age Laws[redacted]18, U.S.C. Sec[redacted]ns 793 and[redacted]. The t[redacted]ission or t re[redacted]lation of[redacted] contents in[redacted] manner to an [redacted]authorized p[redacted]son is prohib[redacted]ed by law.

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CONTRACT FULFILLMENT

This final report completes the fulfillment of Contract NOa(s) 10365.

I. OBJECT

The program of research conducted under Contract NOa(s) 10365 had two primary objectives:

A. To investigate the kinetics of the reaction involved in the thermal decomposition of nitromethane.

B. To evaluate catalytic methods of lowering the L^* required for the combustion of nitromethane in a rocket motor.

II. RESUME

A. An all-glass system, consisting of a reaction cell, a sensitive Bourdon gauge, a greaseless valve, and auxiliary vacuum apparatus, was used in the investigation of the thermal decomposition of nitromethane.

B. Forty-six experiments were conducted in which the kinetics of the decomposition reaction were studied. In many of these experiments, the effect of additives upon the decomposition rate was investigated.

C. The following results were obtained:

1. The thermal decomposition of nitromethane is apparently a first-order reaction, with an activation energy of 53,000 cal/mole.

2. Experiments with additives show that chain processes are suppressed in the decomposition reaction.

3. Stainless steel is a specific catalyst for the decomposition of nitromethane and increases the reaction rate forty fold.

4. Ditertiarybutyl peroxide or chloral in nitromethane doubles the decomposition rate of the mixture.

5. The addition of diacetyl to nitromethane produces a moderate increase in the decomposition rate, but the full effectiveness of this accelerator was not achieved at the test temperature (419°C).

D. A hypothesis which explains the slow decomposition of nitromethane has been proposed as a result of the kinetics study. Nitric oxide, which is one of the decomposition products of nitromethane, is known to inhibit chain reactions; hence nitric oxide may prevent the propagation of long chains, during the decomposition of nitromethane, and in this way may be responsible for the slowness of the over-all reaction.

E. Motor tests of nitromethane containing various additives were conducted in a 50-lb thrust chamber in order to correlate the data obtained from the decomposition tests in the laboratory with motor performance. The results of the limited motor-test program indicate that the additives used did not improve the burning characteristics of nitromethane containing chromium acetylacetonate. Time did not permit the determination of the effect of the additives on nitromethane alone. It may be concluded that the additives did not sufficiently accelerate the decomposition of nitromethane; therefore, other materials, which will produce a greater increase in the decomposition rate, must be developed in the laboratory.

F. The apparatus for the infrared, in situ study of the thermal decomposition of nitromethane was designed and constructed, but certain experimental difficulties prevented an extensive investigation of this portion of the program.

G. Various chemicals were investigated for possible use as aids in the ignition of nitromethane.

1. Sodium-potassium alloy produces an immediate hypergolic reaction with nitromethane and has been used successfully many times in initiating the decomposition of nitromethane in a 50-lb thrust chamber.

2. Concentrated solutions, in ammonia, of lithium, sodium, or potassium produce a hypergolic reaction with nitromethane.

3. Chlorine trifluoride and nitromethane can react explosively under certain conditions.

4. A 3% solution of iron pentacarbonyl in nitromethane was found to be hypergolic with a saturated solution of chromic acid.

H. Dinitrotetrafluoroethane and vanadyl acetylacetonate reduce the thermal stability of nitromethane.

I. Ultrasonic vibrations did not decompose nitromethane during a 30-min exposure period.

J. High-intensity ultraviolet radiation decomposed approximately 3.5% of nitromethane in one hour. The decomposition products had an insignificant effect upon the thermal sensitivity of the nitromethane.

K. The shock-wave phenomenon, as generated in the dual combustion chambers, does not assist appreciably in the decomposition of nitromethane.

III. CONCLUSIONS AND RECOMMENDATIONS

A. The results of the kinetic study of the thermal decomposition of nitromethane have proved the usefulness of this quantitative method of approach to the problem of increasing the rate of decomposition of nitromethane. Within one year, more information was gained regarding the decomposition reaction than had been obtained in all the previous testing. Accordingly, it is recommended that this study be extended, in conjunction with appropriate motor tests, in order to expedite the development of a rocket motor of moderate L* in which complete decomposition of nitromethane will occur.

B. Because of the small amount of decomposition produced by ultrasonic vibrations, ultraviolet radiation, and the shock-wave recompression stimulus, and because of the size and weight of the equipment necessary to initiate decomposition by these methods, it is recommended that further study using these procedures be discontinued.

C. Another test, measurement of burning rates, is recommended for the determination of the effects of soluble additives on the decomposition of nitromethane. Results of these tests must be correlated with small-motor tests in order to assist interpretation of the data.

IV. RESULTS

A. Introduction

Two methods of investigation were pursued in an effort to discover means of lowering the L^* requirements for the combustion of nitromethane in a rocket motor. The first method used was the study of the kinetics of the reaction involved in the thermal decomposition of nitromethane. As a result of this study, it was possible to postulate that certain additives should accelerate the decomposition of nitromethane in a rocket motor. The second method employed was the testing of catalytic substances and procedures which appeared to warrant investigation.

B. Thermal Decomposition of Nitromethane

1. Introduction

The study of the kinetics of the thermal decomposition of nitromethane was conducted in a static system. Two procedures for determining the rate of decomposition were considered: the manometric method, and the infrared, in situ method. The investigation of a reaction by following the pressure changes taking place during the course of the reaction is convenient, but the data obtained in this way should be supplemented and extended by analyses of reactants, intermediates, and end products. Therefore, the in situ, infrared investigation was proposed. Because considerable experimental difficulties are encountered in constructing apparatus for such a study, the program was expedited by studying the reaction, using the manometric method, in a separate all-glass system while the infrared, in situ apparatus was being designed and constructed. There was another reason for following this course. It was necessary to use materials other than glass in the in situ study, and it was believed that the possible influence of these materials on the decomposition of nitromethane should be evaluated in the all-glass system before assembling the in situ apparatus. The same auxiliary equipment was used in both methods of investigation.

2. Manometric Study of Decomposition

a. Introduction

The kinetic study, which used the pressure method of measuring reaction rates, permitted the determination of the order and activation energy of the reaction as well as an investigation of the probable occurrence and extent of free-radical chain reactions.

b. Apparatus

(1) An all-glass apparatus was used in the manometric studies. It included a reaction vessel which was surrounded by a furnace and which was connected to a Bourdon gauge, a greaseless valve, and the auxiliary vacuum apparatus. In order to reduce the volume between the reaction cell and the greaseless valve to a minimum, capillary tubing was used. The complete apparatus is shown in Figure 1.

(2) The cylindrical reaction vessel, which was 19 cm long and had a diameter of 6.5 cm, was constructed of Pyrex glass, and contained an inlet tube and a thermocouple well. The furnace surrounding the reaction bulb consisted of a thick-walled aluminum tube on which a nichrome heating coil was wound. This was surrounded by an outer shell of stainless steel. Sufficient insulation was placed between the shell and the tube to maintain the reaction bulb at a nearly constant temperature. A schematic diagram of the furnace construction is shown in Figure 2.

(3) Because the rates of many reactions approximately double with each 10°C rise in temperature, it was essential to measure and control the temperature in the reaction vessel very carefully. The temperature in the reaction zone was measured by a thermocouple in conjunction with a precision-type, Leeds and Northrup, indicating potentiometer. The temperature was controlled by a resistance thermometer placed close to the outside wall of the aluminum tube. The resistance thermometer was connected to a Leeds and Northrup Electromax controller, which energized a suitable electrical circuit. The wiring diagram for this installation is indicated in Figure 2.

(4) A Bourdon gauge was used for pressure measurements. This device was based on the design of S. G. Foord (Reference 1), but was modified considerably to make it more sensitive and sturdy. A certain amount of experience and skill was required to produce glass Bourdon gauges which were sensitive to very small pressure changes and at the same time were capable of withstanding a considerable differential in pressure. A satisfactory compromise between these two requirements was incorporated in the present gauge. By magnifying the movement of the Bourdon tube with a combination mechanical and optical lever system (Figure 3), a stronger, although less sensitive, tube could be used. The addition of a movement restrictor prevented breakage of the tube by overstraining when large pressure differentials occurred. A metal frame held the gauge and facilitated

installation of a new gauge in case of breakage. In addition, the frame offered a convenient method of mounting the optical and mechanical parts. The stationary mirror was added in order to detect changes in null position of the gauge. Rubber U-cup rings were used to make the vacuum seal between the gauge and the compensating vacuum-chamber (these were found to be very effective seals in a previous application). The vibration-damping vane attached to the bottom of the pointer was necessary because of the sensitivity of the gauge.

(5) It was originally planned to separate the reaction vessel from the rest of the system by a greased stopcock maintained at approximately 60°C (the high temperature is required to prevent condensation of nitromethane). This arrangement has two major disadvantages: it is difficult to maintain a high vacuum with a greased stopcock held at an elevated temperature, and stopcock grease may influence the course of the reaction. For these reasons a greaseless valve similar to the one reported by Alyea (Reference 2) was used. The valve was constructed and operated in the following manner: A small iron bar was placed inside a 20-mm Pyrex tube (approximately 45 cm long), which was sealed at one end. A long, thin capillary was then sealed into the other end of the tube with a ring seal. The valve was connected to the reaction system, and the 20-mm tube was joined to the main vacuum system through a side arm near the ring seal. The valve was sealed by heating the 20-mm tube, under vacuum, above and below the open end of the capillary: this caused the tube to collapse against the capillary and resulted in a gastight seal in this constricted region. The valve was opened by using a magnet in conjunction with the iron bar inside the tube to break the capillary at the point at which it was sealed to the outside walls. Twelve to fifteen tests could be made before the valve had to be replaced.

(6) The vacuum system included the following equipment: (a) outlets for introduction or withdrawal of reactants; (b) a Toepler pump for transfer of products to the gas cell of the infrared spectrophotometer; (c) a McLeod gauge; and (d) a mercury diffusion pump, backed by a mechanical vacuum pump.

c. Experimental Procedure

(1) The nitromethane used in all the experiments was obtained from the Commercial Solvents Corporation and was purified by steam distillation and vacuum distillation in this laboratory. The purified material was then placed in Pyrex bottles and stored in the dark.

(2) Before starting a decomposition-rate test, a pressure of 10^{-4} mm of mercury or less was obtained in the vacuum system. The reaction vessel was then filled with purified nitromethane and evacuated several times. This procedure was adopted in order to remove any traces of oxygen or other impurities that might affect the reaction. At the same time, the temperature of the reaction vessel (approximately 400°C) was

stabilized at the desired level for the test. Because several hours were required to establish complete thermal equilibrium in the furnace, the Electromax controller was preset at the desired temperature and the equipment was allowed to remain at this temperature until the test was initiated. The controller was so efficient that the temperature rarely varied more than ±0.3°C during a test. The capillary tubing connecting the reaction vessel, the Bourdon gauge, the cold trap, and the greaseless valve was electrically heated to approximately 80°C during the tests to prevent condensation of the nitromethane. In Tests A1 to A44, a measured liquid sample of nitromethane, which had been degassed several times, was distilled from the storage flask to a cold finger on the vacuum system. In Tests A45 and A46, the quantity of nitromethane used was determined by measurement of its pressure in a large tube of known volume before transferring the sample to the cold finger. In both procedures, the sample was distilled from the cold finger to a liquid-nitrogen-cooled trap between the greaseless valve and the Bourdon gauge. During the time that the nitromethane remained frozen, the greaseless valve was sealed. After presetting the Bourdon gauge at a value corresponding to half the expected pressure of the nitromethane, the nitromethane was vaporized rapidly into the reaction vessel. As soon as the preset Bourdon gauge reached its rest position, a stopwatch was started to time the reaction. Pressure measurements were taken as rapidly as possible during the first few minutes of the reaction in order to record closely the initial rate of decomposition. A typical set of rate-of-decomposition curves is shown in Figure 4. Several tests were continued until the nitromethane was completely decomposed, in order to obtain the ratio of final to initial pressures. This ratio was used to calculate the fraction of nitromethane decomposed at any given time.

(3) In most of the tests, the initial pressure of nitromethane in the reaction cell was determined by extrapolation of the pressure-time curve to zero time. This method gave consistent results when the initial rate of the reaction was not too high; however, when the rates were of the magnitude encountered in tests in which stainless steel was present, extrapolation became uncertain, as a significant portion of nitromethane decomposed during the interval between zero time and the time at which the first pressure reading was made. Therefore, it was important to obtain the pressure at zero time by some other method. This was accomplished by attaching a large tube of known volume to the vacuum system. A measured quantity of nitromethane was transferred from this tube into the reaction vessel and the initial pressure of nitromethane was computed directly.

d. Experimental Results

(1) Introduction

A total of 46 decomposition tests were conducted during the course of this phase of the program. These tests were made with nitromethane alone and with nitromethane containing additives. In some of the experiments, certain solid materials were added to the reaction vessel to determine whether a heterogeneous reaction occurred. Data for tests in which known failures, such as leakage in the vacuum system or condensation of nitromethane occurred, are not reported.

(2) Nitromethane Tests

(a) The rate of decomposition of nitromethane was measured at a series of temperatures so that the order and activation energy of the reaction could be determined. This also provided a basis for comparison of data obtained in the presence of additives. The results of these experiments are summarized in Table I. In this table, the rate of decomposition of nitromethane is given in terms of the half-life of the decomposition reaction. The half-life is defined as the time interval during which half of the nitromethane decomposes. This was determined from the appropriate rate-of-decomposition curve by the equation

$$P_{t_{50}} = P_o + \frac{1}{2}(P_f - P_o) \qquad (1)$$

where $P_{t_{50}}$ is the pressure corresponding to the decomposition of half of the nitromethane, P_o is the initial pressure of nitromethane, and P_f is the pressure resulting from the complete decomposition of the nitromethane sample (Section IV, Paragraph B-2-d-(2)-(e)).

(b) The over-all activation energy of the thermal decomposition of nitromethane was determined by the following method: The specific reaction rate for a first-order reaction may be calculated from the half-life values by the equation

$$k = \frac{1}{t_{50}} \left(\ln \frac{100}{50}\right) \qquad (2)$$

where k is the specific reaction rate at a particular temperature, and t_{50} is the half-life (Table I). The activation energy, in turn, is obtained from the equation

$$\log k = \frac{E}{2.303R} \frac{1}{T} + \text{constant} \qquad (3)$$

where k is the specific reaction rate, E is the activation energy, R is the gas constant, and T is the absolute temperature. In Figure 5, log k is plotted against $\frac{10^4}{4.574T}$, thus allowing the activation energy to be determined directly from the slope of the line. The results of Tests A8 and A16 (Table I) were not considered in drawing the curve because it was believed that condensation of nitromethane occurred in the tubing between the reaction cell and the greaseless valve during the determinations. The exclusion of these points appears justified, inasmuch as other tests in which liquid nitromethane was known to be present gave false values of k. The specific reaction rate for the decomposition of nitromethane, obtained from the slope and intercept of the line, may be expressed as

$$k = 7.8 \times 10^{15} e^{-\frac{53,300}{RT}} \text{ min}^{-1} \qquad (4)$$

(c) The specific reaction rates computed from the quarter-lives are somewhat higher than those computed from the half-lives (Table I). However, the activation energies derived from the two rate constants are in close agreement. The value for the activation energy based on the quarter-life is 52,700 cal/mole, and that based on the half-life is 53,300 cal/mole. The values of the activation energy obtained in this investigation are in excellent agreement with that reported by Cottrell and Reid (Reference 3). These investigators studied the reaction very recently and obtained a value of 52,700 cal/mole. Taylor and Vesselovsky, in an earlier investigation, had reported a value of 61,000 cal/mole (Reference 4). The agreement between the activation energies calculated from the quarter- and half-lives indicates that a first-order reaction occurs in the decomposition of nitromethane.

(d) In order to determine whether an induction period is responsible for the slow decomposition of nitromethane, one test (A29) was made at 357°C; at this temperature, the rate of decomposition of nitromethane is so slight that any delay in initiation of the reaction could be easily observed. This experiment served to verify the observation made at higher temperatures that there is no perceptible induction period involved in the thermal decomposition of nitromethane.

(e) In order to compute the final pressure in tests that were not carried to completion, it was necessary to know the ratio of final to initial pressure in the complete thermal decomposition of nitromethane. Several tests were made to obtain data for this ratio. The results are summarized in Table II, and agree closely with those found by Taylor and Vesselovsky (Reference 4). These authors have examined the stoichiometry of the reaction and have proposed the equation for the decomposition as

$$10CH_3NO_2 \longrightarrow 6NO + 6H_2O + 4CO_2 + 3C_2H_6 + 2N_2$$

However, because this reaction has a pressure increase inconsistent with that found experimentally, they have postulated other mechanisms. During the current investigation, samples of partially and completely decomposed reaction products were sent to a local laboratory for mass spectrometer analysis, but the spectra were so complex that the products could not be identified. Further consideration was not given to this problem in the manometric study because the determination of the reaction order was only dependent on the initial and final pressures (Section IV, Paragraph B-2-d-(2)).

(f) To show that nitric oxide is produced in the thermal decomposition of nitromethane, a bulb containing the products of decomposition was opened to the air. The colorless gas within the bulb immediately developed the brown color characteristic of nitrogen dioxide. The formation of nitrogen dioxide, which could occur rapidly on admission of air only according to the equation

$$2NO + O_2 \longrightarrow 2NO_2$$

is a direct indication that NO is a product of the thermal decomposition of nitromethane.

(3) Nitromethane Containing Additives

(a) In order to determine the effect of chain promoters and inhibitors on the decomposition reaction, a number of additives, selected because of their known effect on the thermal decomposition of other organic compounds, were tested with nitromethane. These additives included ditertiarybutyl peroxide, diacetyl, ethylene oxide, chloral, iodine, carbon disulfide, and propylene. Reasons for the selection of these additives will be discussed in the section covering the hypothesis that explains the slow decomposition of nitromethane (Section IV, Paragraph B-2-d-(4)). The results of these tests are presented in Table III, in which the rates of decomposition are compared, on the basis of the half-life of nitromethane, with and without additives. It is apparent from these data that ditertiarybutyl peroxide or chloral is most effective, and diacetyl or ethylene oxide is moderately effective in increasing the rate of decomposition, while carbon disulfide, iodine, or propylene either have no effect or have an inhibiting action on the reaction.

(b) For the study of the catalytic influence of stainless steel on the thermal decomposition of nitromethane, a surface of 924 cm^2, approximately twice that of the Pyrex reaction bulb, was provided by packing the bulb with stainless steel strips. Approximately 1.5 millimoles of nitromethane were used in each of the tests comparing the effect of the packed and unpacked bulbs. The results of the decomposition tests are given in Table IV. It should be noted that the ratios of final to initial pressure in the catalyzed and uncatalyzed reactions are not identical; this indicates that two different reactions may be involved. It is believed that stainless steel is a specific catlyst for the thermal decomposition of nitromethane and that its action is not merely the result of the relatively large surface employed. This conclusion is supported by the work of Taylor and Vesselovsky, who reported that packing the reaction vessel with glass did not significantly increase the rate of decomposition of nitromethane (Reference 4). The catalytic action of stainless steel may be attributed to the oxide film adhering to its surface. This is in accord with previous experiments on the influence of metallic oxides on the thermal decomposition of nitromethane (Reference 5).

(c) Because the <u>in situ</u> study required the use of a Pyrex vessel with sodium chloride windows sealed to the glass with silver chloride, it was necessary to investigate the possible effect of these materials on the thermal decomposition of nitromethane. Tests were conducted in the presence of sodium chloride (Tests A21 and A22) and silver chloride (Tests A19 and A20) and are summarized in Table V. Neither material affects the rate of decomposition. The surface exposed to the reaction in these tests was somewhat greater than that which would be present in the reaction cell.

(4) Hypothesis Explaining the Slow Decomposition of Nitromethane

(a) The hypothesis is proposed that free radicals are formed in the decomposition of nitromethane, but that they are prevented from propagating reaction chains by the presence of nitric oxide. This hypothesis explains the slow decomposition of nitromethane and the related large L^* requirements of nitromethane motors.

(b) Many fast vapor-phase decomposition reactions are chain reactions involving free radicals. It is known that small amounts of nitric oxide reduce the rates of these reactions by removing the free radicals, thus terminating the chains (Reference 6). The generation of free radicals from nitromethane is indicated by the presence of methane and higher hydrocarbons among the end products, while nitric oxide is a known product of the decomposition, according to tests performed here and elsewhere (Reference 4). The basis for the hypothesis is thus established. The effects of certain additives on the decomposition of nitromethane provided a test of the hypothesis:

1 Propylene, which is known to inhibit chain reactions, has no appreciable retarding effect on the rate of decomposition of nitromethane (Reference 7). The amount of nitric oxide present should be sufficient to produce maximal inhibition. This belief is consistent with the work of Smith and Hinshelwood which shows, in the case of propionaldehyde, that if the reaction is maximally inhibited by nitric oxide, it is not inhibited further by the addition of propylene (Reference 8).

2 Certain compounds are known for their ability to initiate free radical chains. These include diacetyl, ethylene oxide, and iodine (References 9, 10, 11, 12, 13). When each was added to nitromethane, no significant acceleration in the rate of decomposition was observed. This may be attributed to the inhibiting action of nitric oxide.

3 Ditertiarybutyl peroxide decomposes into free radicals almost instantly above 400°C (References 14, 15). It should, therefore, assist the decomposition of nitromethane before appreciable quantities of nitric oxide form. This may explain the doubling of the rate of decomposition of nitromethane when ditertiarybutyl peroxide is added.

4 When nitromethane is burned with 5% oxygen in a rocket motor, the L^* requirements of the combustion chamber are reduced appreciably (Reference 5). The increased rate of reaction in the presence of small amounts of oxygen may be explained by assuming that the removal of nitric oxide by oxygen permits a chain reaction to develop during the decomposition of nitromethane.

5 When a sufficient quantity of nitric acid is added to nitromethane, results similar to those obtained with oxygen are observed (Reference 16). Presumably, nitric acid is capable of oxidizing nitric oxide during the decomposition process.

6 The thermal stability of nitromethane is appreciably lowered by the addition of 30% ethyl nitrate. In this case also, nitric oxide may be removed by oxidation.

(c) The experimental evidence cited and the theoretical considerations outlined above are in agreement with the hypothesis that nitric oxide is responsible for the slow decomposition of nitromethane. This hypothesis may be applied in several ways:

1 Removal of nitric oxide by oxidation. The addition of nitric acid or ethyl nitrate would probably lower the L* requirements for combustion in a thrust chamber, but the resulting solutions are thermally unstable. However, other oxidizing agents should be considered.

2 Removal of nitric oxide by reduction. It is known that hydrogen reacts with nitric oxide at elevated temperatures (Reference 17). The suitability of various reducing agents should be investigated.

3 Removal of nitric oxide by reaction with another compound. Mallard and Le Chatelier found that a mixture of carbon disulfide and nitric oxide detonates when ignited (Reference 18). Because it appeared possible that carbon disulfide in nitromethane might react with the nitric oxide formed during the decomposition, carbon disulfide was used as an additive. Although the decomposition of nitromethane was not accelerated, the experimental conditions of the two types of tests may have been sufficiently different that the desired effect was not realized. Chloral was also tested, inasmuch as it was assumed (References 19, 20) that the decomposition of chloral in the presence of nitric oxide results in the removal of the latter substance. A relatively large amount of chloral (34%) approximately doubles the rate of decomposition of nitromethane. This is in agreement with the belief that chloral reacts with the nitric oxide and thus increases the rate of decomposition of nitromethane.

4 Removal of nitric oxide by its catalytic decomposition. The free energy equation for the reaction

$$1/2\ O_2 + 1/2\ N_2 = NO$$

$\Delta F^o_{298} = 20{,}650$ cal/mole $\Delta F^o_T = 21{,}600 - 2.50\ T$ (from equilibrium data)

shows that there is a pronounced thermodynamic tendency for nitric oxide to decompose to its elements (Reference 21). This reaction, however, is immeasurably slow at relatively low temperatures because of its high activation energy. Materials that will catalyze the decomposition should be sought.

5 Because the presence of nitric oxide may prevent occurrence of long chains during the decomposition of nitromethane, it may be possible to produce a large number of short chains by generating sufficient quantities of free radicals. Diacetyl appeared to be a promising additive for this purpose, as its decomposition yields free radicals in the

presence of nitric oxide (Reference 10). However, its low rate of decomposition at the temperature at which it was tested (418°C) may be responsible for its relative ineffectiveness. At combustion-chamber temperatures, this may not be the case. The effects of similar additives should be investigated.

6 The production of sufficient quantities of free radicals, before nitric oxide is formed, may result in an appreciable increase in the rate of decomposition of nitromethane. Ditertiarybutyl peroxide yields free radicals at temperatures at which nitromethane is relatively stable. Accordingly, when a mixture of ditertiarybutyl peroxide and nitromethane is heated to 400°C, the former is immediately decomposed, yielding large quantities of free radicals which may initiate chains prior to the time that the nitric oxide is available for inhibiting the propagation of the reaction chain. In the presence of 25% of this additive, the rate of decomposition of nitromethane was doubled. Other additives of this type should be studied.

3. Correlation of Laboratory Tests with Rocket-Motor Tests

The results of the manometric kinetic studies (Section IV, Paragraph B-2-d) and the catalytic study (Section IV, Paragraph C-2-a-(3)) indicated that certain compounds increased the rate of decomposition of nitromethane. In order to obtain a correlation between these results and actual performance in rocket motors, a series of tests was made in a 50-lb, uncooled thrust chamber using nitromethane containing these additives. The time remaining for completion of the contract prevented an extended motor-test program. Accordingly, lower percentages of some additives were used than had been planned originally, in order to avoid appreciable alteration of the propellant characteristics of nitromethane. It has been shown (Reference 5) that in the combustion of nitromethane in a thrust chamber, smooth operation can be realized only if the L* is larger than a certain value for a given chamber pressure, and that the L* required decreases with increasing chamber pressure. It was believed, therefore, that if the addition of these compounds would permit smooth operation at pressures below the value characteristic of the given L*, a thrust chamber of smaller L* could be employed. The thrust chamber used in these tests possessed an L* of 500 inches and would normally operate efficiently at chamber pressures above 400 psia. The procedure in these tests was to determine approximately the lowest chamber pressure at which smooth operation could be achieved. Smoothness of operation is indicated by the percentage variation in chamber pressure during operation. The results of these tests are reported in Table VI, which included, for comparative purposes, results with nitromethane containing 1% chromium acetylacetonate. It is apparent that none of the additives promoted smooth operation at the lower chamber pressures, although marginal operation (combustion continuing for approximately one second after the oxygen used to initiate combustion was shut off) was achieved in most cases. It is concluded, therefore, that the additives used did not increase the rate of decomposition sufficiently, and that other materials that will produce much greater increases in the decomposition rate must be developed in the laboratory.

4. In Situ Decomposition Studies

a. Introduction

(1) It was the purpose of the in situ decomposition study to supplement the information on reaction kinetics obtained by the manometric method. By identifying the intermediate products by their infrared-absorption spectra, and by following the rate of change of concentration of the intermediates by the same method, it was believed that valuable information concerning the mechanism of the decomposition reaction would be obtained. A knowledge of the reaction mechanism would assist greatly in the selection of effective accelerators for the combustion of nitromethane in rocket motors. Inasmuch as this method of investigation is still uncommon, the design and fabrication of equipment presented many difficulties.

(2) In addition to its utility in the in situ study, the infrared spectrophotometer was also of considerable help in the completion of other phases of the program. With the aid of this instrument, it was definitely proved that ultrasonic vibrations produced no decomposition of nitromethane (see Section IV, Paragraph C-3). In the photochemical decomposition of nitromethane, the decomposition products, which were soluble in the solvent, were identified by means of their infrared absorption spectra; this information assisted in the calculation of the amount of decomposition produced (see Section IV, Paratraph C-4). The spectrophotometer also assisted in the identification of the intermediate products formed during the manometric studies (Section IV, Paragraph B-2-d).

b. Apparatus

(1) A Baird infrared spectrophotometer (Figure 6) was selected for this study because the instrument uses the double-beam principle to give direct spectral recordings, and because the spacing of the optical and mechanical system permitted installation of a large absorption cell and furnace without requiring major changes in the instrument. For this study, the sample and reference beams were interchanged, and the source mirrors were moved back to compensate for the thickness of the salt windows on the cell. In addition, a disengaging mechanism was installed on the prism drive, so that the wavelength could be set at a particular value, and the change in absorption could be recorded as a function of time.

(2) At the initiation of the program, an intensive investigation of possible optical systems applicable to this study was undertaken. Several systems were considered, and are discussed in Reference 22, but a large absorption cell, through which passed both the radiation from the source to the source mirror and the radiation from the source mirror to the entrance slit of the monochromator, was selected because of the relative simplicity of the arrangement. The details of the absorption cell and of the remainder of the equipment for this study are given in the following paragraphs.

(3) The apparatus for the <u>in situ</u> study consisted of the furnace, reaction cell, reference cell, Bourdon gauge, and greaseless valve, in addition to the infrared spectrophotometer. The vacuum system used in the manometric investigation was also employed in the <u>in situ</u> studies. Details of construction and use of this system are described in Section IV, Paragraph B-2-b.

(4) The reaction cell and its furnace were mounted on the floor of the spectrophotometer and were traversed twice by the infrared sample beam. The reference cell was similarly located in the reference beam. The pressure gauge and the greaseless valve, which were to be connected to the reaction cell, were located on a shelf on the side of the spectrophotometer.

(5) The construction of the furnace was similar to that of the vertical furnace used in the manometric study. The furnace and the reaction cell are shown in Figure 7. The reaction cell was contained within the tubular aluminum and copper core of the furnace. The metal core was wound with insulated heating coils, and the space between the core and the shell of the furnace was filled with Santocel AO insulation. The shell of the furnace was covered with cooling coils to reduce stray radiation within the spectrophotometer case. The temperature of the furnace was regulated by an Electromax controller actuated by a Thermohm resistance-thermometer located in a slot in the core of the furnace. The gas-duct housings located at each end of the furnace provided a means of maintaining the cell temperature on the outside surfaces of the reaction-cell windows. The construction of the housing was similar to that of the furnace. The gas ducts were perforated tubular rings. The outer rings directed hot gas toward the sodium chloride windows; the inner rings withdrew the hot gas. The open ends of the gas-duct housings were closed with removable covers when the apparatus was not in use.

(6) The reaction cell was a 10-cm-OD Pyrex tube with sodium chloride windows at the ends to permit passage of the infrared radiation. Fused silver chloride was used to seal the windows to the tube. The temperature of the reaction cell was measured by a thermocouple in conjunction with a potentiometer.

(7) The construction of the reference cell was essentially identical with that of the reaction cell. Because a high-temperature seal was not required in this construction, a Glyptal seal was used. The capillary-tube inlet to the cell contained a standard taper joint, so that the inlet could be connected to the vacuum system in order to load the cell with an inert gas or with nitromethane, should this be desired. A special base to hold and position the cell was fabricated.

(8) Considerable effort was expended in attempting to effect a seal between the Pyrex cell and the sodium chloride windows. According to Simard and Steger (Reference 23), the seal can be made by placing a silver chloride gasket between the two surfaces and raising the temperature above the melting point of silver chloride (460°C). In order

to become familiar with the technique, trial seals were made using a small flask with a ground flange and a sodium chloride window which was approximately one inch in diameter. A vacuum-tight seal was formed without difficulty. When an initial attempt was made to make the seal between the reaction cell and the large windows (four inches diameter) that were required for this study, satisfactory seals were not formed. Much information regarding the characteristics of the seal was gained as a result of this attempt and the second attempt to seal the windows to the cell produced a vacuum-tight joint. The furnace and cell were then slowly cooled to approximately 300°C, installed in the spectrophotometer, and connected to the vacuum system. It was soon discovered, however, that the cell could not be evacuated. Subsequent examination revealed that a number of short cleavages had developed in one of the salt windows immediately over the silver chloride joint. It is not definitely known why the window cracked, but it may have been exposed to thermal shock when the cold end-plate and gas-duct housing were bolted in place directly above it. The displacement of the end-plate and gas-duct housing was necessary to permit observation of the melting of the silver chloride, a process which is hidden from view when the end-plate is in its usual position. Because of the expiration of the contract, no further work was undertaken on the *in situ* study. However, so much useful information was obtained during the manometric studies, that a foundation for further developement is firmly established.

C. Catalytic Decomposition of Nitromethane

1. Introduction

Several methods of catalyzing the decomposition of nitromethane were suggested: these included chemical catalysis as well as decomposition induced by ultrasonic vibrations, ultraviolet radiation, and shock-wave recompression stimuli. These studies are described and discussed in the following sections.

2. Chemical Catalysis

a. The action of the following compounds on the thermal decomposition of nitromethane was investigated:

(1) The thermal stability of the dinitrotetrafluoroethane and of its admixtures with nitromethane was determined in the thermal-sensitivity apparatus described in Reference 26. This apparatus was checked, using purified nitromethane; the average temperature of thermal decomposition, 747°F, obtained from 10 tests, agreed within 2°F with that previously found, and had a standard deviation of 3.3°F. Accordingly, tests were continued with the accelerator, and with nitromethane solutions of the material. The accelerator, when thermally decomposed, produced explosions at either of two temperatures, 570°F and 777°F. Nitromethane solutions of the accelerator decomposed explosively at somewhat lower temperatures than did pure nitromethane. Data for these tests are tabulated in Table VII. Unfortunately, a limited supply of dinitrotetrafluoroethane prevented an extended investigation.

(2) The following physical and chemical properties of dinitrotetrafluoroethane were measured:

Boiling point	58.6°C
Freezing point	-32.5°C
Density at 18°C	1.593 gm/cc

Dr. E. T. McBee, of Purdue University, has stated that the inhalation of vapors from this compound will cause palpitation of the heart, headache, a feeling of faintness, and in severe cases, considerable difficulty in breathing.

(3) In reviewing the effect of various metals on the decomposition of nitromethane, it appeared that metallic compounds other than chromium acetylacetonate might be effective in promoting decomposition in a thrust chamber. Accordingly, tests were initiated to determine the thermal sensitivity of nitromethane solutions containing various metallic acetylacetonates. The compounds tested included manganese, cobalt, copper, and vanadyl acetylacetonates. The results of these tests are presented in Table VIII. The solution containing the vanadyl compound was the only one which decomposed at a temperature lower than that at which nitromethane decomposes.

b. Various chemicals were tested which cannot be used as reaction promoters in nitromethane solutions because they react with nitromethane at ambient temperature (References 24 and 25). They may have an important application, however, as hypergolic starting reactants for nitromethane.

(1) Lithium-Ammonia Solution

Lithium is readily soluble in liquid ammonia at room temperature; a saturated solution contains approximately 10% of lithium by weight and has a low vapor pressure at ambient temperatures. This solution has a red color which is characteristic of concentrated solutions of the alkali metals in ammonia. Approximately 15 seconds after nitromethane was dropped into the lithium-ammonia solution in the cup-test apparatus, a hypergolic reaction occurred. A similar result was obtained when the solution was dropped into nitromethane.

(2) Sodium-Ammonia Solution

The boiling point of a solution of sodium in ammonia is below room temperature; therefore, the copper-colored, concentrated solution is maintained at ambient conditions with considerable difficulty. It is believed that in this concentrated solution, the dissolved metal exists in equilibrium with sodium ions and electrons in the ammonia. Such a system is metastable with respect to sodium amide and hydrogen. When nitromethane was dropped into the solution, an immediate hypergolic reaction resulted. A blue, less-concentrated solution of sodium in ammonia, maintained at lower temperatures, reacted with nitromethane without any evidence of combustion. (Metallic sodium reacted slowly with nitromethane, although it is known that under certain conditions an explosive reaction results).

(3) Potassium-Ammonia Solution

The red, concentrated solution of potassium in ammonia is very similar to the sodium solution and is maintained at ambient conditions with great difficulty. It is believed that the test solution contained suspended metal. When nitromethane was dropped into this concentrated solution of potassium in ammonia, an immediate detonation resulted, and the glass beaker containing the reactants was shattered. A dilute, yellow solution of potassium in ammonia appeared to react slowly with nitromethane upon mixing.

(4) Sodium-Potassium Alloy

Clean sodium-potassium alloy was drawn up into a tube from which it was dropped into a beaker containing nitromethane. Upon mixing, an immediate hypergolic reaction resulted; after burning for several seconds, detonation occurred. As a result of these tests, sodium-potassium alloy has been used successfully many times in starting tests with nitromethane in a 50-lb thrust chamber.

(5) Iron Pentacarbonyl

As much as 10% iron pentacarbonyl proved soluble in technical-grade nitromethane. A 3% solution of iron pentacarbonyl in nitromethane proved to be hypergolic with a saturated solution of chromic acid. (The nitromethane itself was not hypergolic with the chromic acid.)

(6) Chlorine Trifluoride

Chlorine trifluoride vapors were directed into an iron crucible. and three drops of nitromethane were added to the crucible; no reaction occurred. The experiment was repeated, using a greater concentration of chlorine trifluoride vapors, and again no reaction was observed. The nitromethane (three drops) was placed in the crucible, and a full stream of ClF_3 was directed upon it; no visible effects were noted. Next, the iron crucible was placed in an ice bath to obtain liquid chlorine trifluoride (boiling point, 11.3°C): about five drops of ClF_3 were condensed in the crucible, and four drops of nitromethane were added; no reaction occurred. The contents of the crucible were mixed by swirling and then thrown on the ground for disposal; at the instant of contact with the warm, dry sand, a sharp detonation occurred.

3. Decomposition by Ultrasonic Vibrations

a. An investigation of the effect of ultrasonic vibrations on the decomposition of nitromethane solutions was conducted. The apparatus used in these experiments is shown in Figures 8 and 9 and consists of a sample tube connected to a mercury manometer. The sample tube was fabricated from a one-inch stainless steel tube, and the bottom of the vessel was made of stainless steel foil (0.002-inch thickness). The sample was exposed to vibrations of 450 kc/sec generated by a Televiso ultrasonic apparatus.

b. The following test procedure was used: Two ml of the nitromethane solution were placed in the sample tube and frozen by immersion in liquid nitrogen. After the apparatus was evacuated, it was inserted in a copper beaker half-filled with insulating oil cooled by water circulating in copper coils. The bottom of the copper beaker was made of 0.001-inch-thick brass foil. The copper beaker containing the test apparatus was placed directly over the quartz crystal in the oil bath of the ultrasonic vibration-generating unit. A potential of 3000v was applied across the crystal and maintained for one-half hour.

c. The following test results were obtained: Purified nitromethane, commercial nitromethane, and commercial nitromethane containing 1% chromium acetylacetonate catalyst were each subjected to the above-described test procedure. The pressure was recorded during each test. The pressure rise during the first few minutes of exposure to ultrasonic vibration was obviously caused by an increase in vapor pressure of nitromethane resulting from an increase in temperature. At the completion of the experiment, a check was made for the presence of noncondensable products by freezing the nitromethane and measuring the pressure; results are recorded in Table IX. Although no increase in pressure occurred after the first few minutes, a measurable amount of noncondensable gas was present at the end of each test. An investigation showed that this residual gas probably results from the outgassing of the rubber tubing connecting the metal apparatus to the manometer. In order to test for possible decomposition, a sample of each solution was examined in the infrared spectrophotometer before and after ultrasonic treatment. The two spectrograms for each solution were recorded on the same chart, and are shown in Figures 10, 11, and 12. If the slight misalignment of the two curves is disregarded, it is clear that no new absorption peaks were produced and that the initial absorption was not appreciably altered. These data indicate that no decomposition of the nitromethane took place. The practicability of applying ultrasonic decomposition is questionable also because of the large amounts of equipment and power that would be required. For these reasons, it is recommended that no additional work be done on this method of initiating decomposition.

4. Decomposition by Photochemical Excitation

a. An investigation of the rate of decomposition of nitromethane by ultraviolet radiation was undertaken with a special apparatus designed to concentrate the radiation on the sample by parabolic mirrors. Photographs of this equipment and the auxiliary vacuum system are shown in Figures 13 and 14. A General Electric, water-cooled, 1000-watt AH-6 lamp was used as the radiation source. A quartz cooling jacket was required to prevent distillation of the nitromethane from the quartz sample holder.

b. The following procedure was used during these tests. One and one-half ml of purified nitromethane was introduced into the sample holder, which then was cooled in a liquid nitrogen bath. After the sample holder was evacuated, the stopcock was closed, and the nitromethane was allowed to warm to ambient temperature. The sample holder was inserted in the cooling jacket and opened to a manometer through the vacuum system. During irradiation, the pressure in the apparatus was recorded at regular intervals. The initial vapor pressure of nitromethane was deducted from the pressure readings in order to determine the estimated amount of decomposition. The data for these tests are plotted in Figure 15.

c. Hirschlaff and Norrish have shown that nitromethane is decomposed by ultraviolet radiation according to the following equation (Reference 27):

$$6\ CH_3NO_2 \longrightarrow 5\ CH_2O + 2\ N_2 + 2\ NO + 4\ H_2O + CO\ .$$

Using this equation and assuming that water and formaldehyde are the major products which are soluble in nitromethane, that none of the products affect the vapor pressure of the solution, and that the temperature of the solution remains constant, the percent of decomposition can be calculated from a knowledge of the pressure, volume, and weight relationships: in Test C6 approximately 3.5% of nitromethane was decomposed in one hour.

d. Portions of the irradiated product were tested in the thermal-sensitivity apparatus to determine whether the products of the radiation-induced decomposition catalyze the thermal decomposition reaction. Results of these tests are tabulated in Table X. It is apparent that the decomposition products have little effect on the thermal sensitivity of nitromethane, inasmuch as the average explosion temperature of 756°F is only slightly different than that of purified nitromethane (745°F). Because the products do not appear to have any catalytic properties and the rate of decomposition by radiation is much too slow for the high flow rates required in rocket motors, these tests were not continued.

e. The infrared spectrogram of a sample of nitromethane that had been exposed to ultraviolet radiation was studied to identify the products of decomposition. This spectrogram was compared with a number of spectrograms of nitromethane containing materials that are possible products of photochemical decomposition. These added materials included acetic acid, water, formic acid, methanol, formaldehyde, carbon monoxide, methane, ethane, nitrous oxide, carbon dioxide, nitric oxide, hydrogen cyanide, ammonium ion (as ammonium hydroxide), and nitrogen dioxide. When the absorption peaks derived from the known diluents were compared with those found in the irradiated sample, strong evidence was obtained that water and formaldehyde are the major decomposition products occurring in the nitromethane solution, thus confirming the results obtained by Hirschlaff and Norrish. The spectrograms for nitromethane, for irradiated nitromethane, and nitromethane containing a small amount of formaldehyde are recorded in Figure 16. It appears that the prepared sample of nitromethane, nearly saturated with formaldehyde, contained less formaldehyde than the irradiated sample. The new peaks occurring in the irradiated sample are assigned as follows:

Water - 2.74 μ, 2.81 μ

Formaldehyde - 5.80 μ, 7.77 μ, 8.62 μ, 8.90 μ, 9.62 μ, 10.09 μ, 11.54 μ.

5. Decomposition by Shock-Wave Recompression Stimulus

a. The belief that nitromethane might be appreciably decomposed by shock waves as it passed through the nozzle of one chamber into another chamber prompted an investigation of this possible means of reducing the L^* requirements of nitromethane motors. The complete thrust-chamber assembly (Figures 17 and 18) consisted of two main components, the preliminary chamber of 50-lb rated thrust and the main chamber of 200-lb rated thrust; these were connected through the water-cooled nozzle of the preliminary chamber. The preliminary chamber was designed for a maximum combustion pressure of 900 psia, an L^* of 765 inches, and ratio of chamber area to throat area, A_c/A_t, of 8.76. The main chamber was designed for a maximum chamber pressure of 450 psia, an L^* of 374 inches, and an A_c/A_t value of 7.6. Both chambers are water-cooled.

b. The preliminary chamber was equipped with two injector systems. The first injector assembly was used for the propellants required for the preliminary chamber. It contained three single orifices for injection of the starting nitromethane, the starting oxygen, and the preliminary nitromethane supply. The second system, used for the injection of the nitromethane into the main chamber, consisted of eight equally spaced orifices located at the entrance of the preliminary chamber nozzle. Nitromethane was injected into the preliminary chamber in a conventional manner, whereas the supply for the main chamber was carried from the preliminary chamber into the main chamber by the combustion gases generated in the preliminary chamber. A shock-wave phenomenon was expected to occur at the exit of the preliminary nozzle. It was further expected that the turbulent mixing of nitromethane injected in the nozzle with the hot combustion gases generated in the preliminary chamber would assist in rapid decomposition.

c. In order to start the thrust chamber, the nitromethane in the preliminary chamber was ignited by a spark in the presence of oxygen. After ignition, the flow of fuel was increased until a chamber pressure of approximately 800 psig developed. As soon as stable operation at rated flow was obtained in the preliminary chamber, nitromethane was introduced through the orifices forward of the throat. Considerable difficulty has always been encountered in starting and shutting down nitromethane thrust chambers and both operations can be relatively hazardous if not properly executed. Recent development programs have produced electronic sequencing units applicable to the automatic governing and timing of rocket-engine operations. On the basis of these developments, a semiautomatic sequencing unit was designed and assembled in order to simplify operation of the nitromethane motor. Numerous uneventful starts and shutdowns proved the utility of this unit.

d. The procedure for the operation of the thrust-chamber assembly and the semiautomatic sequencing unit follows; operations (1) through (4) and operation (9) are manually controlled, the others are automatic.

(1) Start the continuous nitrogen flush of the main nitromethane supply lines.

(2) Close the spark-plug circuit.

(3) Start the oxygen flow.

(4) Initiate the starting nitromethane flow.

(5) A pressure switch automatically actuates the valve of the preliminary nitromethane supply after the pressure in the preliminary chamber reaches 75 psig.

(6) The spark-plug circuit is opened automatically when the preliminary nitromethane supply valve is fully opened.

(7) A pressure switch turns off the oxygen flow automatically after the pressure in the preliminary chamber reaches 550 psig.

(8) A nitrogen flush through the oxygen line is automatically actuated as soon as the flow of oxygen is cut off. The duration of this flush is approximately 1.2 seconds.

(9) Start the main nitromethane flow. The nitrogen flush in these lines is cut off as soon as the main nitromethane valve begins to open.

(10) When the firing switch is manually opened, the operation of the entire thrust-chamber assembly is shut down, and an automatic purge of each of the supply lines is initiated to prevent explosions which might result if the propellants remained in the lines after the valves are closed.

(11) As an additional safety factor, a pressure-actuated malfunction switch is connected to the preliminary chamber. This switch shuts down the entire operation and initiates a purge through each of the supply lines if the pressure in the preliminary chamber drops below a preset value after the thrust chamber is started. The malfunction switch was set at 500 psig during the tests.

e. The test program was carried out in three phases: (1) testing of the starting procedure, (2) operation of the preliminary chamber as a separate unit, and (3) operation of the complete assembly.

(1) The starting procedure was tested several times and, as a result of the incorporation of the sequencing unit, no difficulty was encountered. The weight rate of flow of starting nitromethane was set at approximately 30% of the anticipated total nitromethane flow which was to be injected into the preliminary chamber. The weight rate of flow of gaseous oxygen was 9 - 10% of the weight rate of flow of the starting nitromethane.

(2) Four tests were performed to check the operation and performance of the preliminary chamber at a flow rate of approximately 0.25 lb/sec. The chamber operated satisfactorily with values of the characteristic exhaust velocity, c^*, between 3300 and 4000 ft/sec. Figure 19 shows the variation of the pressure in the preliminary chamber as a function of time after the beginning of injection of the main nitromethane supply. The value of c^*, obtained prior to the injection of the main nitromethane supply, was 3590 ft/sec; it decreased to 1065 ft/sec during the injection. Approximately 8% of the nitromethane introduced at the nozzle entrance was decomposed in the preliminary chamber; the remainder escaped, unburned, through the nozzle of the preliminary chamber into the atmosphere. This phenomenon is expected because it is known that the L^* available (53.5 in.) between the nozzle orifices and the throat is not sufficient for complete decomposition of the nitromethane to occur.

(3) Three tests were made with the complete thrust-chamber assembly; operation was normal in each case until the main supply of nitromethane was introduced. At this point, combustion became unsteady, the flame blew out, and the malfunction switch terminated the tests. In spite of this behavior, the data for these tests were evaluated in order to determine the efficiency of the shock-wave phenomenon; the extent of the decomposition and the data necessary for this calculation are presented in Table XI. The effect of the injection of the main flow of nitromethane on the chamber pressure is shown in Figure 20. The comparison of the observed chamber pressure (corrected for the exhaust pressure from the preliminary chamber) and that calculated for complete combustion of the main flow shows that only

a fraction of the propellant was decomposed in the main chamber. The remainder of this nitromethane escaped, unburned, through the second nozzle into the atmosphere. It is concluded that the shock-wave phenomenon, as generated in the dual combustion chambers, does not assist appreciably in the decomposition of nitromethane.

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TABLE I

HALF- AND QUARTER-LIFE OF NITROETHANE DURING THERMAL DECOMPOSITION AT VARIOUS TEMPERATURES

Test No.	Initial Pressure, mm Hg	Half-Life, min	Quarter-Life, min	Temperature, °C ±0.3°C
A3	77.0	31.8	12.7	390.6
A8	68.0	30.5	9.8	403.0
A16	147.5	22.4	8.8	403.0
A17	132.0	16.7	5.6	403.5
A18	124.5	12.9	4.5	403.3
A26	148.7	8.3	3.0	414.2
A28	144.3	6.3	2.4	418.0
A29	152.0	276.0	96.0	356.9
A30	151.7	10.4	3.9	409.1
A32	149.7	18.7*	7.0	398.0
A41	149.6	6.4	2.4	418.3

* This value was reported erroneously in Progress Report No. 2014-6, Aerojet Engineering Corporation, 3 November 1950.

TABLE II

RATIO OF FINAL TO INITIAL PRESSURE RESULTING FROM COMPLETE THERMAL DECOMPOSITION OF NITROMETHANE

Test No.	Temperature, °C	Initial Pressure, mm Hg	Ratio of Final to Initial Pressure
A28	418.0	144.3	2.36
A29	356.9	152.0	2.31
A32	398.0	149.6	2.41
A41	418.3	149.6	2.36
		Average	2.36

TABLE III

EFFECT OF ADDITIVES ON THE RATE OF THERMAL DECOMPOSITION OF NITROMETHANE

Test No.	Additive	Additive, wt %	Temp. °C, ±0.3°C	Initial Pressure of Nitromethane, mm Hg	Half-Life, min	
					With Additive	Without Additive*
A36	Ditertiarybutyl peroxide	25	418.5	121.5	2.9	6.1
A40	Ditertiarybutyl peroxide	38	418.3	131.5	3.2	6.2
A13	Diacetyl	19	402.8	103.8	12.8	15.4
A35	Diacetyl	15	418.2	146.8	4.8	6.2
A31	Ethylene oxide	6	399.2	157.5	16.7	18.6
A42	Ethylene oxide	10	418.3	147.5	5.2	6.2
A37	Chloral	21	418.8	153.5	4.8	6.0
A43	Chloral	34	419.3	142.0	3.4	6.0
A23	Iodine	7	403.3	142.5	17.6	14.6
A25	Iodine	8	417.7	121.3	7.2	6.4
A33	Carbon disulfide	23	418.3	93.2	6.1	6.2
A7	Propylene	30	401.4	74.0	17.1	16.3
A12	Propylene	24	402.0	105.1	19.1	15.8

* These values are computed for the indicated temperatures from the specific-reaction-rate equation (4) (Section IV, Paragraph B-2-d-(2)), constants for which are derived from the data in Table I.

TABLE IV

CATALYTIC EFFECT OF STAINLESS STEEL ON THE THERMAL DECOMPOSITION OF NITROMETHANE

Test No.	Initial Pressure of Nitromethane, mm Hg	Temp., °C $\pm 0.3^\circ C$	Half-Life, Min		Ratio of Final Pressure to Initial Pressure	
			Packed Vessel[*]	Unpacked Vessel	Packed Vessel	Unpacked Vessel
A45	139.5	402.2	0.4			
--	--	402.2	--	15.8[**]		
A46	130.5	402.2	0.4	--	2.11	
--	--	--	--	--	--	2.36[***]

[*] Reaction vessel filled with 924 cm^2 of stainless steel strips.

[**] Calculated from specific-reaction-rate equation (Section IV, Paragraph B, 2, d, (2)).

[***] Table II.

TABLE V

EFFECT OF SILVER CHLORIDE AND SODIUM CHLORIDE ON THE THERMAL DECOMPOSITION OF NITROMETHANE

Test No.	Temp., °C ±0.3°C	Initial Pressure of Nitromethane, mm Hg	Additive	Half-Life, Min Packed Bulb	Half-Life, Min Unpacked Bulb*
A19	403.5	152.2	30 cm^2 Silver Chloride	15.2	14.5
A20	403.0	142.0	30 cm^2 Silver Chloride	17.5	15.1
A21	403.3	126.0	212 cm^2 Sodium Chloride	15.8	14.8
A22	403.5	142.0	212 cm^2 Sodium Chloride	13.6	14.5

* These values are computed for the indicated temperatures from the specific-reaction-rate equation (4) (Section IV, Paragraph B-2-d-(2)), constants for which are derived from the data in Table I.

TABLE VI

THRUST-CHAMBER TESTS USING NITROMETHANE CONTAINING ADDITIVES

Run No.	Nitromethane Composition (by weight)	Chamber Press, psia	Variation of Chamber Press, %	Duration of Self-Sustained Combustion, sec
45	99.0% Nitromethane 1.0% Chromium Acetylacetonate	452	± 6	2.35*
46	99.0% Nitromethane 1.0% Chromium Acetylacetonate	356	± 8	1.0
47	99.0% Nitromethane 1.0% Chromium Acetylacetonate	330	± 7	1.5
48	99.0% Nitromethane 1.0% Chromium Acetylacetonate	330	± 10	1.1
42	99.0% Nitromethane 1.0% Vanadyl Acetylacetonate	457	± 5	2.8*
43	99.0% Nitromethane 1.0% Vanadyl Acetylacetonate	365	± 9	1.4
44	99.0% Nitromethane 1.0% Vanadyl Acetylacetonate	335	± 9	0.9
49	84.3% Nitromethane 14.7% Ditertiarybutyl Peroxide 1.0% Chromium Acetylacetonate	495	± 3	2.8*
50	84.3% Nitromethane 14.7% Ditertiarybutyl Peroxide 1.0% Chromium Acetylacetonate	465	± 5	3.5*
51	84.3% Nitromethane 14.7% Ditertiarybutyl Peroxide 1.0% Chromium Acetylacetonate	---	---	<0.1
52	84.3% Nitromethane 14.7% Ditertiarybutyl Peroxide 1.0% Chromium Acetylacetonate	---	---	<0.1

* Successful run, terminated by test engineer.

(cont.) Table VI

TABLE VI (cont.)

Run No.	Nitromethane Composition (by weight)	Chamber Press, psia	Variation of Chamber Press, %	Duration of Self-Sustained Combustion, sec
53	84.3% Nitromethane 14.7% Ditertiarybutyl Peroxide 1.0% Chromium Acetylacetonate	----	---	< 0.1
54	84.3% Nitromethane 14.7% Chloral 1.0% Chromium Acetylacetonate	485	± 3	0.85
55	84.3% Nitromethane 14.7% Chloral 1.0% Chromium Acetylacetonate	542	± 3	2.6*
56	94.0% Nitromethane 5.0% Diacetyl 1.0% Chromium Acetylacetonate	420	± 10	2.7*
57	94.0% Nitromethane 5.0% Diacetyl 1.0% Chromium Acetylacetonate	375	± 12	0.5
58	94.0% Nitromethane 5.0% Diacetyl 1.0% Chromium Acetylacetonate	405	± 10	0.5
59	84.3% Nitromethane 14.7% Diacetyl 1.0% Chromium Acetylacetonate	420	± 8	0.3
60	84.3% Nitromethane 14.7% Diacetyl 1.0% Chromium Acetylacetonate	452	± 3	0.55
61	84.3% Nitromethane 14.7% Diacetyl 1.0% Chromium Acetylacetonate	375	± 6	0.75

* Successful run, terminated by test engineer.

TABLE VII

THERMAL SENSITIVITY OF NITROMETHANE-DINITROTETRAFLUOROETHANE SOLUTIONS

Solution	Test No.	Rate of Heating, °F/min	Block Temp. Start, °F	Block Temp. at Explosion, °F
100% Nitromethane	B-1	19	410	745
	B-2	19	409	744
	B-3	20	409	744
	B-4	21	418	745
	B-5	20	409	746
	B-6	22	410	748
	B-7	22	414	748
	B-8	19	412	745
	B-9	22	414	755
	B-10	21	412	750
	Standard Deviation = 3.3°F		Average =	747
80% Nitromethane 20% Dinitrotetrafluoroethane	B-51	19	411	696
	B-52	19	413	697
	B-53	20	418	579
	B-54	20	413	697
	B-55	20	415	699
	B-56	21	410	705
	B-57	19	412	700
	B-58	20	425	705
	B-59	17	418	708
	B-60	17	420	717
	Standard Deviation = 6.5°F (Test No. B-53 omitted)		Average	703
60% Nitromethane 40% Dinitrotetrafluoroethane	B-41	19	410	678
	B-42	18	415	681
	B-43	20	408	610
	B-44	21	415	695
	B-45	20	414	695
	B-46	19	420	690
	B-47	18	412	680
	B-48	19	410	680
	B-49	17	415	687
	B-50	18	412	680
	Standard Deviation = 8.6°F (Test No. B-43 omitted)		Average	685

TABLE VII (cont.)

THERMAL SENSITIVITY OF NITROMETHANE-DINITROTETRAFLUOROETHANE SOLUTIONS

Solution	Test No.	Rate of Heating, °F/min	Block Temp. Start, °F	Block Temp. at Explosion, °F
40% Nitromethane 60% Dinitrotetrafluoroethane	B-31	17	411	700
	B-32	19	416	706
	B-33	20	416	675
	B-34	19	412	675
	B-35	17	427	675
	B-36	17	408	675
	B-37	19	415	681
	B-38	19	410	676
	B-39	19	412	670
	B-40	18	408	670
	Standard Deviation = 9.4°F			Average = 680
20% Nitromethane 80% Dinitrotetrafluoroethane	B-21	17	420	734
	B-22	12	413	517
	B-23	19	415	722
	B-24	18	414	725
	B-25	21	415	725
	B-26	18	415	725
	B-27	20	417	730
	B-28	18	415	730
	B-29	19	420	750
	B-30	20	415	712
	Standard Deviation = 9.7°F (Test B-22 omitted)			Average = 728
100% Dinitrotetrafluoroethane	B-11	20	413	576(I)
	B-12	17	414	769(II)
	B-13	20	414	570(I)
	B-14	20	414	571(I)
	B-15	20	419	570(I)
	B-16	19	415	570(I)
	B-17	18	417	785(II)
	B-18	18	415	777(II)
	B-19	16	421	564(I)
	B-20	17	417	777(II)
	Standard Deviation Group I = 3.5°F Group II = 8.0°F			Average Group I = 570 Average Group II = 777

TABLE VIII

THERMAL SENSITIVITY OF NITROMETHANE SOLUTIONS CONTAINING METAL ACETYLACETONATES

Additive, wt %	No. of Tests Conducted	Average Explosion Temperature, °F	Standard Deviation, °F
1% Chromium Acetylacetonate	10	655	54
1% Manganese Acetylacetonate	5	645	20
1% Cobalt Acetylacetonate	2	748	3
Approx. 0.1% (saturated) Copper Acetylacetonate	2	740	0
1% Vanadyl Acetylacetonate	6	561	5

TABLE IX

DECOMPOSITION OF NITROMETHANE SOLUTIONS BY ULTRASONIC VIBRATIONS

Test No.	Sample Material	Solution Temp. °C	Time of Exposure, min	Pressure, mm Hg	On Crystal Potential, KV	On Crystal Milli-amperes
1	**Purified Nitromethane**	-196	0	1	—	—
	↓	ambient	0	27	3.0	225
		ambient	2	38	3.0	225
		ambient	30	38	3.0	250
		-196	30	4	—	—
2		-196	0	0	—	—
		ambient	0	36	3.0	250
		ambient	2	55	3.0	250
		ambient	30	47	2.6	250
		-196	30	4	—	—
3		-196	0	0	—	—
		ambient	0	48	3.0	240
		ambient	2	84	3.0	240
		ambient	30	66	3.0	230
		-196	30	4	—	—
1	Commercial Nitromethane	-196	0	1	—	—
	↓	ambient	0	35	2.9	250
		ambient	2	56	2.9	250
		ambient	30	56	2.9	250
		-196	30	13	—	—
2		-196	0	0	—	—
		ambient	0	40	2.8	250
		ambient	2	70	2.8	250
		ambient	30	61	2.9	250
		-196	30	4	—	—
3		-196	0	0	—	—
		ambient	0	39	3.0	215
		ambient	2	66	2.8	250
		ambient	30	55	2.8	250
		-196	30	5	—	—

TABLE IX (cont.)

DECOMPOSITION OF NITROMETHANE SOLUTIONS BY ULTRASONIC VIBRATIONS

Test No.	Sample Material	Solution Temp., °C	Time of Exposure, min	Pressure, mm Hg	On Crystal Potential, KV	On Crystal Milliamperes
1	Commercial Nitromethane Plus 1% Chromium Acetyl Acetonate	-196	0	2	—	—
	↓	ambient	0	28	3.0	230
		ambient	3	41	3.0	240
		ambient	30	41	3.0	245
		-196	30	9	—	—
2		-196	0	0	—	—
		ambient	0	31	3.0	230
		ambient	3	41	3.0	250
		ambient	30	37	3.0	250
		-196	30	6	—	—
3		-196	0	0	—	—
		ambient	0	30	3.0	210
		ambient	2	37	2.8	250
		ambient	30	32	3.0	250
		-196	30	7	—	—
	Water	-196	0	0	—	—
	↓	ambient	0	25	3.0	230
		ambient	2	44	3.0	240
		ambient	30	33	3.0	260
		-196	30	5	—	—
	None	-196	0	0	—	—
	↓	ambient	0	21	3.0	220
		ambient	2	20	3.0	220
		ambient	30	18	2.9	250
		-196	30	4	—	—

TABLE X

THERMAL SENSITIVITY OF IRRADIATED NITROMETHANE SOLUTIONS

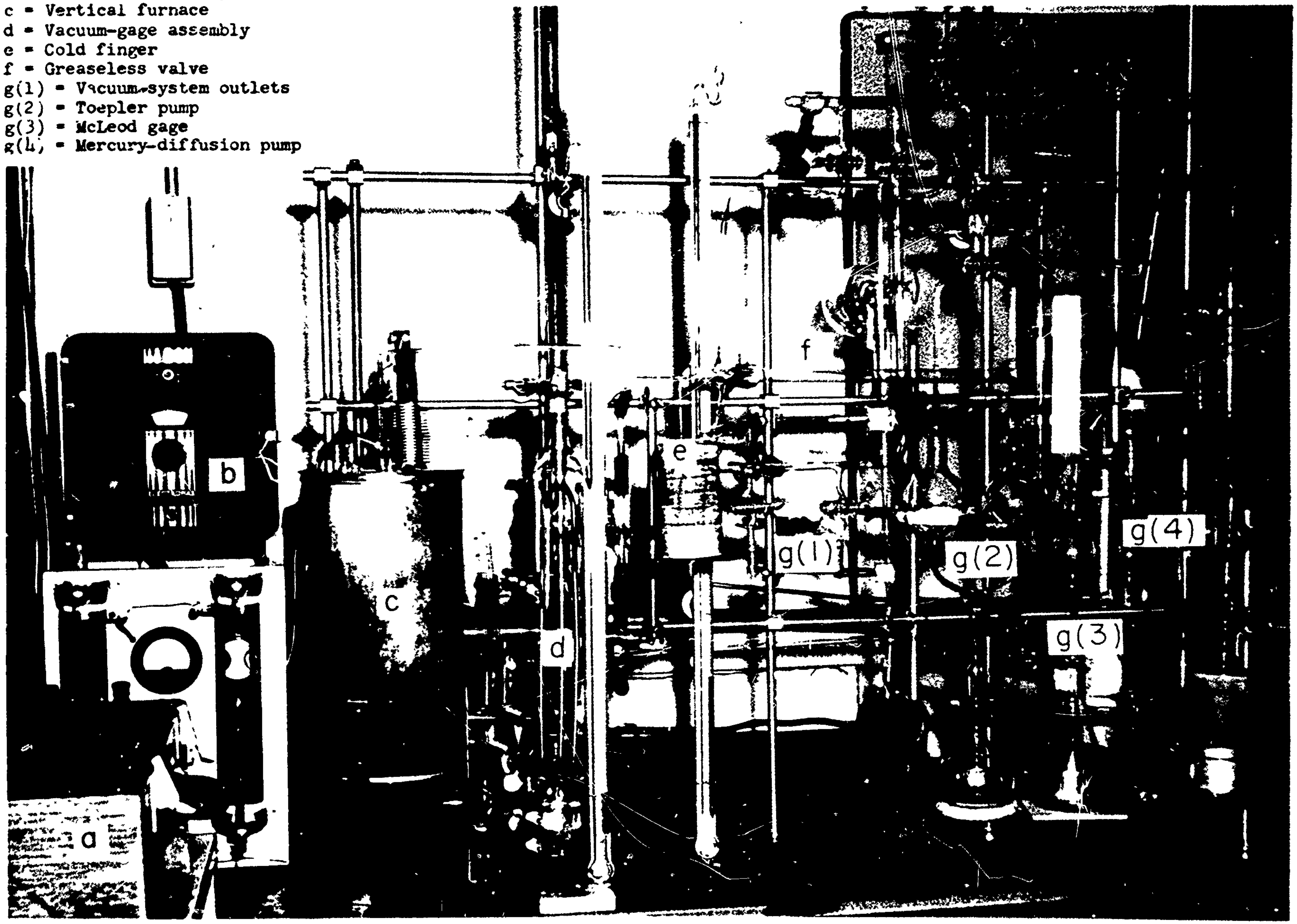
Test No.	Rate of Heating, °F/min	Block Temp. Start, °F	Block Temp. at Explosion, °F
V1	20	401	753
V2	20	398	770
V3	20	401	773
V4	18	400	772
V5	12	425	763
V6	16	450	743
V7	15	400	745
V8	19	400	740
V9	19	400	746
	Standard Deviation = 12.7°F	Average	756

TABLE XI

DECOMPOSITION OF NITROMETHANE IN SHOCK-WAVE RECOMPRESSION TESTS

Test No.	Nitromethane Flow Rates, lb/sec				Main Chamber Press. Resulting from Main Flow, psi		Nitromethane Decomposed in Main Chamber, %
	Starting	Prelim. Chamber	Main Chamber	Total	Meas.	Calc.	
D22-24	0.074	0.190	0.658	0.922	28	191	14.6
D22-25	0.066	0.166	0.401	0.633	38	114.5	33.1
D22-26	0.071	0.190	0.621	0.882	40	177.5	22.5

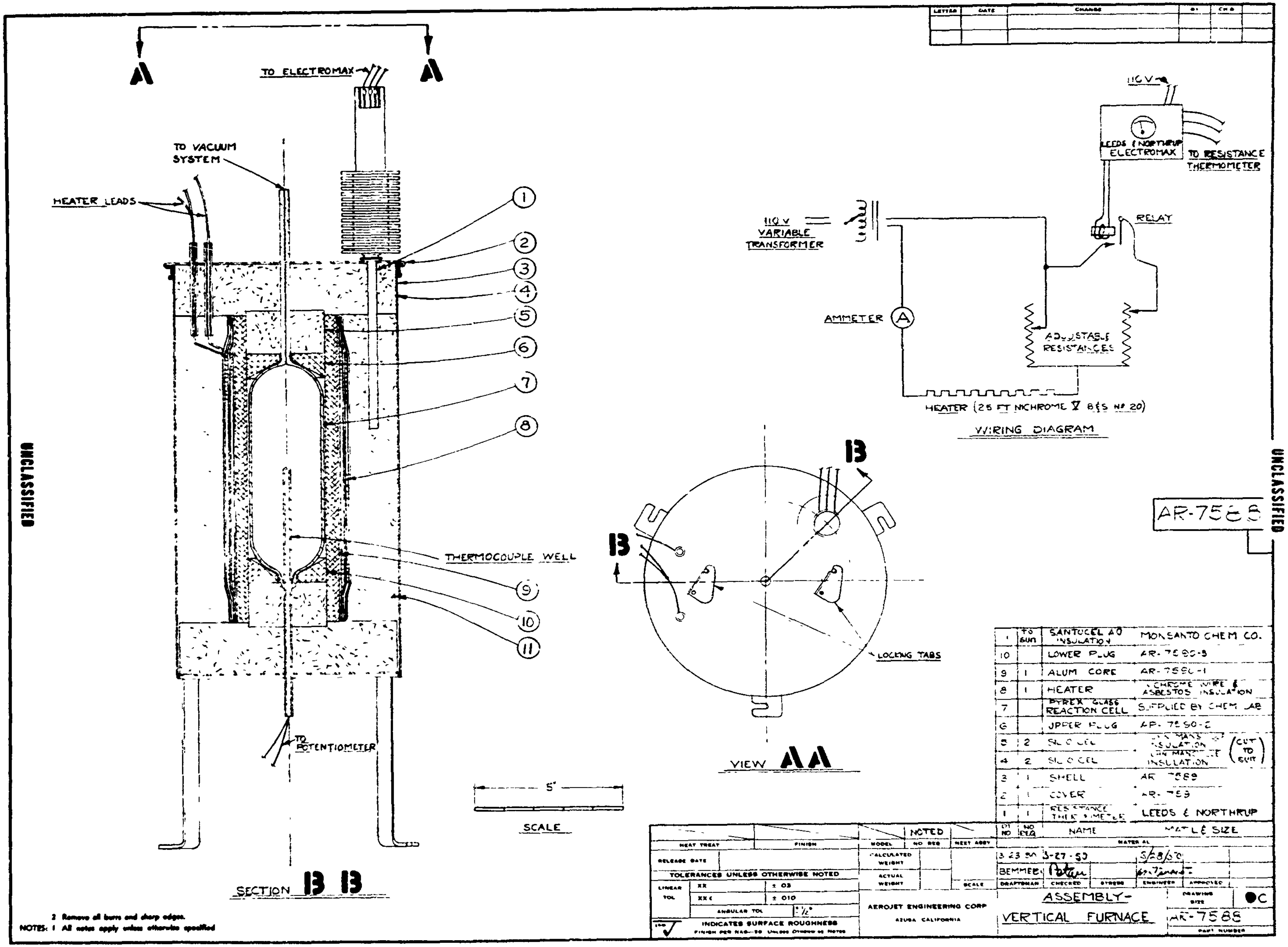
a = Leeds and Northrup Potentiometer
b = Leeds and Northrup Electromax
c = Vertical furnace
d = Vacuum-gage assembly
e = Cold finger
f = Greaseless valve
g(1) = Vacuum-system outlets
g(2) = Toepler pump
g(3) = McLeod gage
g(4) = Mercury-diffusion pump



Apparatus for Manometric Decomposition Studies

Figure 1

UNCLASSIFIED

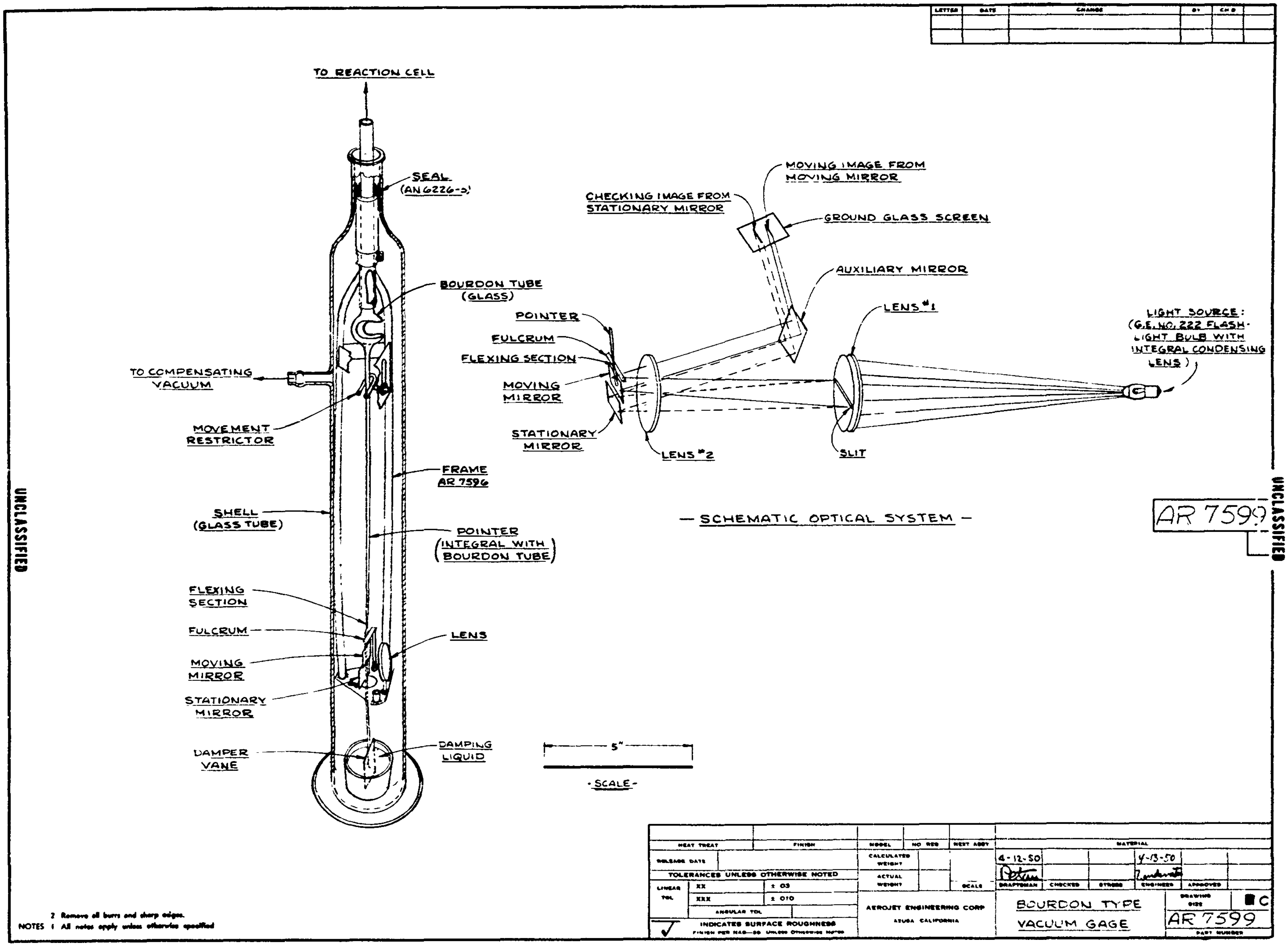


DT NO	NO REQ	NAME	MAT'L & SIZE
11	TO SUIT	SANTOCEL AO INSULATION	MONSANTO CHEM CO.
10		LOWER PLUG	AR-7590-3
9	1	ALUM CORE	AR-7590-1
8	1	HEATER	NICHROME WIRE & ASBESTOS INSULATION
7		PYREX GLASS REACTION CELL	SUPPLIED BY CHEM LAB
6		UPPER PLUG	AR-7590-2
5	2	SIL O CEL	JOHNS MANVILLE INSULATION (CUT TO SUIT)
4	2	SIL O CEL	JOHNS MANVILLE INSULATION (CUT TO SUIT)
3	1	SHELL	AR 7589
2	1	COVER	AR-759
1	1	RESISTANCE THERMOMETER	LEEDS & NORTHRUP

UNCLASSIFIED

Figure 2

UNCLASSIFIED



UNCLASSIFIED

Figure 3

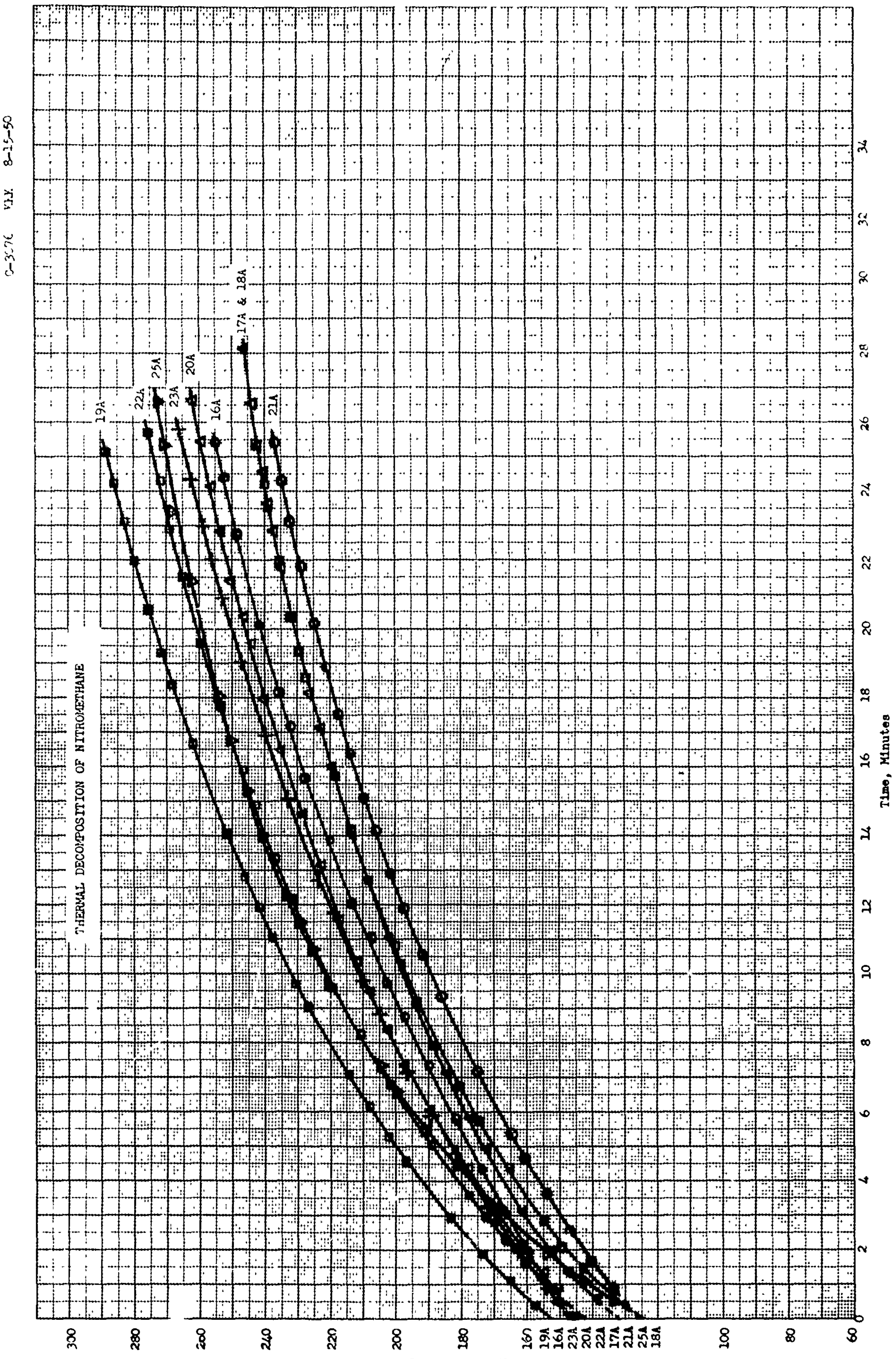
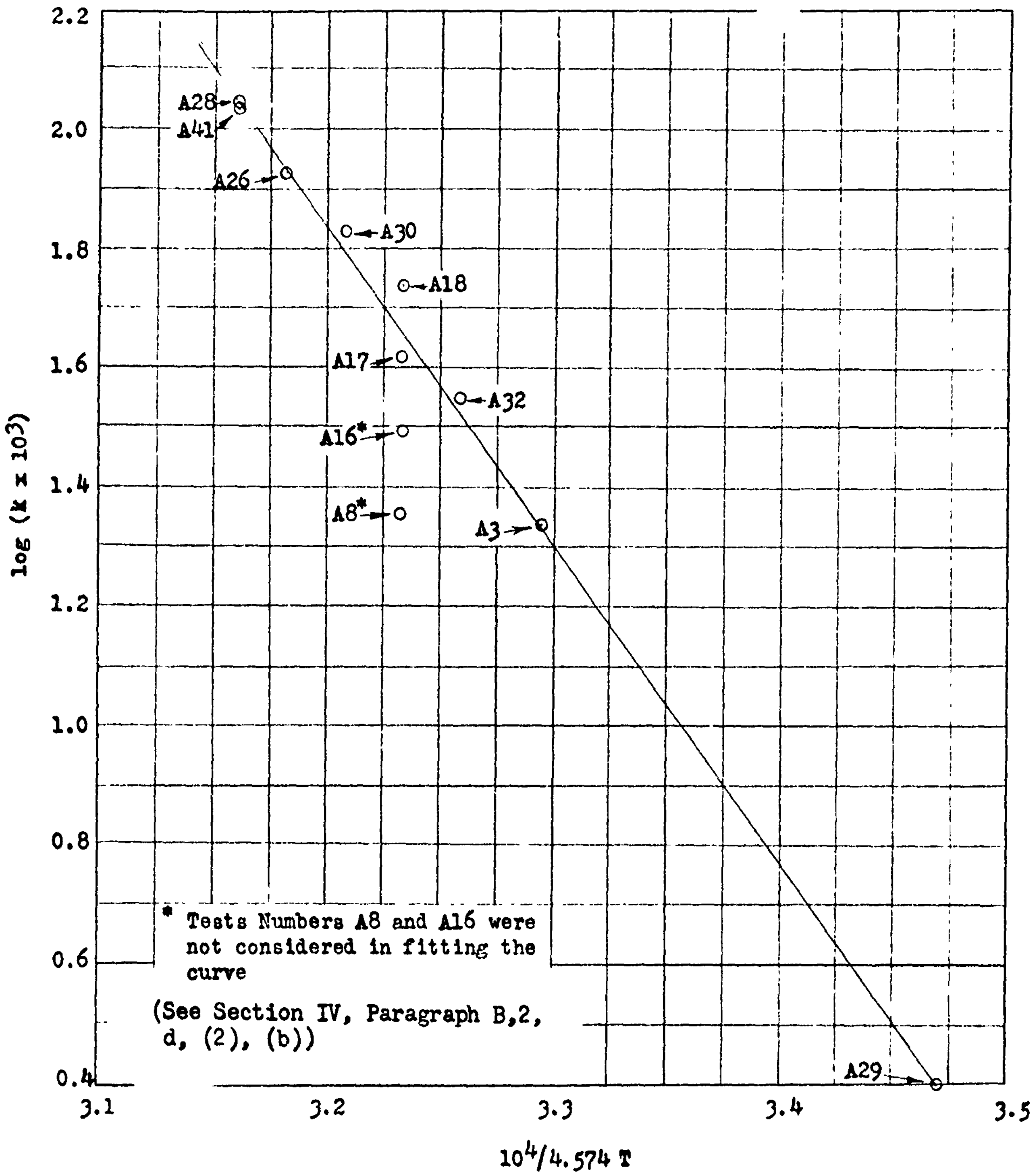
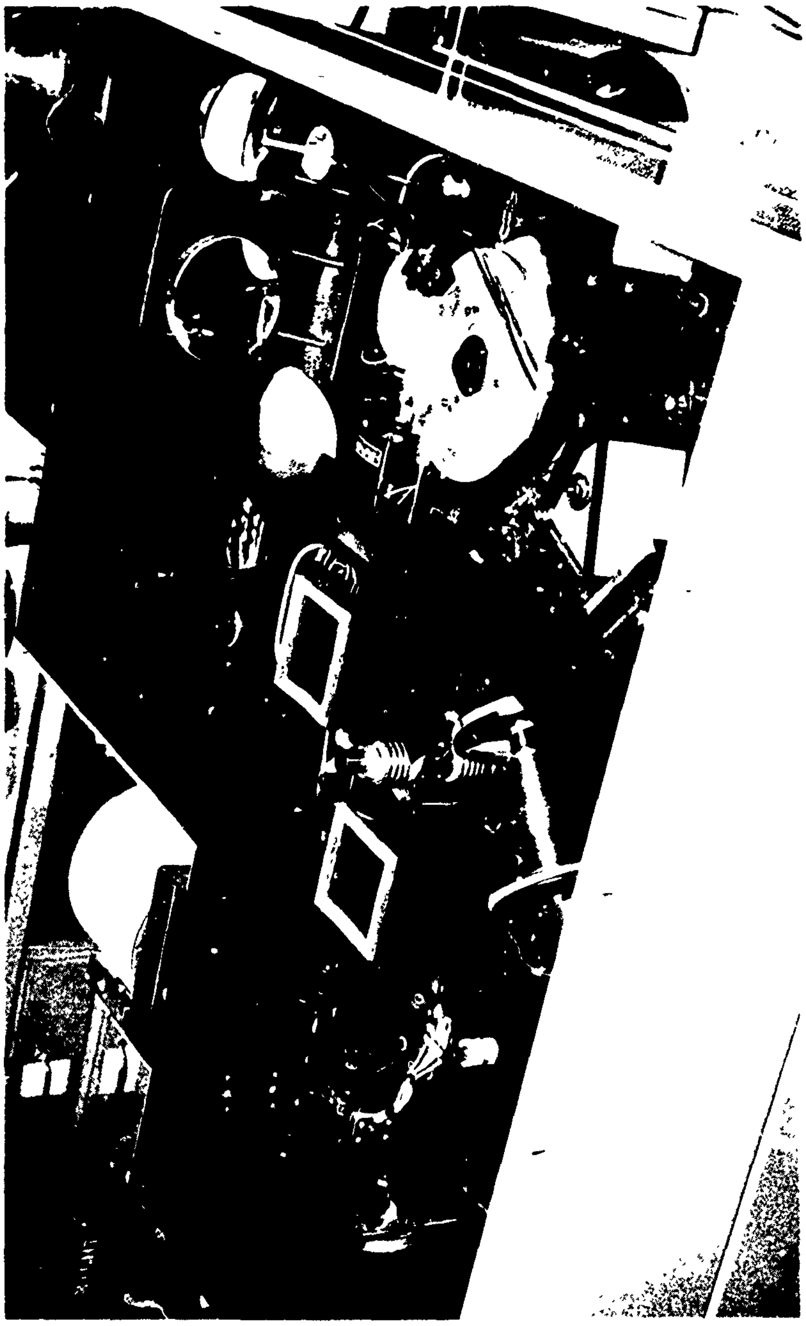

C-3076 VJK 8-15-50
THERMAL DECOMPOSITION OF NITROMETHANE
19A
22A
25A
23A
20A
16A
17A & 18A
21A
Time, Minutes
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
Pressure, mm Hg
300
280
260
240
220
200
180
160
19A
16A
23A
20A
22A
17A
21A
25A
18A
100
80
60

Figure 4

C-3083 HMK/MP 10-14-50

SPECIFIC REACTION RATE (AT HALF-LIFE) OF NITROMETHANE AS A FUNCTION OF TEMPERATURE

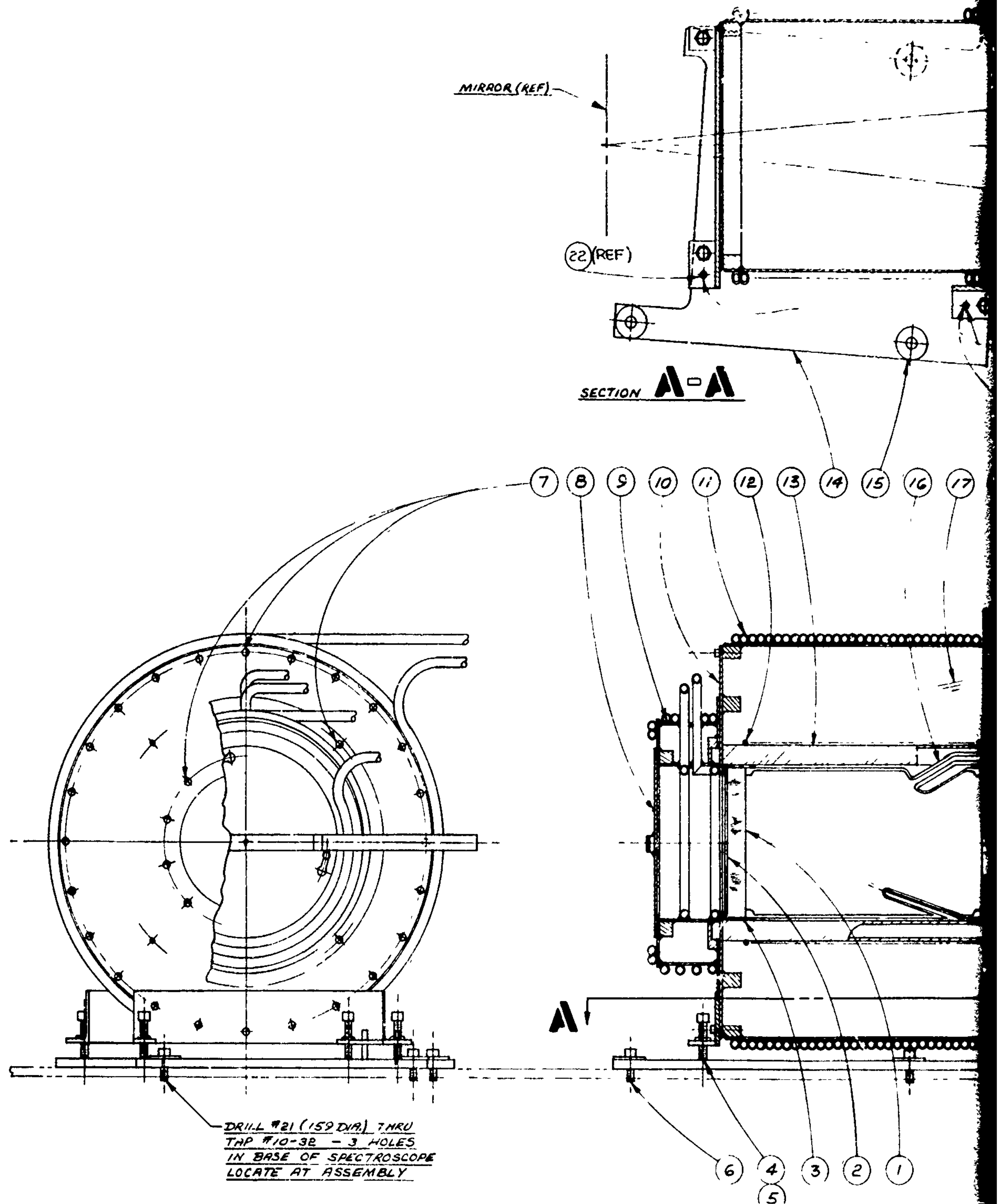




Side View of Baird Infrared Spectrophotometer, Top Removed

Figure 6

UNCLASSIFIED



2 Remove all burs and sharp edges.
NOTES 1 All notes apply unless otherwise specified

LET	DATE	CHANGE	BY	[illegible]

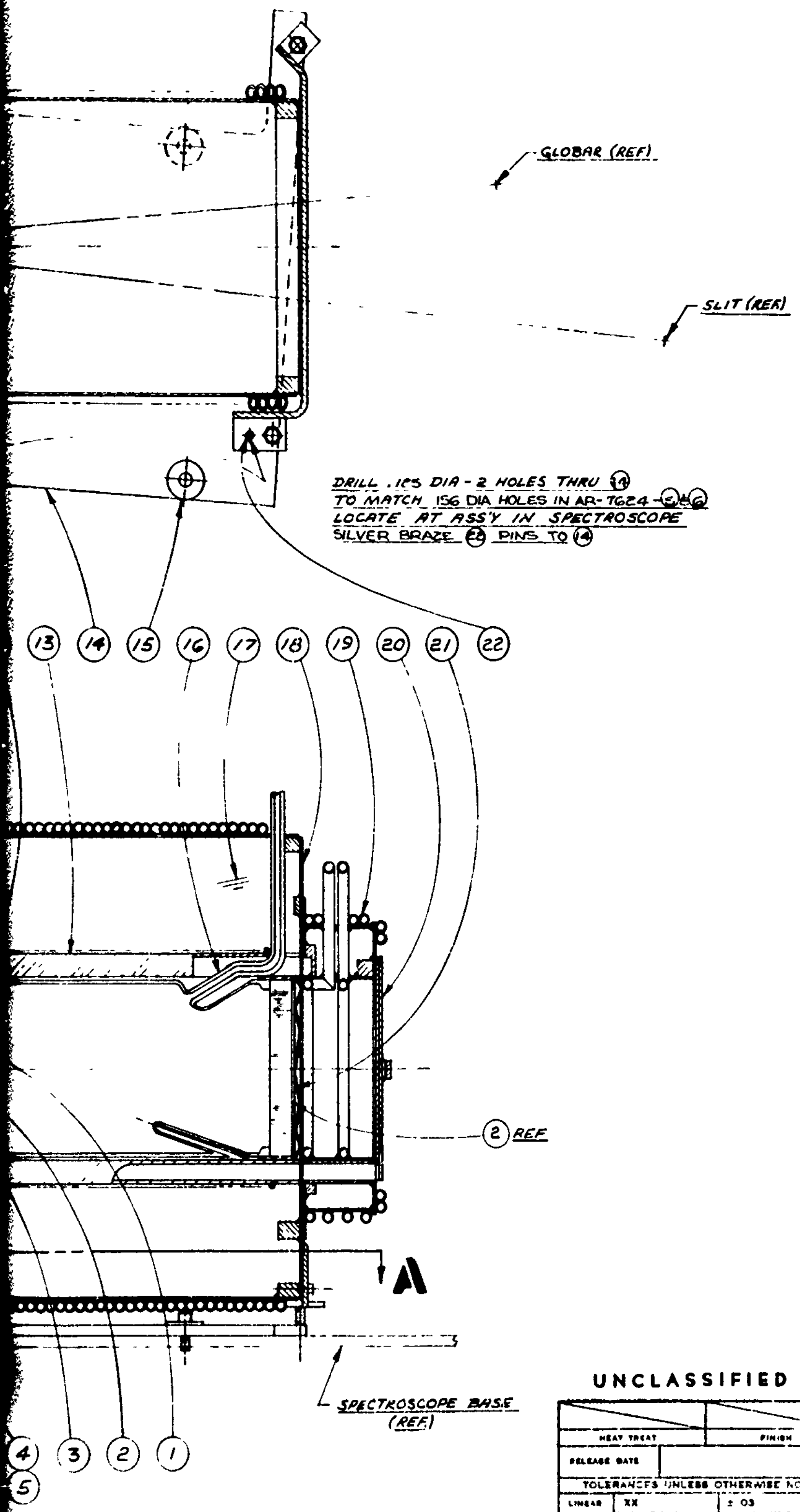


Figure 7

PART NO.	NO. REQ	NAME	MATERIAL & SIZE
22	2	DOWEL PIN	SAE 1020 STL. .125 OD x 1.00 LONG
21	1	WASHER	AR 7629-2
20	1	LOCKING PLATE	AR 7630-4
19	1	GAS DUCT HOUSING	AR 7627-2
18	1	COVER ASSY	AR 7624-2
17	AS REQ.	INSULATION	SANTOCEL A O.
16	1	REACTION CELL	AR 7622
15	3	WASHER	AN-970-3
14	1	BASE PLATE	AR 7625-5
13	1	FURNACE CORE	AR 7623
12	AS REQ.	HEATER	ELECTRIC HEATING WIRE
11	1	SHELL ASS'Y	AR 7625-1
10	1	COVER ASS'Y	AR 7624-1
9	1	GAS DUCT HOUSING	AR 7627-1
8	1	LOCKING PLATE	AR 7630-1
7	79	SCREW	STEEL SOC. HEAD CAP SCREW 5-44 N.F. x .25 LONG
6	3	SCREW	STEEL SOC. HEAD CAP SCREW 10-32 N.F. x .62 LONG
5	4	NUT	COMM. STEEL #10-32 N.F.
4	4	SCREW	STEEL SOC. HEAD CAP SCREW 10-32 N.F. x 1.00 LONG
3	2	SPACER	ASBESTOS 12.00 x .75 x .062 THICK
2	AS REQ.	ASBESTOS RING	AR 7629-1
1	2	WINDOW	AR 7621

AR-7620

UNCLASSIFIED

HEAT TREAT	FINISH	MODEL	NO. REQ.	NEXT ASSY
			1	

MATERIAL

RELEASE DATE

CALCULATED WEIGHT

ACTUAL WEIGHT

SCALE

TOLERANCES UNLESS OTHERWISE NOTED

LINEAR TOL.	XX	± .03
	.XXX	± .010
	ANGULAR TOL	

√ INDICATES SURFACE ROUGHNESS FINISH PER NAS 30 UNLESS OTHERWISE NOTED

DRAFTSMAN	CHECKED	STRESS	~~ENGINEER~~	APPROVED
6-21-50	6-23-50			
BOOTHMAN	[illegible]		[illegible]	

AEROJET ENGINEERING CORP
AZUSA CALIFORNIA

HORIZONTAL FURNACE ASS'Y

DRAWING SIZE: D

AR-7620
PART NUMBER

Disassembled Ultrasonic-Decomposition Apparatus

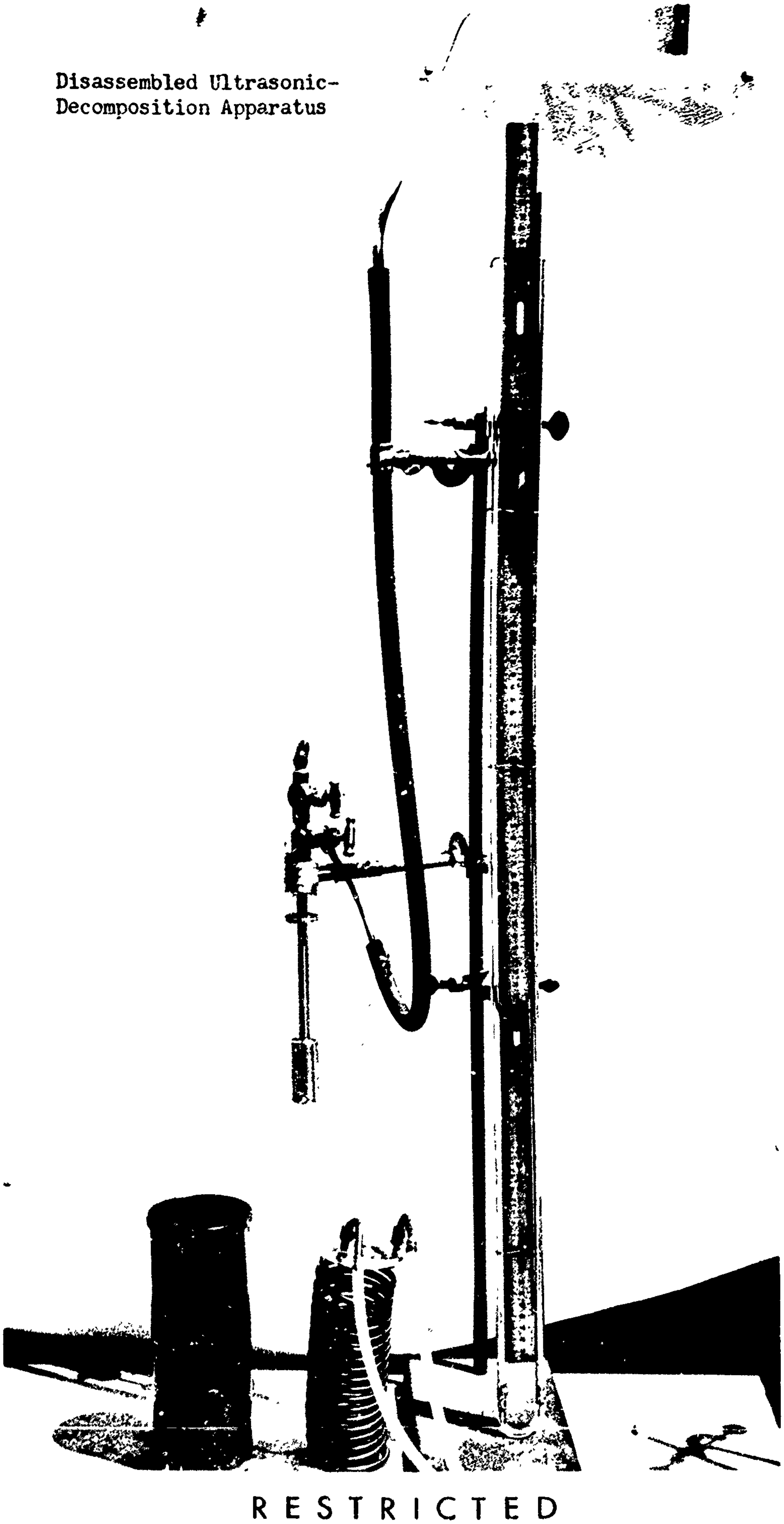
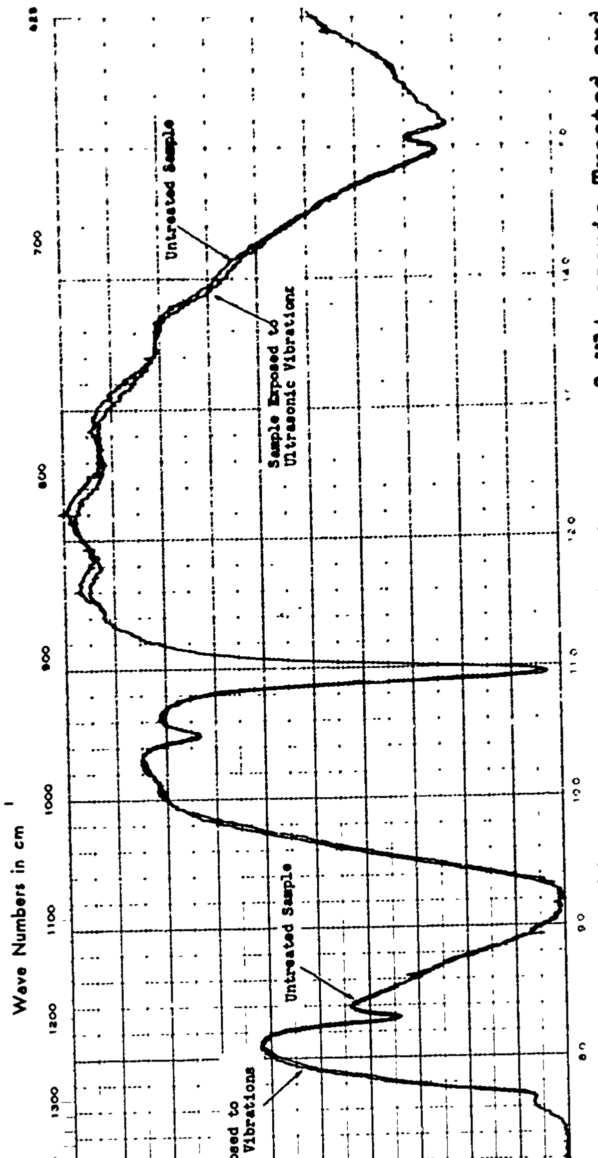
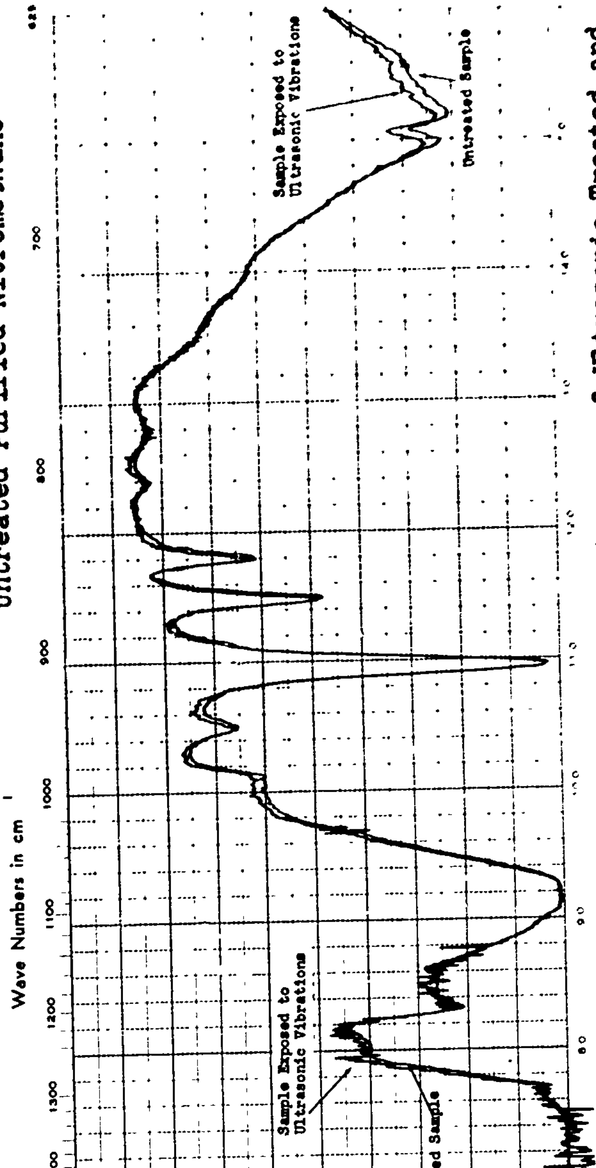


Figure 8



No. 12; 11 April 1950; Scan, 24 Minutes
Samp. Cell - 0.1 mm; Comp. Cell - N_2 0.1 mm

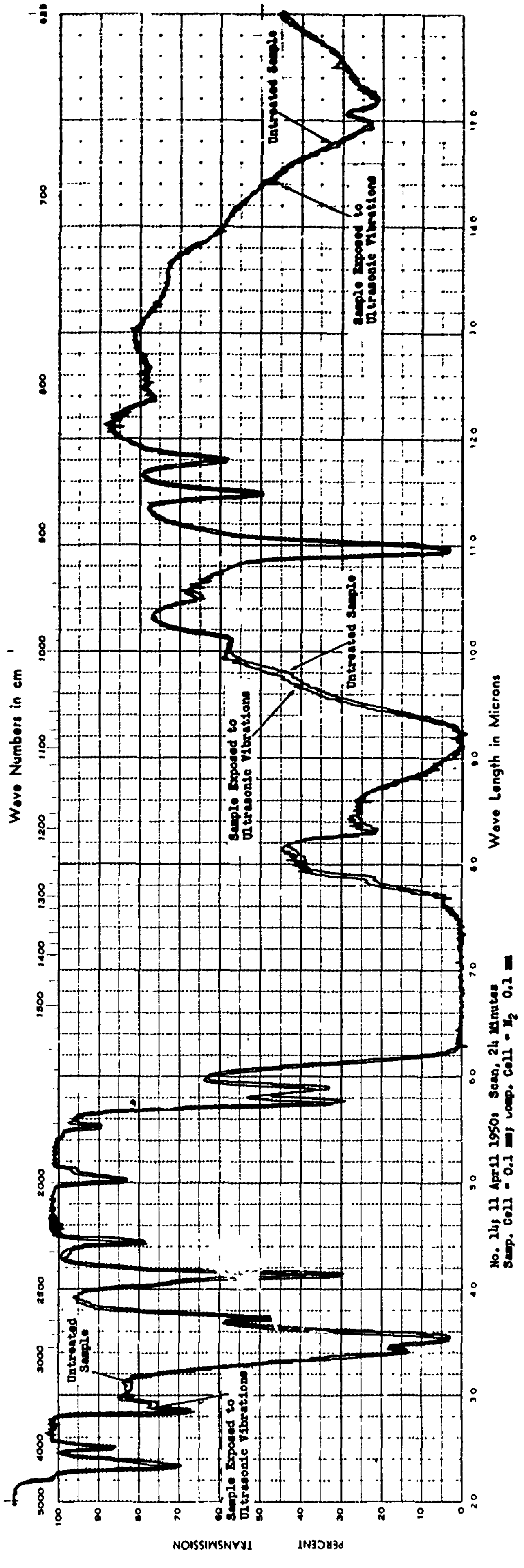
Fig. 10 Spectograms of Ultrasonic-Treated and Untreated Purified Nitromethane



No. 13; 11 April 1950; Scan, 24 Minutes
Samp. Cell - 0.1 mm; Comp. Cell - N_2 0.1 mm

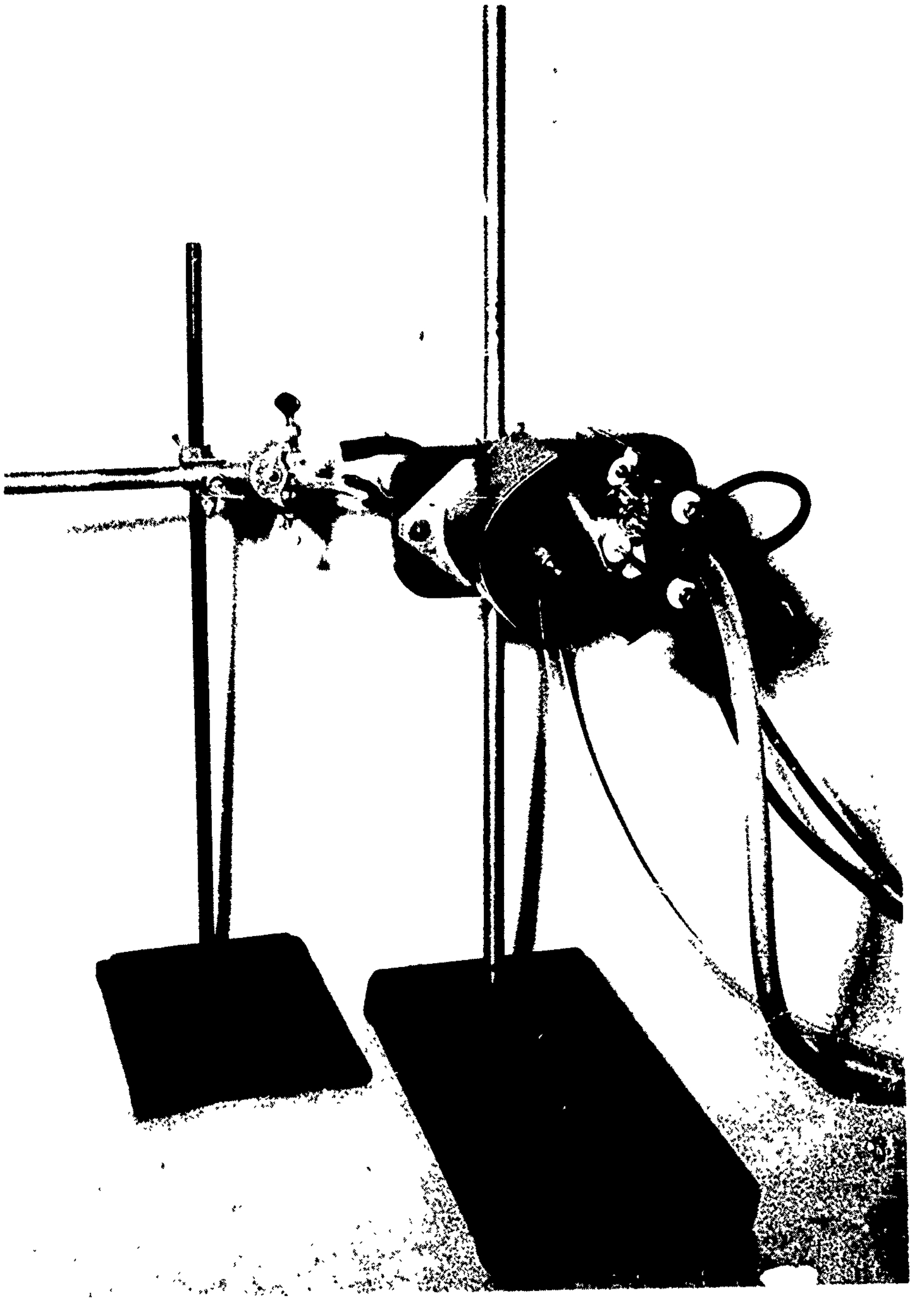
Fig. 11 Spectograms of Ultrasonic-Treated and Untreated Commercial Nitromethane

Figures 10 and 11

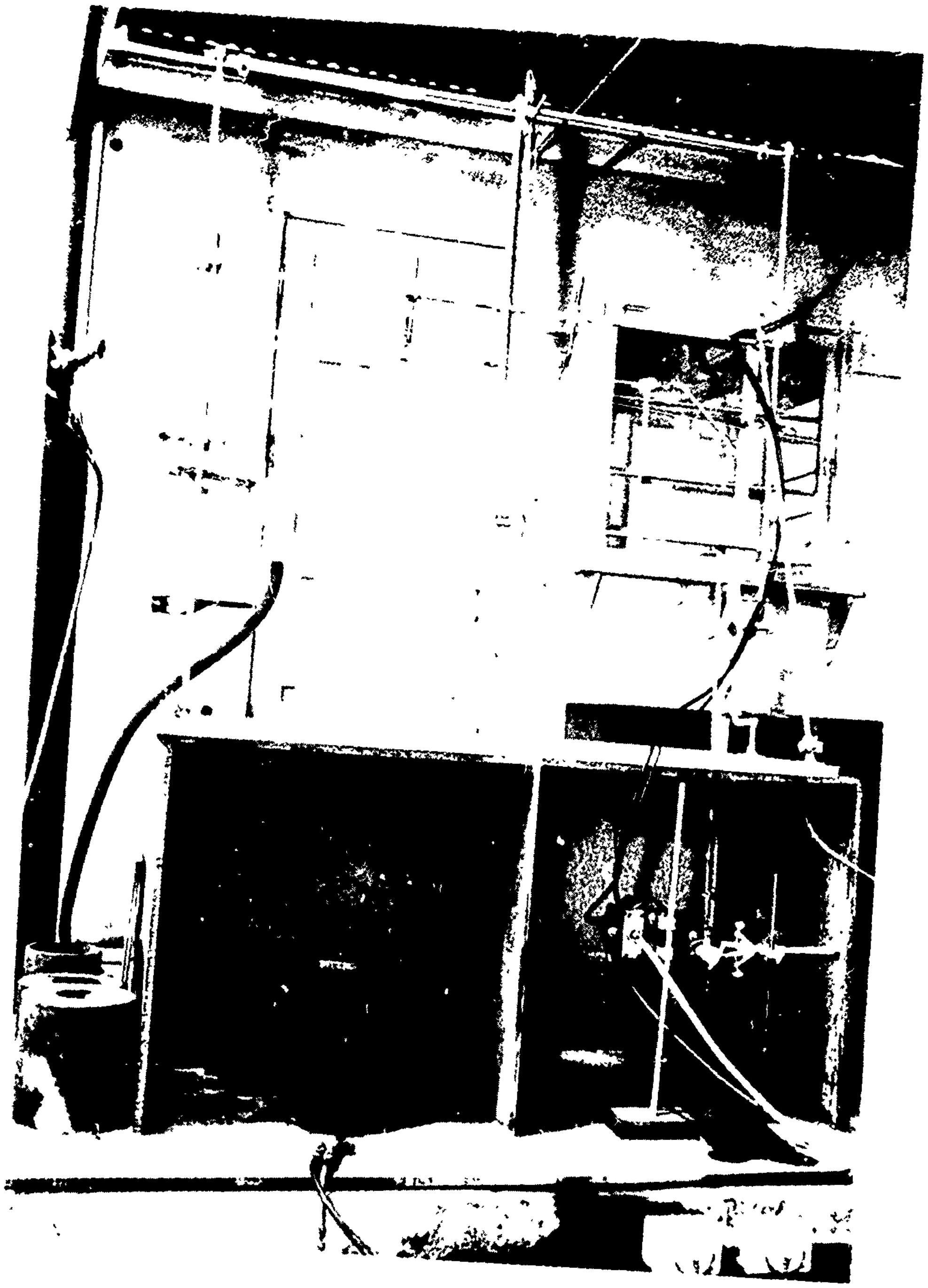


Spectograms of Ultrasonic-Treated and Untreated Commercial Nitromethane Containing 1% Chromium Acetylacetonate

Figure 12



Ultraviolet Radiation Device



Ultraviolet Radiation Apparatus

Figure 14

C-3075 HMK 8-11-50

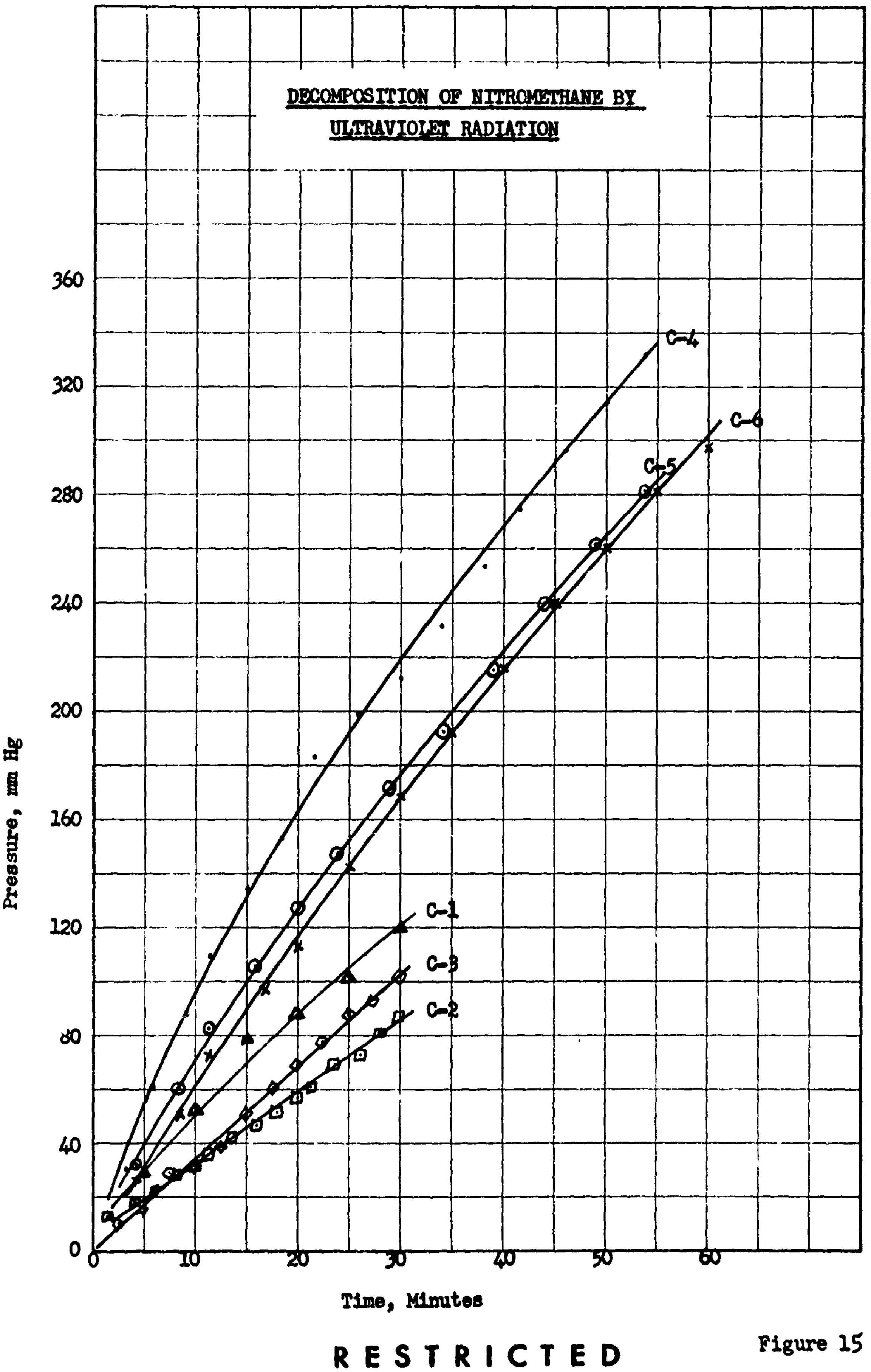


Figure 15

No. 35

DATE: 11 August 1950
INDEX:

SAMPLE

A- Nitromethane

B- Nitromethane Exposed to Ultraviolet Radiation

From Aerojet Engineering Corp.

Samp. Cell = 0.05 mm. cms.

Comp. Cell = Salt Block mm. cms.

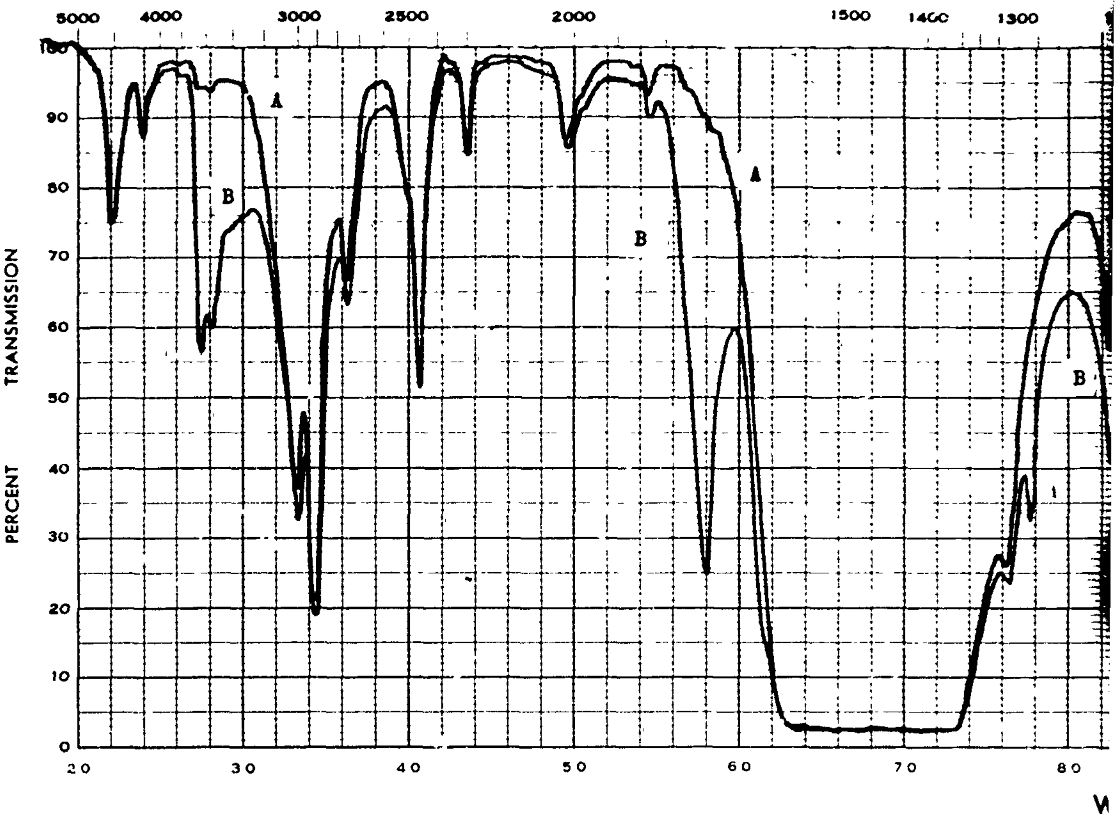
Chem. mg. mg

Solv.

Vol. c.c. % c.c. %

F.S. Solid °C. Gas mm.

BAIRD ASSOCIATES
I R SPECTROPHOTOMETER
NA CL PRISM



No. 39

DATE: 17 August 1950
INDEX:

SAMPLE

Nitromethane Nearly Saturated With Formaldehyde

Scan - 12 Minutes.

From Aerojet Engineering Corp.

Samp. Cell = 0.05 mm. cms.

Comp. Cell = Salt Block mm. cms.

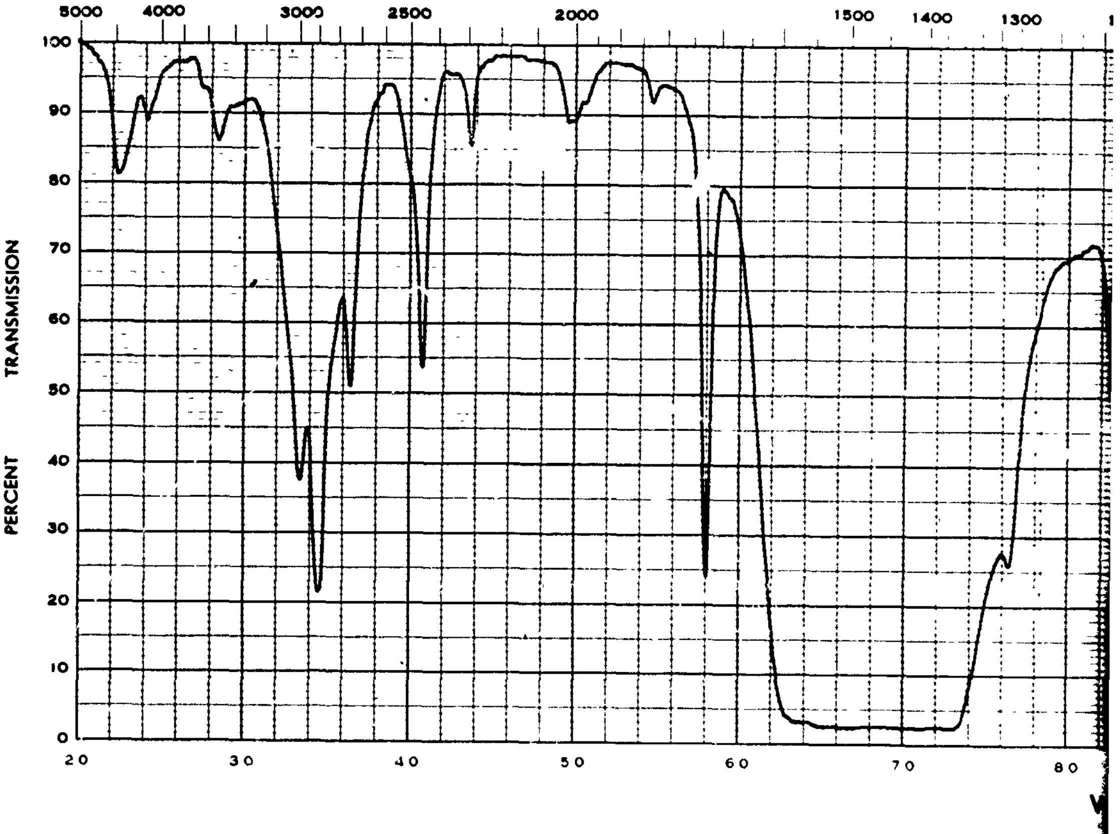
Chem. mg. mg.

Solv.

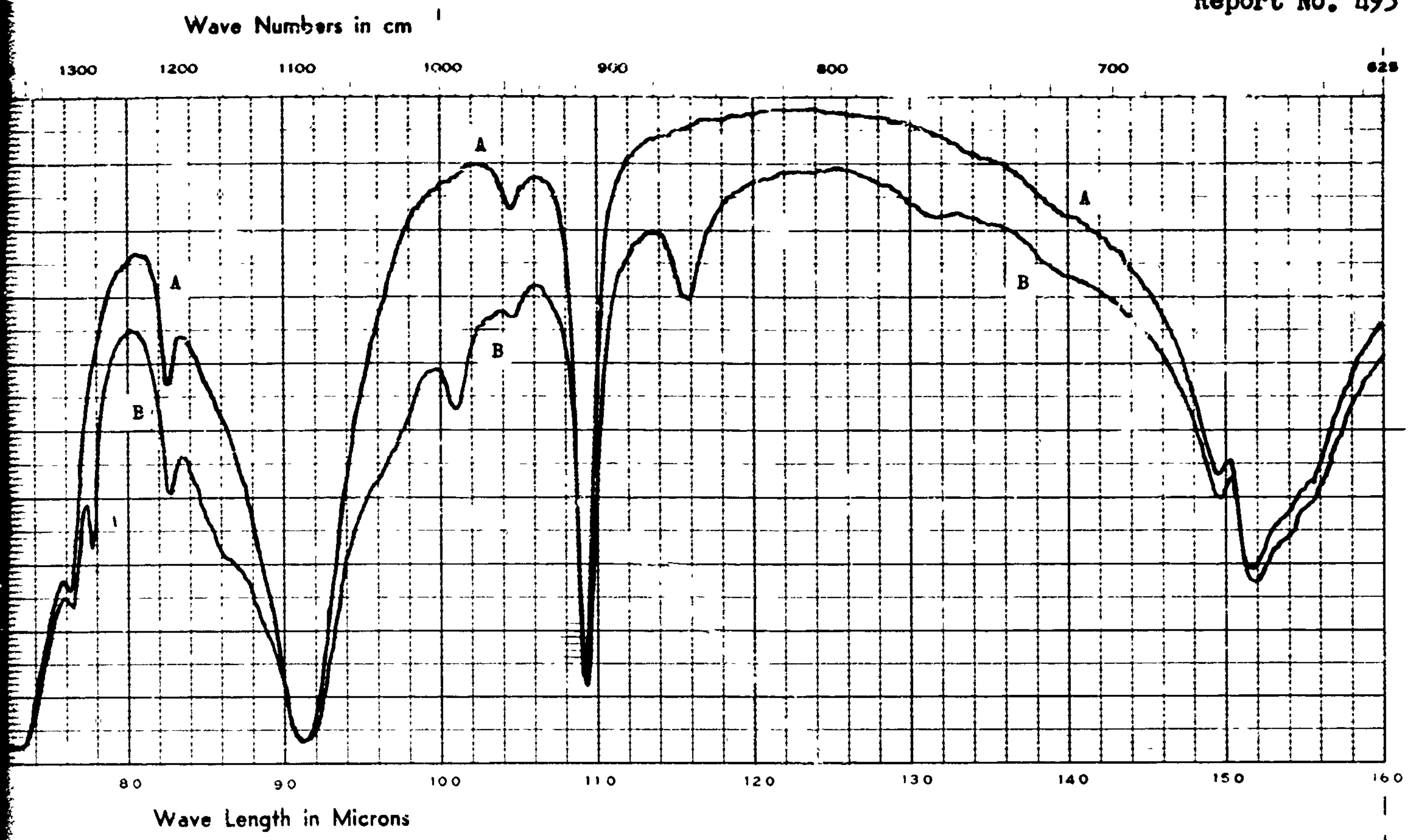
Vol. c.c. % c.c. %

F.S. Solid °C. Gas mm.

BAIRD ASSOCIATES
I R SPECTROPHOTOMETER
NA CL PRISM



1



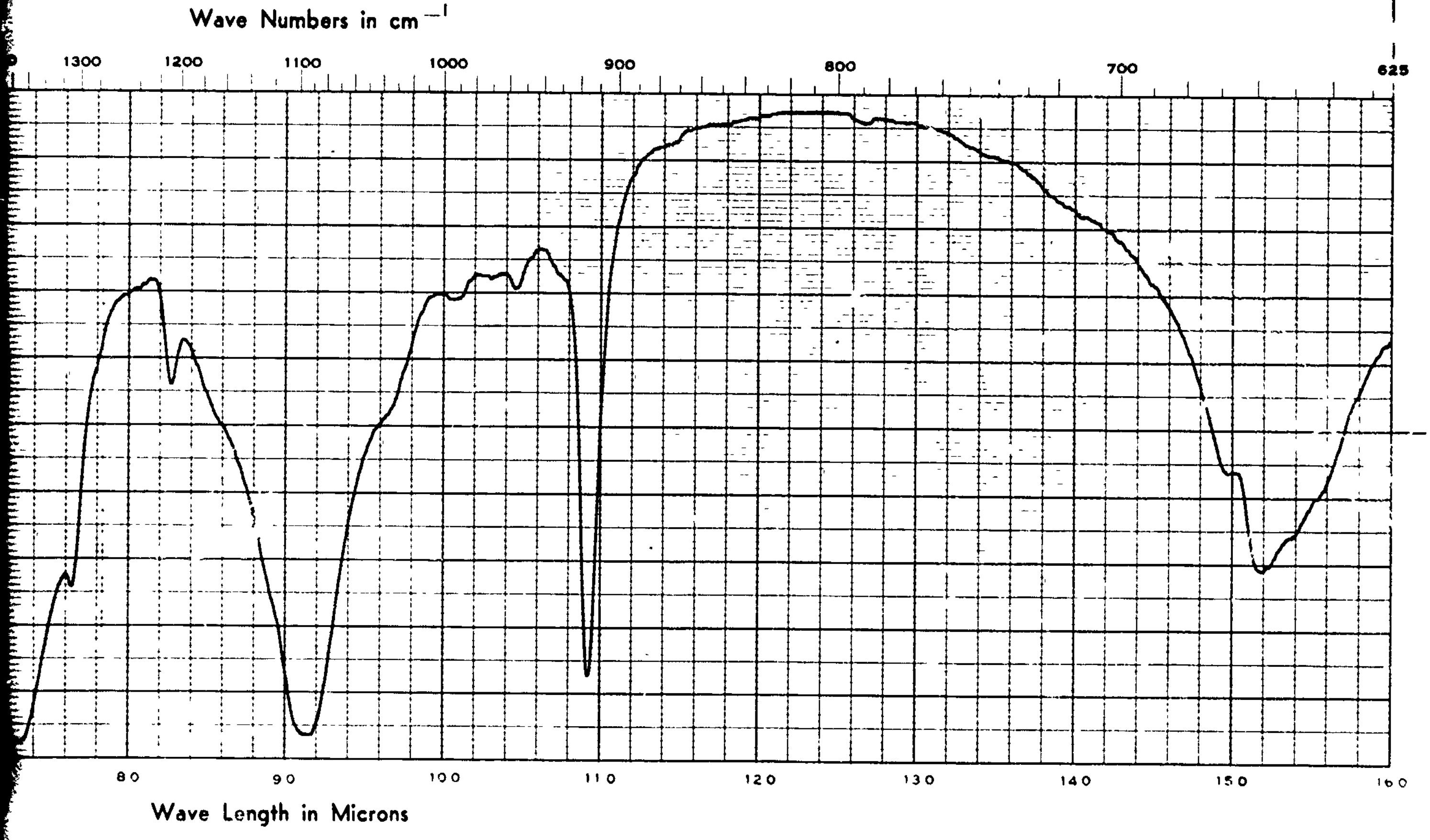
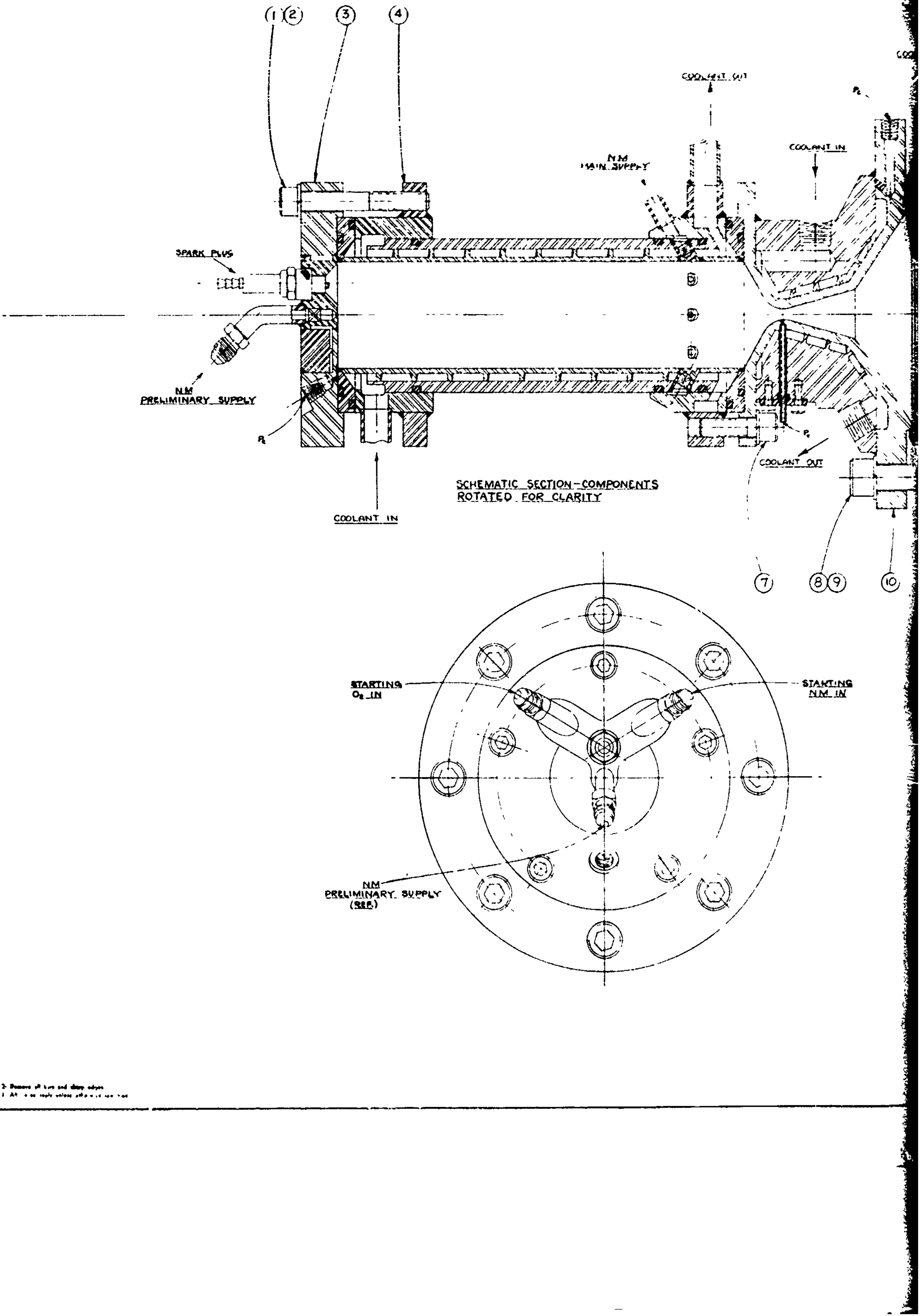


Figure 16

Infrared Spectrograms of Nitromethane Solutions

RESTRICTED

[illegible]



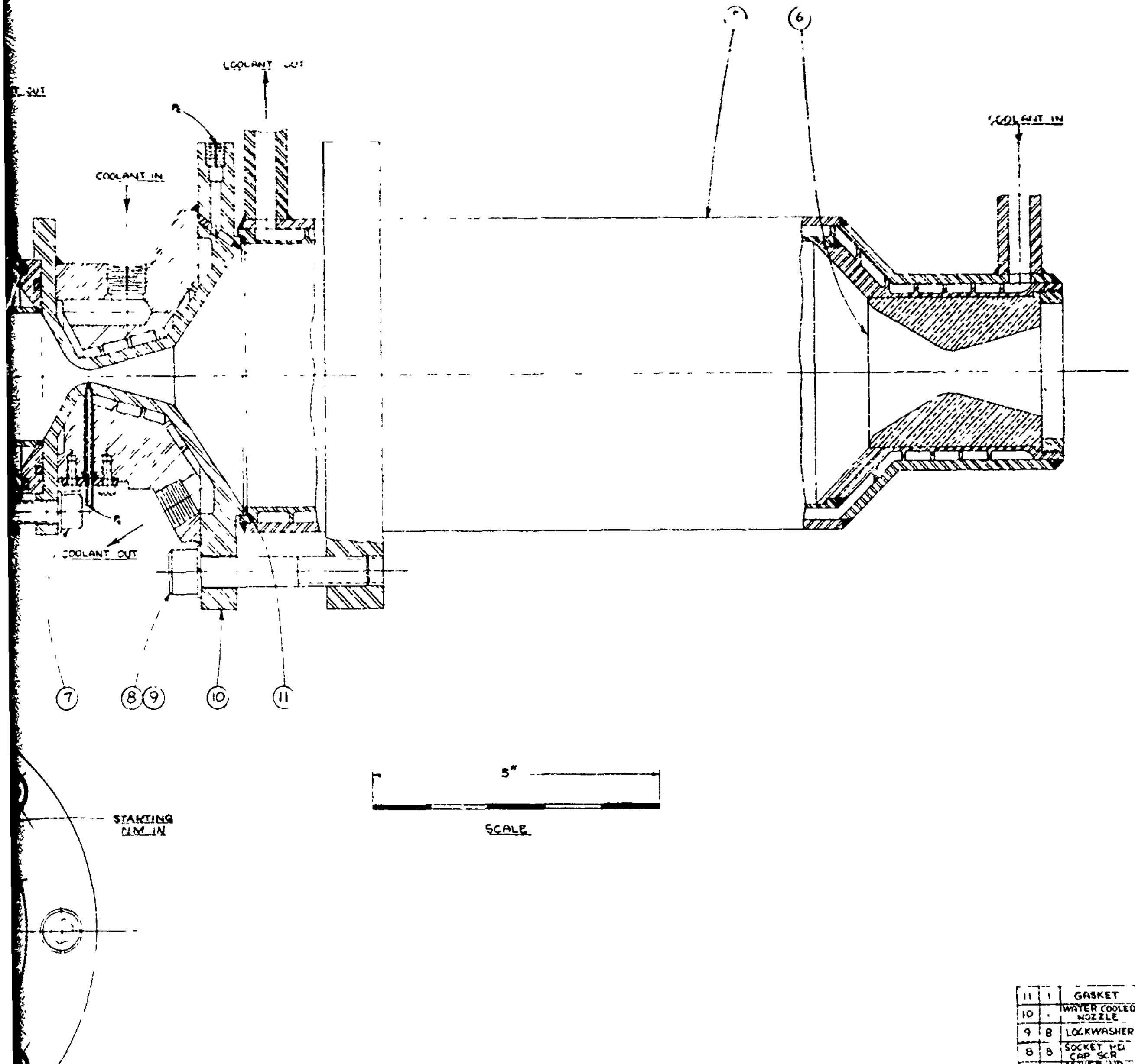
SCHEMATIC SECTION–COMPONENTS
ROTATED FOR CLARITY

2. Remove all burs and sharp edges

NOTES: 1. All [illegible] apply unless otherwise specified

LTR	DATE	CHANGE	BY	CKD

Report No. 493



AR-3580

Figure 17

PT Nº	Nº REQ	NAME	MATERIAL & SIZE
11	1	GASKET	SOFT COPPER [illegible] THK
10	1	WATER COOLED NOZZLE	AR-3581
9	8	LOCKWASHER	COMM STL CAD PLATE FOR ½ BOLT
8	8	SOCKET HD CAP SCR	COMM STL CAD PLATE ½-13NC × 3.00 LG
7	4	SOCKET HD CAP SCR	COMM STL CAD PLATE [illegible] NF × 1.25 LG
6	1	NOZZLE	AR-3585
5	1	MODEL "B" 200# MOTOR	AE-4988
4	1	COMBUSTION CHAMBER	AR-3590
3	1	INJECTOR ASSY	AR-3586
2	11	LOCKWASHER	COMM STL CAD PLATE FOR ⅜ BOLT
1	5	SOCKET HD CAP SCR	COMM STL CAD PLATE ⅜-24NF [illegible] LG

RESTRICTED

HEAT TREAT | FINISH

RELEASE DATE

TOLERANCES UNLESS OTHERWISE NOTED

$\surd$ INDICATES SURFACE ROUGHNESS

MODEL | NO REQ | NEXT ASSY

CALCULATED WEIGHT

ACTUAL WEIGHT

SCALE

AEROJET ENGINEERING CORP
AZUSA, CALIFORNIA

MATERIAL

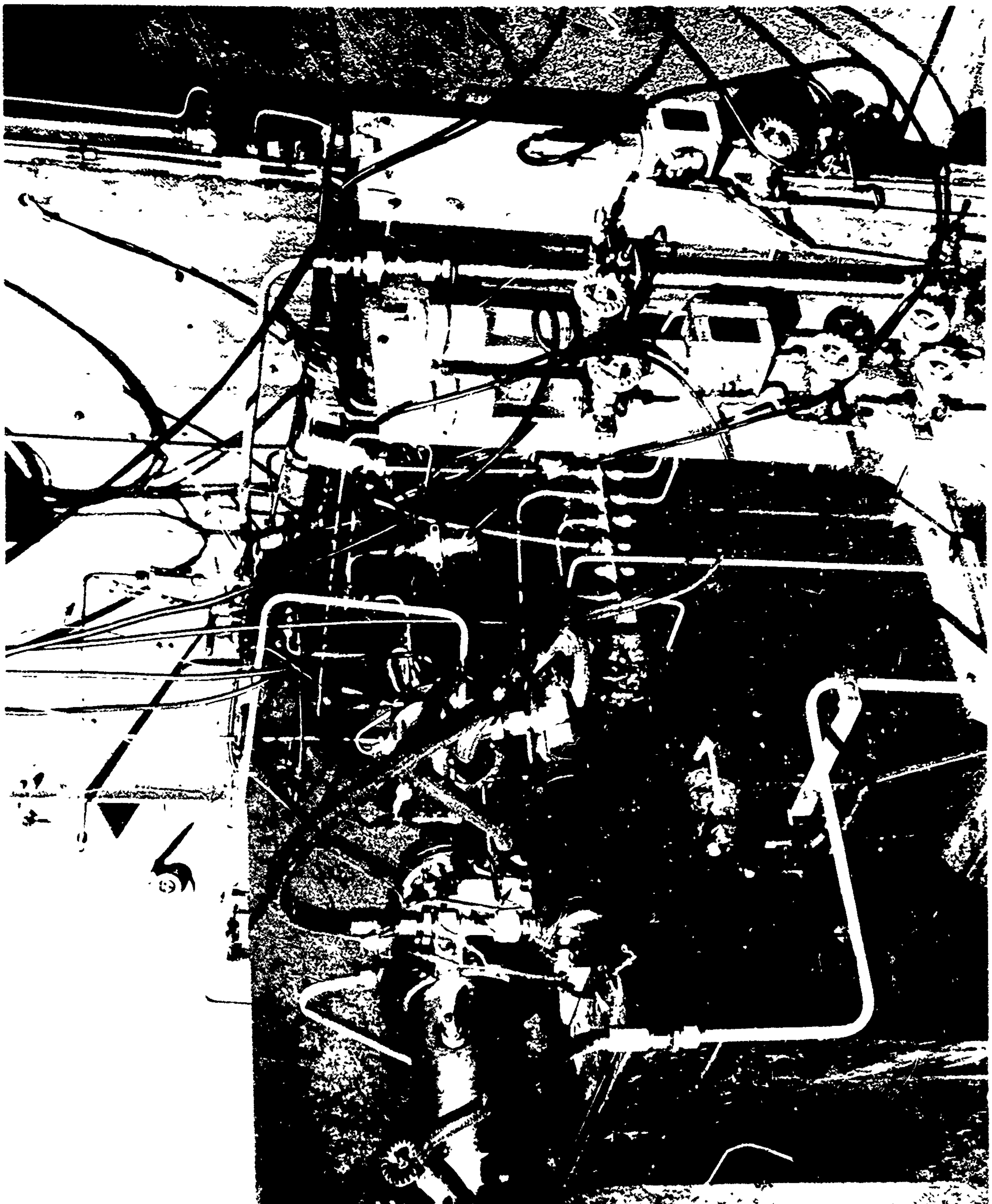
DRAFTSMAN	CHECKED		ENGINEER	APPROVED
8-29-50	9-1-50		12 SEPT 50	
M. KRESS	[illegible]		R GORDON	RH

- THRUST CHAMBER -
NITROMETHANE SHOCK WAVE
RECOMPRESSION

DRAWING SIZE E

AR-3580

2



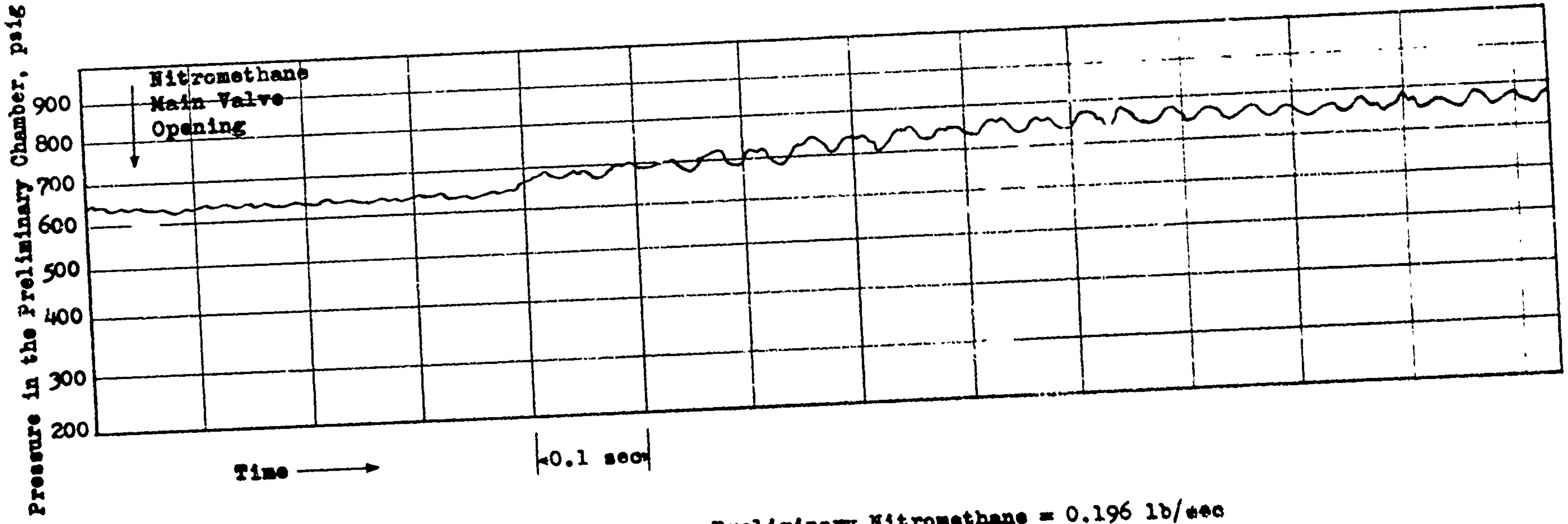
Shock-Wave Recompression Thrust-Chamber Assembly

Figure 18

C-8386 PPD/ewb 1-4-52

NITROMETHANE SHOCK-WAVE RECOMPRESSION TEST PRELIMINARY CHAMBER ALONE WITH INJECTION OF BOTH PRELIMINARY AND MAIN NITROMETHANE SUPPLY

Test Number D22-23



Flow Rates: Preliminary Nitromethane = 0.196 lb/sec
Main Nitromethane = 0.632 lb/sec

Figure 19

[redacted] UNCL[illegible]IED

0-8305 PPD/ewb 1-4-51

NITROMETHANE SHOCK-WAVE RECOMPRESSION TESTS
COMPLETE THRUST-CHAMBER ASSEMBLY

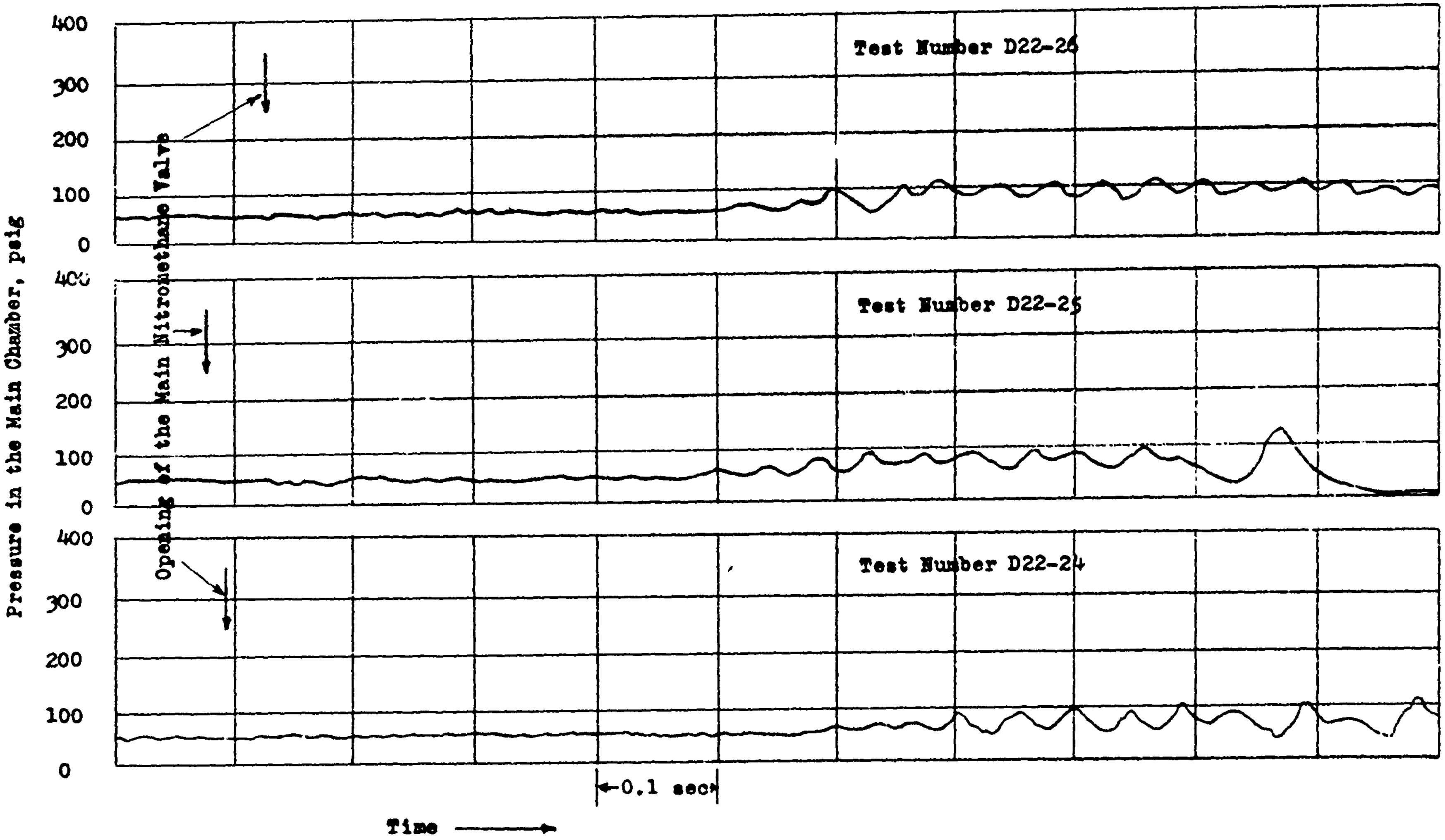


Figure 20

[redacted] UNC[illegible]IED