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DIFFERENTIAL THERMAL ANALYSIS AS A

RESEARCH TOOL IN CHARACTERIZING

NEW PROPULSION SYSTEMS

by

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ABSTRACT. Differential thermal analysis (DTA) techniques are applied to the characterization of advanced propellant systems. From the thermogram of a material (propellant or a propellant ingredient), the temperature at which a reaction will rapidly occur can be studied.

It is shown in this study how a DTA thermogram can be used to obtain activation energy, E (the energy barrier opposing the reaction), the frequency factor, A (the measure of the probability that a molecule having E will participate in a reaction), and, from the degree of asymmetry of the thermogram, the apparent reaction order.

This information (from small samples), along with other thermodynamic properties and theoretical equations relating size and shape to temperature rise, is used in predicting behavior during storage of large propellant motors. The extrapolation is checked by scaled sizes of propellants and cook-off data using derivative differential thermal analysis.
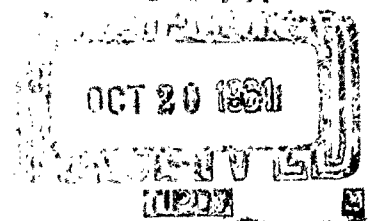
U.S. NAVAL ORDNANCE TEST STATION

China Lake, California

October 1961

FOREWORD

During February 1961, a continuing project was started at the Naval Ordnance Test Station that has as its goal the prediction of the critical temperature (temperature that, if exceeded, will result in spontaneous combustion) and the behavior of large-diameter propellants during storage.

This report describes the usefulness of DTA as a method of thermally characterizing new propellant materials and as a rapid, accurate method of determining reaction kinetic data.

This work is being done under Bureau of Naval Weapons Task Assignment RMMP-21-001/216-1/F009-01-016.

This report is transmitted for information only and does not represent the official view or final judgment of this Station. It presents information released at the working level that is still subject to modification and withdrawal.

13 Chief, Bureau of Naval Weapons
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    RM-3 (1)
    RM-35 (1)
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CONTENTS

ACKNOWLEDGMENT

INTRODUCTION

Borchardt (Ref. 1) states that differential thermal analysis (DTA) is a method for observing the transitions and reactions that a substance undergoes on heating. This is accomplished by placing the substance and an inert reference in a furnace. The two materials, though separated, experience the same heating effects from the furnace. A difference in temperature occurs when the active material undergoes a transformation or reaction. If the active material undergoes an endothermic reaction, such as the loss of water of hydration, its temperature lags behind that of the inert material. When the chemical reaction is completed, no more heat is absorbed; and a steady state is again attained where the difference in temperature, ΔT, is zero. Hence, a curve that goes from zero, rises to a maximum, and drops to zero is expected.

The origin of DTA, its use, theory, and a list of publications from 1877-1957 are given by Smothers and Chiang (Ref. 2).

Briefly, DTA was proposed in 1877 as a method of investigating complex inorganic minerals. Between 1877 and 1912, methods and equipment were improved to such a degree that DTA was accepted by the mineralogical laboratories as a rapid and convenient method for recording the thermal effects that occur when a mineral is heated.

Until recent years, limited use of DTA was made. During the period 1877-1950, only 384 publications appeared. Between 1950 and 1957, more than 1,100 publications were presented. At present, DTA is used in both organic and inorganic research in such varied fields as geology, agriculture, pharmaceutical research, ceramics, nuclear physics, and metallurgy.

In 1944, Spiel (Ref. 3) derived equations showing that the area under a peak in the DTA thermogram is proportional to the heat of reaction. Borchardt and Daniels (Ref. 4) and Freeman and Carroll (Ref. 5) are but a few who have recently published papers relating the application of DTA to the study of thermodynamics and reaction kinetics.

1

In recent years, DTA has been employed in conjunction
with X-ray and thermogravimetric methods of analysis. The
latest combination of apparatus with DTA utilizes a gas-
sweeping system and gas-detector cell. Ayres and Bens
(Ref. 6) report on thermograms and gas profiles that can be
obtained with this type of equipment.

A study is being conducted at the Naval Ordnance Test
Station on the safe curing and storing temperatures of
cast composite and cast double-base propellants. Through
this study, the behavior of large, solid-propellant motors
during storage can be predicted. Predictions are made on
the basis of data collected on small samples, thermodynamic
properties, theoretical equations relating size and shape
to temperature rise, and nomographs prepared from theoretical
and empirical calculations. The extrapolation is checked by
scaled sizes of propellants and cook-off data using
derivative differential thermal analysis (Ref. 7).

In this study, DTA is used to obtain the activation
energy, E (the energy barrier opposing the reaction), and
the frequency factor, A (the measure of the probability
that a molecule having E will participate in a reaction).
The parameters E and A are two of the many needed to relate
size, shape, and environment to the thermal properties of a
propellant.

From thermograms obtained during DTA, the apparent
reaction order is determined by the degree of asymmetry as
described by Kissinger (Ref. 8). (The work of Kissinger
(Ref. 8) is summarized in the Appendix.) It is also
possible to determine from the thermograms the temperature
at which a reaction occurs and to characterize a new
propellant rapidly. This information is an important part
of the evaluation that a propellant undergoes during its
development. The heat of reaction, which is proportional
to the area under the peak (Spiel, Ref. 3), can be obtained
also.

APPARATUS AND INSTRUMENTATION

APPARATUS

The apparatus consists of a furnace, heating block,
thermocouple probe, sample sleeve, and main sample tube.

The electric furnace[1] has a working area 3 inches in diameter and 5 inches deep. The maximum safe working temperature is 1850°F. A screwdriver adjustment permits its operation on 110 or 220 volts. The resistance wire in the furnace (725 watts) is noninductively wound, and the windings are power matched to the heating control system.

The heating block is of Carpenter glass-sealing steel (No. 42). It is 2.85 inches in diameter and 5.40 inches long. The sample wells are 2.0 inches deep and 0.40 inch in diameter and are positioned 90 degrees apart on a 1.975-inch diameter. There is a 1.0-inch hole through the center, running the entire length of the block. (This permits the use of quartz immersion heaters for certain applications.)

The thermocouple probe (Fig. 1) is of Pyrex; thus, the Chromel-Alumel thermocouple is protected from damage by the reacting material. In the thermocouple, No. 5 mil wire is used.

The sample sleeve (Fig. 2) is normally used to hold the sample. By use of this sample sleeve, a small quantity of material can be used to obtain a thermogram. Two types of sleeves are shown in Fig. 2; the one with the pointed tip is preferred, but the round one is used for liquid samples or for samples that cannot be reduced to a powder.

The main sample tube (Fig. 3) used for each test is of Pyrex and is constructed in such a manner that the volatiles can be collected. It holds the sample sleeve and the thermocouple probe and keeps them in proper alignment. When a material cannot be reduced safely to a fine powder or must be analyzed in an inert oil, the sample sleeve is not used, but the material is placed directly in the main sample tube. The glassware for the probe, sleeve, and tube is shown in Fig. 4.

The main sample tube and inert reference are placed in the heating block.

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[1] The furnace is a product of the Hevi-Duty Electric Co., Milwaukee, Wis., Type 86.

INSTRUMENTATION

The accuracy of the DTA depends, in a large measure, on the precision at which a uniform heating rate can be maintained. The instrumentation for the heating control system consists of a controller-recorder equipped with an Electr-O-Volt unit[2], a proportional time controller[3], a magnetic amplifier, and a saturable-core reactor. Controls have been developed to give continuously variable heating rates over a range of 0.1 to 20.0°F/min. A block diagram of the heating control system is shown in Fig. 5.

Power is transmitted to the electric furnace through a saturable-core reactor. The thermocouple in the heating block, symmetrically positioned to the sample and the inert reference in the heating block (Fig. 6), senses the temperature in the furnace and transmits its signal to the controller-recorder (Fig. 7). This signal is then compared in the controller-recorder with that of the programmed temperature indicator. The extent of any deviation between these two signals is then transmitted to the Electr-O-Volt unit, which in turn sends the corrected d.c. signal to the magnetic amplifier.

Amplification System. The 225-va magnetic amplifier and the 500-va saturable-core reactor have two sets of windings, the control and the power windings. The d.c. signal to the control windings of either dictates the amount, or the percent, of saturation of the a.c. allowed to pass through the power windings. As more d.c. passes through the control windings, more a.c. is allowed to flow through the power windings. The throttling control possibilities are infinite, eliminating any step control. The magnetic amplifier is essentially a saturable-core reactor but with its own d.c.-rectifying circuit on the power windings.

Program Timer. The circuits of the proportional time controller proportion the power input to the advance

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[2] A product of the Minneapolis-Honeywell Regulator Co., Brown Instruments Div.

[3] A product of Automatic Timing and Controls, Inc., Prussia, Pa.

motor in the recorder. When at 100%, the advance motor is fed power continually and the heating rate is maximum. The proportional time controller can be set from 0 to 100%.

Controller-Recorder. The controller-recorder[4] compares the output of the control and of the recorded temperatures, and the differential signal from this comparison is fed to the Electr-O-Volt unit.

The Electr-O-Volt unit uses a proportional-reset mode of control, with an additional rate-time adjustment. This proportional control adjustment makes the corrective action (in this case, the amount of current flowing to the magnetic amplifier) in direct proportion to the magnitude of the deviation of the recording and controlling temperatures. The reset-rate adjustment controls the rate of change of the corrective action, and the rate-time adjustment advances the proportional correction based on its rate of deviation.

Thermogram Recorder. A Brown recorder[5], with a range of 0-5 or 0-55 mv from a center tap, is used. The thermogram produced on this recorder is the signal received from the thermocouples (sample and inert reference connected in series opposed), as the temperature of the system is increased in a linearly controlled manner.

PROCEDURE

When possible, the sample is ground in a mortar to about 100-200 mesh size. Experimental propellant and explosive materials are run as received, or a sample is obtained after an operation that leaves a powdered residue. Usually, a 20-25 mg sample is used. The sample is placed in the sample sleeve and tamped into place. The thermocouple probe is then pushed through the center of the

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[4] The controller-recorder (range, 0-1000°F) used in this work was a Brown ElectroniK, Type K, a product of the Minneapolis-Honeywell Regulator Co., Brown Instruments Div.

[5] A product of the Minneapolis-Honeywell Regulator Co., Brown Instruments Div.

sample material. Since the thermocouple is encased in glass, the inert reference material is not mixed with the sample. Glass beads 0.05 mm in diameter were used as the inert reference material. (The beads had been digested in nitric acid, washed with distilled water, rinsed in acetone, and stored in a vacuum oven at 70°C until ready for use.)

The sample sleeve and thermocouple probe assembly is then placed in the main sample tube (Fig. 4). When the sample is placed in the sleeve, the beads are put between the main sample tube and the sleeve.

The sample and the inert reference material with thermocouple series opposed and the thermocouple to the controller-recorder are placed in the heating block of the furnace, and the heating control system is connected.

The thermocouples in the sample and in the inert reference material transmit signals to the recorder, which produces a thermogram as the temperature of the system is increased in a linearly controlled manner. The thermogram is removed from the recorder, and the graph is transferred to the DTA record sheet. This sheet can be duplicated, and a typical sample sheet is presented in Fig. 8.

DISCUSSION

Figure 9 is a representative thermogram. The straight horizontal line, which indicates no reaction or transformation is occurring, is called the base line. Base-line drift is a small but measurable change that may occur before, after, or during a reaction for one or more of the following reasons: the sample and inert reference have different heat capacities and thermal conductivities; the sample reacts with the thermocouple; or the particle size and packing density of the samples and the position of the thermocouples are not identical. After a reaction, base-line drift is usually attributed to a change in the sample. The shape of the peak may vary with the position of the thermocouple in the sample.

The onset temperature, T, is the first indication that a reaction has started. This transition temperature is often difficult to recognize because of base-line drift. Smothers and Chiang (Ref. 2) present several methods for locating this temperature. It should be noted that this

6

temperature is greater than the true transition temperature, because a heat change must occur before it can be detected by the thermogram recorder. For this reason, the heating rate and mechanism also affect the transition temperature.

By convention, exothermic deflections are recorded above the base line and endothermic below. The point of maximum deflection of each is called a peak (Fig. 9).

The first deviation from the base line, T, is sometimes called the reaction temperature. This temperature is the temperature at which a reaction will take place rapidly enough to be detected.

It is often difficult to detect T because of base-line drift. Base-line drift can be controlled by proper selection of inert reference and by instrumentation design; it cannot be eliminated, however, because the thermal properties of the inert reference and the sample will not be the same before and after a reaction.

The heating rate, if very slow, will result in a thermogram in which the peaks may appear to be base-line drift. The heating rate, if fast, may cause the peaks to overlap. Therefore, some peaks may not be detected at certain heating rates.

A source of concern in DTA is the variation in results obtained on the same material when analyzed at different laboratories. This is due, in part, to sample preparation, response lags in the various instruments, choice of reference material, choice of apparatus, and position of the thermocouple in the sample. This shortcoming is not serious since each setup can be standardized.

The order of the reaction is indicated by the degree of asymmetry of the thermogram peak. Kissinger (Ref. 8) discusses this and develops a method of determining the reaction order by the "shape index." In this method, the absolute value of the ratio of slopes of tangents to the curve at the inflection points is used to derive an equation that relates the shape index to the reaction order.

To determine the heat of reaction by DTA, a standard material such as benzoic acid or silver nitrate is ground to a fine powder (100-200 mesh). A known quantity is mixed with an equal quantity of inert reference material (also 100-200 mesh). This blended sample is analyzed by DTA.

7

The total heat absorbed from the sample is calculated from the known heat of reaction. This, together with the measured peak area, gives the area per calorie absorbed. With this calibration, a known quantity of another material can be used and the peak area measured. From the peak area and the prior calibration, the total heat absorbed is calculated. The accuracy is 90-95%.

RESULTS[6]

A series of thermograms obtained from a propellant under development gave the results listed in Table 1.

TABLE 1. Results of Individual Thermal Analysis

Run	ϕ, °C/min[a]	T_m, °K	ϕ/T_m^2, °C/min	$1/T_m$ x 10^3	T_m^2, °K
1	0.756	443.2	3.86 x 10^{-6}	2.257	1.981 x 10^5
2	1.720	452.1	8.41 x 10^{-6}	2.212	2.033 x 10^5
3	2.775	458.2	13.2 x 10^{-6}	2.183	2.090 x 10^5
4	2.810	458.7	13.4 x 10^{-6}	2.180	2.100 x 10^5

[a] Heating rate.

The data from this table are plotted in Fig. 10. Calculation of the activation energy yielded a value of 32.9 kcal/mole. The apparent value of A is 1.8 x 10^{13} sec⁻¹.

A less elaborate treatment, i.e., the determination of T is routinely performed on all new materials. This initial thermogram plus the vacuum stability and the friction, electrostatic, and impact sensitivities are used to characterize new propellants and explosives.

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[6] Since this report is Unclassified, no actual results are presented. A report is being prepared, which lists the materials analyzed during the past year.

Three separate thermograms taken on the same material are shown in Fig. 11. These thermograms demonstrate the stepless control and reproducibility of the apparatus and instrumentation used in DTA.

CONCLUSION

The use of DTA is a valuable tool for the study of the reactions and transformations that propellants and propellant ingredients undergo at elevated temperatures.

The determination of the onset (reaction) temperature should be part of the required procedure used in the characterization of new propellant and explosive materials.

If used throughout a propellant development program, DTA can detect latent instabilities early enough for corrective action. If used continually in a supporting applied research program, DTA has the potential of reducing propellant development time. Continued evaluation of material, steady flow of thermal and kinetic reaction data, and a thermal-behavior-prediction program reduce immeasurably the cost and time required for developing a new propellant.

Appendix

KISSINGER'S METHOD OF STUDYING REACTION KINETICS

After establishing the validity of the assumption that the peak temperature T_m occurs at the maximum reaction rate (maximum deflection on the thermogram), Kissinger (Ref. 8) developed a method of studying reaction kinetics. He used DTA and variable heating rates. His work is summarized below.

Most reactions of the solid $\longrightarrow$ solid + gas type can be described by the following differential equation

$$\frac{dx}{dt} = A(1 - x)^n e^{-E/RT} \tag{1}$$

where $\frac{dx}{dt}$ is the rate, x is the fraction reacted, n is the empirical order of the reaction, R is the gas constant, and T is the Kelvin temperature.

With a rise in temperature during the reaction, the reaction rate $\frac{dx}{dt}$ will rise to a maximum value, then return to zero as the reactant is exhausted. The maximum rate occurs when $\frac{d}{dt}\left(\frac{dx}{dt}\right)$ is zero. If the temperature rises at a constant rate ϕ, then by differentiation of Eq. 1

$$\frac{d}{dt}\left(\frac{dx}{dt}\right) = \frac{dx}{dt}\left[\frac{E\phi}{RT^2} - An(1 - x)^{n-1}e^{-E/RT}\right] \tag{2}$$

The maximum rate occurs at a temperature T_m defined by setting Eq. 2 equal to zero.

10

$$\frac{E\,\phi}{RT_m{}^2} = An(1 - x)_m{}^{n-1}\, e^{-E/RT_m} \tag{3}$$

This general expression is for any order reaction and differs from the first order case, Eq. 8, by the product $n(1 - x)_m{}^{n-1}$. The temperature T_m is the sample temperature at which the peak DTA deflection occurs. The amount of material left unreacted, $(1 - x)_m$, is not readily determined from the DTA analysis pattern.

Equation 1 can be integrated, assuming a constant heating rate ϕ, to determine the extent of reaction as a function of temperature. The resulting integration, however, is of an exponential type, which complicates the expression. A satisfactory approximation can be obtained by successive integration by parts (Eq. 8). A rapidly converging series results, so that little error results if all terms after the second are dropped. Using Eq. 7, integration of Eq. 1 results in

$$\frac{1}{n-1}\left(\frac{1}{(1-x)^{n-1}} - 1\right) = \left(\frac{ART^2}{E\,\phi}\, e^{-E/RT}\right)\, 1 - \frac{2RT}{E} \tag{4}$$

For $n = 0$, integration yields

$$x = \frac{ART^2}{E\,\phi}\ e^{-E/RT}\ \left(1 - \frac{2RT}{E}\right) \tag{5}$$

For $n = 1$

$$\ln\left(\frac{1}{1-x}\right) = \left(\frac{ART^2}{E\,\phi}\, e^{-E/RT}\right) 1 - \frac{2RT}{E} \tag{6}$$

At the temperature T_m (where the maximum reaction rate occurs) the value of $(1 - x)_m$ is given by Eq. 4. If Eq. 3 is combined with Eq. 4, the following result is obtained for $n \neq 0$ and $n \neq 1$.

$$\frac{1}{n-1}\left(\frac{1}{(1-x)_m{}^{n-1}} - 1\right) = \frac{1}{n}\left(\frac{1}{(1-x)_m{}^{n-1}}\right)\left(1 - \frac{2RT_m}{E}\right) \quad (7)$$

which simplifies to

$$n(1-x)_m{}^{n-1} = 1 + (n-1)\frac{2RT_m}{E} \quad (8)$$

The heating rate ϕ is not involved in Eq. 8, except as it affects T_m, and the product $n(1-x)_m{}^{n-1}$ is not only independent of ϕ, but is very nearly equal to unity. Therefore, substituting this value of unity in Eq. 3 and differentiating (neglecting small quantities), the following is obtained

$$\frac{d\left(\ln\frac{\phi}{T_m{}^2}\right)}{d\left(\frac{1}{T}\right)} = -E/R \quad (9)$$

regardless of the reaction order. If the reaction order is zero, the peak occurs when the material is exhausted, i.e., when $x = 1$ and Eq. 9 can be obtained from Eq. 5. This is the same expression as derived earlier for the first order case, Eq. 4. Equation 9 makes possible the determination of E for a simple decomposition reaction regardless of reaction order by making DTA patterns at a number of heating rates.

Therefore, from Eq. 9, the slope of the plot of $\ln(\phi/T_m{}^2)$ versus $1/T_m$ is seen to be equal to $-E/R$. Knowing E, Eq. 3 is used to calculate A.

The above treatment is taken as adequate justification for the use of DTA to determine A, E, T, T_m, n, and the heat of reaction.

8.00 ± 0.50 IN.

OD NOT CRITICAL IF
ID GREATER THAN 0.075 IN.

12/18 ₹ MALE JOINT

5/12 ₹ STRAIGHT-THROUGH
MALE JOINT

4.60 ± 0.02 IN.

LENGTH OF TAPER 0.50 IN.
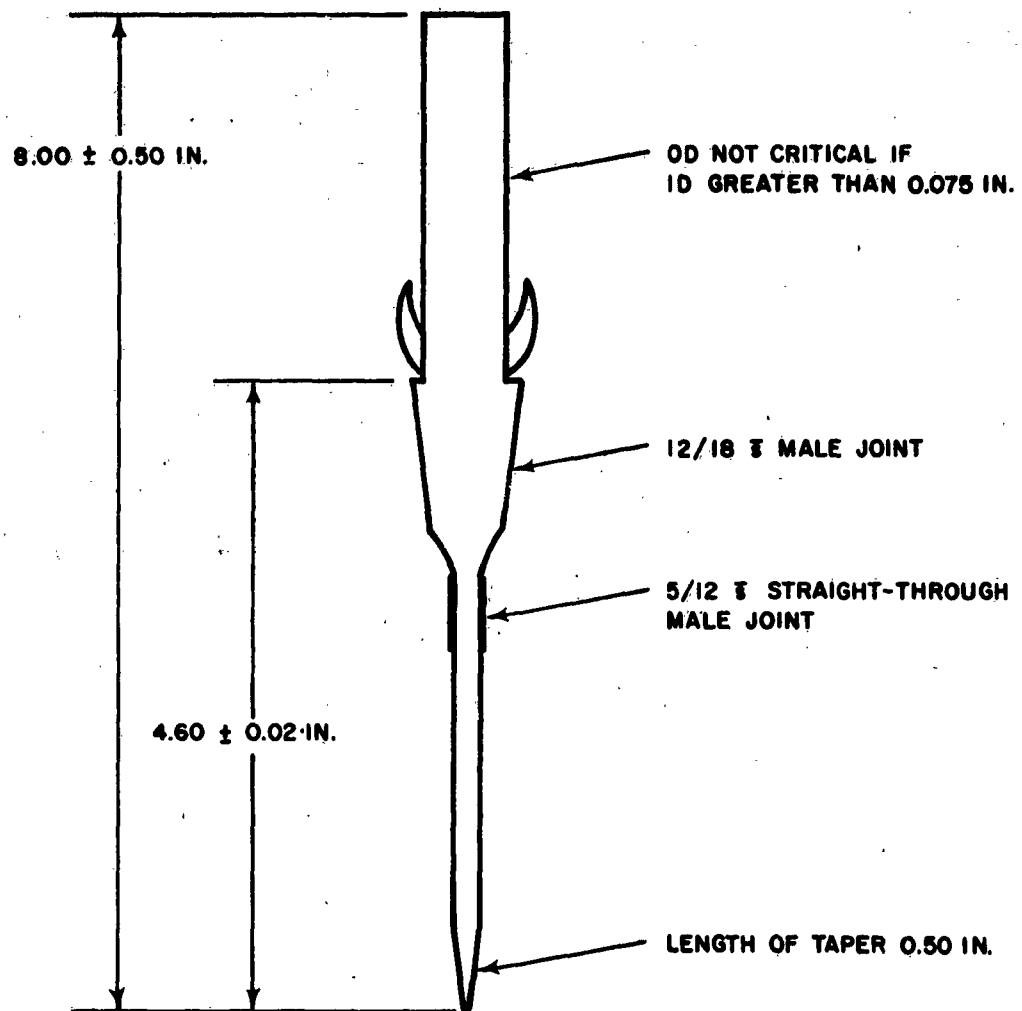
FIG. 1. Schematic of Thermocouple Probe.

OD MAX. 0.390 IN.

5/12 ₸
FEMALE JOINT

ONE
HOLE →

3.85 ± 0.02 IN.

0.25 IN. OD
(MIN. ID 0.162)

TYPE I

OD MAX. 0.390 IN.

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ONE
HOLE →

3.90 ± 0.02 IN.

0.25 IN. OD
(MIN. ID 0.162)

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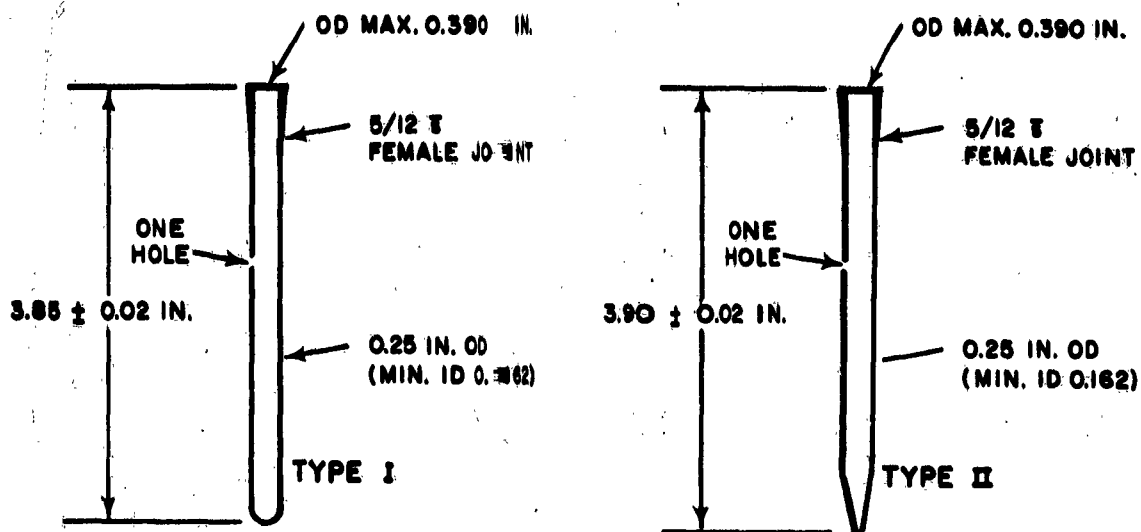
FIG. 2.   Schematic of Sample Sleeve.

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3.00 IN.

4.90 ± 0.02 IN.
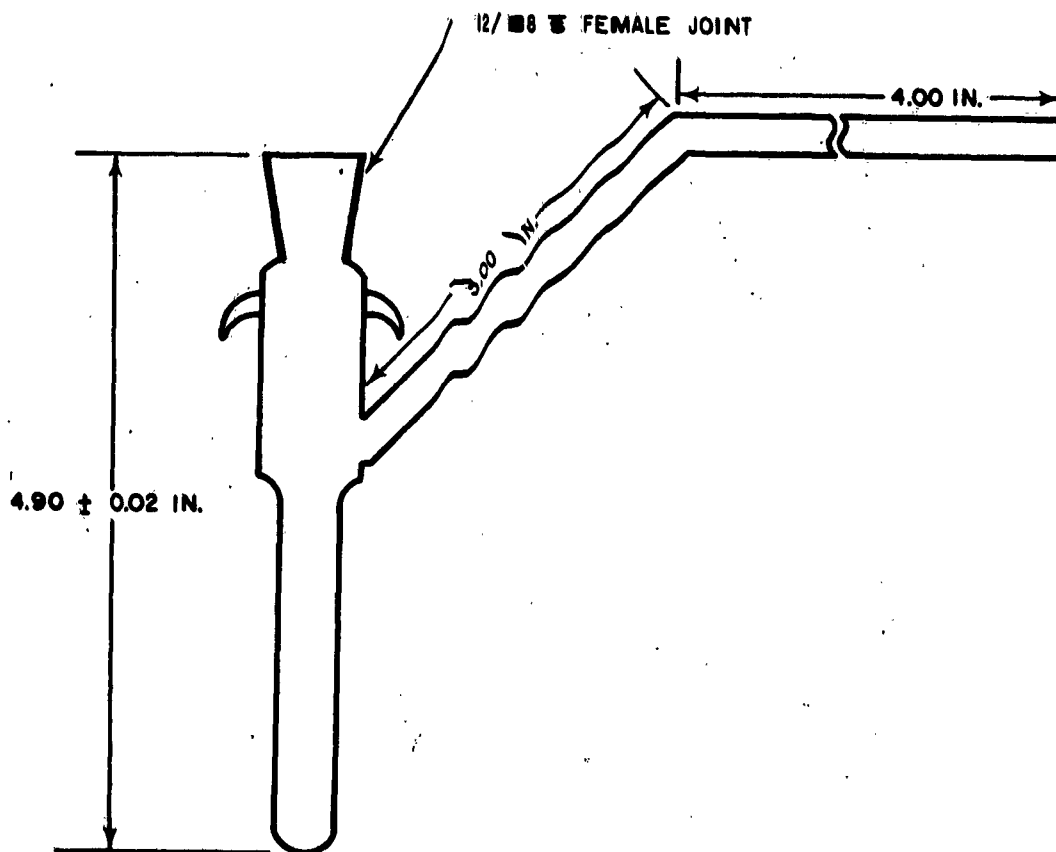
FIG. 3.   Schematic of Main Sample Tube.
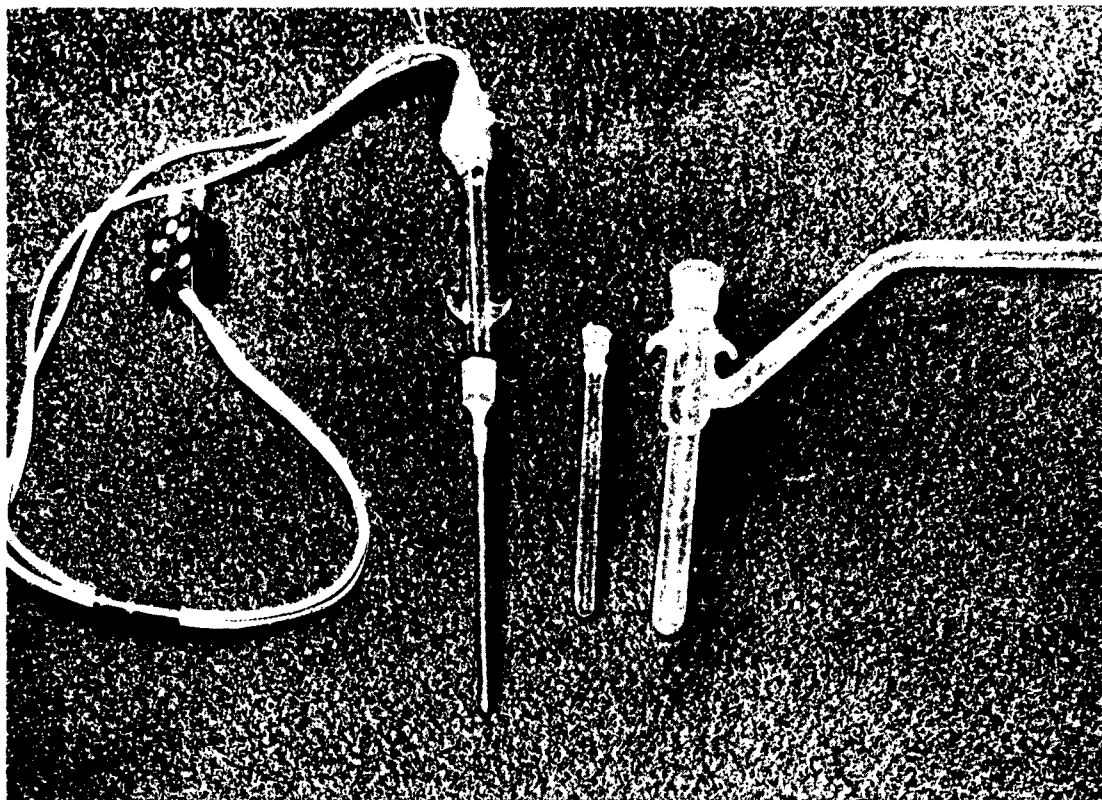
FIG. 4. Thermocouple Probe, Sample Sleeve,
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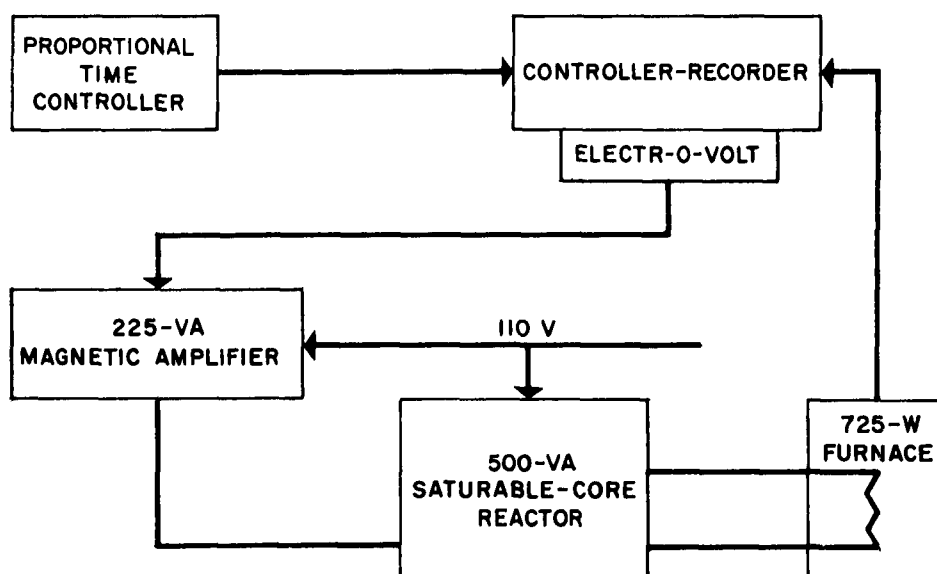
FIG. 5. Block Diagram of Heating Control System.
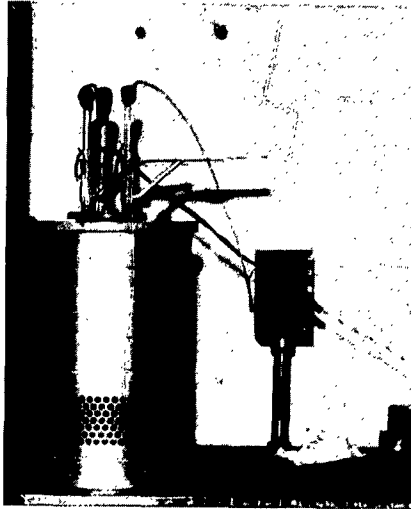
FIG. 6. Test Setup.
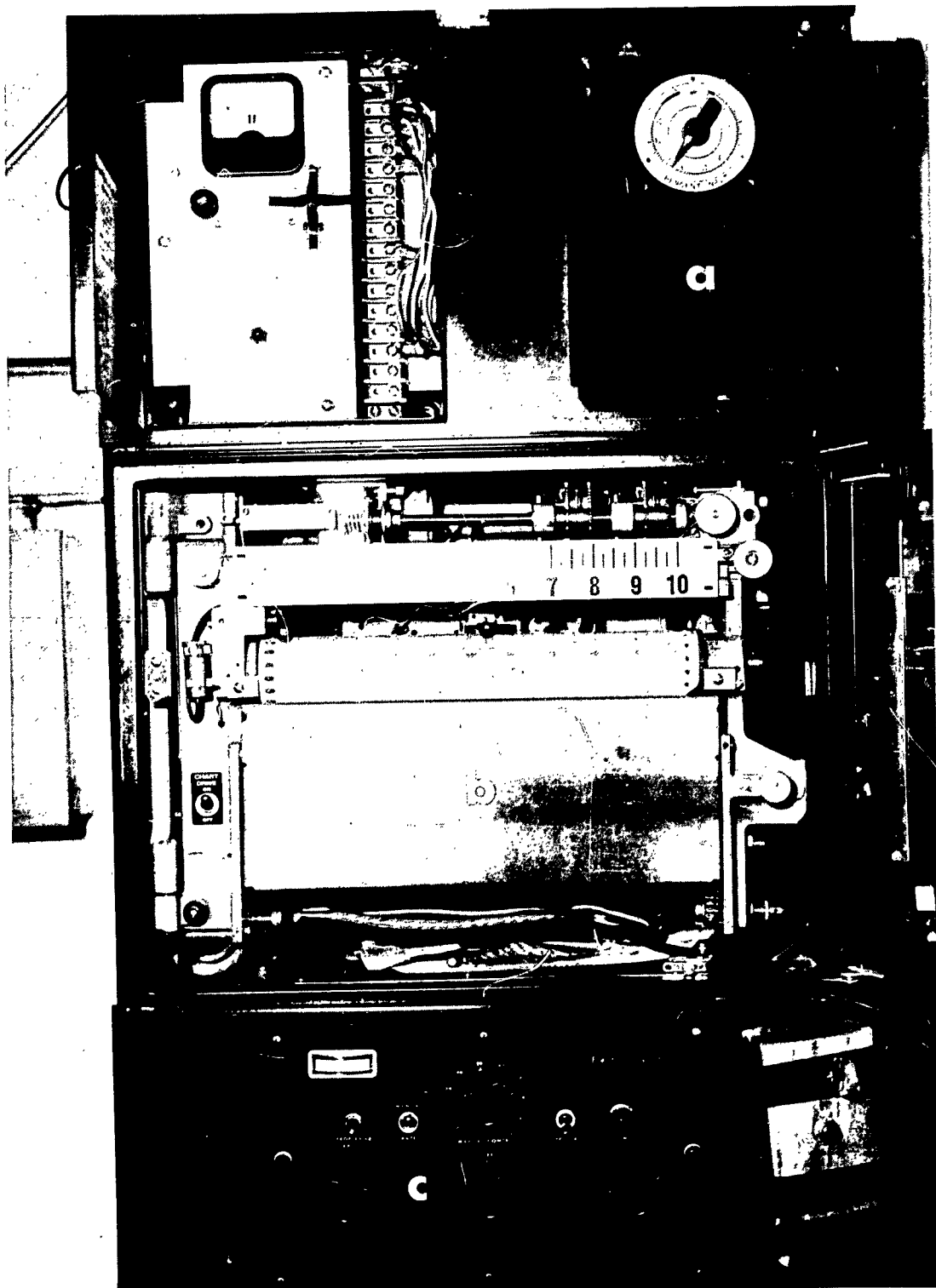
FIG. 7. Controller-Recorder and Electr-O-Volt Unit.
(a) Proportional Time Controller; (b) Controller-
Recorder; (c) Electr-O-Volt Unit.

SAMPLE IDENTIFICATION	MIX TAMA	EXOTHERMS			ENDOTHERMS	
		ONSET	PEAK		ONSET	PEAK
RUN NUMBER	127	330°F	420°F		183°F	196°F
RUN DATE	11 MAY 1961				553±2°F	590°F
HEATING RATE	5.00°F PER MIN					
SAMPLE WEIGHT	16.9 MG's					
REFERENCE	GLASS BEADS					
AMPLIFICATION	9.75					
BLOCK NUMBER	8					
FURNACE WATTAGE	125					
CONTACT	CODE 4532					
COMMENTS:						
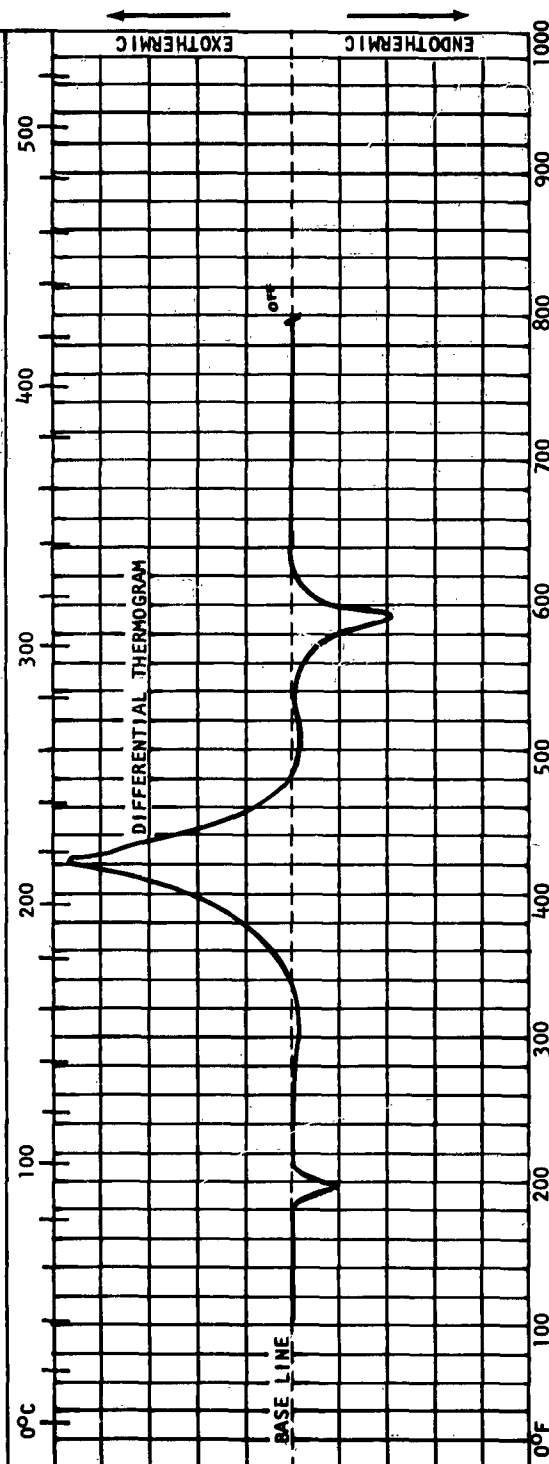
FIG. 8. Typical Sample Data Sheet.

18
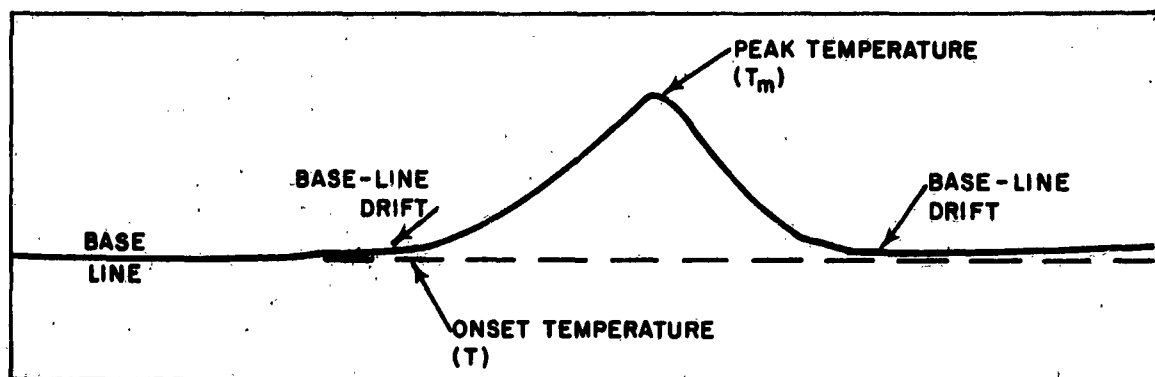
FIG. 9. Representative Thermogram.
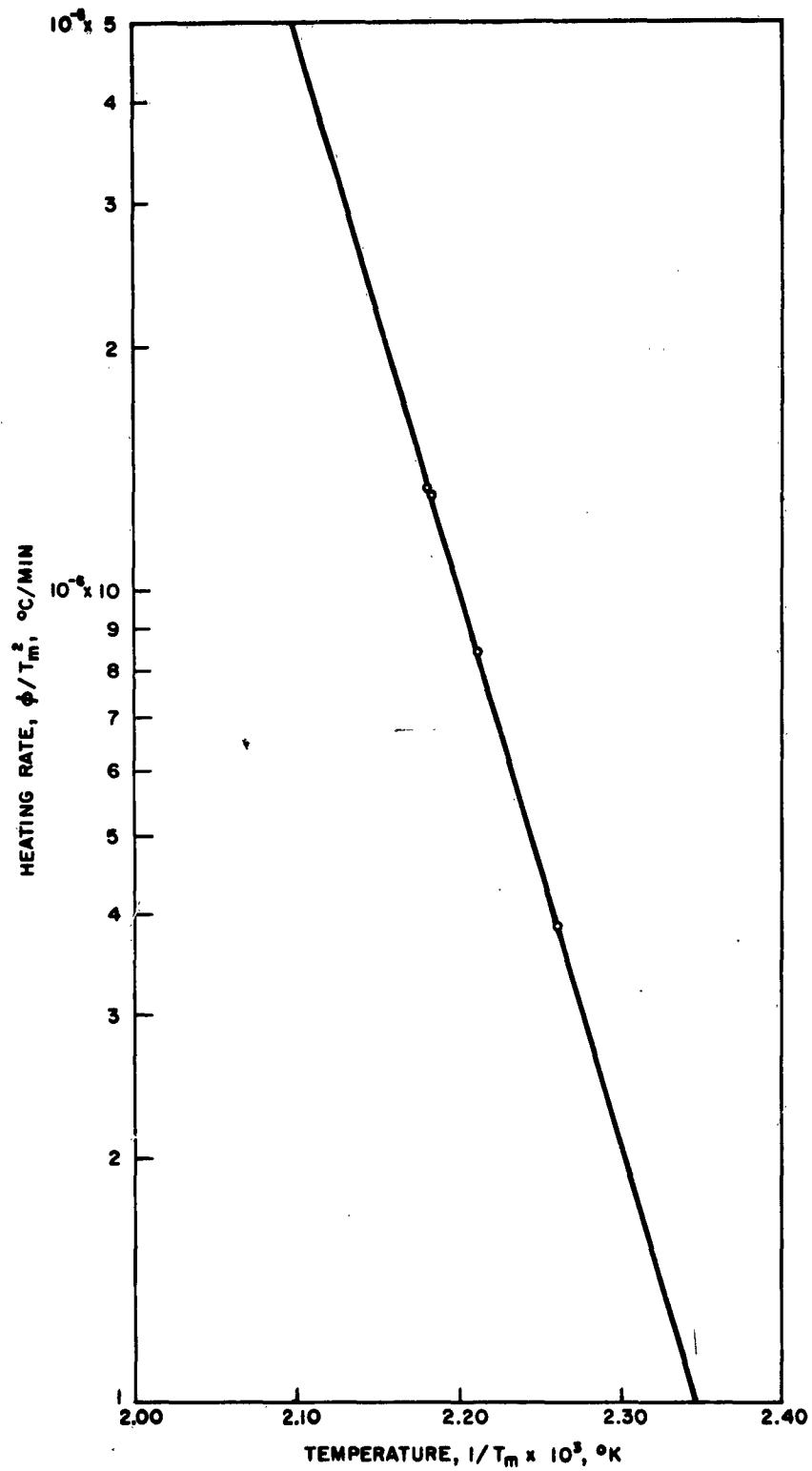
FIG. 10. Heating Rate Versus
Temperature for Determining
Activation Energy.
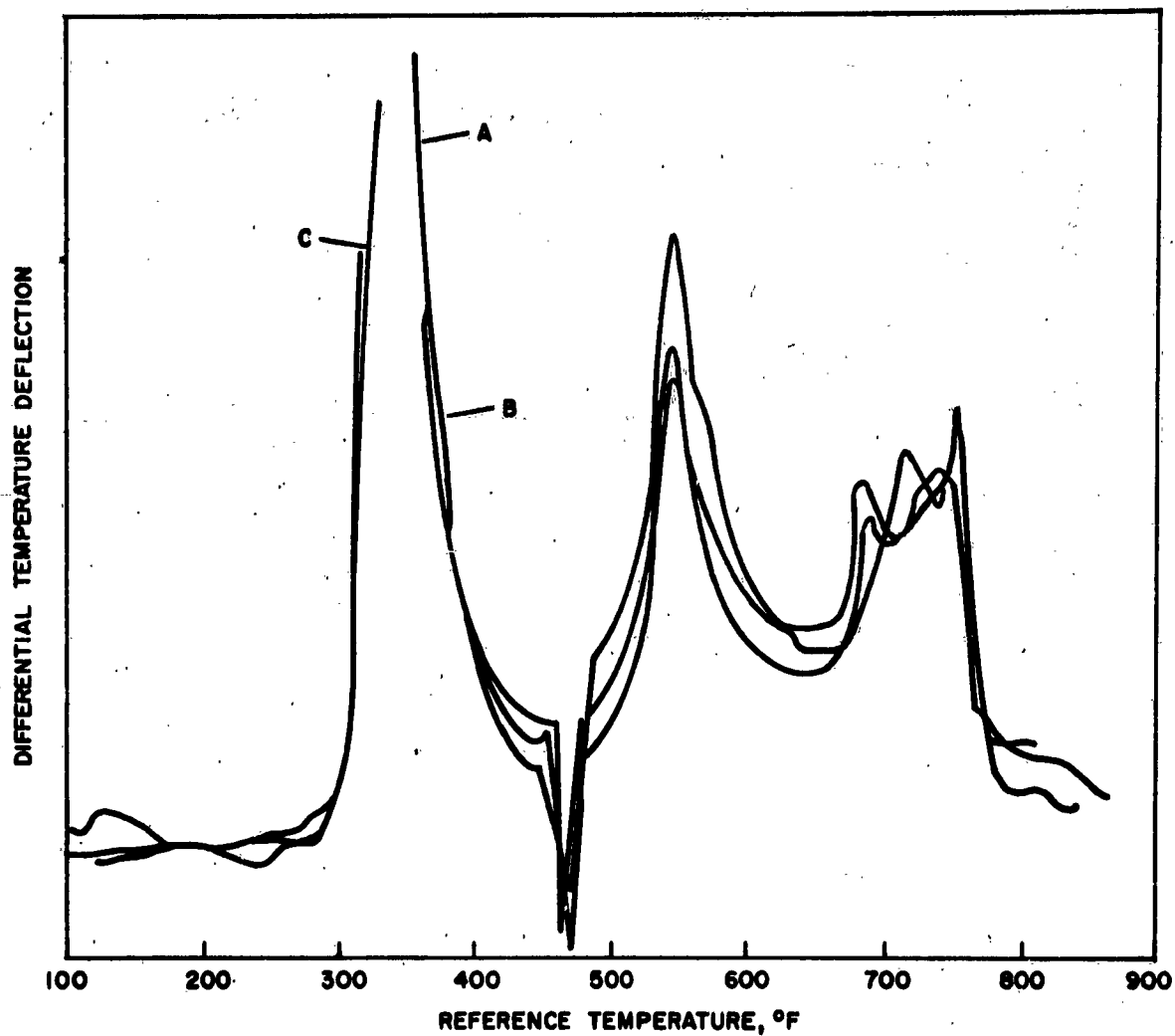
FIG. 11.   Differential Thermogram
of Runs Made on the Same Material
Showing Reproducibility of
Instrumentation.

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NEGATIVE NUMBERS OF ILLUSTRATIONS

Fig. 1, none; Fig. 2, none; Fig. 3, none; Fig. 4, L066454; Fig. 5, none; Fig. 6, L066456; Fig. 7, L066455; Fig. 8, none; Fig. 9, none; Fig. 10, none; Fig. 11, none.

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energy, E (the energy barrier opposing the
reaction), the frequency factor, A (the
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