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EVALUATION OF METHODS FOR RAPID DETERMINATION OF FREEZING POINT OF AVIATION FUELS

by B. Mathiprakasam

MIDWEST RESEARCH INSTITUTE

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
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PREFACE

This report documents the activities of a project, "Evaluation of Methods for Rapid Determination of Freezing Point of Aviation Fuels," sponsored by the National Aeronautics and Space Administration, Lewis Research Center, Cleveland. The objectives of the project were (a) the analytical evaluation and selection of practical methods to determine the freezing point of aviation fuels which are suitable for rapid and field testing, (b) the experimental evaluation of selected methods, and (c) the design of concepts for a self-contained, portable model for rapid freezing point measurement.

The program was conducted in the Energy Systems Section under the general supervision of Dr. J. L. Beeson. This section is a part of the Energy and Materials Science Department, Dr. K. P. Ananth, Director. Dr. B. Mathiprakasam, Senior Energy Engineer, served as project leader and principal investigator, and was assisted by Dr. T. Sutikno, Mr. William Jellison, Mr. A. Chui, and Mr. P. Hogan.

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September 1982

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SUMMARY

A number of methods were evaluated to identify the more promising concepts for the development of a portable instrument to rapidly determine the freezing point of aviation fuels. The evaluation process consisted of: (a) the collection of information on the techniques employed in the past to determine the freezing point; (b) screening and selection of these techniques for further evaluation of their suitability in a portable unit for rapid measurement; and (c) an extensive experimental evaluation of the selected techniques, and the final selection of the most promising technique for design into a portable unit.

Information was obtained for several techniques and two of these were chosen for experimental evaluation in the initial phase of the work. These were differential thermal analysis (DTA) and an optical technique. The DTA method recorded the temperature difference between the sample and a nonfreezing reference fuel. A maximum in the temperature difference occurs at the freezing point. The optical technique observed the change in light transmission through the sample during the phase change. A test apparatus employing these techniques was designed and built. The apparatus consisted of test and reference cells placed between thermoelectric coolers, a laser light source, an optical detector, and associated measuring instruments. An ice-water bath was used as the heat sink for the thermoelectric coolers. Both techniques gave satisfactory results for fuels, but the optical technique inexplicably failed for pure species. Because of its simplicity and superior results, the DTA method was chosen for additional tests. Further tests using the DTA method indicated that the cooling rate of the sample and reference fuel were not equal. No solution to the problem was found. As an alternate approach, the reference fuel was eliminated and the data for the sample was digitized, and the point of inflection obtained. The point of inflection represented the freezing point. The results using this method compared well with results obtained elsewhere by the ASTM D-2386 method and differential scanning calorimetry. A conceptual design of a portable instrument incorporating this technique was presented.

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I. INTRODUCTION

It is likely that in the future as high quality petroleum crude oils become scarce and more costly, they will be replaced with lower grade crudes, or synthetic crudes which are similar to low grade crudes. These will require additional refinery processing to meet the present day specifications for aviation turbine fuels, and would increase the fuel cost. As a possible alternative to additional refinery processing, some recent research efforts have been directed toward investigating the consequences of relaxing the present day property requirements. One of these is the possibility of increasing the maximum allowable freezing point temperature. If this were done, the temperatures of the fuel tanks could reach or exceed the freezing point of the fuel. If this should occur, the pumpability of the fuel could deteriorate markedly. The possiblity of such a situation indicates that it would be important to know the actual freezing point of the fuel at the time of delivery to the aircraft, and suggests the need for a portable instrument for rapidly determining the freezing point of the fuel.

Currently, the freezing points of aviation fuels are measured using the method described in ASTM D-2386. This laboratory method, though sufficiently accurate, is relatively slow and unsuited for field measurements. Freezing points of fuels at the time of delivery to the aircraft will probably have to be measured in less than 10 min.

NASA - Lewis Research Center, Cleveland, has contracted with Midwest Research Institute (MRI) to evaluate methods for rapid determination of freezing point of aviation fuels to meet the above requirements.

The objectives of the contract program were: (a) the analytical evaluation and selection of practical methods to determine the freezing points of aviation fuels suitable for rapid measurement in field testing, (b) experimental evaluation of selected methods, and (c) the design of a self-contained, portable model for rapid freezing point measurement.

MRI has successfully completed the scheduled technical activities of this program to attain the program objectives. Subsequent sections of this document present the details of the technical activities performed. Chapter II of this document describes the literature search, the analysis of various methods of freezing point measurement, and the selection of promising methods for experimental evaluation. In Chapter III, the laboratory test apparatus used to carry out the experimental work is described, and the experimental data and analysis of the test data are presented in Chapter IV. The concepts for the design of the portable freezing point apparatus are provided in Chapter V. Finally, a summary of the conclusions and recommendations arising from this study are presented in Chapter VI. A list of publications referenced in the report can be found in Chapter VII.

II. BASIC ANALYSIS AND SELECTION OF PROMISING METHODS

The selection of promising concepts for the experimental evaluation of freezing point measurement methods requires a knowledge of the concepts that have been employed in earlier investigations and an analysis of these concepts to determine their suitability for predicting the freezing point of multicomponent substances such as aviation fuels. A literature search was therefore made to identify and collect the technical papers, notes, reports, and textbooks relevant to freezing point measurement. Related literature on aviation fuel properties was also collected.

A. Analysis of Various Methods of Freezing Point Measurement

A detailed review of literature revealed that, in the past, a number of techniques have been employed for the determination of freezing point of different substances. These techniques cover a wide range of temperatures for a variety of applications such as phase transformation studies (solid-solid or solid-liquid), latent heat of fusion studies, and melting and freezing point studies. We classified these methods into the following three groups: (a) thermal methods, (b) optical methods, and (c) other methods. Those techniques which employ the inflection behavior of temperature-time history due to the absorption/release of latent heat during solid-liquid phase transition were classified as "thermal methods." The techniques which "observe" the disappearance of the solid crystals during warming a partially crystallized fuel by means of optical instruments were classified as "optical methods." All techniques which do not belong to either thermal or optical were classified as "other methods."

1. Thermal methods: In thermal methods, the freezing point of a given sample is determined by measuring the specific heat of the sample while warming a sample which was cooled to well below its freezing point. When a liquid substance is heated or cooled, the sensible heat is absorbed or released; but when a substance melts or freezes, the latent heat of fusion is absorbed or released. In the case of mixtures, melting or freezing processes involve not only the latent heat of fusion but also the sensible heat change over the melting or freezing temperature range. Therefore, the melting processes of pure species and those of mixtures are associated with increased specific heat. For example, the specific heat of n-octadecane reported by Tanasijczuk and Oja (ref. 1) is shown in Figure 1. For a one-component system, melting occurs at a single temperature. For this case, the specific heat approaches theoretically infinity at the freezing point. In Figure 1, a rapid change in specific heat near the end of melting is observed at ~ 29°C. This value is observed as the freezing point of n-octadecane. The increase in specific heat also occurs for mixtures; however this effect is not as pronounced as for pure species because melting occurs over a temperature range which in turn spreads out the impact on the specific heat. Thus, mixtures such as aviation fuels should show an increase in specific heat during melting, though not as pronounced an effect as for pure species such as n-octadecane.

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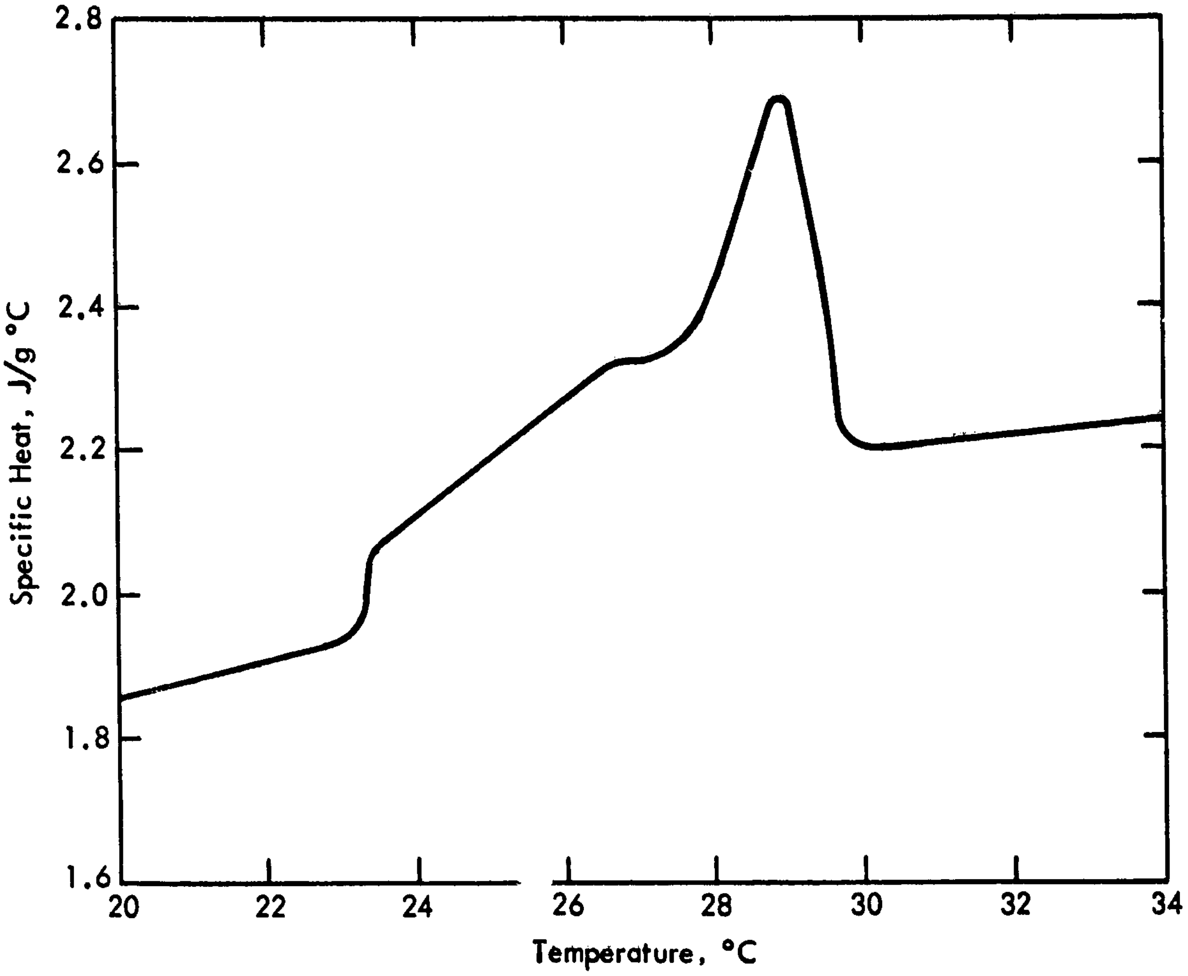

Figure 1 - Specific Heat of n-Octadecane Near the Freezing Point

The specific heat of liquids or solid-liquid mixtures can be measured in several different ways. Some of the methods found in the literature are:

- Adiabatic calorimetry,
- Thermal relaxation calorimetry, and
- Differential scanning calorimetry or differential thermal analysis.

The basic principles of each of the above methods are described below. In all these methods, the heat capacity, which is the product of the mass of the sample and its specific heat, is measured. The specific heat can then be deduced from the heat capacity values.

a. Adiabatic calorimetry: In adiabatic calorimeters, the heat added in the system is completely used to raise the enthalpy of the sample. It is assumed that no heat leaks from the system which is very well insulated. The conservation of heat energy in this case gives the equation:

$$\dot{Q} = C \frac{dT}{dt} \qquad (1)$$

where: $\dot{Q}$ = Rate of heat supply, kW

C = Heat capacity of the sample, kJ/°C

T = Temperature of the sample, °C

t = Time, sec

The system can be monitored in two different ways. Case (a): constant rate of increase of the sample temperature. In this case, dT/dt is independent of time, but $\dot{Q}$ is a function of time. Case (b): constant rate of power supply. In this case, $\dot{Q}$ is independent of time, but dT/dt is a function of time.

Case (a): In this case, the sample is warmed so that its temperature varies linearly with time. The power supply is adjusted continuously to meet this requirement. Through proper instrumentation, a plot of heat supplied $\dot{Q}$ versus time t is obtained. Since T and t are proportionally controlled, t-axis will also represent T-axis with a modified scale. Similarly, as can be seen from equation (1), $\dot{Q}$ is proportional to C (since dT/dt is a constant) and, therefore, $\dot{Q}$-axis will also represent C-axis in some other scale. Therefore, the $\dot{Q}$-t plot and C-T plot are similar. If the objective of the experiment is to determine the freezing point but not the heat capacity, then a transformation to C-T plot is not needed; the freezing point can be observed directly from the $\dot{Q}$-t plot.

Case (b): In this case, heat is added to the sample at a constant rate. The temperature will vary as a function of time. With the necessary instrumentation, a plot of the temperature T versus time t is first obtained. From this plot, dT/dt is calculated and another plot of dT/dt versus t is prepared. Since $\dot{Q}$ is constant, as can be seen from equation (1), the heat capacity C is inversely proportional to dT/dt; hence, C can be obtained as a function of temperature. If the requirement is for the determination of freezing point but not heat capacity values, it is possible to observe the freezing point either directly in T-t plot or after differentiating to a dT/dt-t plot. The determination of the freezing point by Glasgow et al. (ref. 2) is based on observing the curve in a T-t plot.

b. Thermal relaxation calorimetry: In thermal relaxation calorimeters, the system does not operate on an adiabatic mode. A small heat leak of thermal conductance K is incorporated into the system. The heat leaks between the sample and a thermal reservoir which is maintained at a temperature of T_o. In the literature, several calorimeters were found which used thermal relaxation to test samples undergoing phase transition. The basic equation governing the transport of heat is given by:

$$\dot{Q} = C \frac{dT}{dt} + K(T - T_o) \tag{2}$$

The ratio C/K is called relaxation parameter. Both C and K are functions of temperature T. The measurement of C in the thermal relaxation method involves basically two steps of experimentation. In step (1), the value of K=K(T) is determined. Then in step (2), the value of C=C(T) is determined.

Step (1): In step (1), the calorimeter is operated at steady-state conditions. The heat supply rate $\dot{Q}$ is so adjusted that dT/dt is zero at a desired temperature T. In other words, the entire heat supply is leaked to the thermal reservoir at T_o without increasing the enthalpy of the sample. Since dT/dt is zero, K is given by:

$$K = \dot{Q}/(T - T_o) \tag{3}$$

The experiment is repeated for a set of steady-state temperatures T, so that K is determined as a function of T.

Step (2): In step (2), the heat supply to the sample from the power source is stopped (Q=0), and the reservoir temperature, which has previously been raised to a sufficient value by separate heating systems, is used to warm up the test substance through the heat leak. Equation (2) then takes the form:

$$C \frac{dT}{dt} + K(T - T_o) = 0 \tag{4}$$

The heating capacity C can be determined from equation (4) as:

$$C = K(T_o - T)/(dT/dt) \tag{5}$$

During the experiment, the temperature of the test substance T is measured continuously as a function of time. From this measurement, dT/dt can be determined, and the specific heat C can then be calculated using equation (5). The freezing point can then be observed from the specific heat values. Sometimes, depending upon the behavior of the sample near the freezing point, it may be possible to observe the freezing point from the plot of T versus t directly.

Though the basic principle of thermal relaxation calorimetry is the same, wide variation in the operation of calorimeters was found in the literature. Some of these calorimeters were used to study samples undergoing phase transition. Moses et al. (ref. 3) used a constant heat supply (Q constant), whereas Buckingham and Edwards (ref. 4) used a constant rate of increase of temperature (dT/dt constant). Tanasijczuk and Oja (ref. 1) employed an alternating current supply at different frequencies. Griffing and Shivashankar (ref.5) reported a scheme for monitoring the sample temperature and reservoir temperature for use in studying phase transition. Calorimeters developed for special applications are also reported (ref. 6-9).

c. Differential scanning calorimetry (DSC) and differential thermal analysis (DTA): In differential systems (both in DTA and DSC), the principal components of the apparatus are a sample cell and a reference cell. The sample cell contains a test substance whose calorimetric data are to be determined; the reference cell contains a known material which undergoes no thermally induced event such as phase transition, or exothermic or endothermic reaction in the temperature range under study. The sample and reference holders are insulated from each other and are always maintained at the same temperature by closely controlling the heat supplied to each of the holders. With the aid of proper instrumentation, the rate of change of the cells' temperature is set constant (dT_p/dt = constant). Depending upon the thermal resistance between the reference holder and the reference material, the temperature of reference material T_r will lag by a finite amount from the programmed temperature T_p. However, the rate of change of the temperature of reference material will be the same as that of the holder, i.e., $dT_r/dt = dT_p/dt$ where t represents time. The sample temperature T_s will also lag from the programmed temperature T_p; but in this case, $dT_s/dt = dT_p/dt$ only during the time when the sample is not undergoing any thermal changes. When a thermal event such as a phase transitions occurs, the rate of change of sample temperature will be different from the programmed rate (i.e., $dT_s/dt \neq dT_p/dt$). The heat associated with the thermal event (latent heat in the case of a phase transition) can be related to those deviations which are measurable in the system.

The principal quantity measured in a differential thermal analyzer is the difference in temperature between the reference and sample. The temperature difference is measured continuously as a function of time (or programmed temperature). In a Differential Scanning Calorimeter, one measures the difference between the heat supplied to the sample and the heat supplied to the reference material.

The energy conservation equations representing the heat transfer processes in the sample and in the reference are:

$$\dot{Q}_s = C_s \frac{dT_s}{dt} + \frac{dh}{dt} \tag{6}$$

$$\dot{Q}_r = C_r \frac{dT_r}{dt} \tag{7}$$

where: $\dot{Q}_s$ = Heat supplied to the sample

$\dot{Q}_r$ = Heat supplied to the reference

C_s = Heat capacity of the sample, based on the sensible heat only

C_r = Heat capacity of the reference

dh/dt = Rate of heat absorption (latent heat)

Assuming that the thermal resistance between the sample holder and the sample is R, we obtain the relation:

$$R\,\dot{Q}_s = T_p - T_s \tag{8}$$

Since the arrangement of sample in the sample holder is identical to that of the reference material in the reference holder, the thermal resistance between the reference holder and the reference material is the same as that between the sample and sample holder. Therefore, we have:

$$R\,\dot{Q}_r = T_p - T_r \tag{9}$$

In equations (8) and (9), R is the thermal resistance. Using equations (8) and (9), in equations (6) and (7), and by subtracting equation (7) from (6), we get:

$$-(T_s - T_r) = R\,C_s \frac{dT_s}{dt} - R\,C_r \frac{dT_r}{dt} + R \frac{dh}{dt}$$

$$\Delta T + R\,C_s \frac{d\Delta T}{dt} = -R \quad (C_s - C_r) \frac{dT_r}{dt} + \frac{dh}{dt} \tag{10}$$

where ΔT is the differential temperature $(T_s - T_r)$ measured in the DTA apparatus. It can be seen from equation (10) that the rate of latent heat adsorbed dh/dt is a direct function of ΔT, and this can be calculated from the ΔT-t plots. By definition, the freezing point of the sample is the temperature at which the last crystal disappears while warming. At the freezing point, the absorption of latent heat is complete and dh/dt=0. This point can be observed in the plot of ΔT-t where ΔT attains a peak. This is how the freezing point is measured in the DTA apparatus.

The principle on which the DSC apparatus is based is presented next. The differential heat supplied between the sample and the reference $\Delta\dot{Q}=(\dot{Q}_s-\dot{Q}_r)$ is related to ΔT, as shown below:

$$\Delta\dot{Q} = -\Delta T/R \qquad (11)$$

Substituting equation (11) in equation (10), one obtains:

$$\Delta\dot{Q} + R\,C_s \frac{d\Delta\dot{Q}}{dt} = (C_s - C_r)\frac{dT_r}{dt} + \frac{dh}{dt} \qquad (12)$$

From equation (12), we find that the rate of latent heat absorbed dh/dt is a direct function of the differential heat supplied $\Delta\dot{Q}$ and can be calculated from the $\Delta\dot{Q}$-t plots. The freezing point is then observed from this plot by noting the point where dh/dt=0 or where $\Delta\dot{Q}$ attains a peak.

A DSC record ($\Delta\dot{Q}$-t plot) is analogous in many respects to that obtained in a DTA plot (ΔT-t plot); yet there are differences between the two methods. A DTA apparatus is a temperature measuring device, whereas a DSC apparatus is a heat measuring device. In both systems, a thermal lag occurs due to the finite value of the thermal resistance R. One can minimize the thermal lag by reducing R to the smallest possible value. However, in DTA, the sensitivity is reduced as R is reduced, but in DSC, the sensitivity is increased as R is reduced. The calibration constant required to estimate latent heat values in a DSC is a constant which is an electrical conversion factor, whereas that required in DTA is a thermal constant.

Numerous reports which document the determination of latent heat, heats of reaction, and transition temperatures (melting and freezing points) using either the DTA or DSC have been found in the literature (ref. 10-12). In particular, most of the reports in the 1970's have used DSC techniques because of the inherent advantages.

In a differential thermal system (either DTA or DSC), if the analysis requires several hundred milligrams of sample, the analysis is deemed macroanalytical in nature. In contrast, if a method requires only a few milligrams of sample, then the method is called microanalytical. In macromethods, the use of an appreciable amount of sample causes a nonuniform distribution of sample temperature and results in nonreproducibility. Therefore, since 1961, the trend in quantitative thermal analysis is toward reducting the sample size. The decrease in the sample weight to the microscale ensures a better homogeneity of the temperature distribution within the sample, a greater accuracy in temperature measurement, and an increased resolution and reproducibility of results. However, microanalytical methods require the homogeneity of reference and analyzed sample so that the small weight used in the analysis will be representative of the bulk reference and sample. Low heat capacity and conductivity of the sample and reference holders and an accurate determination of the position of thermocouples are also important.

In actual tests, the correct transition temperatures do not occur at the peak points of DTA or DSC curves as would be expected theoretically. The major factor influencing this effect is the programmed heating rate. Usually temperature corrections, based on the heating rate, are made to determine the correct phase transition temperatures.

d. Effect of cooling rate on the freezing point: It has been experimentally shown by Coley et al. (ref. 13) that the size of crystals formed during cooling depends strongly on the rate of cooling. Coarse crystals are formed at fast cooling rates, and fine crystals are formed with very slow cooling rates. When the fuel is rewarmed to observe the point at which the last crystal disappears, the temperature observed at this point (freezing point) may or may not depend on the size of crystals that were formed during cooling. In other words, the observed freezing point of a fuel may or may not depend on the prior rate of cooling. There are reports in the literature for polymers and milk fat showing that the observed freezing point can vary from 1 to 1.5°C while changing the cooling rates from 5 to 40°C/min.

2. Optical methods: A number of technical papers and reports were identified in the literature which described various optical techniques for determining phase transition temperatures. Basically one of the following three techniques was used in earlier work to determine phase transition temperatures: (a) optical transparency changes in the material during the process of phase transition, (b) variation in X-ray absorption of materials during melting, and (c) changes in index of refraction of materials during transition from solid to liquid states. These methods are described below in detail.

a. Transparency methods: Novak et al. (ref. 14) developed an apparatus to measure the transparency of materials at any specific wavelength as a function of temperature. They illustrated the procedure by measuring the transmission properties of (a) phenyl benzoate, and (b) butyl p-(p-ethoxyphenoxycarbonyl)-phenyl carbonate and by showing that abrupt changes in the transmission of light occurred when changing from solid to mesophase or isotropic liquid. The anhydrous salts of the long chain fatty acids have been studied using light transmission techniques by Benton et al. (ref. 15) to observe general mesomorphic forms between the true crystalline solid and the isotropic liquid. The transition temperatures determined by the light transmission method were found to be close to data determined by other methods.

Miller (ref. 16) measured the depolarized light transmission of several substances using thermal depolarization analysis (TDA). The measurement is affected by the scattering intensity and appear to be depolarizing further. The results of Miller for benzoic acid using both TDA and DTA are presented in Figure 2. It can be seen from this figure that the peaks generated by both TDA and DTA responses are close to each other and predict the same value of freezing point (~ 125°C).

b. X-ray absorption methods: Kobayashi (ref. 17) determined the melting points of ice droplets, powdered benzene, and p-xylene using this principle. In his experiment, solid particles of the chosen sample were melted and spread into a layer having a thickness sufficient to cut off X-rays. X-rays were absorbed more effectively by the spread layer than by the solid particles.

The plots of temperature and ionization current as a function of time during melting benzene, as presented by Kobayashi, are shown in Figure 3. The limitations of X-ray absorption methods are the requirement that the sample be in powder form and the need for an X-ray source and related instruments.

c. Method of index of refraction: Marcoux (ref. 18, 19) reported that certain substances have higher indices of refraction in the solid phase than in the liquid phase. Measurements have been made in molten salts at temperatures close to the melting point while the solid was melting. A simple method of measuring the index of refraction was also described in his paper.

Boxman (ref. 20) described a technique for measuring the variation of refraction index of a liquid as a function of temperature. The principal difficulty of obtaining a uniform temperature along the optical path in the sample liquid while simultaneously varying the temperature at a reasonable rate is overcome in his apparatus by heating the liquid in a separate vessel and injecting the heated fluid into the test vessel as a series of jets to encourage turbulent mixing.

Beysens (ref. 21) developed a simple and sensitive interferometer which provides high accuracy measurements of the refractive index of liquids with temperature. The temperature gradients within the sample are minimized in Beysens' apparatus by using a very small heating rate ($< 10^{-3}$ °C/sec). The technique of light scattering has also been employed to determine contamination particle sizes (ref. 22-24).

3. Other methods: The number of techniques found in the literature other than calorimetric or optical used to evaluate the freezing point of substances was limited. Some of the techniques that have been used in the past are (a) fuel composition (the total content of the last three members of the n-paraffin series in the fuel); (b) changes in magnetic permeability and/or electrical resistivity; and (c) density. Properties of fuels such as thermal conductivity, and viscosity and their changes, if

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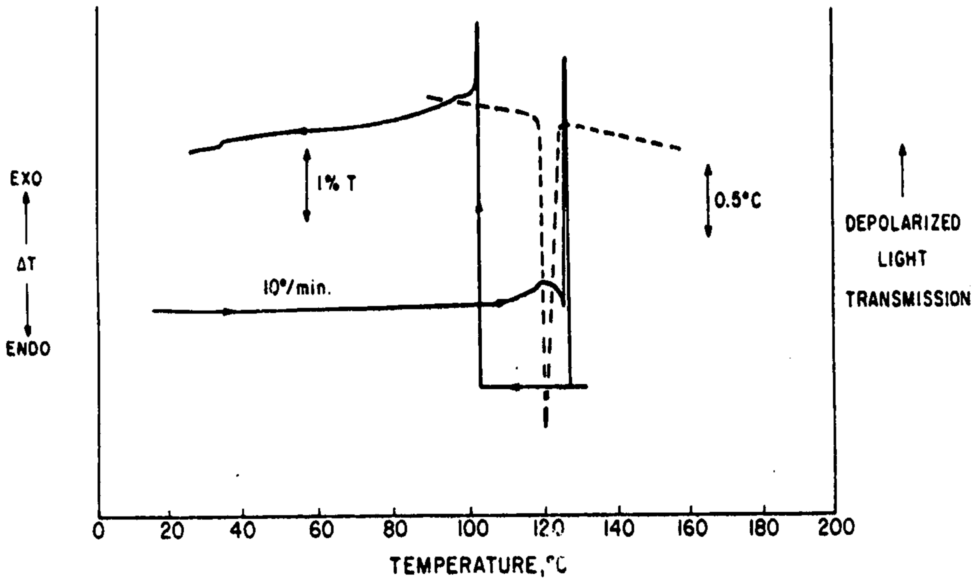

Figure 2 - TDA and DTA Responses of Benzoic Acid.

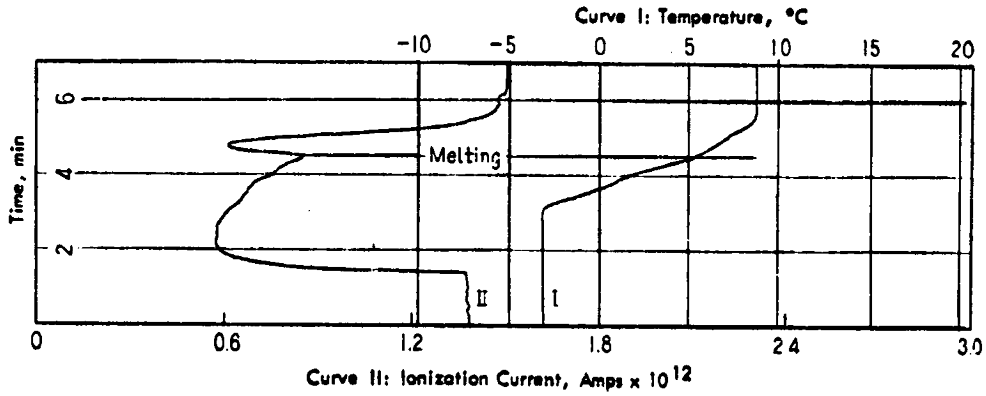

Figure 3 - Determination of the Melting Point of Benzene

any, during melting have not been used to observe the freezing point, though one must consider these properties in the evaluation process.

a. Fuel composition: Petrovic and Vitorovic (ref. 25) proposed a method for estimating freezing points of jet fuels, based on a linear relationship between experimental freezing points and the total content of the last three members of the n-paraffin series in the fuel. Antoine (ref. 26) has presented a plot of the sum of C_{14} to C_{17} n-alkanes concentration against freezing points as shown in Figure 4. A reasonably straight line can be fitted to the data for the shale and the COED fuels. Therefore, the freezing point does have some dependence on the amount of larger hydrocarbons present in the fuel. In case of jet fuels derived from alternate energy sources, the total n-alkane concentration does not provide a significant relationship with freezing point.

b. Electrical resistivity: Valenzuela and Miller (ref. 27) reported an apparatus for detecting solid state phase transformation which was based on the changes in magnetic permeability and/or electrical resistivity accompanying the phase transformation. The method was demonstrated on a 1020 steel (Fe + 0.2 wt % carbon) in cooling it from the austenite (Υ) region. The nonmagnetic ferrite (α) precipitation from austenite (Υ) changed the electrical resistivity of the sample, thus changing the output signal. Ranco, Inc., Controls Division, Ohio (ref. 28) uses the difference in electrical resistance between water and ice to control the thickness of ice in commercial ice bank, ice harvest, or liquid level equipment. The data on electrical properties of aviation fuels near their freezing point are, however, not available.

c. Density: No literature was found that show following density changes during the phase transition as a possible technique for determining the freezing point of fuels. However, instruments have been developed for the continuous volume measurement of samples as a function of temperature (ref. 29). Reilly and Rae (ref. 30) have described a dilatometer method to determine the transition point of the double salt system ($Na_2SO_4 \cdot 10\ H_2O + MgSO_4 \cdot 7\ H_2O$) which is stable above 21.6°C but separates to two simple salts below 21.6°C. An abrupt change in density of the sample was measured by the dilatometer at 21.6°C.

d. Viscosity: In our literature review, we were unable to find any work that was designed to observe the freezing point using viscosity measurements. However, the transition point of solutions of sodium ammonium tartrate has been estimated by measuring the viscosity of the sample and noting a break at 28.3°C (ref. 30). Thomas et al. (ref. 31) studied the viscosity temperature behavior of isomeric substituted benzenes and have shown that no abnormal increase in viscosity occurs in the proximity of the freezing point. Studies on viscosity behavior of fuels near the freezing point indicates that this behavior is very complex and depends on many factors, including the composition of the fuel. The details of viscosity behavior of aviation fuels near the freezing point are presented in Appendix A.

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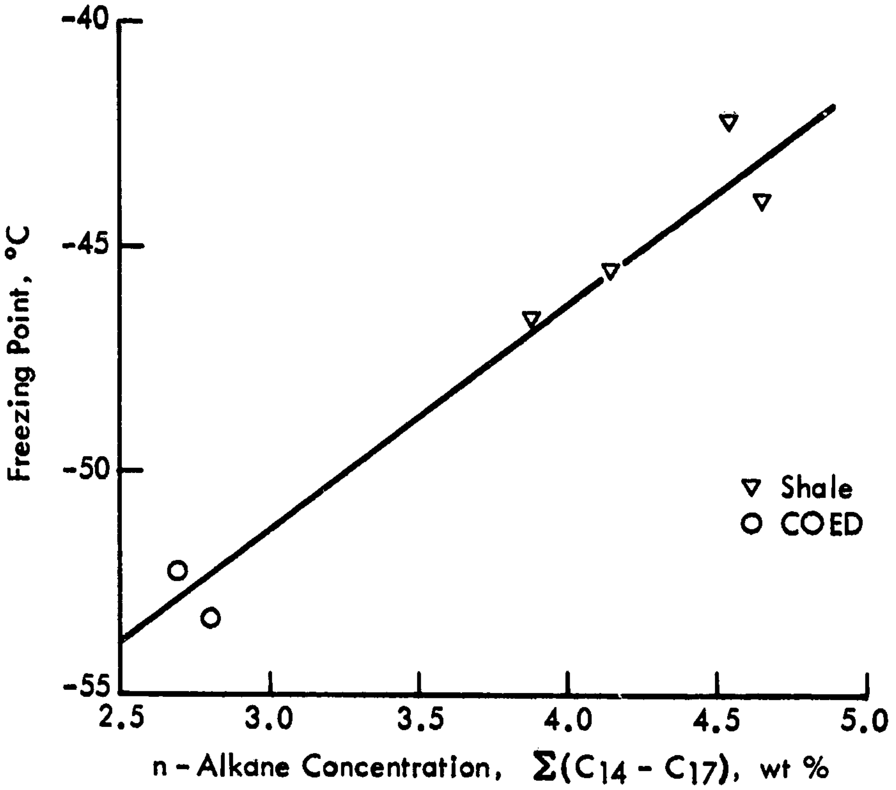

Figure 4 - Change in Freezing Point with n-Alkane Concentration

e. Thermal conductivity: It can be expected that some substances may undergo abrupt changes in their thermal conductivity during melting/freezing. The work of Hattori et al. (ref. 32) on heat conduction properties during melting/freezing processes showed the thermal conductivity of tuna fish and glucose solutions change abruptly at the freezing point. Figure 5 shows the thermal conductivity of the water content of tuna; the freezing point of this water is indicated as -1.2°C. Thermal conduction properties of aviation fuels in the near freezing point are, however, not known.

B. Selection of Methods for Experimental Evaluation

Several practical methods for the evaluation of the freezing point of substances were identified in the literature search, and these have been presented earlier. In all these methods, the primary requirement is the cooling of the sample fuel to the freezing temperature. Due to supercooling, crystallization in the liquids being cooled generally begins several degrees below the freezing point. Therefore, the measurement of freezing temperatures should be based on melting rather than freezing to avoid the possible errors introduced by supercooling. Measuring the freezing point during melting requires the rewarming of sample fuel which has previously been cooled sufficiently below its freezing point. Therefore, in any freezing point apparatus, cooling and rewarming devices are required irrespective of the techniques that are employed to observe the freezing point.

The following subsections present the selection of cooling and rewarming devices and also the selection of techniques for the evaluation of the freezing point.

1. Selection of cooling/rewarming devices: A number of methods can be employed to cool and rewarm the aviation fuel to the desired temperature. Generally, the devices performing the cooling and rewarming must have the following essential characteristics.

- Since an apparatus for field testing is to be developed, the cooling/rewarming devices must be simple, small in volume, and highly reliable.

- Because of the rapid testing capability requirement, cooling/rewarming devices must have a high rate of cooling/heating capacities.

- It is highly desirable, though not essential, to have a single device which can perform both cooling and rewarming, with the particular operation being set by the operator at his will.

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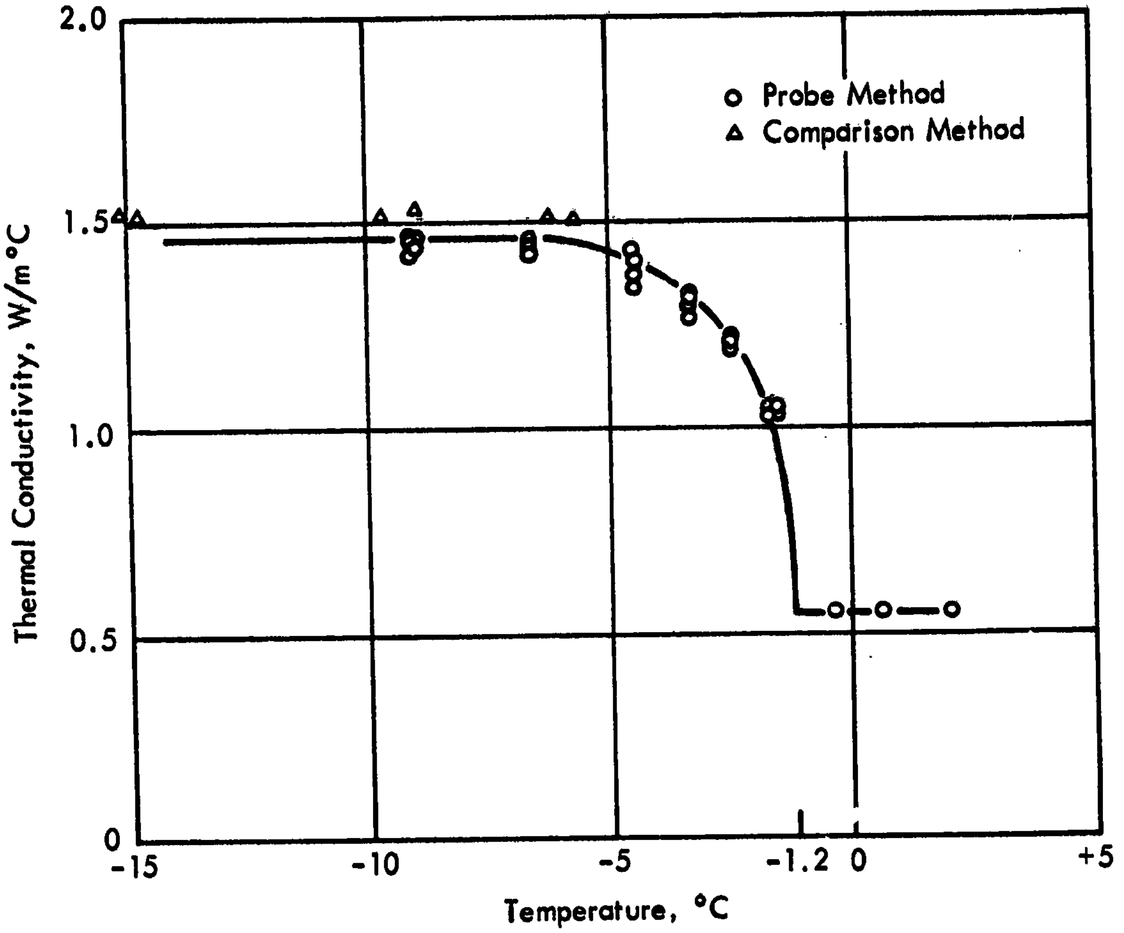

Figure 5 - Thermal Conductivity of Tuna

Commercially available cooling devices include (a) cooling baths, (b) mechanical refrigerators, and (c) thermoelectric heat pumps.

In cooling baths, cooling is obtained by using ultracold refrigerants which have been chilled to a predetermined low temperature. Examples of this method of cooling are liquid nitrogen--solid carbon dioxide with a liquid whose freezing point is -50°C or lower. The driving force for the rapid cooling of the fuel is substantially higher in the case of liquid nitrogen (-195°C) or solid carbon dioxide (-78°C). Acetone or alcohol is also suitable for cooling when used with solid carbon dioxide, and specific liquids can be partially frozen to provide slurries with definite temperatures. The advantage of using ultracold refrigerants lies in the rapid rate of cooling obtainable because of the high overall heat transfer coefficients. The main drawbacks of these methods are the size of the cooling vessels needed and handling problems for field operations.

Cooling can also be obtained by employing simple mechanical refrigeration systems. In the present-day market, mechanical refrigeration packages are available for cooling to temperatures as low as -100°C. "Flexi-cool" manufactured by FTS Systems is one example. Mechanical systems have a number of advantages over the liquid cooling systems, the main advantage being mechanical refrigeration systems can be operated at lower temperatures. Other advantages are rapid cooling and control of the cooling rate. The main drawback, however, is that the units are not simple enough to be used in portable test instruments.

Electrical refrigeration units are solid state devices which make use of thermoelectric (TE) materials. TE cooling devices are uniquely suited for a wide range of applications for which other cooling methods are either impractical or undesirable. TE cooling offers several advantages such as small size and weight, high reliability, simplicity, convenient power requirements, ease of temperature control, and wide operating range, and thus making them attractive for many applications. In addition to the above advantages, TE coolers are compatible with freezing point identifications and temperature measurements. Simple reversal of the current flow through the TE modules switches the system to the heating mode. Thus, a simple device can perform both cooling and rewarming of fuel during the experiment.

Based on these factors, we selected TE heat pumps for our application in this program. A conceptual design of the system configuration showing the TE heat pumps is shown in Figure 6. The unit is rectangular in shape, having a central specimen chamber. The width of the chamber can be varied by adjusting the position of the two TE heat pumps. For normal operation, the width may range from 1 to 5 mm. The length of the chamber will be large compared to the width and may be about 50 to 80 mm. During cooling, TE heat pumps draw the heat from the specimen in the chamber and pump the heat to the ice kept on the other side of the heat pumps. The volume of ice required will be large enough to receive the heat pumped during specimen cooling and yet to remain at the melting point. The height

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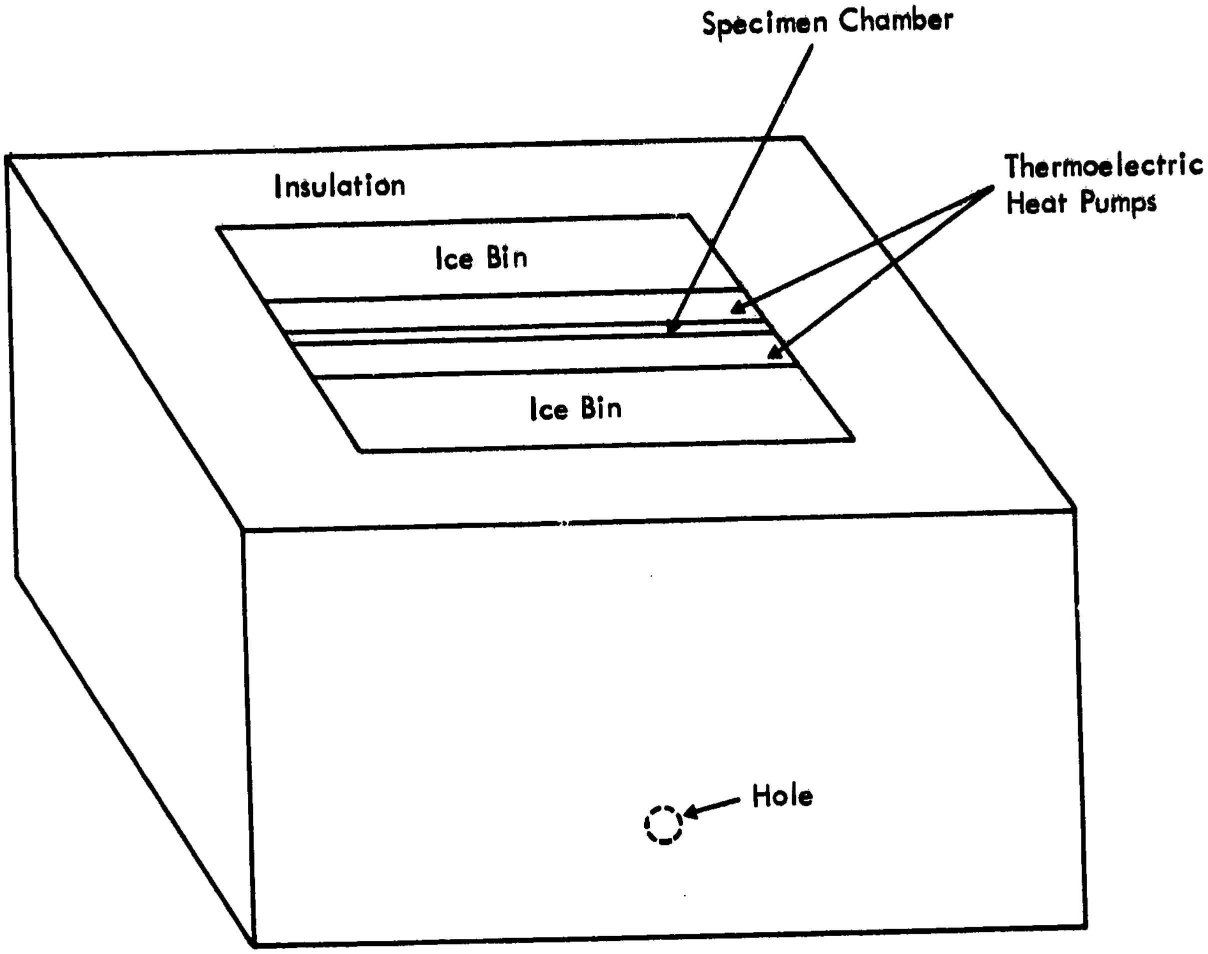

Figure 6 - Cooling and Rewarming Device

of the unit excluding insulation will be of the order of 50 to 80 mm. The bottom of the unit will have a fixed insulation, and the top will have removable insulation. For optical observations, a transverse hole, shown as a dotted line in the figure, will be provided. The electrical power needed to activate the heat pumps will be supplied by batteries (not shown).

2. Selection of concepts for freezing point determination: Based on the literature survey, concepts appearing to be more promising were selected for further experimental evaluation. In all these concepts, cooling devices comprised of TE modules can be used to both cool and rewarm the test fuel.

a. Thermal methods: Our literature survey indicates that most of the earlier work on the determination of freezing point and latent heat of fusion of several one-component and multicomponent substances employed thermal techniques. In thermal methods, the ability of substances to absorb the latent heat of fusion and thus to exhibit an inflection in the temperature-time behavior is used to identify the freezing point. Thermal methods are, in general, direct and simple and require only a few instruments to measure and control temperatures and/or heat fluxes. By virtue of its simplicity and use by earlier workers, we selected thermal methods as one option to be further evaluated experimentally under the current program.

Among the thermal methods, there are different techniques by which the freezing point can be measured, as discussed in Section A of this chapter. These techniques are adiabatic calorimetry, thermal relaxation calorimetry, and differential thermal techniques (both DTA and DSC). Among these techniques, the differential thermal technique has been widely used in the measurement of the freezing point and latent of melting. Therefore, we selected the differential thermal technique as one possible concept among the calorimetric techniques for further evaluation. We specifically favored the DTA method over the DSC, since the former requires only the measurement of temperatures, whereas the latter requires the measurement of both temperature and heat fluxes. The general arrangement of the test setup using the calorimetric technique is shown in Figure 7.

When extensive experimental evaluation was made on this thermal method (the details of which are presented in Chapter IV), it was found that this method has some basic problems. Therefore, the chosen thermal method was slightly modified from the originally planned DTA-type method. In the modified method, the inflection in the temperature-time behavior is directly used to identify the freezing point.

b. Optical methods: As indicated earlier, past work on the determination of the freezing point used mostly calorimetric methods. Next to the calorimetric methods, optical methods were popular. In this method, the process of the visual observation of the disappearance of crystals was replaced by suitable optical sensors which can "observe" the crystals and melting phenomenon. Light scattering, X-ray absorption, and index of refraction were some of the techniques used in optical studies; the description of these methods to measure the freezing point has been presented

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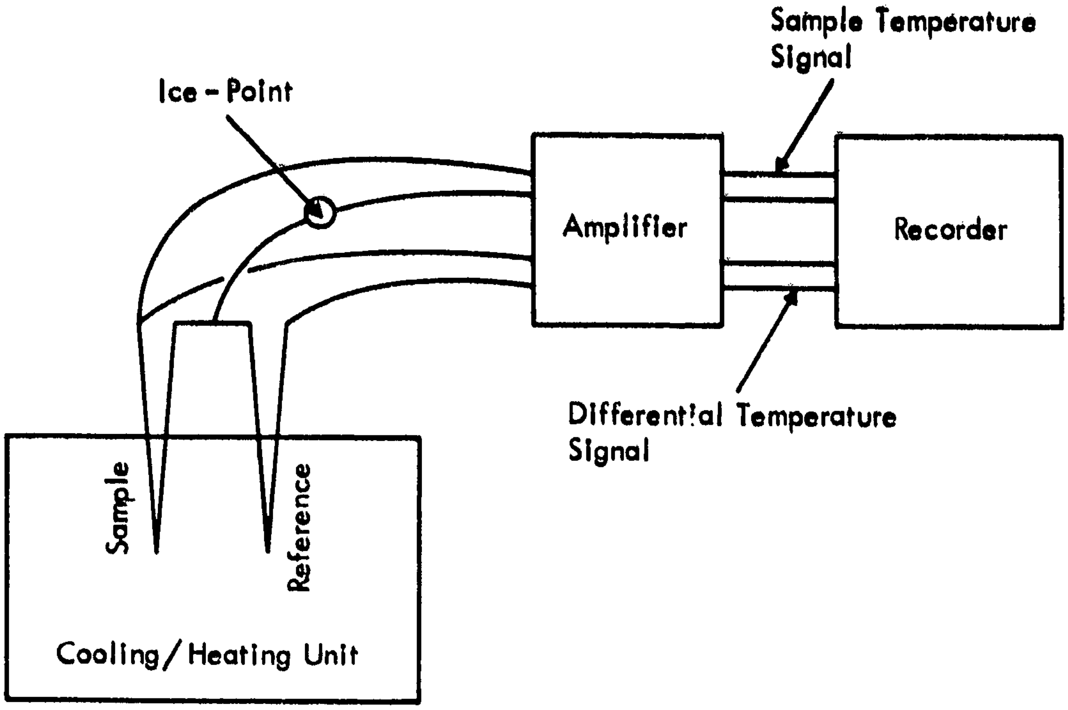

Figure 7 - Schematic of Thermal Method

earlier. Among these techniques, we selected the light-scattering method for our further experimental evaluation, based on the following factors.

The method of X-ray absorption appears to be complex and not suited for field applications. The method requires the sample in the form of powder or frozen droplets deposited on an optical plate. A radioactive α source and the associated control devices are also needed in the apparatus.

The technique of measuring the index of refraction has been widely used in the past. In simple systems, the sample is contained in a cylindrical tube, and the light is passed in the transverse direction so that the sample column will act as a lens in the optical path. When the sample is heated in a cylindrical container, the temperature gradients in the radial direction can cause errors in temperature measurement unless the tube is very small in diameter. The design of the TE unit becomes critical if a small diameter tube for the sample is selected. Therefore, this technique was not considered as a candidate for our further experimental evaluation.

Light-scattering techniques measure the changes in transparency during heating a sample. In this case, the sample is contained in a thin flat surfaced cell and held in the path of light. The TE unit, described earlier in this section, can be used easily in this scheme with minor modifications. An optical path is needed to "see" through the sample while it is being heated, and this can be accomplished by having a hole in the insulation and designing the TE unit with corresponding holes in each. This method was chosen for further investigation. The schematic of the test setup is presented in Figure 8.

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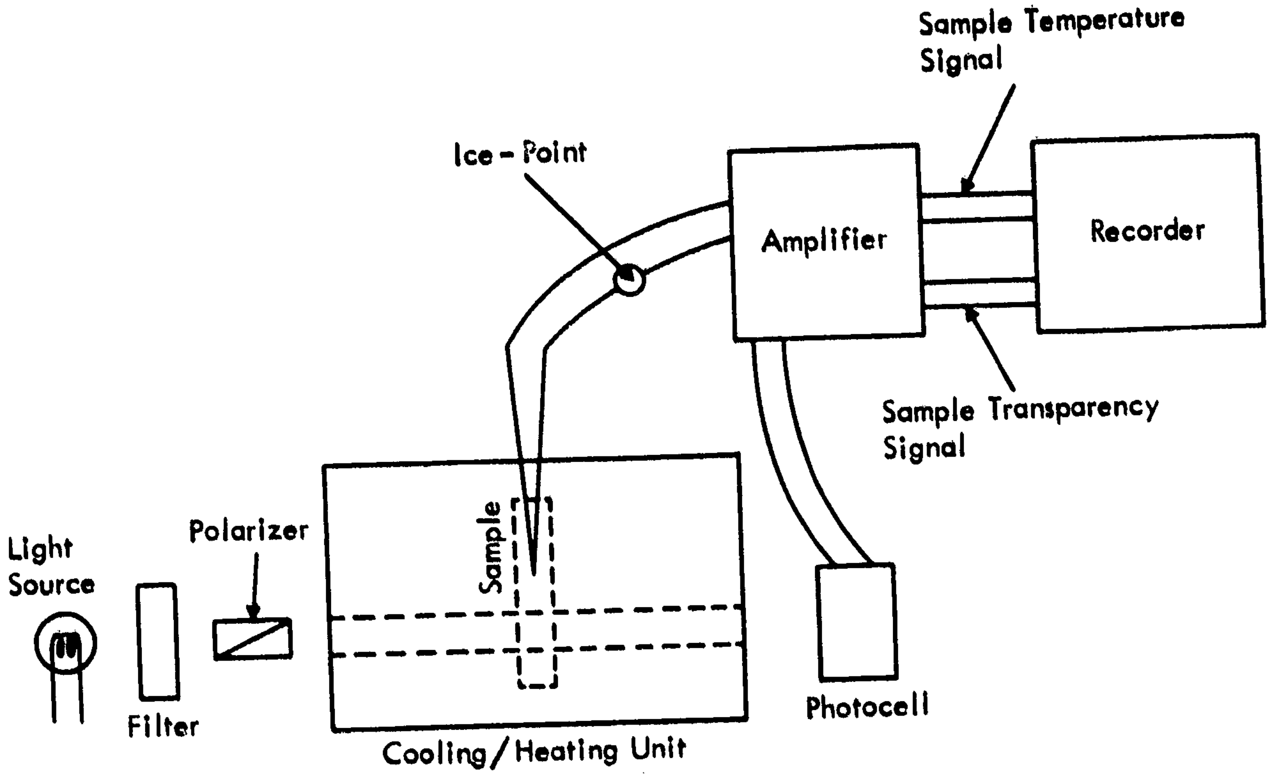

Figure 8 - Schematic of Optical Apparatus

III. LABORATORY TEST APPARATUS

A laboratory test apparatus was designed and fabricated to experimentally evaluate the thermal and optical concepts selected on the analysis described in Chapter II. In both thermal and optical methods, the fundamental requirement was a TE cooling and rewarming device. During the design process, it was observed that the test setup can be designed incorporating both thermal and optical techniques in one unit. In such a test setup, the values of the freezing point of a test fuel can be determined simultaneously from these two independent techniques. Integrating two different methods into a single test unit offers several advantages. The total number of tests to be performed to evaluate the two methods are reduced by a factor of two, since each single test is equivalent to two tests if they were conducted in different test setups. Comparison of the results obtained by the calorimetric and optical methods is more meaningful, since all measurements are taken under identical conditions for both cases. Therefore, we decided to incorporate both thermal and optical techniques into a single test unit.

A. TE Cooler

The principal element in the cooling and rewarming device of the test setup is the TE cooler. The functions of the TE cooler are: (a) to cool the test fuel and the reference to a temperature below the anticipated freezing point, and (b) to rewarm the sample fuel and the reference to observe the melting phenomenon and thus to determine the freezing point. A duration of 5 min was selected in the design to cool the fuel and reference. Another 5-min duration is required to observe the melting and record the freezing point. Thus, we estimated that a single test can be completed in about 10 min time.

While cooling the test fuel (and reference), the heat is removed from the fuel, and this heat plus the heat added in the form of electric power to the modules are rejected to ice which was maintained at 0°C in the ice bin. We assumed the minimum temperature to which fuel may have to be cooled is -50°C. An important parameter in the design of TE coolers is the difference in temperature between the cold side and hot side of the cooler. The maximum difference in the present case is [0 - (-50)] 50°C. For temperature differences as high as 50°C, coolers must be constructed by cascading the modules into two stages. In the first stage, the heat will be pumped from -50°C to an intermediate temperature (about -25°C); and in the second stage, the heat will be pumped from the intermediate temperature to 0°C. Under steady-state conditions, the second stage will have to pump approximately three times the heat that is pumped by the first stage. Therefore, the number of elements in the second-stage modules was three times that in the first stage.

Several TE modules manufactured by different companies were considered in the analysis. We obtained the performance curves of different modules from the manufacturers. From these curves, the property values such as Seebeck coefficient, thermal conductance, and electric resistance of each element in the module were calculated. Using these property values, the performance curves of a two-stage cascaded cooling unit were generated. Figure 9 shows one such performance curve. For this case, the ratio of the number of elements in the second stage to that in the first stage is 3.043. The plot gives the heat pumping rate in watts by one TE module having 35 elements. It can be seen from the figure that the heat pumping rate is a function of supply voltage and the fuel temperature T_c. At an instant, when the fuel temperature is 7°C (280 K), each module (of 35 elements) will pump 9 W of heat, whereas the same module will pump only 2.5 W when the fuel temperature is -53°C (220 K). These values represent the performance only under steady-state heat transfer conditions. These plots are not directly usable for our application, since the actual heat transfer process is not steady state. Performance data were not generated for TE coolers operating under transient conditions, since the modeling of such heat transfer processes is very elaborate and would require considerable technical effort. Instead, calculations were made to determine the cooling load based on average properties. These calculations showed that the average cooling rate required to cool the sample to about -50°C in 5 min design time was 20.55 W.

We assumed that this entire load of 20.55 W would be applied at the cold junction of first-stage modules. This is a conservative assumption, and the actual performance was expected to be better than that predicted with this assumption.

Each module of first stage can pump heat initially at the rate of 8 W when the cold junction is at 0°C, and the rate reduces gradually to 2.5 W when the cold junction reaches -50°C (see Figure 9). The average rate of cooling of each module would then be 5.25 W. Therefore, four first-stage modules would be able to pump a total heat of 21 W.

The general arrangement of TE coolers is shown in Figure 10, and the components of the cooler on one side of the sample and reference holders are shown in Figure 11.

1. Sample holder: The sample holder accommodates the fuel to be tested. The sketch of the sample holder is also shown in Figure 11. The holder has a length of 3 cm, a height of 4 cm, and a width of 0.4 cm (outer dimensions). The holder was made of stainless steel sheets 0.5-mm thick. Two end pieces and one bottom piece was first bent to the shape of a bracket, then soldered to the two main plates in position.

Two optical windows were then mounted on the main plates as shown in the figure. The windows were glued to the plates using adhesives such as Super Glue.

2. Reference holder: The reference holder resembles the sample holder in all respects except that the reference holder does not have optical windows. Figure 11 shows the sketch of the reference holder also.

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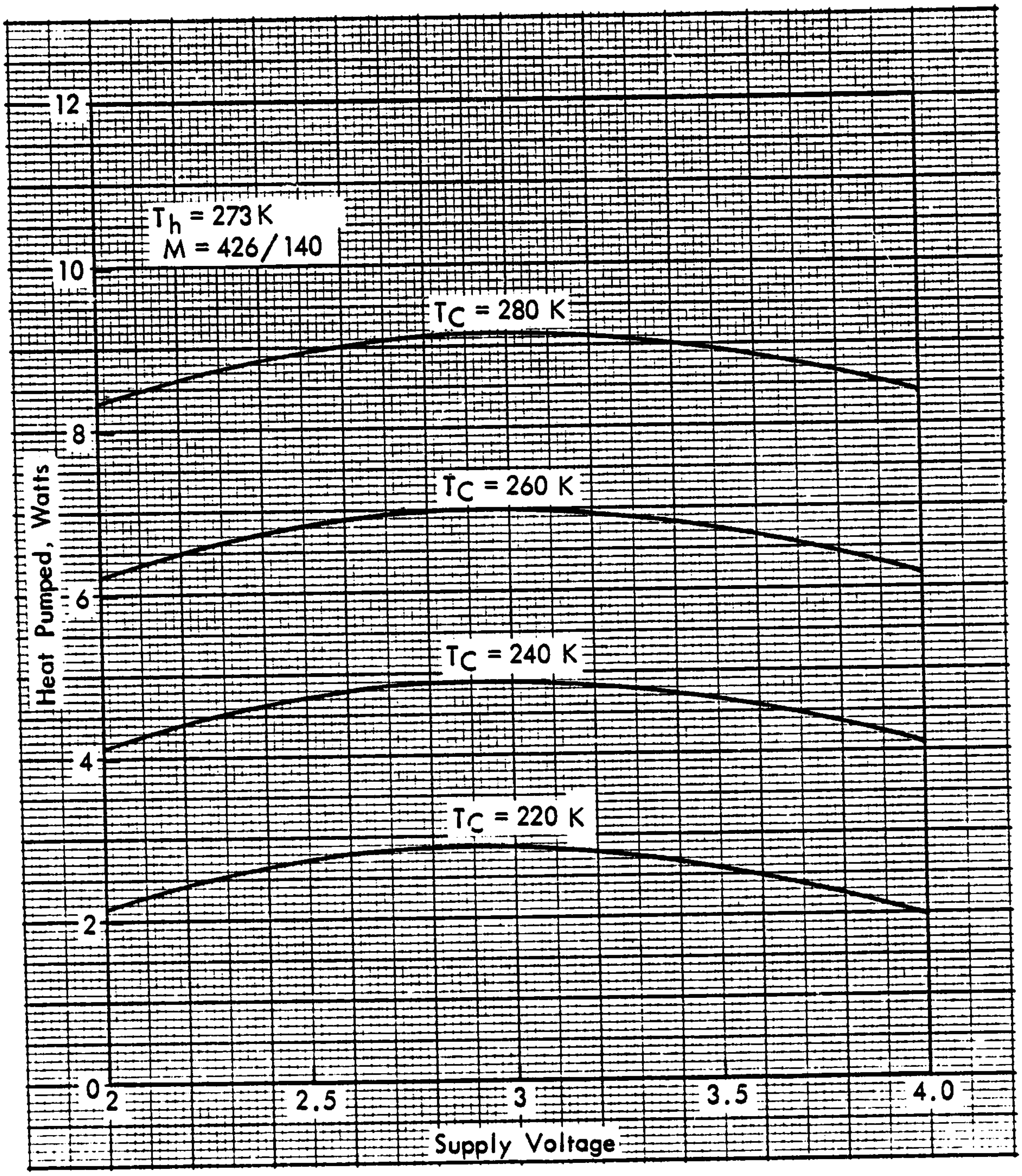

Figure 9 - Heat Pumping Capacity of Two-Stage TE Cooler

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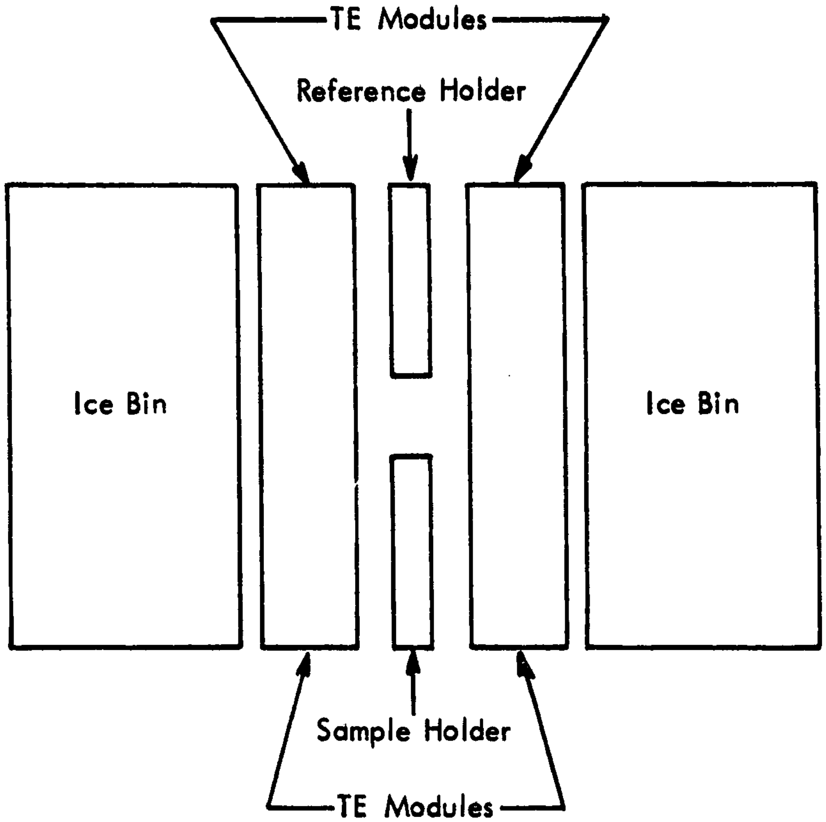

Figure 10 - Two-Stage TE Cooler

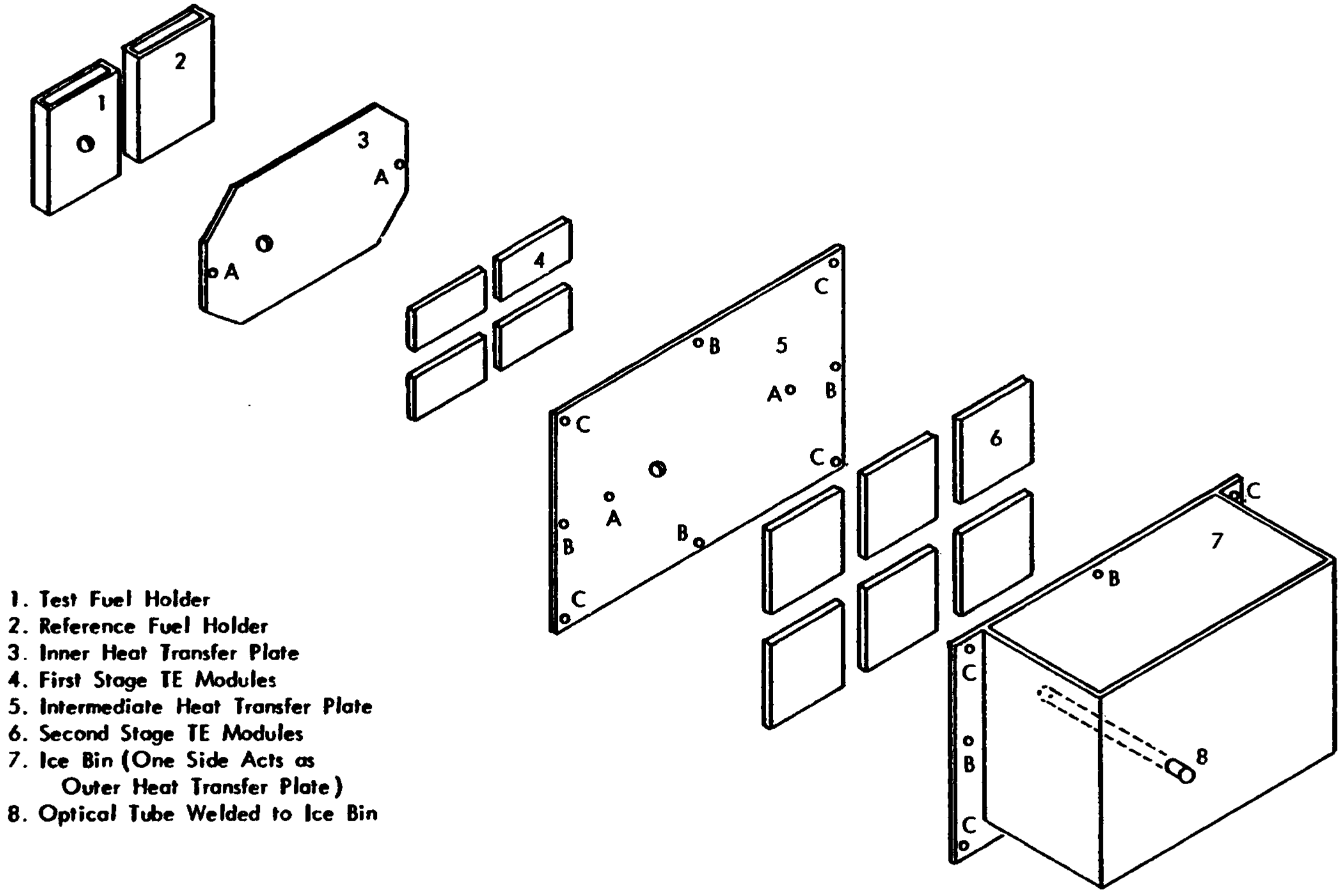

Figure 11 - TE Cooler Assembly

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3. Heat transfer plates: Two heat transfer plates are required in the cooler assembly on each side. An inner heat transfer plate conducts the heat from the sample and reference holders to the first stage of TE modules. Another intermediate heat transfer plate serves to conduct the heat from the first stage to the second-stage TE modules. The heat transfer from the second stage to the ice bath is carried through the wall of the ice bin itself. The heat transfer plates 3 and 5 (see Figure 11) are made of copper. The thickness of these plates are 1.6 mm. This thickness was found sufficient to maintain a flat surface when screws were tightened, and at the same time low enough to minimize the heat capacity. (The heat capacity of different components must be kept minimum so that the cooling rate can be very high for the given capacity of TE modules.)

4. TE modules: The TE modules manufactured by Melcor Materials Electronic Products Corporation was used in the test setup. Modules (Catalog No. CP1.4-35-06L) have the base dimensions of 1.5 x 3.0 cm, and four of these were used in the first stage. Modules (Catalog No. CP1.4-71-06L) have the base dimensions of 3 x 3 cm, and six of these were used in the second stage. For both the sides of the specimen chamber, a total of 20 TE modules were used.

The optimum operating voltage for first-stage modules was found to be 3 V (see Figure 9). Hence, all the four modules could be connected in series to a 12-V DC battery. The optimum operating voltage for second-stage modules is 6 V. Therefore, two modules can be connected in series, and three such series circuits can be connected in parallel in a 12-V battery.

5. Ice bin: The ice bin is a rectangular box having a length of 12 cm, a width of 4.4 cm, and a height of 8 cm. Two ice bins were required in the test setup. The bins were constructed of brass sheets. One face of the ice bin had eight holes drilled on it so that ice bins could be fastened to the TE cooler with the help of screws. In fact, all the elements of the TE cooler, along with the two ice bins, can be assembled with eight screws. The metal tube provided in the cooler extended through the ice bins as shown in Figure 11.

6. Procedure to assemble the cooler: The various components of the cooler were assembled in the following manner. First of all, the inner plate "3", first-stage TE modules "4", and the intermediate plate "5" are fastened together by using two screws through the holes "A." Then, this subassembly, second-stage modules, and the ice bin were fastened together by four screws through the holes "B." The new subassembly forms one side of the TE cooler. Another symmetrical subassembly forms another side, using the same fastening methods. Finally, the two sides were fastened together using four screws through the holes "C." Four nylon spacers were used along with screws at "C" between the two inner heat transfer plates that provide space for accommodating the test and reference fuel holders. During the test, unscrewing the top two screws in the holes "C" permitted the unloading or reloading of fuel samples.

7. Locator for specimen holders: Placing the test fuel holder and reference fuel holder quickly and accurately in their places is possible if we use a locator (Figure 12). Two rectangular slots in the locator can accommodate the test and reference fuel holders. The locator, along with specimen holders, can be inserted into the cooler unit easily and is located in correct position by the heads of the screws through the holes "A." Two small holes provided in the locator top serve to accommodate the thermocouples.

8. Test cooler electrical connections: The electrical series and parallel connections for the TE modules in the first and second stages of one side of the cooler are shown in Figure 13. In each series circuit there were three second-stage modules and two first-stage modules. Four such series circuits (two of them are shown in Figure 13; the other two come from the other side of the cooler) are connected in parallel.

B. Other Components in the Test Setup

A number of components, in addition to the TE coolers and the associated accessories, were required in the laboratory test setup. These included temperature measuring and recording devices, and optical components that were needed to perform optical tests.

1. Temperature measuring and recording devices: A basic requirement during the conduct of freezing point tests (both thermal and optical) was the continuous measurement of the temperature of the test sample during cooling and rewarming as a function of time. For this purpose, we used hypodermic thermocouples manufactured by Omega Engineering, Inc., Model No. HYP-1. This thermocouple was a type T (copper-constantan) grounded junction probe. The thermocouple is kept inside a stainless steel 30-gauge x 12-mm needle that can provide a very fast response. Because of the extreme small size of the needle, it is less likely that it would disturb the surrounding temperature field. One thermocouple is needed to measure the test sample temperature in optical tests and two thermocouples are needed, one to sense the temperature of test sample and another for the reference sample in thermal tests. The thermocouple measuring the temperature of the test sample was also connected to an electronic ice point that eliminated the need for an additional thermocouple and icewater box. The thermocouple measuring the temperature of the reference sample in thermal tests did not require an electronic ice point; this thermocouple is differentially connected to the test sample thermocouple so that the resulting signal is a direct measure of the difference in temperature.

For recording the temperature signals, a strip chart recorder was used. The chart recorder required two channels when the test was conducted using either the thermal or optical technique. When thermal tests were conducted, the two signals recorded were (a) the temperature of the test fuel, and (b) the difference in temperature of the test and reference fuels. When optical tests were conducted, the two signals recorded were (a) the temperature of the test fuel, and (b) the signal, representing the transparency of the fuel, as measured by the optical detector. When a test was

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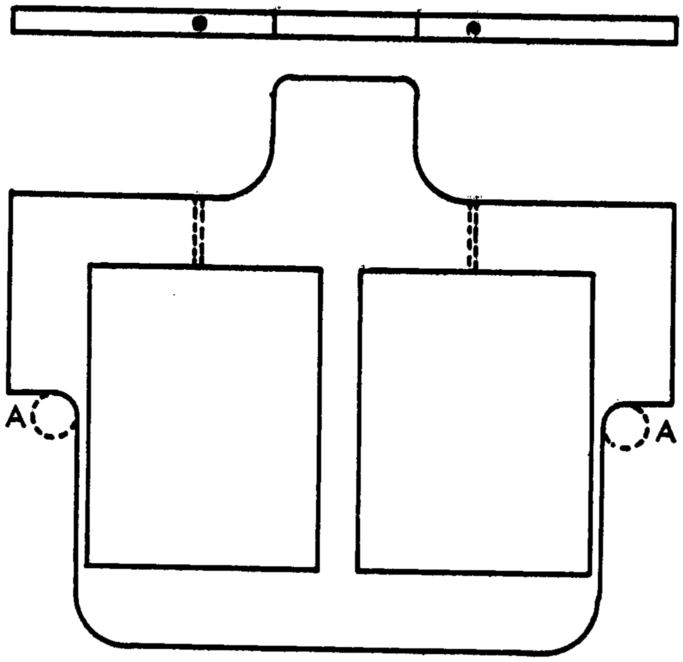

Figure 12 - Locator for Specimen Holders

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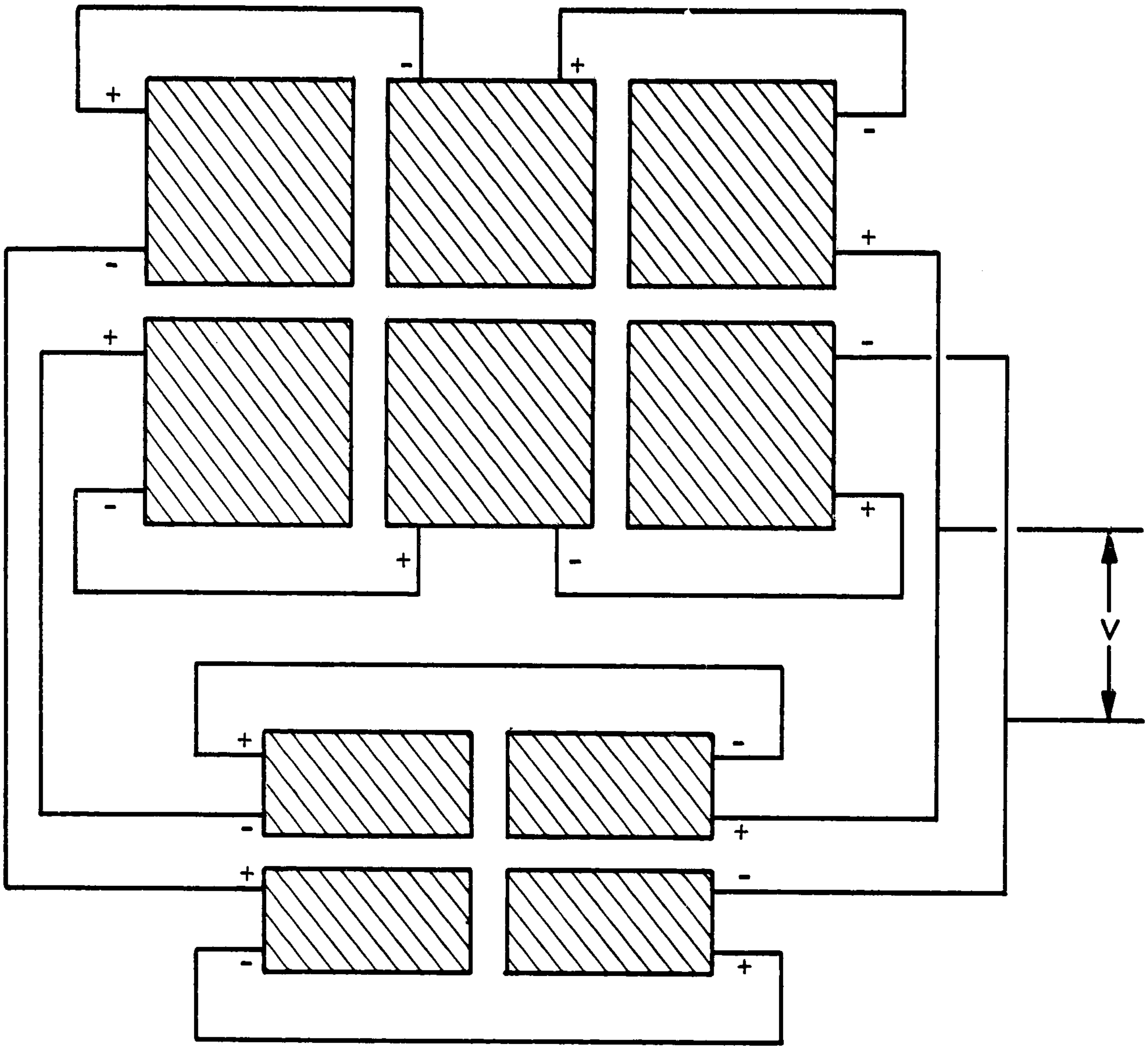

Figure 13 - Electrical Connection to TE Modules

conducted employing both thermal and optical methods, the setup required either a recorder having three channels or two recorders each having two channels. In our test setup, we used two recorders.

2. Optical componets: A number of optical componets were required in the test setup to "observe" the melting phenomenon to determine the freezing point. The essential components were (a) light source, and (b) detector assembly. The details and specifications of optical components are described below.

a. Light source: A requirement in the optical system was a linearly polarized light that would traverse a small diameter hole over a distance of some 16 cm before reaching the sample.

Because of thermal considerations, the bore hole had to be on the order of 5 mm diameter. We could not simply construct an incoherent "lightpipe" to reach the sample, as the state of polarization would then not be reliably known. It would be most difficult, if not impossible, to collimate light from a tungsten lamp well enough to avoid significant grazing reflections off the inner wall of a 5-mm diameter bore hole over a 16-cm path. Further, light exiting the sample must traverse an equivalent 16-cm path through a 5-mm bore hole to reach the analyzer and detector apparatus, where its state of polarization was to be measured. A small, low-power gas laser met the requirement for a highly directional, small-diameter collimated beam.

The use of a laser further simplified the overall design in two ways. The light emitted from a helium neon gas laser was inherently monochromatic, eliminating the need for narrow bandpass filters, and we could easily specify a laser of the type which is highly polarized, which eliminated the need for prism or film polarizers at the source end of the system.

Throughout the process of component selection, we kept in mind the eventual design of a field portable system. Here we specified a laser which may be operated either from 117 VAC or from a 12-V battery.

We narrowed our choices among suitable DC-powered lasers by giving attention to the physical ruggedness of the design. The Hughes Model 3222-H-PC was designed for such applications as field surveying instruments and construction site alignment equipment. The wave length of the laser light is 6328 angstroms. Along with its small size, it suited our purposes in the laboratory test setup.

b. Detector assembly: At the time of selecting a suitable detector assembly, we did not know what range of sensitivity was needed at the detector end of the optical system. We therefore looked for a type of detector that gives maximum sensitivity and allows for easy scale-down of overall sensitivity should that prove necessary. A photomultiplier tube, together with an adjustable high-voltage power supply and a multirange amplifier, was found to meet this requirement. Laboratory-grade photomultiplier systems are readily available, but we also had in mind an eventual design suitable for field portable use. We identified one particular system meeting our requirements for sensitivity, scaling, and physical size, the Model 21-150 integrated detector assembly from Research Support Instruments. This device is provided in a potted module approximately 5 x 3.8 x 10 cm overall. Within that small rugged package were included the adjustable high-voltage power supply, a tri-range linear amplifier, and a power supply regulator. Input power requirements are 12 to 30 V DC at 15 mA. The 9-mm diameter active face of the photomultiplier tube allowed for simple alignment fixtures as we measured the intensity of a laser beam nominally 0.64 mm in diameter. Optionally, we provided a small optical diffuser to spread the laser beam over a larger fraction of the photomultiplier tube face.

c. Assembly of optical components: The arrangement of various components used in the optical portion of the test setup are shown in Figure 14. The polarized light source (laser) and a red filter were placed on one side of the TE cooler. Two neutral density filters, a mirror-reflex housing, glass diffuser, analyzer, electronic shutter, and the photomultiplier tube are placed on the other side.

The function of the laser was to provide a monochromatic light which is highly polarized. The laser eliminates the need for polarizers and narrow filters at the source end. A red filter is mounted, however, at the source end to eliminate the small amount of incoherent, residual blue light which is emitted from the laser. At the receiving end, two neutral density filters have been mounted to adjust the intensity of light transmitted by the fuel sample within the acceptable range of the detector. Following the filters was a mirror-reflex housing, incorporated in the optical path to aid in the proper alignment of the system. A glass diffuser was added next that would spread the pencil-thin beam over the entire sensing area of the photomultiplier tube. The diffusion of light also helped to protect the localized sensing area of the detector from burning that could be otherwise caused by the pencil-thin incident light. The analyzer was mounted following the diffuser and the purpose of the analyzer was to achieve nearly complete extinction of light by mounting its axis at 90 degrees to the axis of polarization of the laser source. The photomultiplier tube sensed the light incident over its face and provided a voltage signal proportional to the incident light. The unit had an integrated high-voltage power supply and a 3-decade linear amplifier. The output signal of the photomultiplier tube was fed to the chart recorder.

During the conduct of experiments, the optical path was supplied with nitrogen from a bottle so as to keep the optical passage free from moisture deposition at low temperatures.

C. Modified TE Cooler

The two-stage TE cooler, described in Section A of this chapter, was used to conduct several thermal and optical tests. The results of these tests can be found in Chapter IV. An important observation that was made in the operation of this TE cooler was that the cooler was not capable of

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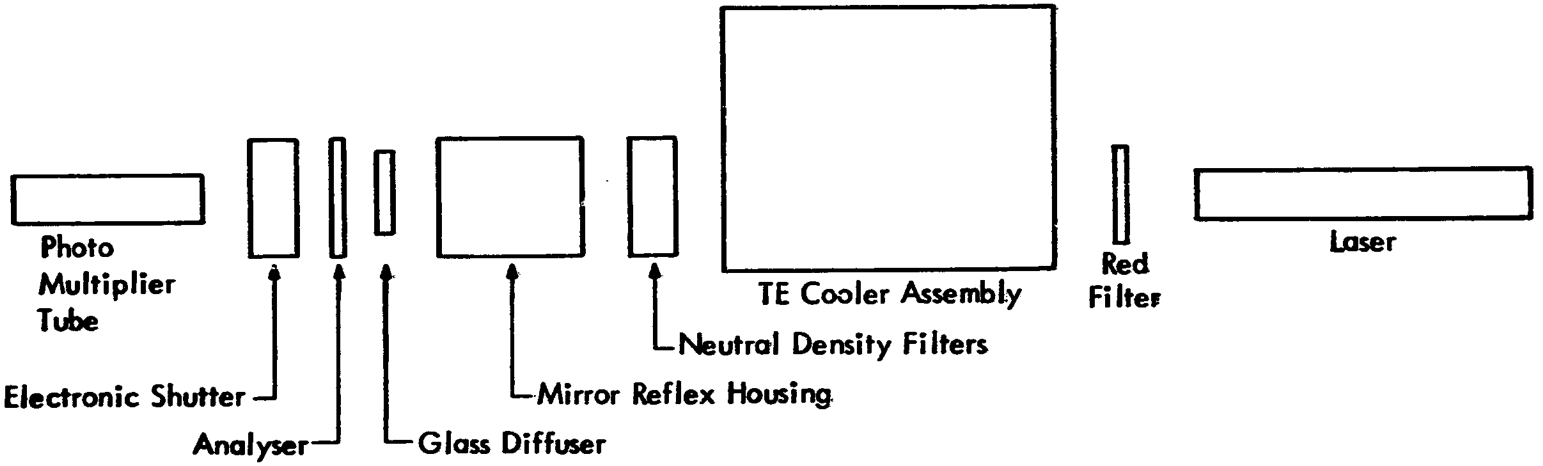

Figure 14 - Arrangement of Optical Components

attaining the design low temperature of -50°C. The minimum temperature attainable in this unit was on the order of -45°C. Because of this drawback, we were unable to test aviation fuels whose reported freezing points were below approximately -35°C. For the purpose of extending the freezing point tests to fuels whose freezing point was as low as -42°C, a TE cooler that can attain a low temperature of -50°C or below was needed. At the time when this need was felt, it was also decided that the new TE cooler be designed for conducting thermal tests only. By doing so, the configuration of the TE modules in different stages can be much simplified because of the absence of an optical path in the unit.

The new TE cooler configuration is shown in Figure 15. The new unit had three stages of TE modules to pump the heat from the fuel to the ice-water mixture. A three-stage cooler can attain a lower temperature than that attainable in a two-stage cooler. The unit was also designed so that no inner or intermediate heat transfer plates were required to connect the three stages. This was accomplished by providing identical TE modules in each stage. The DC power supplied to each stage was, however, varied; the first stage was supplied with a small amount of power, the second stage with medium power, and the third stage with a large amount of power. The electric circuit for TE modules provided in the new cooler unit is shown in Figure 16. The unit had a total of 12 TE modules, six of which were used for the test fuel and another six for the reference fuel. These modules were purchased from Melcor Materials Electronic Products Corporation (Catalog No. CP1.4-71-062).

The size of the sample holder and reference holder was also changed to 3 x 3 x 0.4 cm to accommodate these two holders in the new configuration of TE modules.

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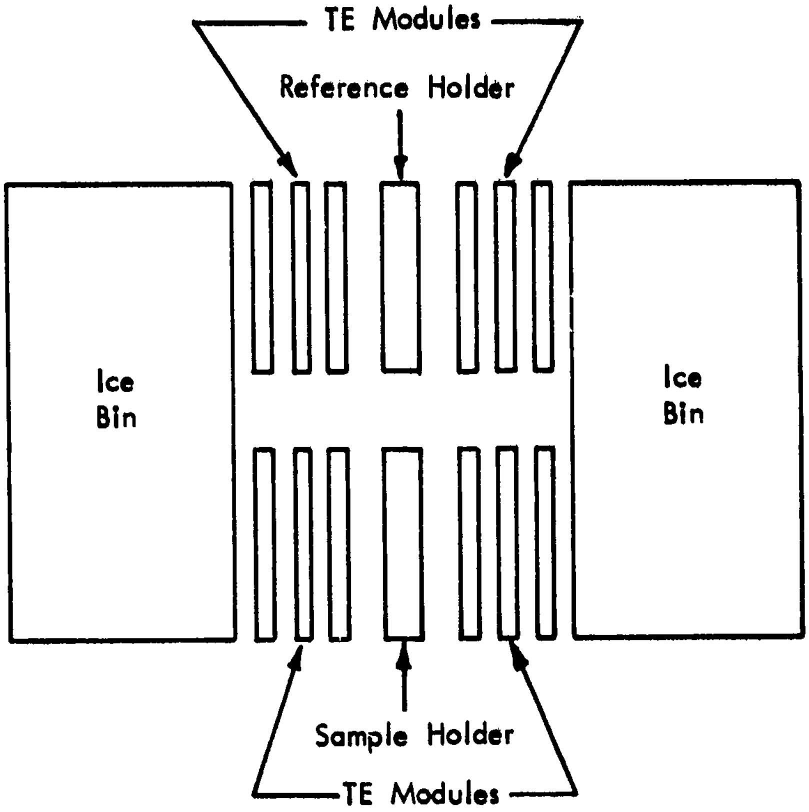

Figure 15 - Three-Stage TE Cooler

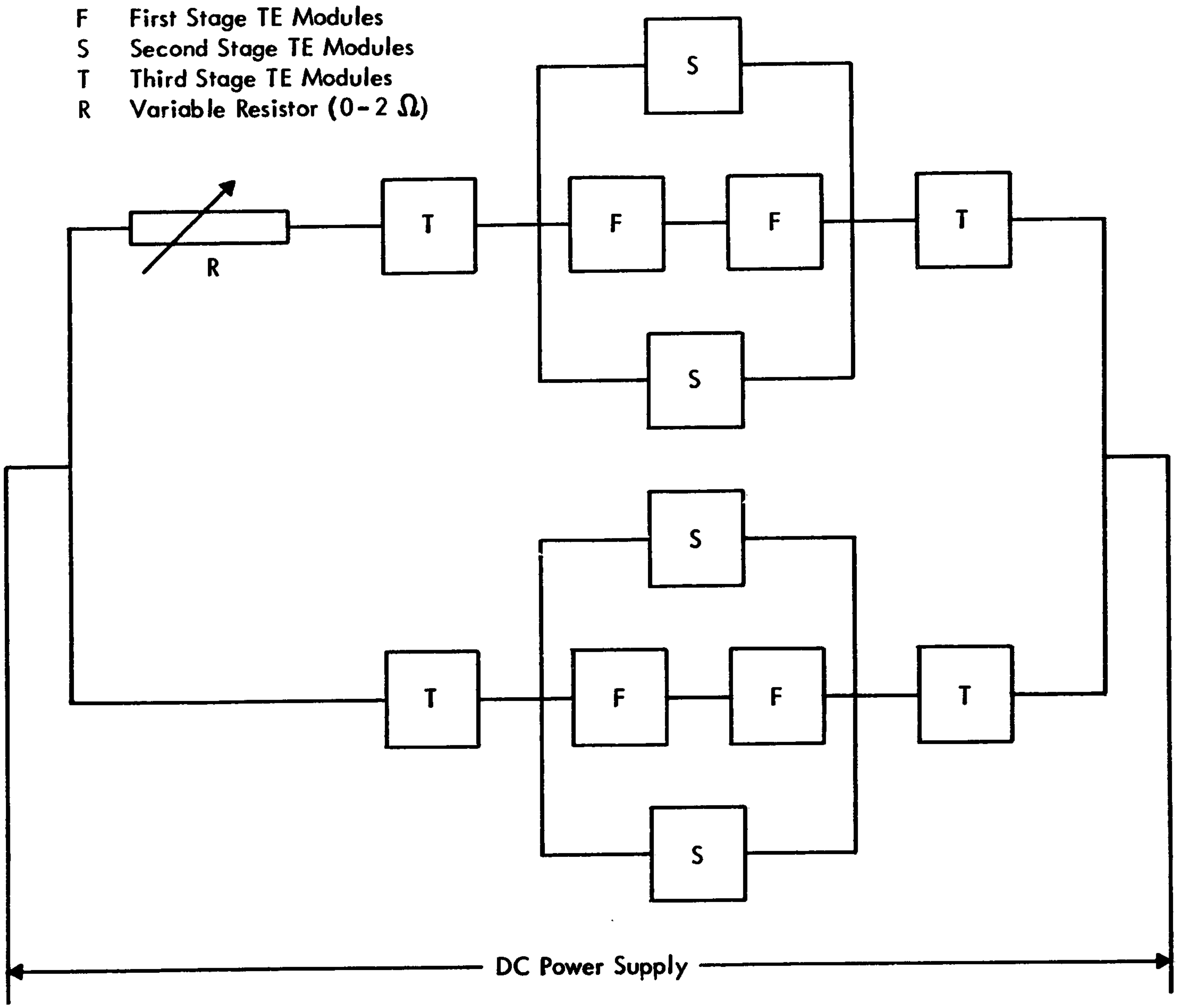

Figure 16 - Electrical Circuit for TE Modules

IV. EXPERIMENTAL DATA AND ANALYSIS

Based on the literature review and the analysis of various methods of freezing point measurement, we selected thermal and optical techniques for further experimental evaluation. The details of the analysis and the rationale for selection were presented in Chapter II. Subsequently, we proceeded to design and construct the laboratory test setup in which both thermal and optical techniques can be evaluated experimentally. In Chapter III, the description of the laboratory test setups have been presented. In this chapter, the test procedures, the results obtained, problems encountered, and the conclusions based on the results are presented.

A. Thermal Tests - Differential Thermal Analysis Approach

In this approach, the test required the use of a reference fuel in addition to the test fuel. When the test and reference fuel were heated or cooled at the same rate, the difference between the temperatures of the test fuel and reference fuel would be constant as long as no thermal event occurred in the test fuel. When a thermal event occurred (such as freezing or melting) the difference in temperature increased and attained a maximum at the end of the thermal event. The freezing point was therefore related to the occurrence of maximum temperature difference.

The reference fuel for these tests must be so chosen that it does not undergo any thermal event such as freezing or melting during the test. For our tests, isooctane $(CH_3)_3C \cdot CH_2 \cdot CH:(CH_3)_2$, was chosen as the reference fuel; isooctane's reported freezing point is -107.4°C which is much lower than the temperatures at which all our tests were to be conducted.

1. Principle involved: The principle involved in thermal tests using the differential thermal analysis approach is illustrated in Figure 17. In this figure, typical plots showing the temperature of the fuel (T) and the temperature difference (ΔT) between the test and reference fuels are shown as a function of time for a hypothetical one component and a hypothetical multicomponent substance. In the plots shown for one component substance in Figure 17(a), it is assumed that the substance has previously been frozen completely to solid phase. When the test and reference fuel is rewarmed, the temperature of the fuel increases until the melting begins. The temperature difference stays constant and minimum. As soon as the melting process commences, the temperature of the fuel remains constant and the entire heat absorbed is used as latent heat. However, since the reference fuel do not undergo any thermal event, the temperature of the reference continues to go up, thus exhibiting an increase in ΔT as shown. The increase in ΔT continues until melting is completed. When the melting is completed, the test fuel absorbs no further latent heat, and therefore its temperature rises again; this is followed by a reduction in ΔT. Therefore, the time at which ΔT attains a maximum corresponds to the end of melting process. By definition, the temperature at this point is the freezing point.

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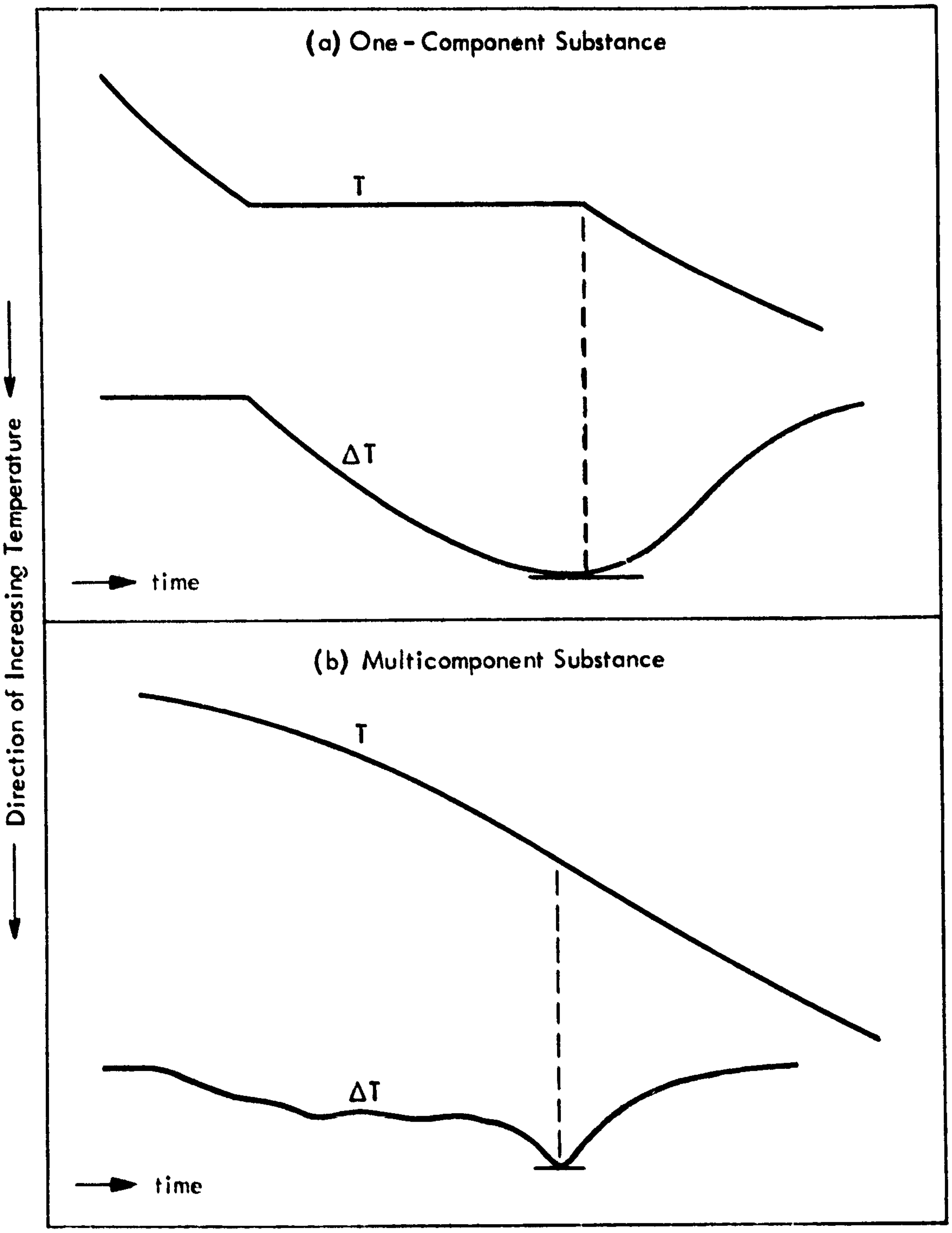

Figure 17 - Illustration of the Thermal Method

In the plots shown for multicomponent substance in Figure 17(b), it is assumed that the substance has previously been frozen either partly or completely. When the test and reference fuel is rewarmed, the temperature of the fuel increases. The increase in temperature occurrs whether or not the fuel undergoes melting. However, the rate of increase of temperature will be relatively less if the fuel undergoes melting since the fuel absorbs both sensible and latent heat. In contrast, the reference fuel absorbs only the sensible heat; therefore, as the test fuel melts, the difference in temperature deviates from the minimum value. The changes in ΔT was not usually uniform since different components may melt at different temperatures absorbing different latent heats. When the melting of all components is completed, the rate of increase of test fuel's temperature again increases which leads to the reduction in ΔT. Therefore, ΔT attains a maximum when the melting is complete. By definition again, the temperature at this point is the freezing point.

In actual lab experiments T and ΔT curves were generated by the chart recorder; the freezing point was then observed by noting the time at which the ΔT attained a maximum and by reading the fuel temperature at that time.

2. Test procedure: In the thermal method the test sample holder was filled with the fuel to be tested and the reference holder with isooctane. The holders were then placed in position into the locator (see Figure 12). The locator, carrying the holders, was then carefully placed inside the TE cooler in the space between the two inner heat transfer plates. The screws were then tightened to keep the holders in good contact with inner plates. Thermocouple probes were then inserted through the holes in the locator into the test fuel and reference fuel. The ice bins were filled with a mixture of ice and water (about 20% water by volume). The setup was at this point ready to conduct the tests.

The power supply (either a DC battery or a DC power supply) was switched on so that the current flow to the TE modules cooled the fuels (test and reference). The chart recorder was also switched on so that both the temperature of the test fuel and the difference in temperature between the test and reference fuels were recorded continuously as a function of time. When the temperature of the fuel reached a temperature about 10 to 20°C below its anticipated freezing point, cooling was stopped and the rewarming started. Reversing from cooling to rewarming was achieved by reversing the current flow to the TE module. The chart recorder continued to record the T and ΔT signals. Rewarming was continued until the ΔT signal exhibits a maximum and then returned towards the baseline. The experiment was stopped at this time. The freezing point was observed by noting the time at which the ΔT attained a maximum and by reading the fuel temperature at that time.

3. Test results: Several thermal tests using the DTA technique were conducted to evaluate the suitability of this method for developing a portable, rapid freezing point apparatus. Test samples included both single component and multicomponent substances. The results are shown for the following test fuels.

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(a) One component: Tridecane, dodecane, water, and tertiary butyl alcohol.

(b) Multicomponent: Aviation fuels designated as LFP-1, LFP-4, LFP-6, LFP-7, LFP-9, ERBS, and Fuel No. 8.

Figures 18 through 26 show the plots obtained in thermal tests conducted on several test samples. In all these plots, the curves that appear light and thin show the actual temperature of the test fuel as a function of time. The curves that appear dark and thick show the difference in temperature between the test sample and isooctane as a function of time. In the chart recorders that were used in these tests, arrangement of tracing pens was such that, at a given instant of time, the pen tracing the T curve occupied a position which was 2.5 subdivisions (in the background graph) ahead of the pen tracing the ΔT curve. Therefore, a point in the ΔT curve and a point displaced to the right by 2.5 subdivisions in the T curve correspond to the same instant of time. About five tests were conducted on each test fuel.

Table 1 shows the results obtained in these freezing point tests. The results shown in this table for LFP-1 and LFP-9 were obtained in the three-stage TE cooler and associated accessories. The results of all other fuels were obtained in the two-stage TE cooler which was constructed first. Pure species such as water, dodecane, and tridecane, exhibit a plateau in the temperature-time history while absorbing or releasing the latent heat. Thus, it was possible to determine the freezing point of these pure species by directly observing the temperature at which the plateau occured. Table 2 shows the results so obtained.

TABLE 1

RESULTS OBTAINED IN TESTS USING THERMAL METHOD
(Freezing Point in °C)

		Test						
S No.	Test Fuel	No. 1	No. 2	No. 3	No. 4	No. 5	Average	Reported*
1	Tridecane	-5.3	-5.3	-5.3	-5.3	-5.3	-5.3	(-5.5)
2	Dodecane	-8.9	-8.9	-8.6	-8.5	-8.9	-8.8	(-9.6)
3	Water	0.4	0.8	1.4	0.8	0.5	0.8	(0.0)
4	Butyl alcohol	24.3	24.3	23.7	23.7	-	24.0	(25.5)
5	LFP-1	-42.2	-42.2	-41.5	-42.2	-41.7	-42.0	
6	LFP-4	-12.3	-13.6	-13.1	-13.6	-13.1	-13.1	
7	LFP-6	-24.5	-23.9	-25.0	-26.1	-25.5	-25.0	
8	LFP-7	-13.1	-14.1	-13.8	-13.4	-13.4	-13.6	
9	LFP-9	-43.6	-44.3	-40.7	-42.2	-42.9	-42.7	
10	ERBS	-21.7	-21.7	-22.8	-23.4	-22.8	-22.5	
11	Fuel No. 8	-33.7	-32.0	-32.0	-33.7	-	-32.8	

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* Literature reported values.

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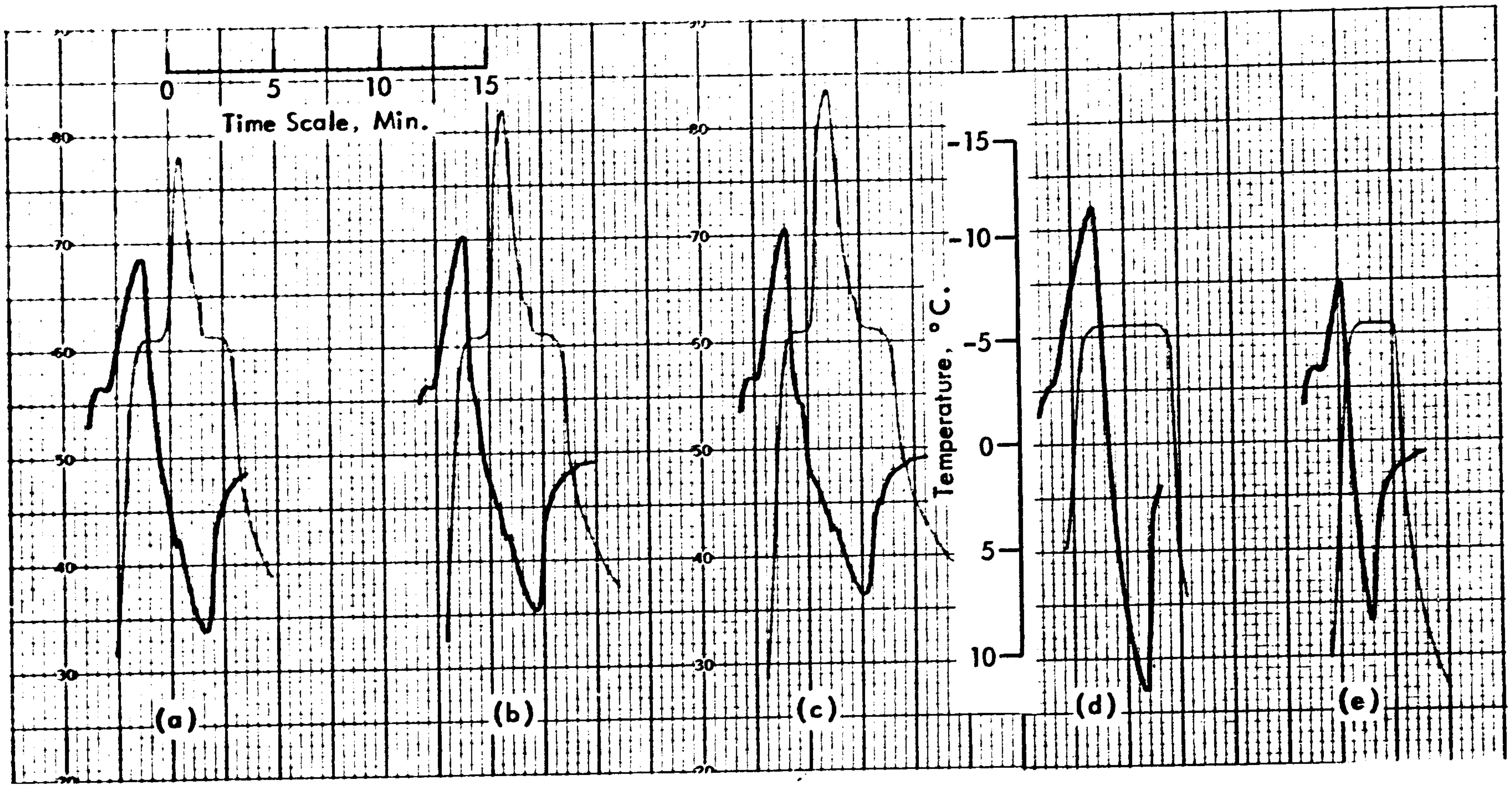

Figure 18 - Results of Thermal Tests on Tridecane

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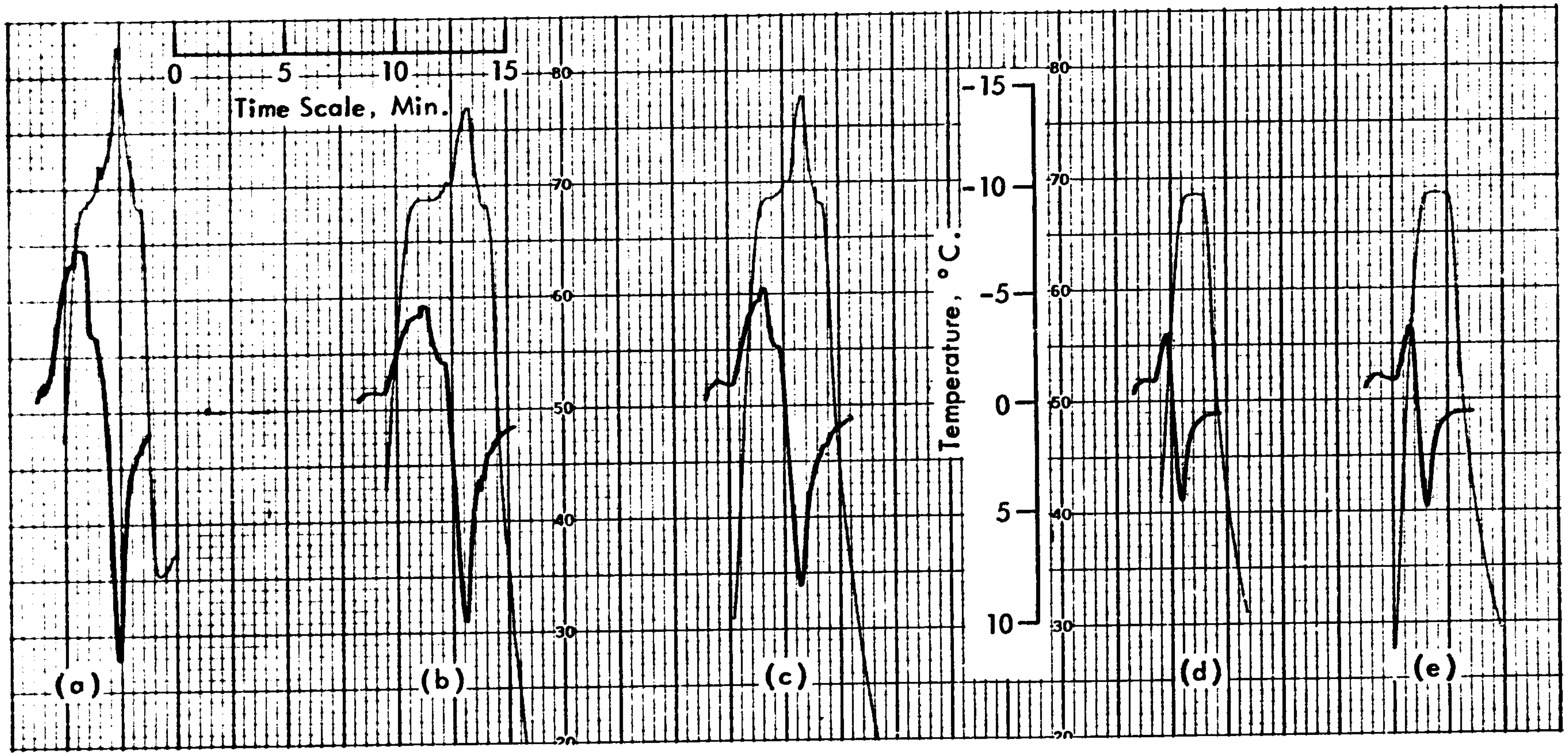

Figure 19 - Results of Thermal Tests on Dodecane

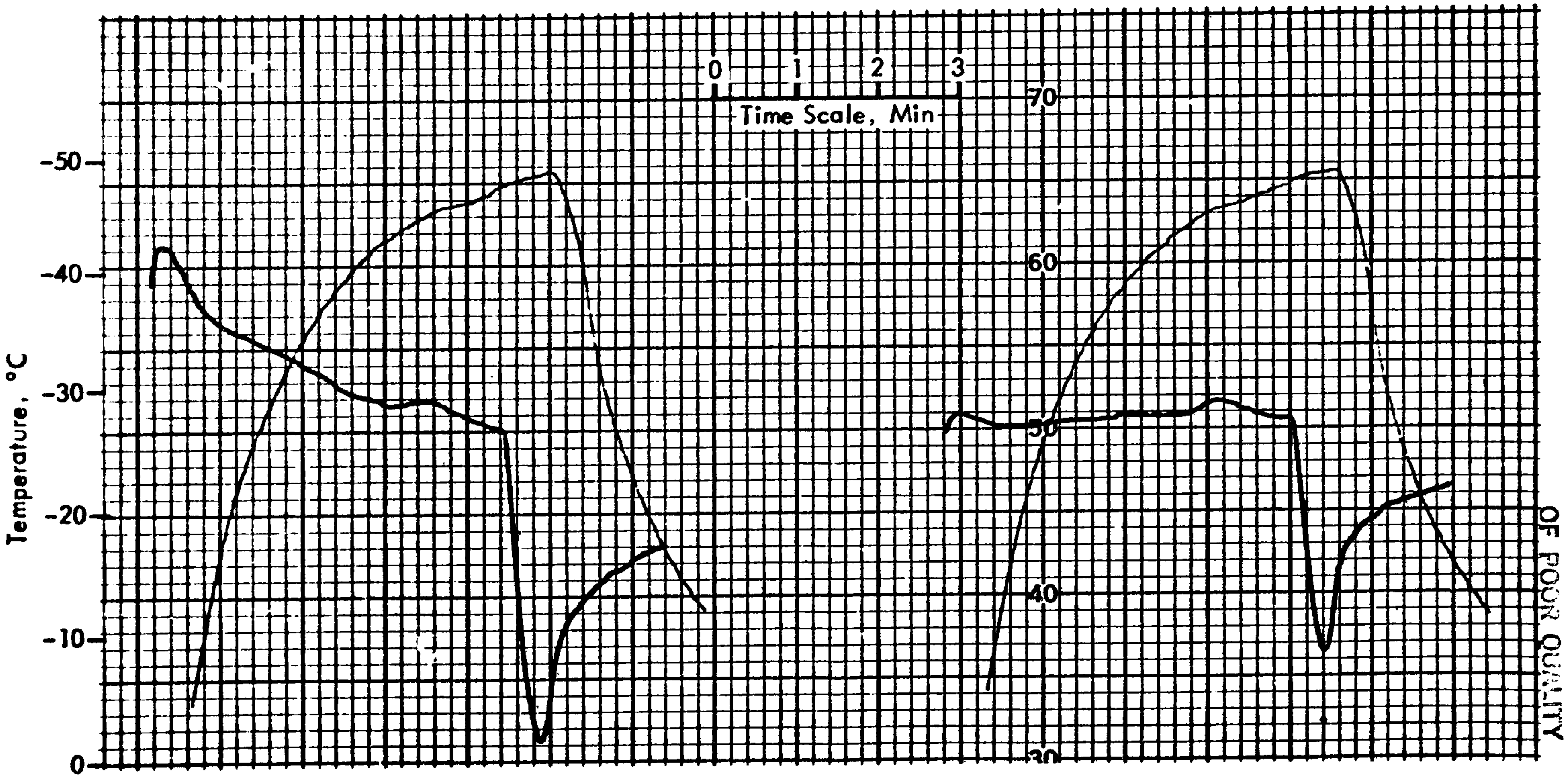

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Figure 20 - Results of Thermal Tests on LFP-1

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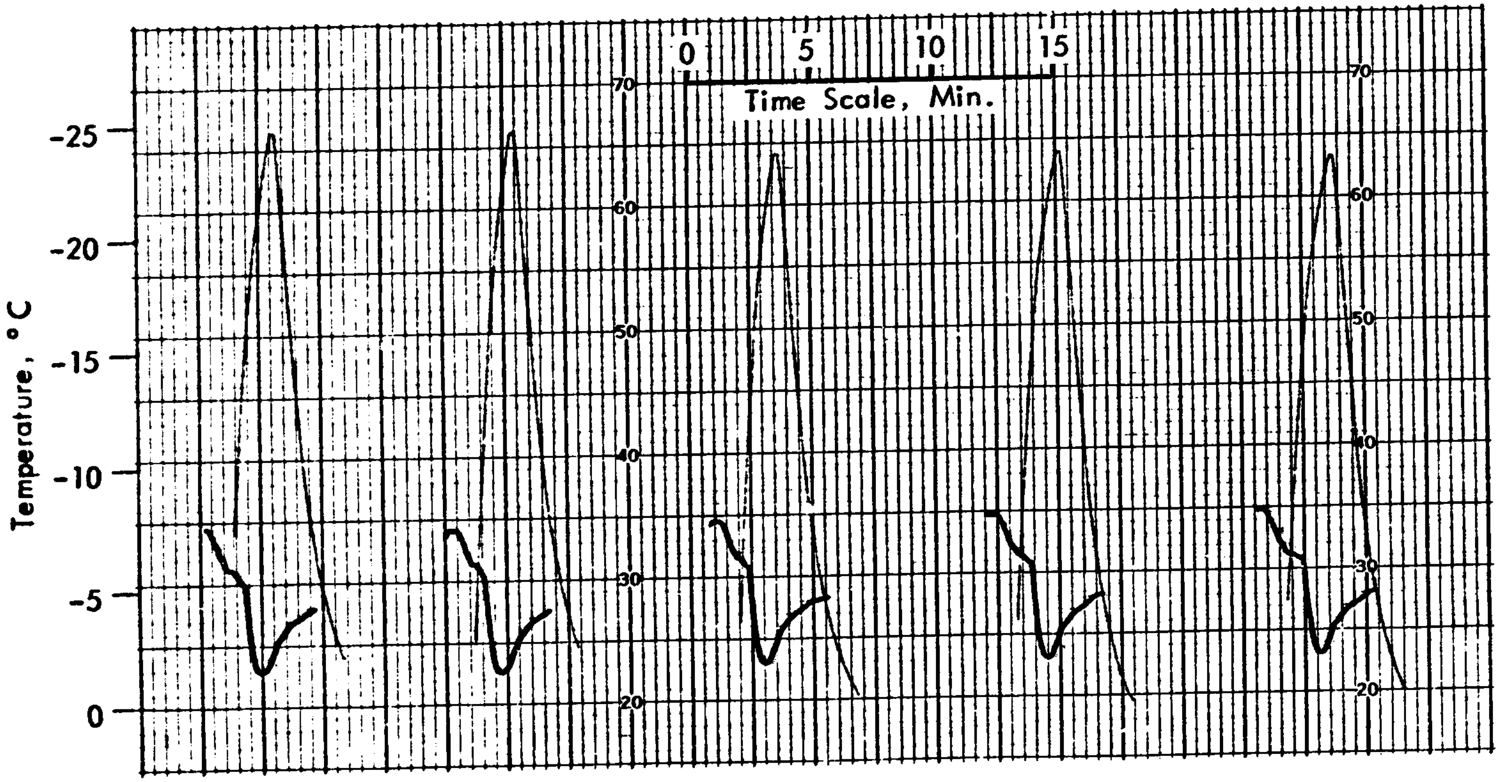

Figure 21 - Results of Thermal Tests on LFP-4

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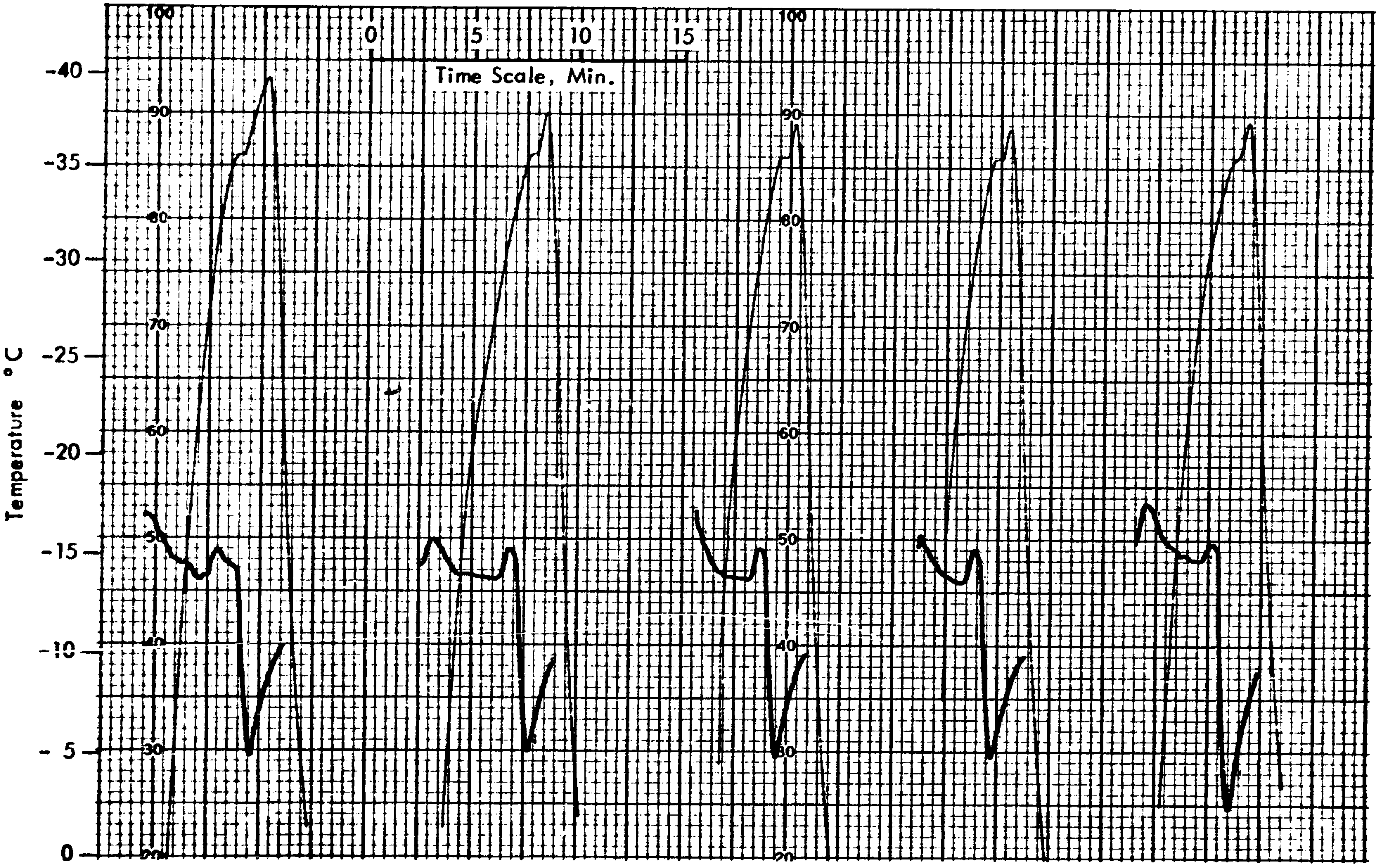

Figure 22 - Results of Thermal Tests on LFP-6

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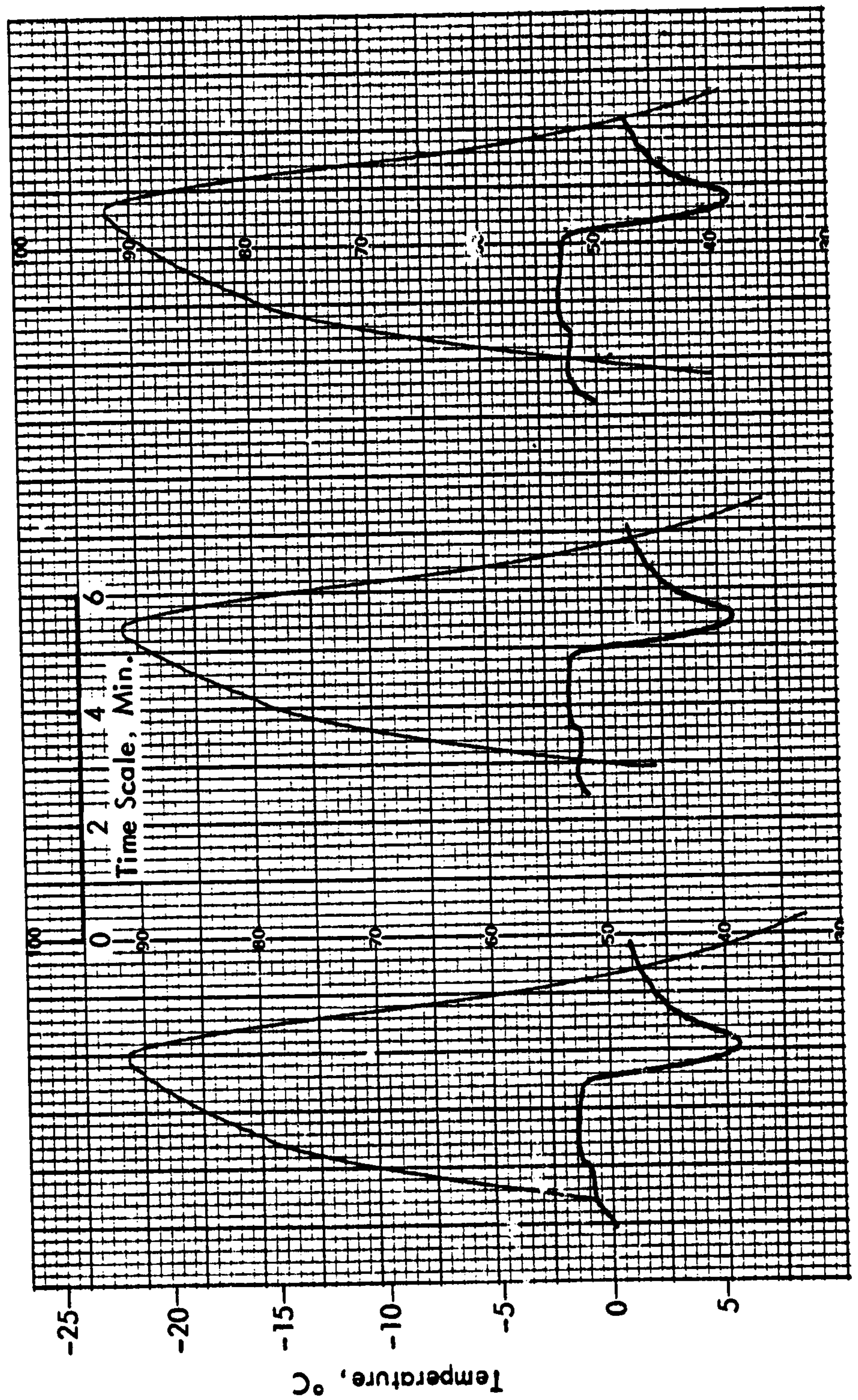

Figure 23 - Results of Thermal Tests on LFP-7

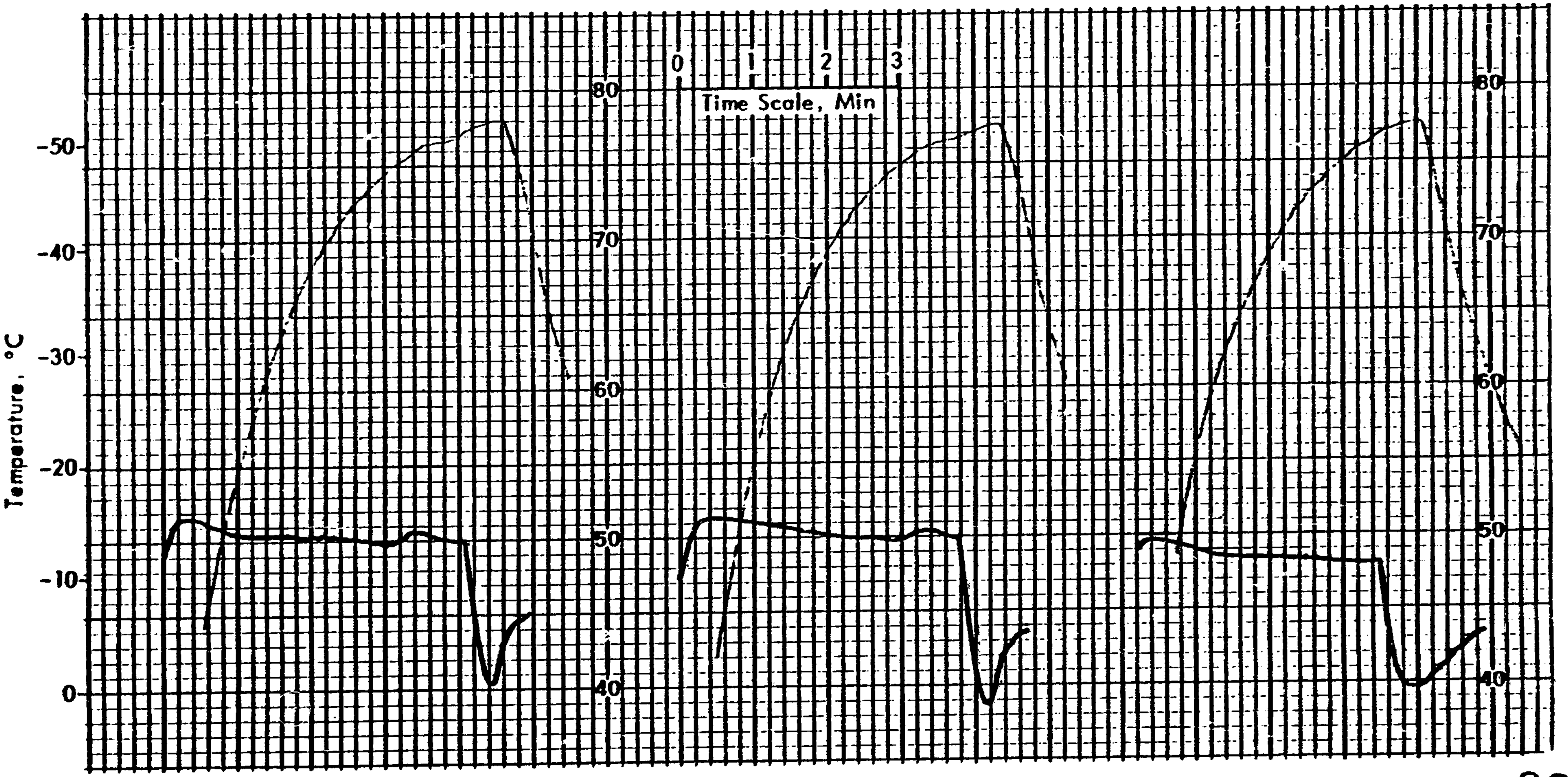

Figure 24 - Results of Thermal Tests on LFP-9

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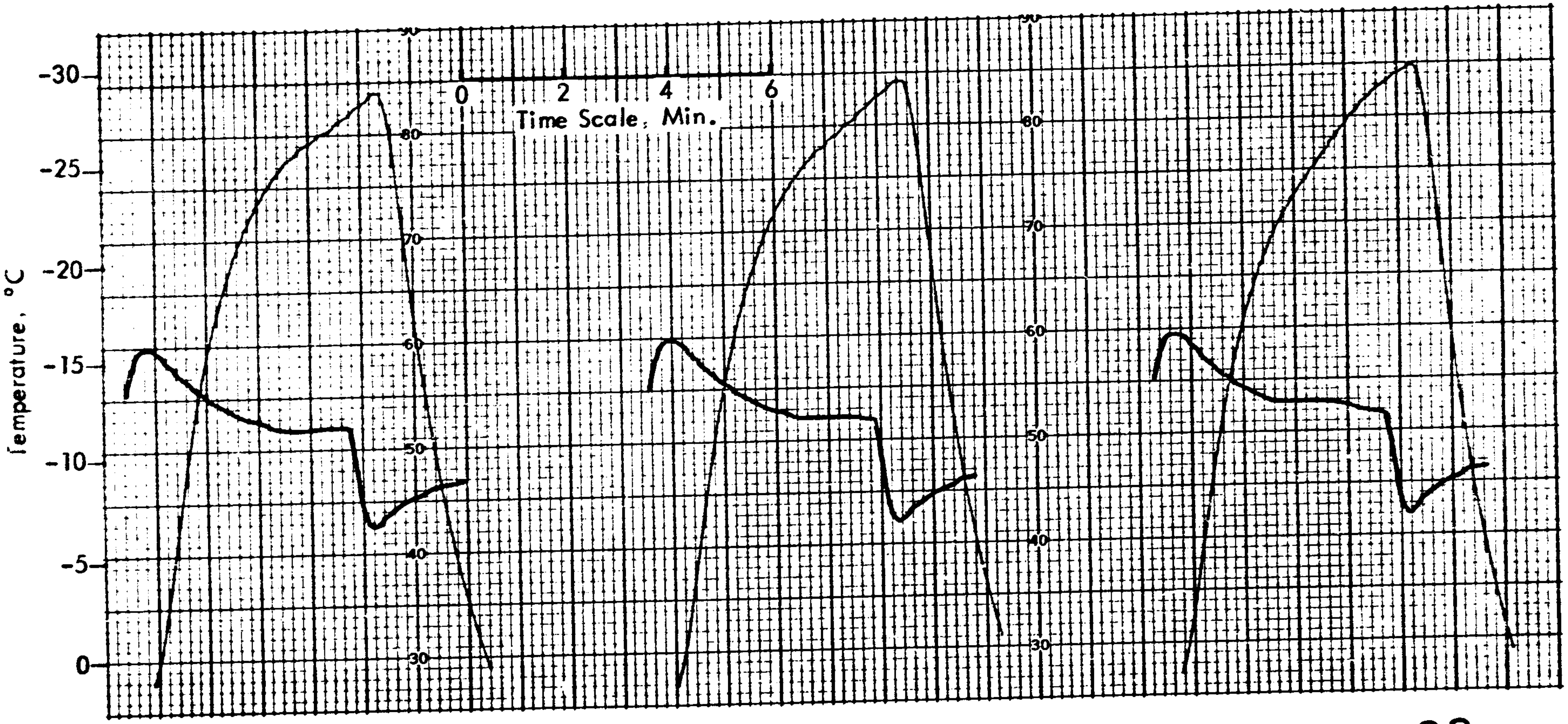

Figure 25 - Results of Thermal Tests on ERBS

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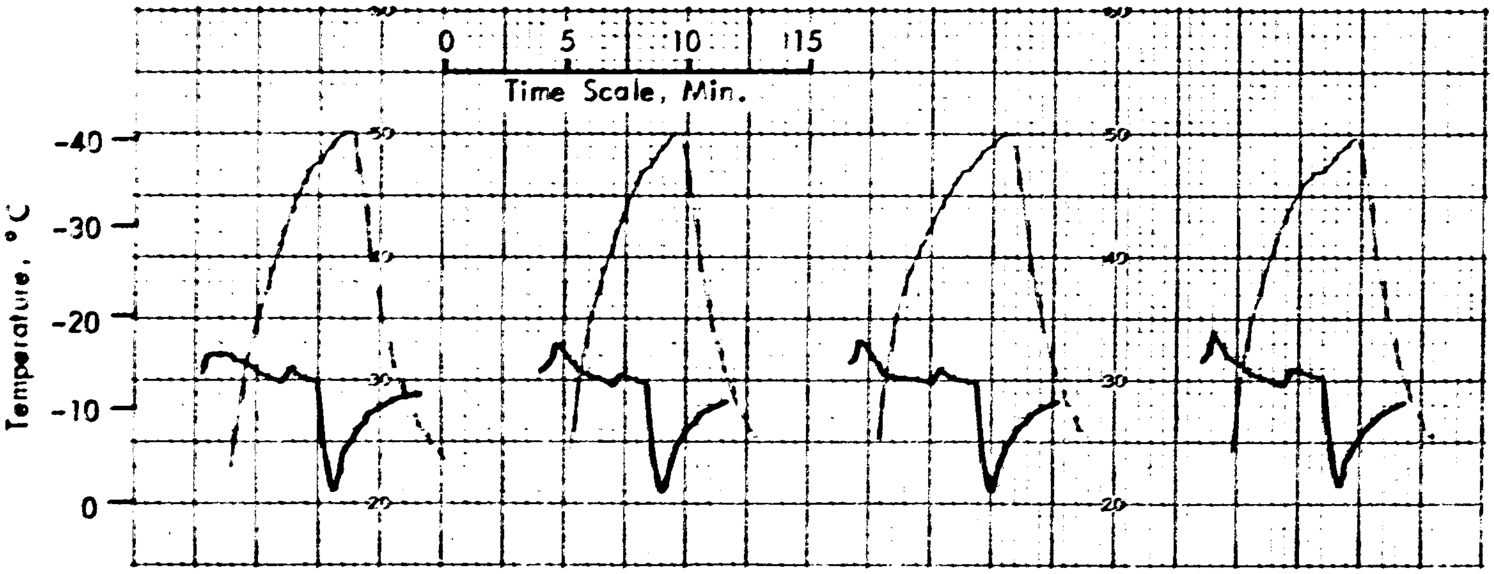

Figure 26 - Results of Thermal Tests on Fuel No. 8

TABLE 2

RESULTS OBTAINED IN TESTS USING THE TEMPERATURE PLATEAU

(Freezing Point in °C)

S No.	Test Fuel	Test No. 1	 No. 2	 No. 3	 No. 4	 No. 5	Average
1	Water	0.36	0.39	0.21	0.22	0.10	0.26
2	Dodecane	-9.4	-9.5	-9.4	-9.7	-9.7	-9.5
3	Tridecane	-5.7	-5.6	-5.9	-5.7	-5.8	-5.7
4	Ter.-Butyl Alcohol	(no plateau observed)					

B. Optical Tests

Originally, it was planned to measure the freezing point of test fuels by what is known as the depolarization technique. In this technique, at the beginning of a freezing point test, the polarization angle between the laser light and the analyzer would be set at 90 degrees, thus extinguishing the light; the detector would, at this time, record close to zero signal. With this setting, the test fuel would be cooled in the TE cooler unit. There would be no change in the recorded signal until the fuel starts freezing. When the freezing commences, the crystals that are formed would depolarize the incident light and this could be observed by noting a change in the recorded signal delivered by the detector. When switching is made from cooling mode to the rewarming mode, it was expected that there would be another change in the recorded signal when the test crystal disappeared. When preliminary tests were conducted employing this technique, it was found that the changes in the intensity of depolarized light were too small during freezing and melting to generate a meaningful signal, and therefore this technique was unable to identify the freezing point accurately.

The successful optical technique that did predict the freezing point of test fuels was the application of changes in the intensity of transmitted light through the test fuel that occurred when the fuel was melting or freezing. In this technique, at the beginning of a test, the laser was rotated so that a reasonable amount of light could pass through the analyzer and allow the detector to record and indicate an output signal. With this setting, the test fuel was cooled. There was not any change in the intensity of transmitted light until the fuel started freezing. When the fuel froze the crystals that were formed reduced the intensity of transmitted light, and therefore the detector sensed a change in the output signal. When the switch was made from cooling mode to rewarming mode, the intensity of transmitted light increased as soon as the last crystal melted. The temperature of the fuel at the time when the light intensity increased again was recorded as the freezing point. This optical technique was used throughout this program.

1. Test procedure: In this optical method the test sample holder that had been fitted with clear optical windows was filled with the fuel to be tested. If it was desired to conduct the optical test along with the thermal test, the reference holder was also filled with isooctane. The

holder is then placed in position into the locator as before. The locator, carrying the holder(s), is then carefully placed into the TE cooler in the space provided, and the screws tightened to keep the holders in good contact with the heat transfer plates. Thermocouple probes were then inserted into the test fuel. The ice bins were filled with a mixture of ice and water as before.

The power supply was switched on so that the current flow to the TE modules cooled the test fuel. The chart recorder was also switched on so that the temperature of the test fuel and the intensity of transmitted light (measured in millivolts) recorded continuously as a function of time. When the temperature of the fuel reached a temperature about 10 to 20°C below its anticipated freezing point, cooling was stopped and the rewarming started. The chart recorder continued to record both signals. Rewarming was continued until the optical signal showed an increase from its minimum value. The experiment was stopped at this time and the freezing point determined as the time at which the optical signal moved from its minimum value and reading the fuel temperature at that time.

2. <u>Test results</u>: Several optical tests were conducted using the optical technique to evaluate the suitability of this method for developing a portable, rapid freezing point apparatus. Test fuels included both single component and multicomponent substances. The results are shown for the following test fuels.

(a) One component: Tridecane and tertiary butyl alcohol.

(b) Multicomponent: Aviation fuels designated as LFP-4, LFP-6, LFP-7, ERBS, Fuel No. 7, and Fuel No. 8.

Figures 27 through 33 show the plots obtained in optical tests conducted on several test samples. In all these plots, the curves that appear light and thin show the actual temperature of the test fuel as a function of time. The curves that appear dark and thick show the intensity of transmitted light through the test fuel as a function of time. The chart recorder used in the optical tests is identical to the one used in thermal tests so that a point in the light intensity curve and a point to the right by 2.5 subdivisions on the temperature curve correspond to the same instant of time. About five tests were conducted on each test fuel. Table 3 shows the results obtained in the optical tests. In all these tests, the two-stage TE cooler was used. Only the test fuels, whose reported freezing point was more than -35°C, could be tested in this unit.

A detailed comparison of our test results with the values reported by others is presented in Section D (page 74). At this point, it can be seen that the results obtained for tridecane, and butyl alcohol are not in good agreement with the values reported in the literature. However, the results obtained for all aviation fuels (which are multicomponent substances) are within acceptable limits when compared with the reported values. Our tests on other pure species, such as dodecane and water also indicated that the optical technique could not measure the freezing point

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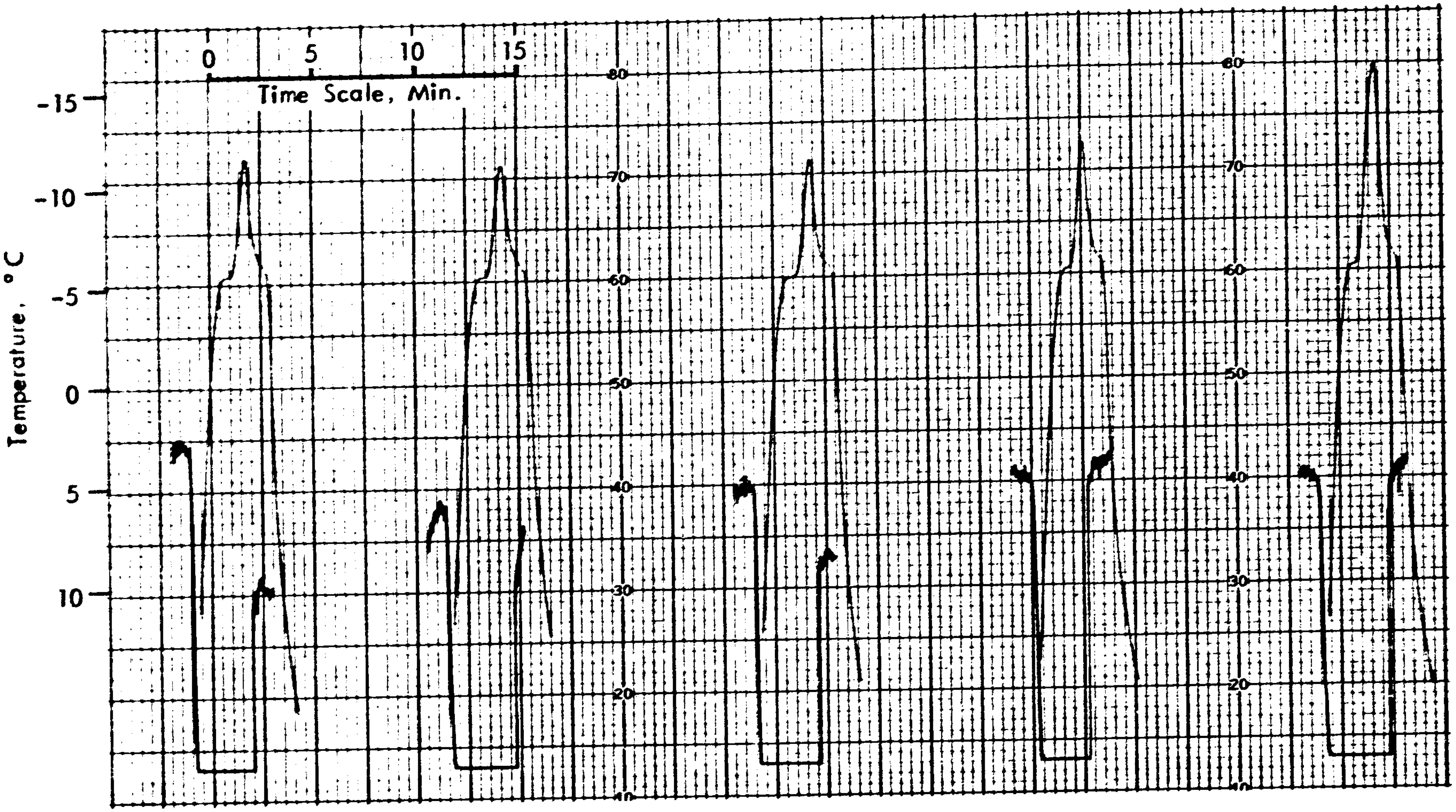

Figure 27 - Results of Optical Tests on Tridecane

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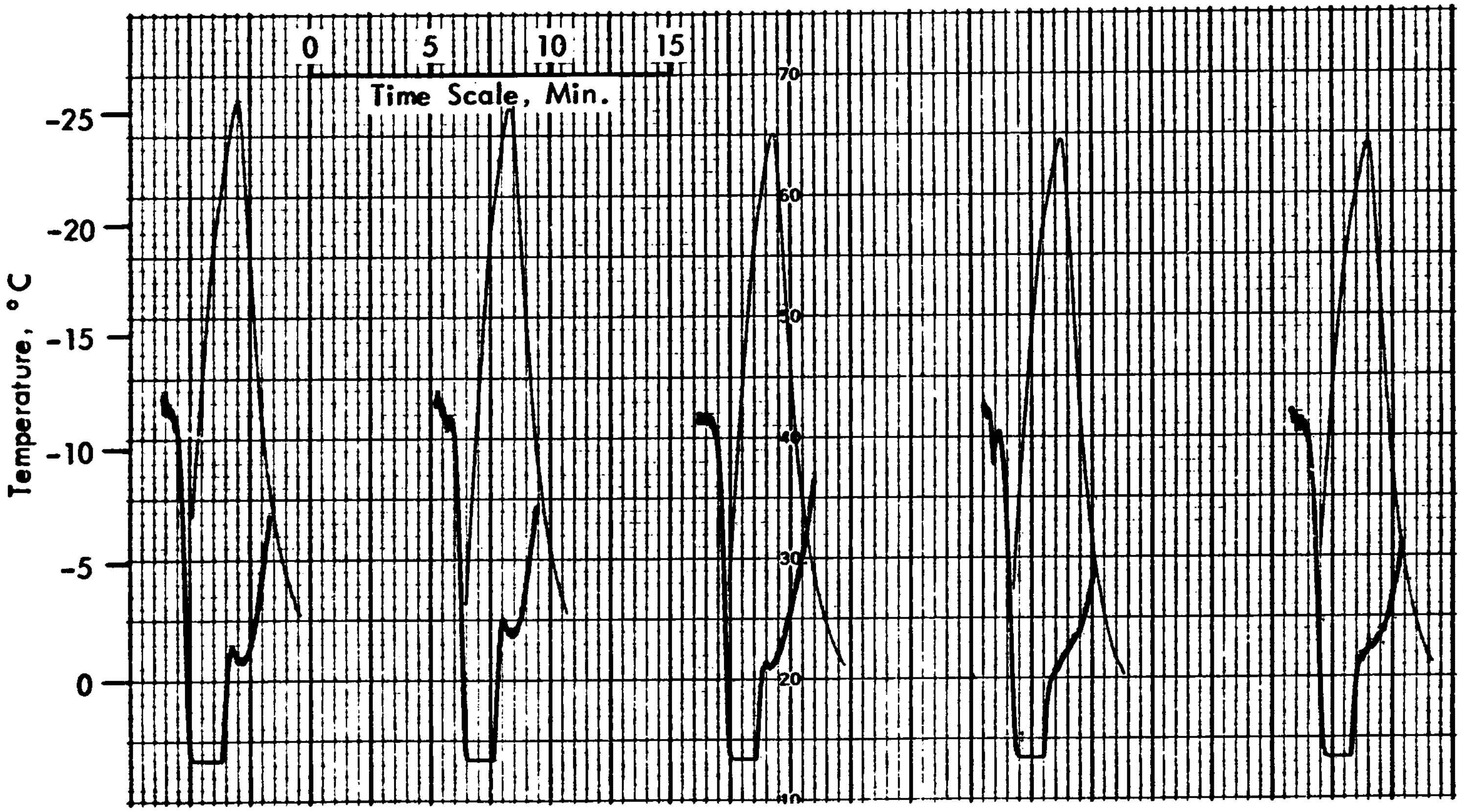

Figure 28 - Results of Optical Tests on LFP-4

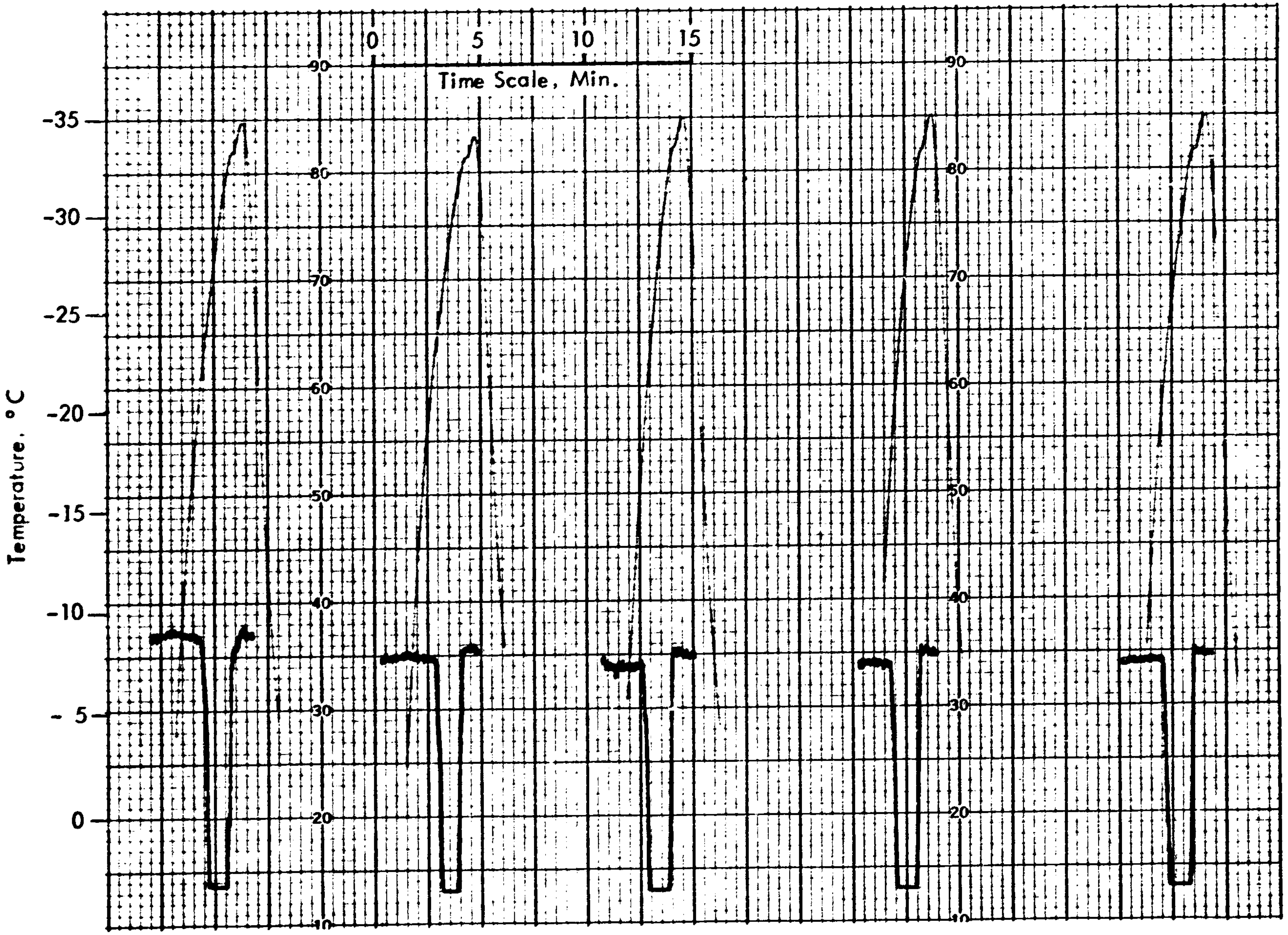

Figure 29 - Results of Optical Tests on LFP-6

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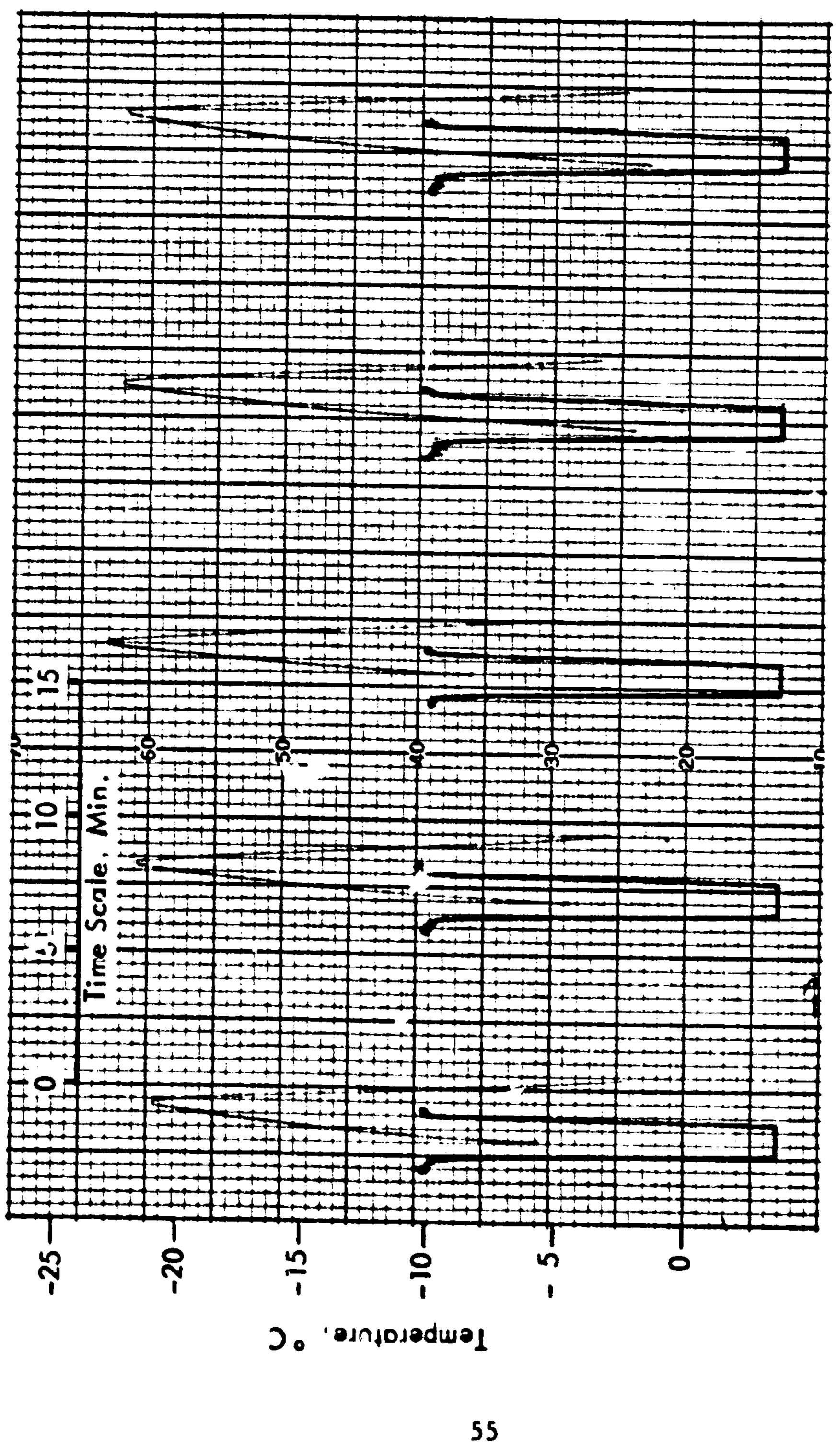

Figure 30 - Results of Optical Tests on LFP-7

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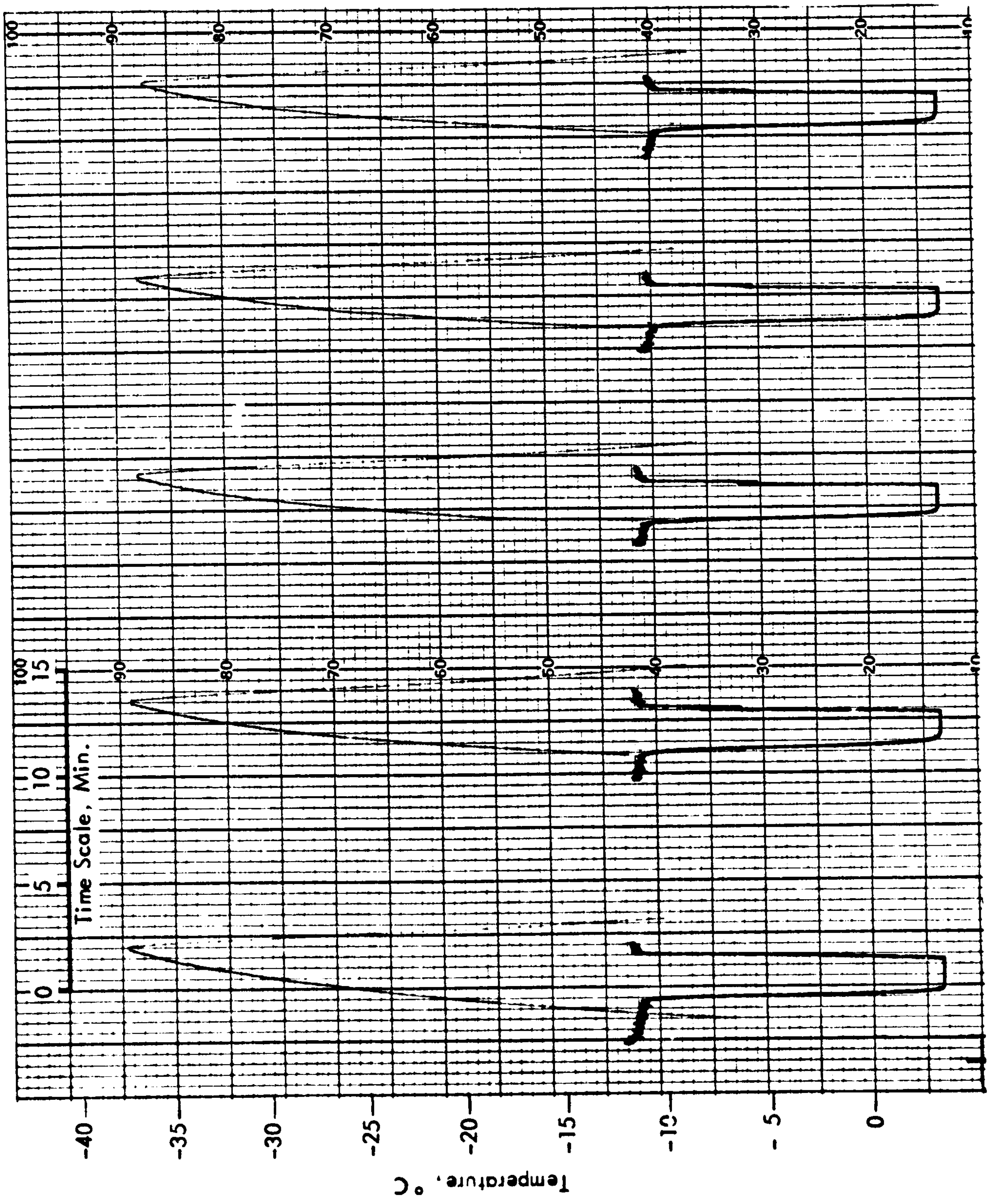

Figure 31 - Results of Optical Tests on ERBS

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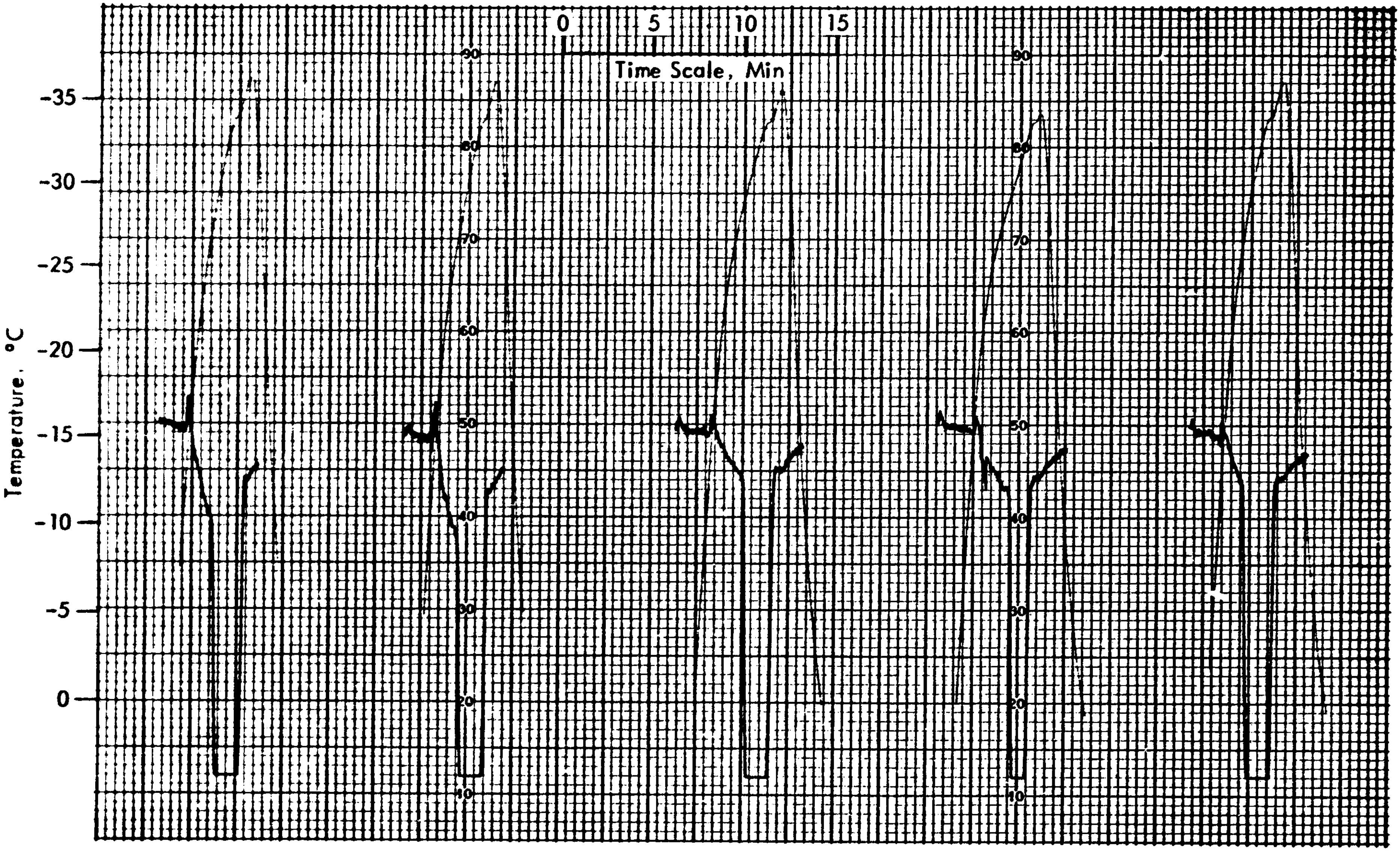

Figure 32 - Results of Optical Tests on Fuel No. 7

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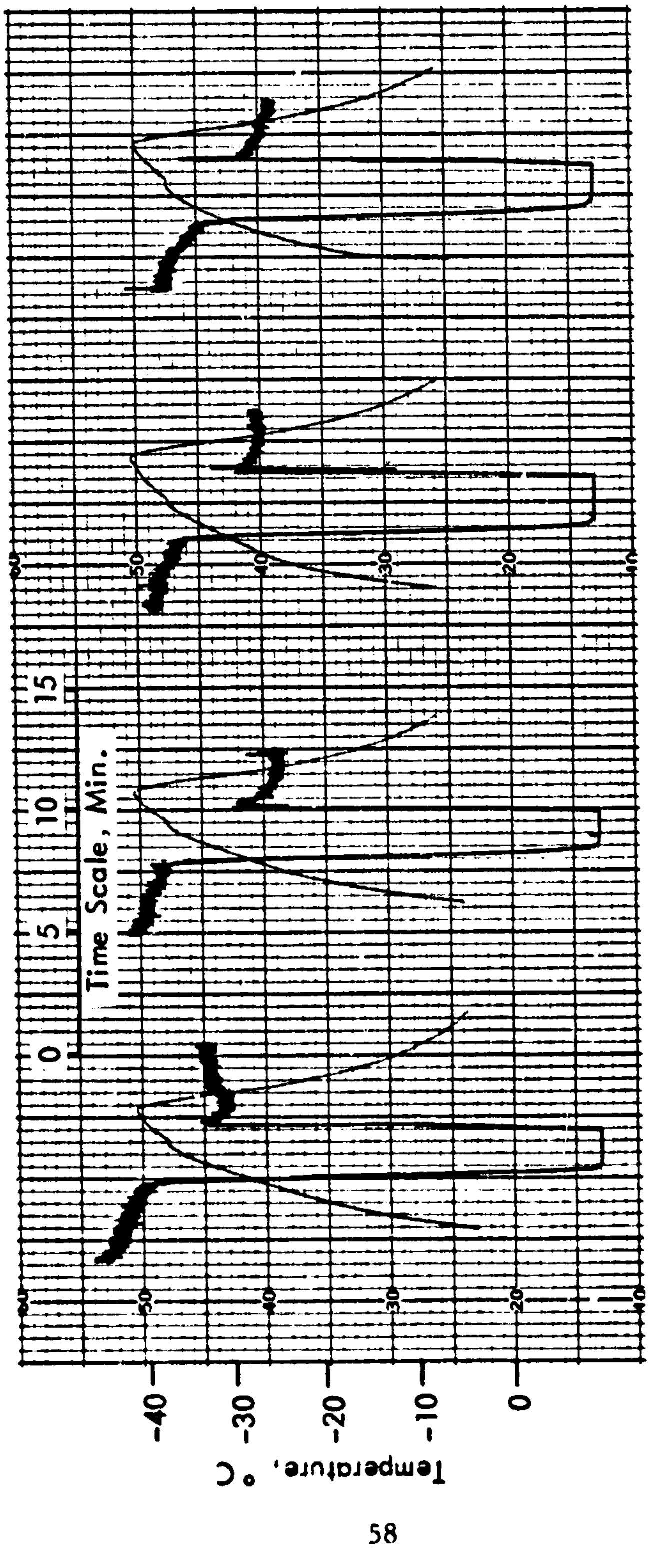

Figure 33 - Results of Optical Tests on Fuel No. 8

TABLE 3

RESULTS OBTAINED IN TESTS USING THE OPTICAL METHOD
(Freezing Point in °C)

S No.	Test Fuel	Test No. 1	No. 2	No. 3	No. 4	No. 5	Average	Reported*
1	Tridecane	6.3	7.6	6.0	6.0	9.5	7.1	(-5.5)
2	Butyl alcohol	30.7	31.0	31.5	28.0	28.0	29.8	(25.5)
3	LFP-4	-13.5	-12.0	-11.6	-12.0	-12.0	-12.2	
4	LFP-6	-29.5	-28.0	-26.2	-27.0	-27.0	-27.5	
5	LFP-7	-9.4	-10.0	-10.4	-12.1	-11.0	-10.6	
6	ERBS	-27.0	-26.0	-25.7	-25.0	-24.0	-25.5	
7	Fuel No. 7	-25.5	-24.5	-25.0	-25.5	-26.6	-25.5	
8	Fuel No. 8	-33.5	-33.5	-31.0	-30.0	-	-32.0	

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* Literature reported values.

accurately for one component substances. The reason why the optical technique could predict satisfactory results for the case of aviation fuels and fails to predict satisfactory results for the case of pure species is not known.

C. Thermal Tests - Point of Inflection Approach

It was originally planned to conduct all the thermal tests using only the DTA approach. However, an extensive evaluation of the DTA approach indicated that there was a specific problem associated in this approach. Therefore, we proceeded to evaluate a new thermal method which we call the point of inflection approach.

1. Problem in the differential thermal method: The problem associated with the DTA approach was identified when a parametric analysis involving the study of the effect of cooling rate, warming rate, and the minimum temperature attained was performed. The parametric analysis was made to make sure that the operating variables involved in the test do not influence the measured value of freezing point. Figure 34 shows the effect of supply voltage during cooling, supply voltage during rewarming, and of temperature attained at the end of cooling on the measured freezing point. The fuel used for this parametric study was aviation fuel ERBS. Three tests were conducted to study the effect of supply voltage during cooling. As this voltage increases, the time required to cool the test fuel to the desired low temperature decreased. In all these three tests, rewarming the fuel was done with a 'zero' rewarming voltage. (Zero rewarming voltage means that the TE cooler was not supplied with any power to heat the fuel; the flow of heat from the ice-water mixture to the fuel is solely due to the existing temperature gradient.) The minimum temperature to which the

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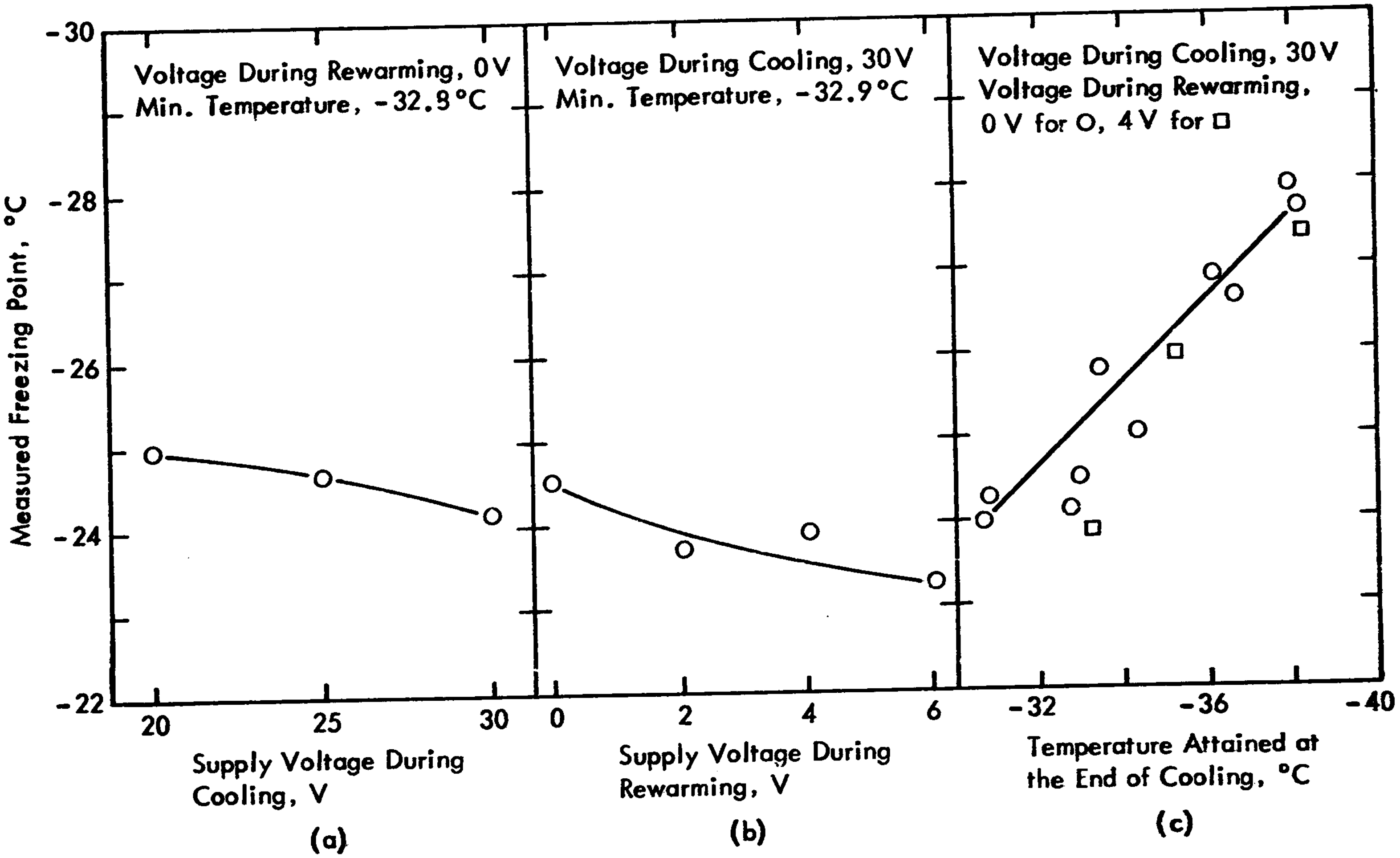

(a) (b) (c)

Figure 34 - The Effect of Cooling Rate, Warming Rate, and Minimum Temperature

fuel was cooled before switching to rewarming mode was about -32.8°C. The results obtained in these three tests indicated that the measured freezing point was not sensitive to the supply voltage during cooling; therefore, we concluded that the effect of cooling rate did not influence the measured freezing point.

The effect of supply voltage during rewarming was studied by conducting four tests on ERBS. The time required to rewarm the fuel from the minimum temperature to any desired high temperature will be less, as the supply voltage during rewarming increases. In all these tests, the supply voltage during cooling was kept at 30 V. The minimum temperature to which the fuel was cooled was about -32.9°C. The results obtained in these tests showed that the effect of rewarming voltage on the freezing point is not significant. Therefore, we also concluded that the effect of rewarming rate on the freezing point can be ignored.

The effect of the minimum temperature attained at the end of cooling (just before switching to the rewarming mode) on the measured value of freezing point was also studied. More than 10 tests were conducted in this parametric study. The minimum temperature attained varied from -30.5 to -38.2°C. The supply voltage during cooling was set at 30 V and the supply voltage during rewarming was 0 V for some tests and 4 V for other tests. The results of this study showed that the minimum temperature attained at the end of cooling did influence the measured freezing point and this effect cannot be ignored. For every 1°C lowering of the minimum temperature, there was a corresponding lowering of measured freezing point of approximately 0.5°C.

To identify the causes that influence the measured freezing point, a chain of tests were conducted on a pure substance, dodecane, in which the minimum temperature attained at the end of cooling was varied over a wide temperature range. The plots obtained on this sample are shown in Figure 35. It shows the T and ΔT signals generated when the sample was cooled and rewarmed several times. The lowest temperature attained was -35°C during the first cycle and was progressively higher during the subsequent cycles. In each cycle, as can be seen from Figure 35, two ΔT signals have been generated during cooling (curves A and B) and two other ΔT signals during heating (curves C and D). The dominant ΔT signal during cooling (curve B) is that generated by the latent heat effect and the weak ΔT signal during cooling (curve A) is that generated by some unknown operating variables. Similarly, the dominant ΔT signal during heating (curve D) is that generated by the latent heat effect and the weak ΔT signal during heating (curve C) is again the one caused by some unknown factors. In an ideal freezing point apparatus, the curves B and D will be generated but not the secondary curves A and C. It can be noticed that the curve A has been generated at the beginning of cooling and the curve C at the beginning of heating.

When the minimum temperature attained at the end of cooling was increased the secondary signals A and C continued to exist; however, the signal C was progressively superimposed on the main signal B. When the system was switched from the cooling to the rewarming mode, before the sample attained the freezing point, there were no latent heat signals but the disturbing signals were still present.

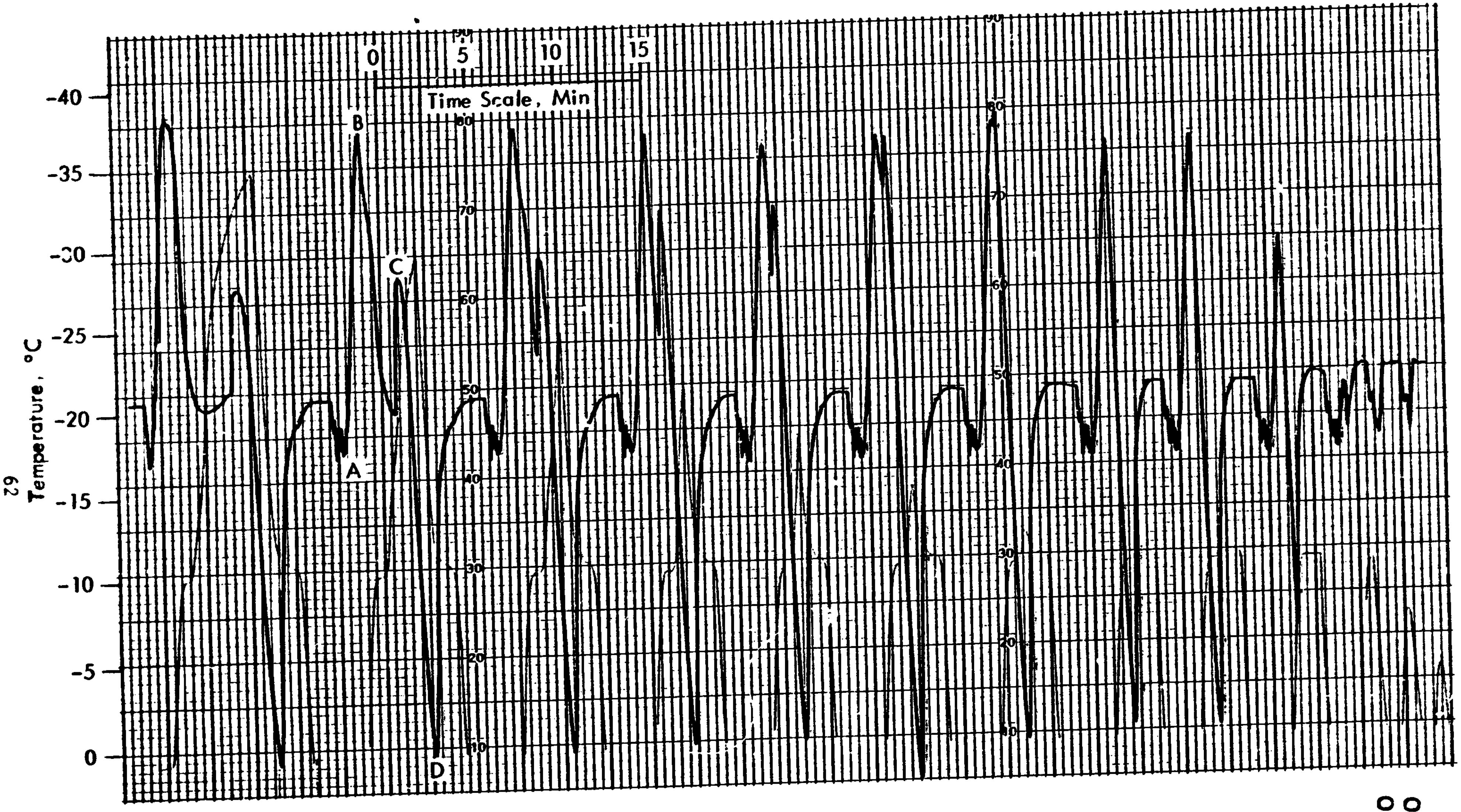

Figure 35 - Thermal Tests on Dodecane

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To gain more insight of the thermal process, another experiment was made on dodecane. This time the sample cell containing dodecane was placed in that portion of the TE cooler where we used to place the reference fuel. In turn, the reference cell containing isooctane was placed in the TE cooler in the portion usually occupied by the test cell. In all other respects, the test procedure was the same as that of the first test. The plots obtained in this second test are shown in Figure 36. In this test also, there are two ΔT signals generated during cooling and two other ΔT signals generated during heating. The main difference is that the sign of the secondary signal A in Figure 36 generated during cooling is opposite to that of signal A in Figure 35. During heating also, the sign of the secondary signal C in Figure 36 is opposite to that of signal C in Figure 35. The sign reversal in signals made the greater part of signal A to merge with the main signal B and the greater part of signal C to merge with the main signal D. The existence of unwanted signals A and C can be noticed for all minimum temperatures attained. In the last two cycles, when switching from cooling to rewarming mode was done before the sample attained the freezing point, there were no latent heat signals but still signals A and C were present.

A third experiment that was conducted to understand the process was on isooctane. In this experiment, both test fuel and reference fuel were the same. The plots obtained in these tests are presented in Figure 37. The plot on the left shows the results obtained when the test cell was placed in the usual test cell position and the one on the right shows the results obtained when the test cell was placed in the reference cell position. In an ideal TE cooler unit, if the heating and cooling were performed cyclically, no ΔT signal should be generated, since no latent heat is involved in the process. However, in our TE cooler unit, ΔT signals were not zero, thus confirming the existence of an unknown problem.

The above experiments indicate that the TE cooler elements provided for the test cell and those elements provided for the reference cell do not have the same cooling capacity. With unequal cooling capacities, one of the two cells is cooled faster than the other during cooling and is warmed faster during heating. In turn, this difference in the cooling/warming rate generates ΔT signals similar to curves A and C in Figures 35 and 36. Other than the difference in cooling capacity of the TE cooler elements, the possible factors that can generate the disturbing signals are nonuniformity in the thickness of the test and reference cell, the difference in heat capacity of the test and reference fuels, and the existence of large temperature gradients in the test and reference fuel.

For pure components such as dodecane, the main latent heat signal is very dominant, and therefore even though the secondary signal is present, its magnitude is very low and as such it cannot strongly influence the measured freezing point. However, for aviation fuels the latent heat signal is very weak, and therefore the secondary signal is of considerable relative magnitude and thus influences the freezing point. Since the secondary signal is generated at the time of switching from cooling to rewarming, the location of the peak of the secondary signal is dependent on the minimum temperature attained at the end of cooling; thus the measured freezing point

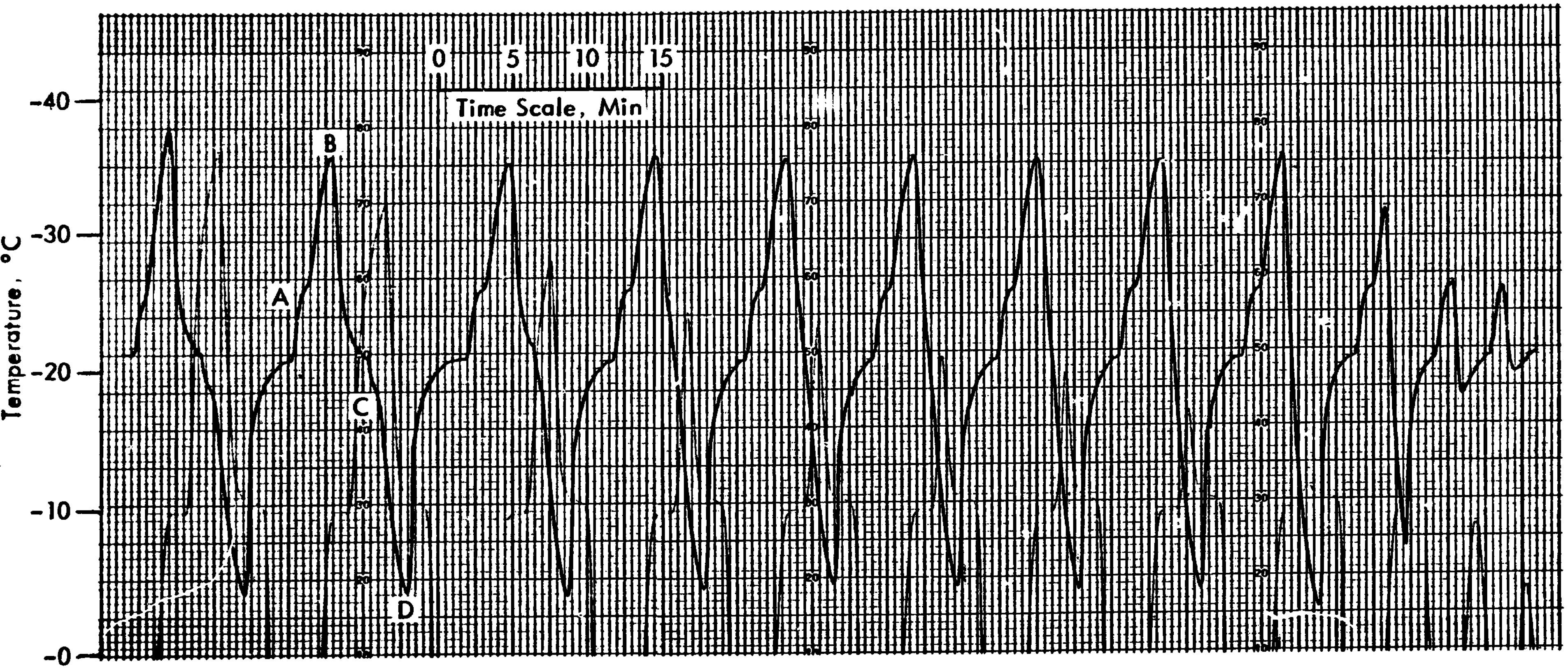

Figure 36 - Thermal Tests on Dodecane that Confirmed the Existence of Secondary Signals - Cell Position Exchanged.

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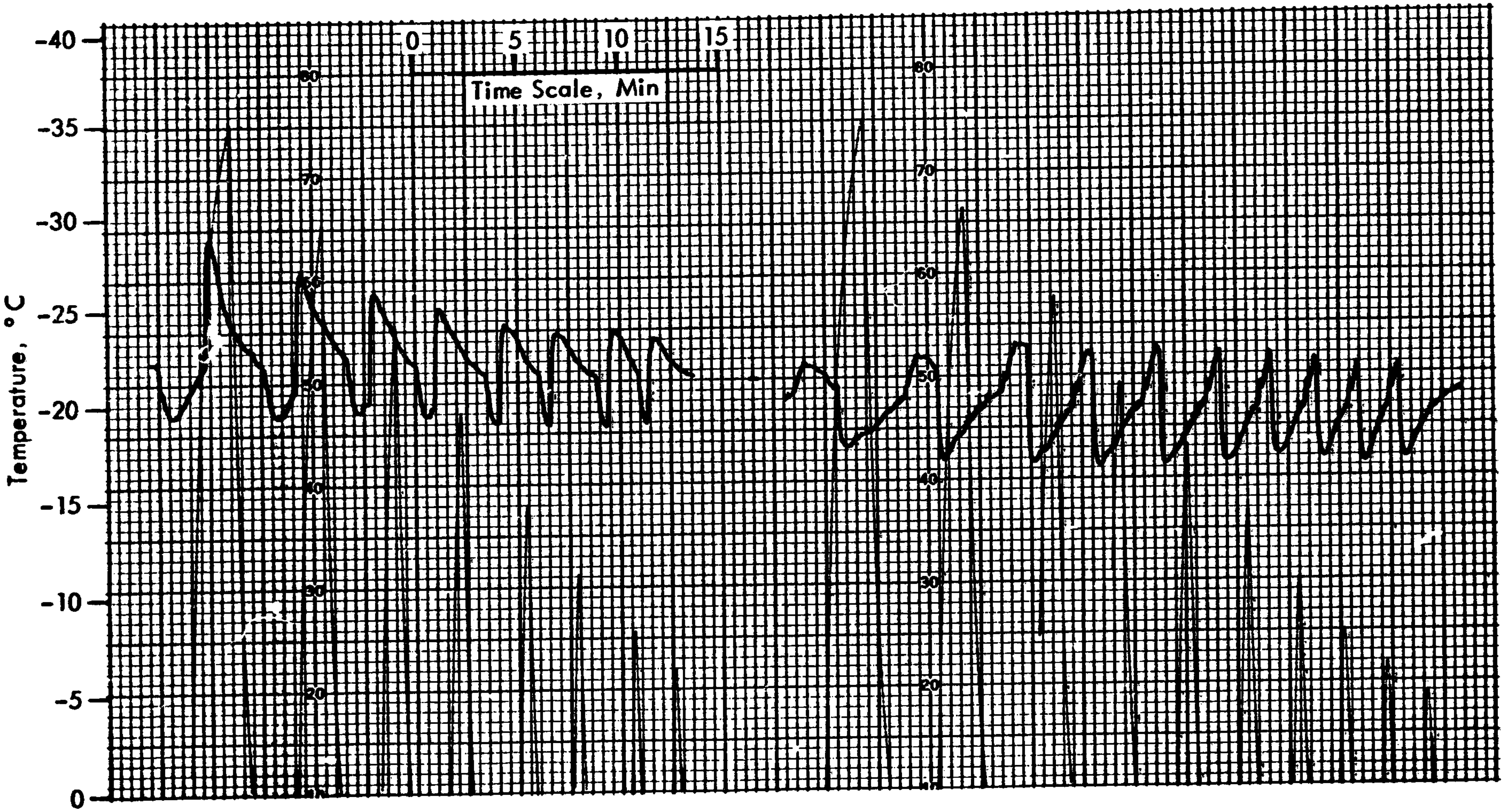

Figure 37 - Secondary Signals Observed on Isooctane.

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is observed to be dependent on the minimum temperature attained. Our extensive experimental analysis, performed subsequently, showed that the secondary signal arises from several sources. The major sources are: (a) unequal cooling capacities of TE coolers; (b) large temprature gradients due to thicker cells; and (c) the difference in thermal conductivity between test and reference fuels. Our attempts to overcome these problems were not successful.

2. Principle involved in the point of inflection technique: Let us consider a substance which has been partially frozen and is being rewarmed in a device similar to our TE cooler. At time, $t = 0$, the substance is at some temperature T ($T < 0°C$) and the heat source (ice) is at 0°C. The heat flows from the ice into the sample either unaided (zero volt supplied to the TE modules) or pumped (by supplying a voltage across the modules). The temperature of the heat source is maintained constant at 0°C. Under these conditions, we can analyze the rewarming process for: (a) a single component substance; and (b) a multicomponent substance.

Figure 38(a) shows typical change in temperature with time and derivatives of the change in temperature with respect to time for the case of a single component substance. In the initial state the substance is a partially frozen mixture of liquid and solid phases, and during rewarming, the time temperature would exhibit a plateau representing the melting process. Once melting has been completed, the temperature will increase again, approaching either the source temperature of 0°C or a temperature (> 0°C), as determined by the voltage supplied to the TE modules. In an ideal melting process, there would be a sharp change in the slope of the temperature-time curve at the freezing point (the point where the last solid crystal would disappear), but in actual experiments the sharp corners would be rounded as shown in the figure. It is interesting to observe that in both ideal and actual experiments, the time derivative of temperature exhibits maxima at the melting point. In other words, the temperature of the substance at a time t when dT/dt attains a maximum, represents the freezing point.

Figure 38(b) shows the temperature-time histories and derivatives for the case of a multicomponent substance, such as an aviation fuel. In the initial state, the substance is a partially frozen mixture of liquid and solid phases. During the initial rewarming, solid crystals are melted, but melting does not take place at constant temperature. The heat added to the substance is used both to increase the bulk temperature and also to provide the latent heat necessary for melting. Since the heat added during melting is used in two ways, the rate of temperature increase would not be as high as when there is no melting phenomenon. When melting has been completed, the heat added to the substance would be used solely to increase temperature and this would result in an increase in the rate of heating at the end of melting. In ideal and actual experiments, the slope of the temperature-time curve's derivative dT/dt would exhibit a change at the freezing point. In this case, the difference between the ideal and actual experiments is less noticeable than for pure species. The important observation is that in both ideal and actual experiments, the time derivatives of temperature exhibit maxima at the melting point. Thus, the freezing point can be determined as the temperature of the test substance at the time when dT/dt attains a maximum.

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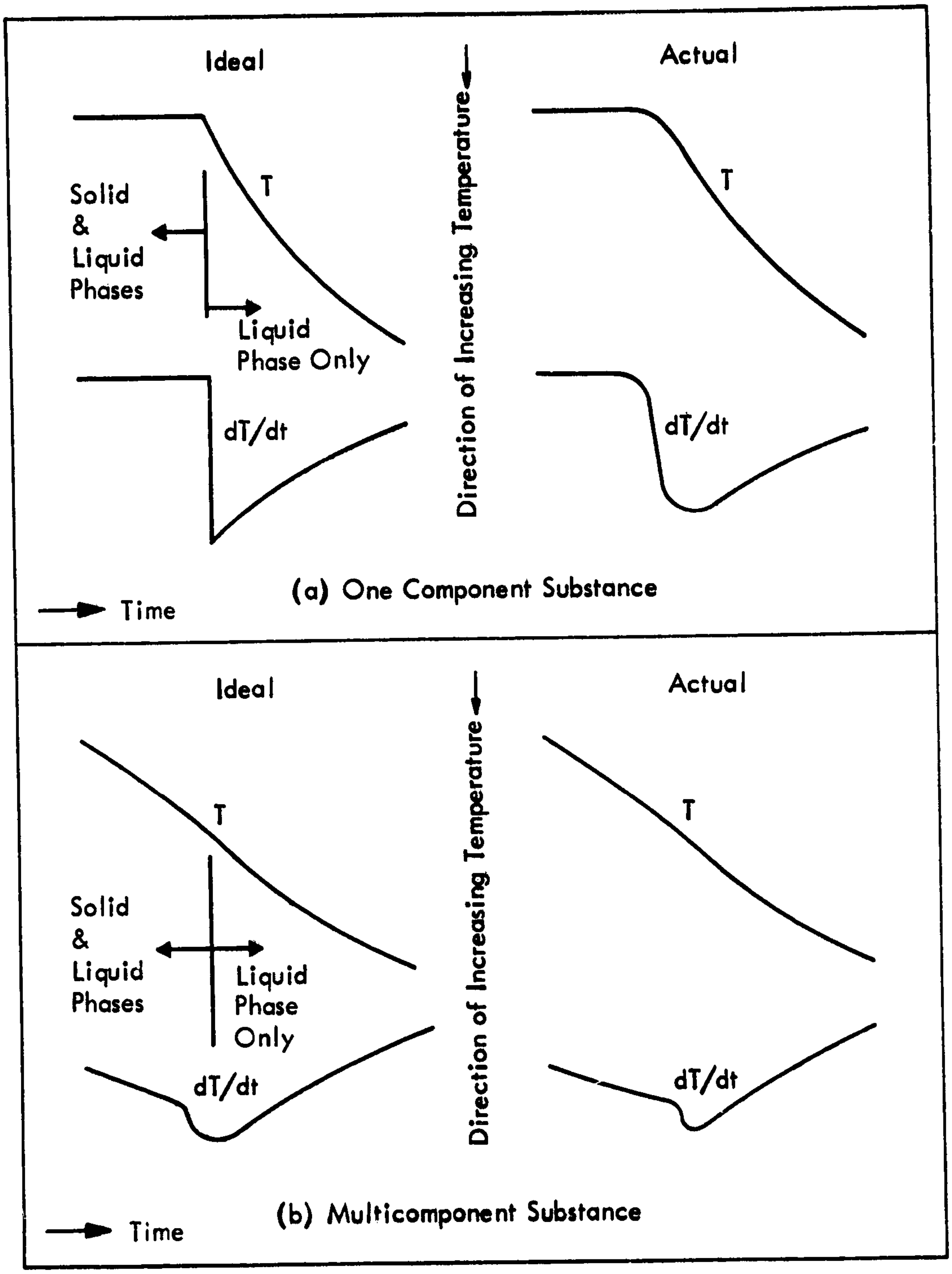

Figure 38 - Illustration of the New Thermal Technique

In this new thermal technique, no reference substance is needed, and problems with the superposition of secondary signals arising from the use of a reference material do not occur. Moreover, the TE cooler unit is simpler in construction since only one set of TE modules (to cool the test substance) are needed. Our earlier version required two sets of TE modules, one to cool the test substance and another to cool the reference.

A number of trial tests were conducted on aviation fuels to evaluate the accuracy of the new thermal technique. Figure 39 shows the plots of the temperature of LFP-7 obtained on a typical test and its time derivate. The temperature of the fuel in this test was measured at intervals of 3 sec and recorded using a data logging system. The slope was then determined using the finite difference scheme. As expected, the time derivate curve exhibited a maximum (in Figure 39, the maximum of dT/dt is located at time between 42 and 45 sec). By suitable interpolation, we determined the temperature of the fuel at which dT/dt is maximum; this temperature was found to be -9.8°C. This value compares very well with the reported freezing point of LFP-7.

3. Test results: Several tests were conducted on aviation fuels to evaluate the accuracy of the new thermal technique. The results of these tests were also used to study the effect of supply voltage during cooling, supply voltage during rewarming, and the minimum temperature attained at the end of cooling. The measured values of freezing point were compared with those reported by others (the details of comparison are presented in Section D).

Figure 40 shows the results of tests conducted to study the effect of supply voltage during cooling. Table 4 shows the values of freezing point obtained on tests whose data points are given in this figure. It can be seen from Figure 40 and Table 4 that the supply voltage during cooling did not significantly affect the measured freezing point. The effect of varying the supply voltage during rewarming was also studied on all the aviation fuels. It was found in these tests that the supply voltage during rewarming must be set so that the rewarming rate at the time of crossing the freezing point was at an optimum value. In other words, the first derivate of temperature (dT/dt) must be an optimum value when the temperature of the fuel is equal to its freezing point. This can be achieved either by adjusting the supply voltage during rewarming depending on the anticipated freezing point of the test fuel or by providing necessary control in the electrical circuit so as to provide a constant rate of rewarming (independent of the fuel temperature).

The effect of varying the minimum temperature attained at the end of cooling was also studied on aviation fuels. Figure 41 shows the results of tests conducted to study this effect. Table 5 shows the values of freezing point obtained on tests whose data points are given in Figure 41. The new thermal technique is much less sensitive to the minimum temperature attained at the end of cooling. Since our TE cooler can lower the fuel's

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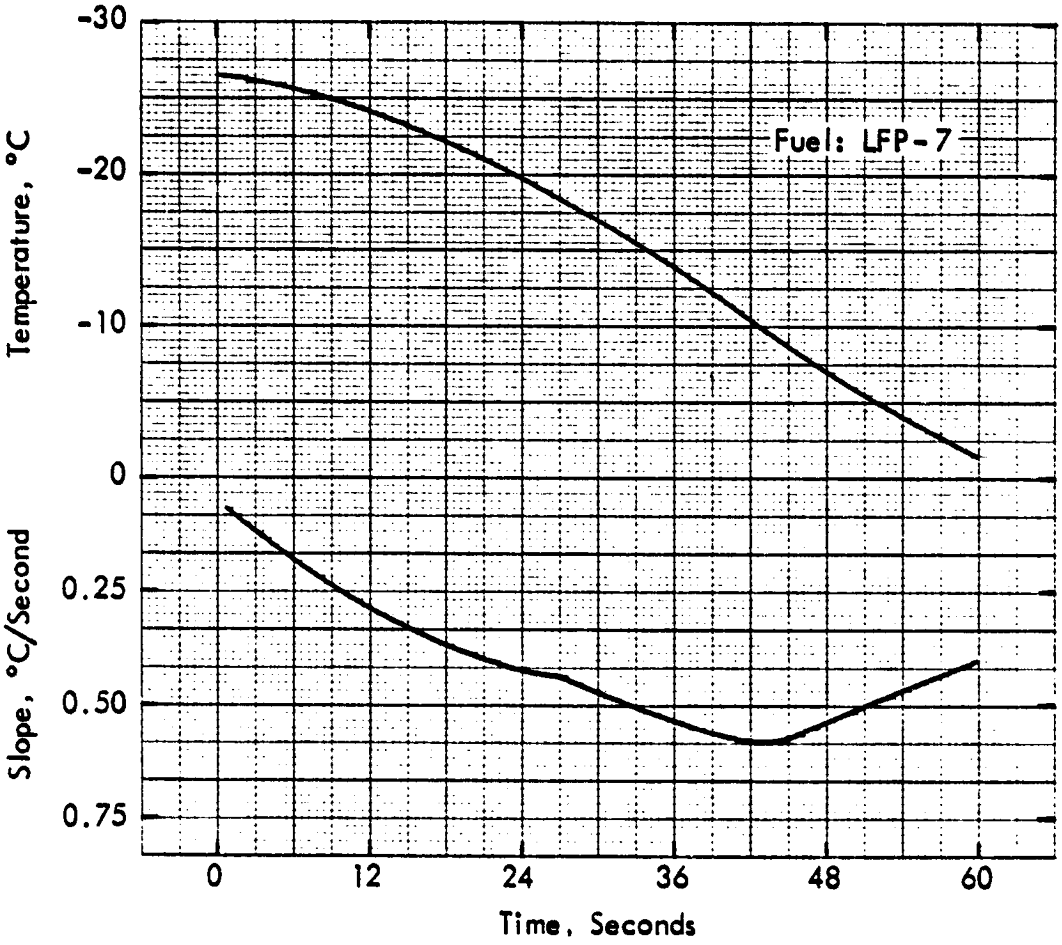

Figure 39 - Test Results of LFP-7

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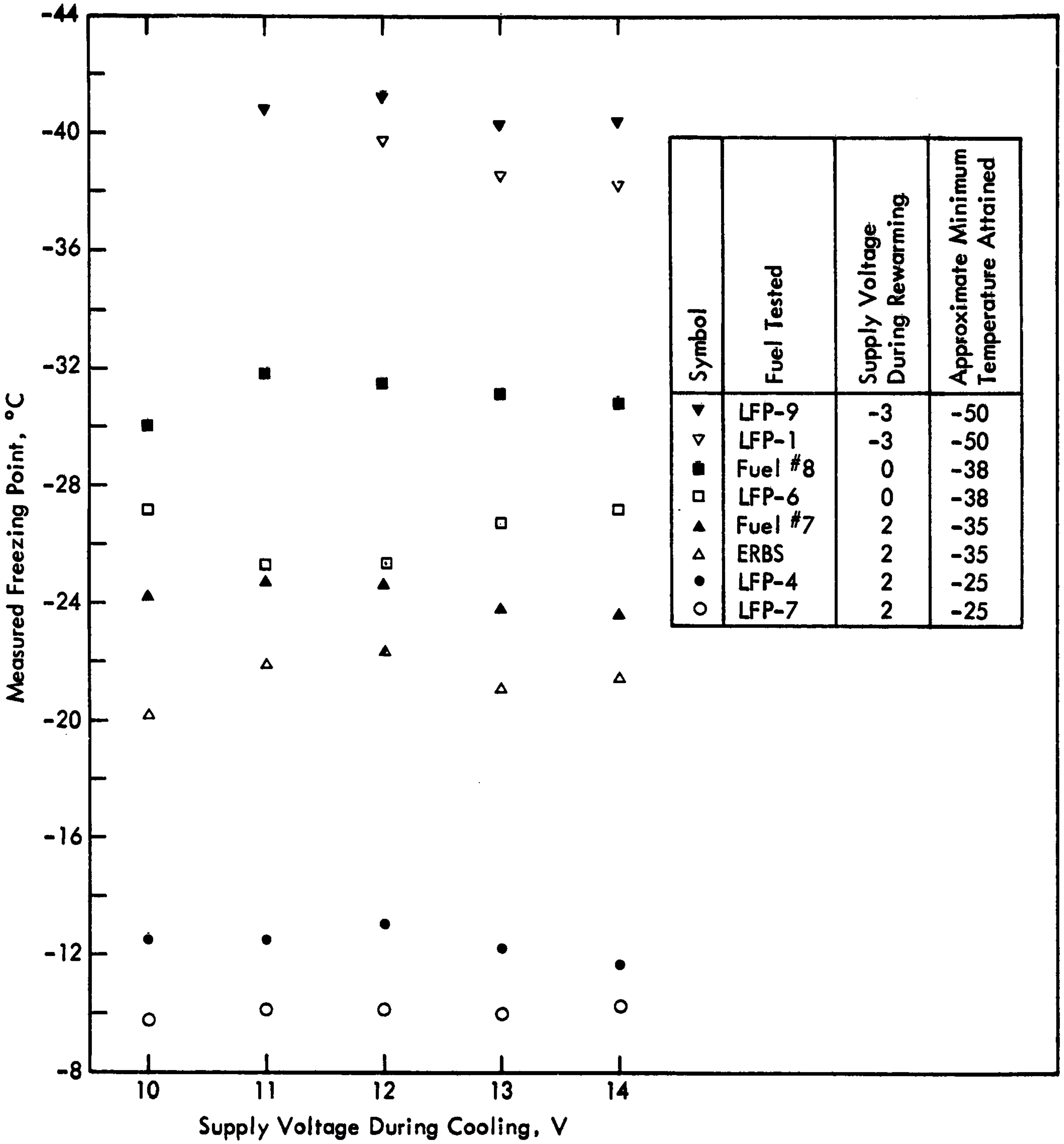

Symbol	Fuel Tested	Supply Voltage During Rewarming	Approximate Minimum Temperature Attained
▼	LFP-9	-3	-50
▽	LFP-1	-3	-50
■	Fuel #8	0	-38
□	LFP-6	0	-38
▲	Fuel #7	2	-35
△	ERBS	2	-35
●	LFP-4	2	-25
○	LFP-7	2	-25

Figure 40 - The Effect of Cooling Rate on Measured Freezing Point

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TABLE 4

EFFECT OF VARYING THE SUPPLY VOLTAGE DURING COOLING

(Freezing Point in °C)

		Supply Voltage, V				
S. No.	Test Fuel	10	11	12	13	14
1	LFP-1	-	-	-39.8	-38.5	-38.1
2	LFP-4	-12.6	-12.6	-12.9	-12.2	-11.8
3	LFP-6	-27.2	-25.1	-25.3	-26.9	-27.1
4	LFP-7	-9.8	-10.2	-10.3	-10.0	-10.3
5	LFP-9	-	-40.9	-41.2	-40.3	-40.4
6	ERBS	-20.2	-22.0	-22.4	-21.1	-21.5
7	Fuel No. 7	-24.4	-24.8	-24.6	-23.9	-23.8
8	Fuel No. 8	-30.0	-31.8	-31.5	-31.3	-30.9

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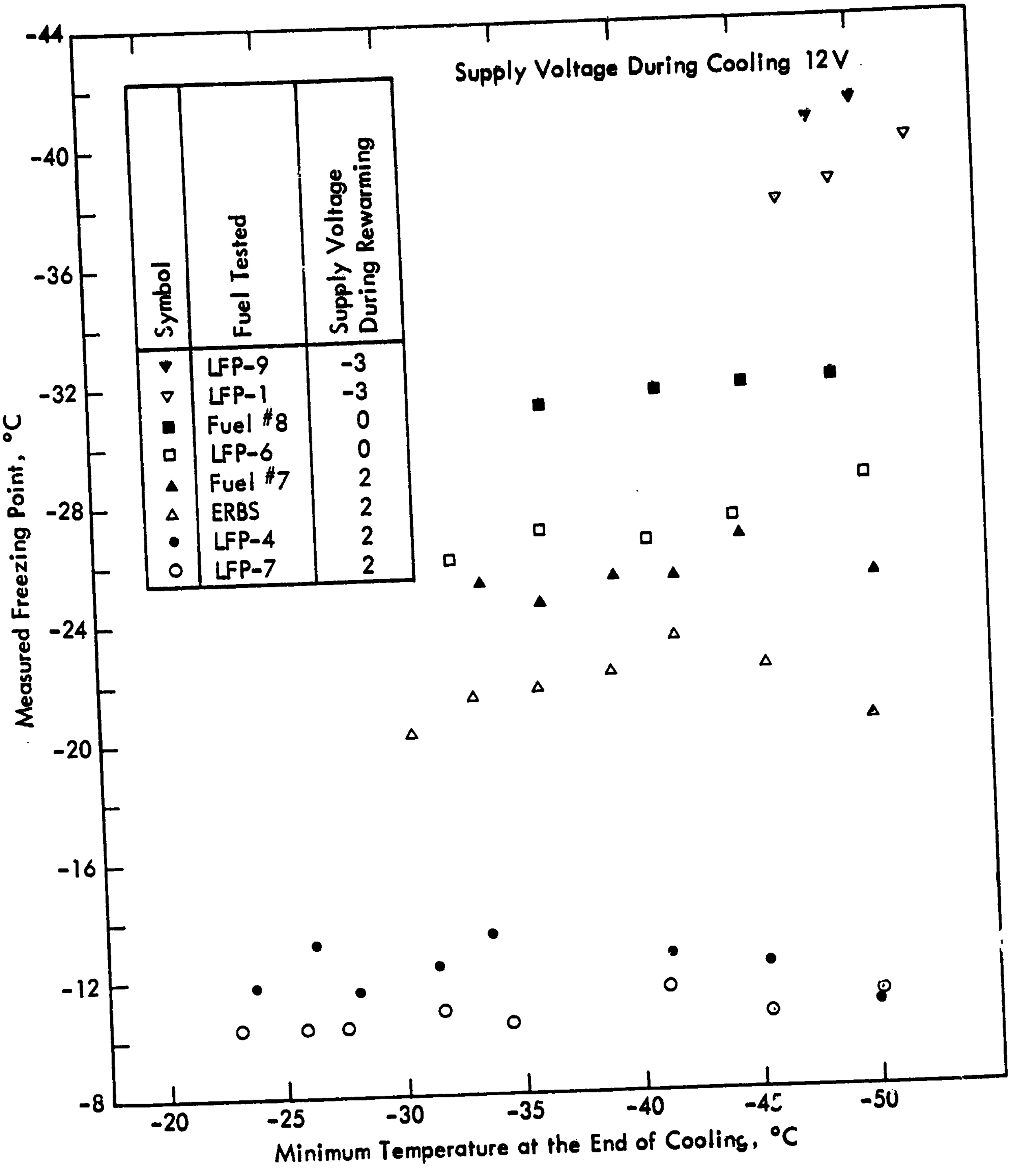

Figure 41 - The Effect of Minimum Temperature on Measured Freezing Point

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TABLE 5

EFFECT OF VARYING THE MINIMUM TEMPERATURE ATTAINED AT THE END OF COOLING

(Freezing Point in °C)

S. No.	Test Fuel	Test No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	Freezing Point*
1	LFP-1	-38.0 (-46.5)†	-38.5 (-49.0)	-39.8 (-52.0)	-	-	-	-	-	-41.9
2	LFP-4	-11.9 (-23.7)	-13.2 (-26.3)	-11.7 (-28.3)	-12.5 (-31.5)	-13.4 (-33.9)	-12.8 (-41.2)	-12.3 (-45.0)	-10.8 (-50.0)	-12.4
3	LFP-6	-26.1 (-32.8)	-27.0 (-36.2)	-26.6 (-40.8)	-27.3 (-44.3)	-28.5 (-49.9)	-	-	-	-27.7
4	LFP-7	-10.4 (-23.1)	-10.4 (-25.8)	-10.3 (-27.4)	-10.9 (-31.7)	-10.5 (-34.3)	-11.6 (-41.6)	-10.6 (-45.3)	-11.2 (-49.9)	-10.5
5	LFP-9	-40.6 (-48.3)	-41.2 (-50.0)	-	-	-	-	-	-	-44.4
6	ERBS	-20.2 (-30.6)	-21.6 (-33.4)	-21.8 (-36.0)	-22.1 (-39.0)	-23.4 (-41.9)	-22.1 (-46.2)	-20.7 (-50.0)	-	-21.8
7	Fuel No. 7	-25.3 (-33.9)	-24.6 (-36.2)	-25.3 (-39.4)	-25.3 (-41.9)	-26.9 (-44.7)	-25.2 (-50.0)	-	-	-25.4
8	Fuel No. 8	-31.3 (-36.7)	-31.5 (-41.4)	-31.9 (-45.1)	-32.1 (-48.9)	-	-	-	-	-[illegible]1.9

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* The values of freezing point, given in this column, are those interpolated or extrapolated (LFP-1, LFP-9) from the observed data to a minimum temperature of approximately 15°C below the anticipated freezing point.

† Numbers in paranthesis represent the minimum temperature attained at the end of cooling.

temperature to about -50°C, it was possible to conduct 5 to 8 tests on those fuels whose freezing points are above -30°C. Only a few tests were conducted on fuels whose freezing points are below -30°C. In general, when the fuel was cooled to a temperature, which is less than 15°C below the freezing point of the test fuel, the measured freezing point was found to be higher than reported values, showing that the minimum temperature attained is not sufficient. However, when the fuel was cooled to a temperature which is more than 15°C below the freezing point, the measured freezing point was found to be close to the reported values. Therefore, we concluded that the test fuel must be cooled to a temperature at least 15°C below the anticipated freezing point.

The values of freezing point shown under the column "freezing point" in Table 5 are those interpolated or extrapolated from the test data to a point where the minimum temperature attained was 15°C below the freezing point. For the fuels LFP-1 and LFP-9, extrapolation was used and for all other fuels, interpolation was used.

D. Comparison of Measured Values with Reported Data

Eight aviation fuels were tested using the thermal and optical techniques at our facilities to evaluate the suitability of these methods to develop a portable freezing point apparatus. For the purpose of studying the accuracy of the results obtained using these conceptual methods, arrangements were made to test these eight fuels at other facilities where the fuels can be tested using the established test methods, such as ASTM-2386 and DSC. Samples of these eight fuels were sent to the Materials Science laboratory at Rensselaer Polytechnic Institute (RPI) at Troy, New York. Samples of these fuels were also available at the fuels research laboratory, NASA, Cleveland. Tests were conducted independently on these fuels at RPI and the freezing points measured using the ASTM method and DSC method were sent to us. Similarly, tests were conducted at NASA and the freezing point values measured using the ASTM method and DSC method were provided by the NASA project manager.

Table 6 summarizes the measured freezing point of eight aviation fuels at MRI, NASA, and RPI. The results shown under the thermal technique of MRI are those obtained using the new thermal method (point of inflection). A comparison of the values measured at MRI using the experimental techniques with those measured at NASA and RPI using the ASTM and DSC methods indicate that both thermal and optical techniques are capable of predicting the freezing point of aviation fuels satisfactorily. The comparison of MRI's freezing points with those obtained by RPI and NASA is also presented in the form of a 45 degree line of perfect agreement in Figures 42 through 45.

E. Conclusions

A number of conclusions can be drawn based on the results obtained in the thermal and optical methods compared with other reported values. First of all, we find that the thermal technique provides a satisfactory correlation with ASTM D-2386 method. For six out of the total eight fuels

TABLE 6

COMPARISON OF TEST DATA WITH REPORTED VALUES
(Freezing point in °C)

		MRI		NASA		RPI	
S No.	Test Fuel	Thermal	Optical	ASTM	DSC	ASTM	DSC
1	LFP-1	-41.9	-	-39.0	-38.5	-41.0	-40.2
2	LFP-4	-12.4	-12.2	-11.0	-13.7	-12.6	-11.8
3	LFP-6	-27.7	-27.5	-24.0	-27.2	-29.1	-26.3
4	LFP-7	-10.5	-10.6	-9.5	-13.0	-12.6	-12.1
5	LFP-9	-44.4	-	-40.5	-43.0	-45.1	-43.6
6	ERBS	-21.8	-25.5	-21.0	-23.0	-24.6	-22.8
7	Fuel No. 7	-25.4	-25.5	-26.7	-26.8	-27.9	-28.7
8	Fuel No. 8	-31.9	-32.0	-29.0	-31.8	-34.6	-31.4

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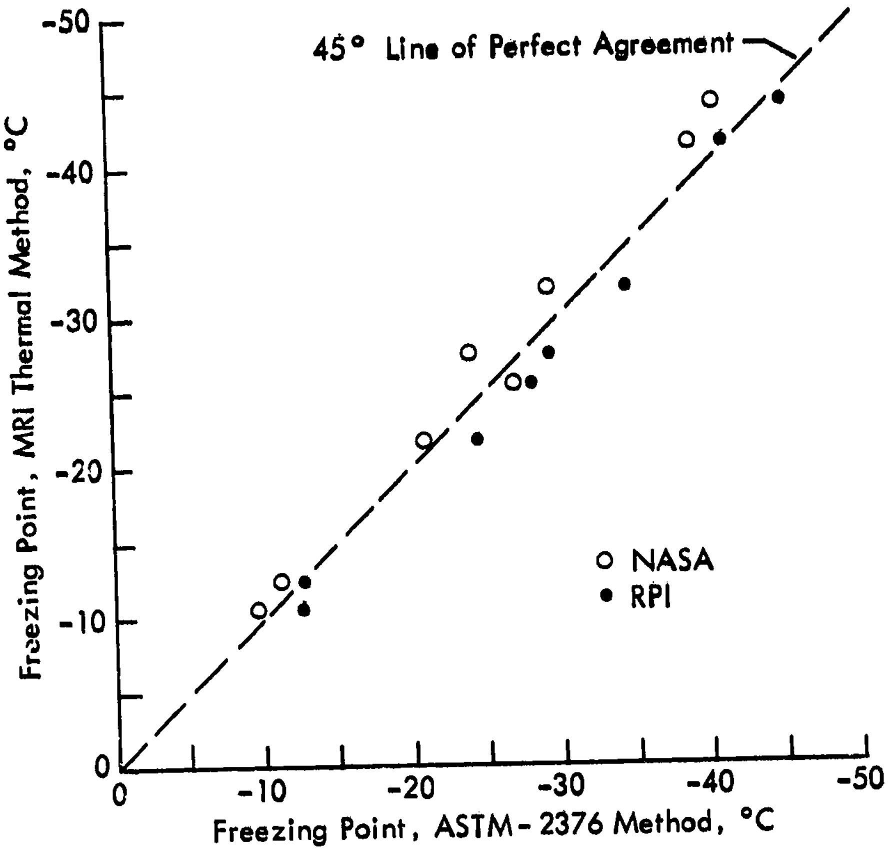

Figure 42 - Comparison of the Results of MRI Thermal Method with Those Obtained by ASTM Method

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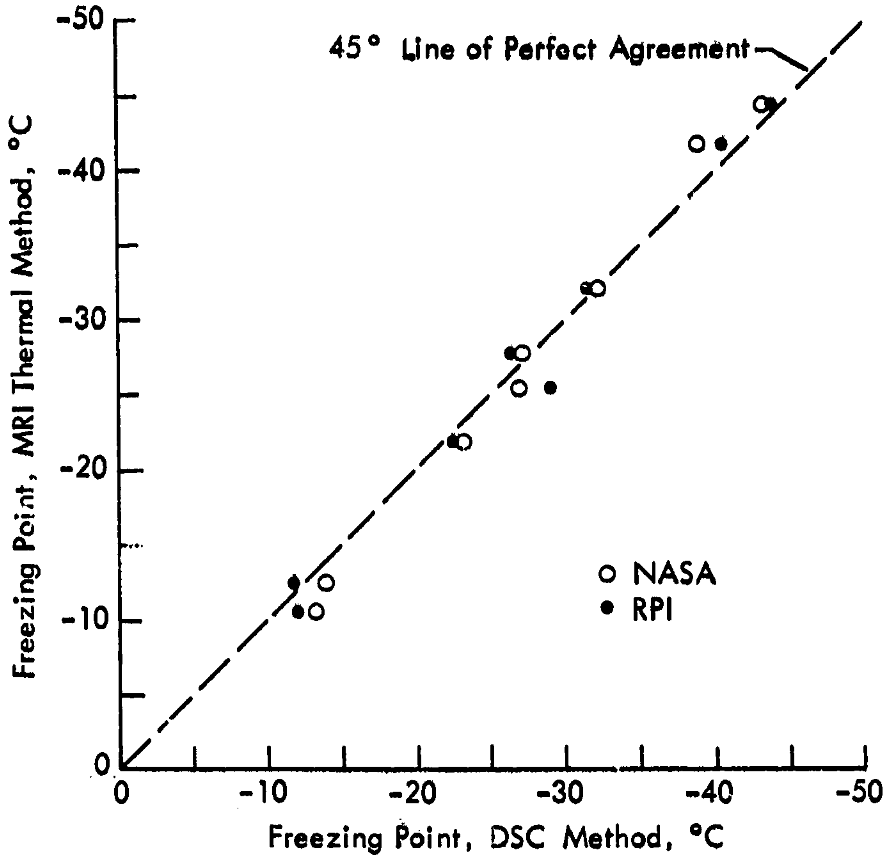

Figure 43 - Comparison of the Results of MRI Thermal Method with Those Obtained by DSC Method

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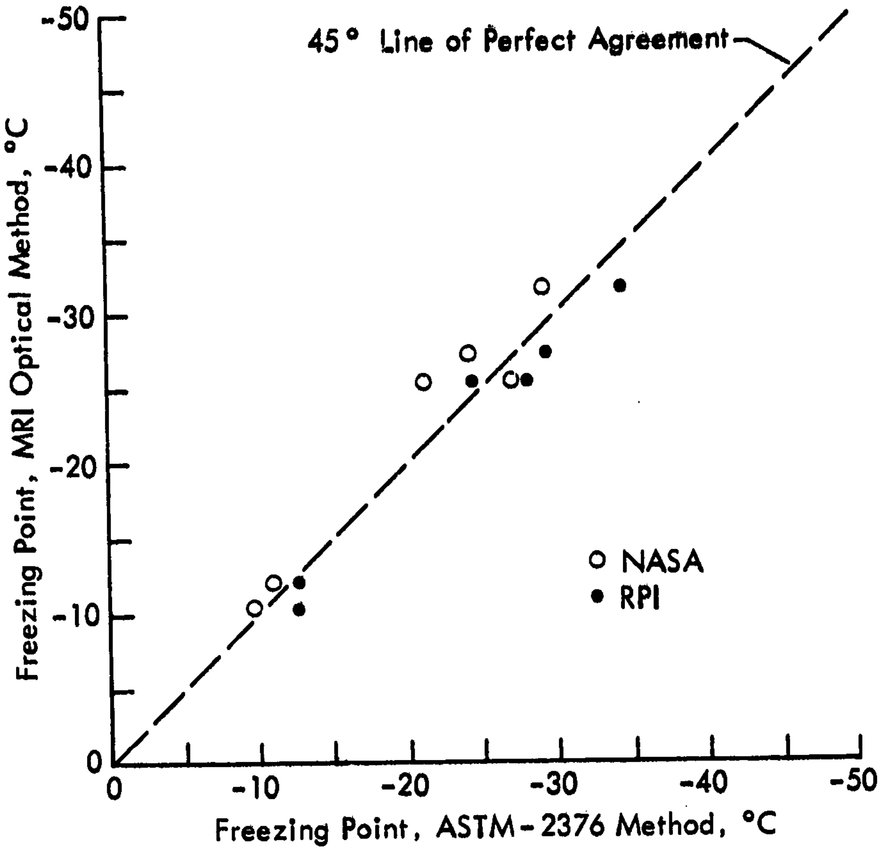

Figure 44 - Comparison of the Results of MRI Optical Method with Those Obtained by ASTM Method

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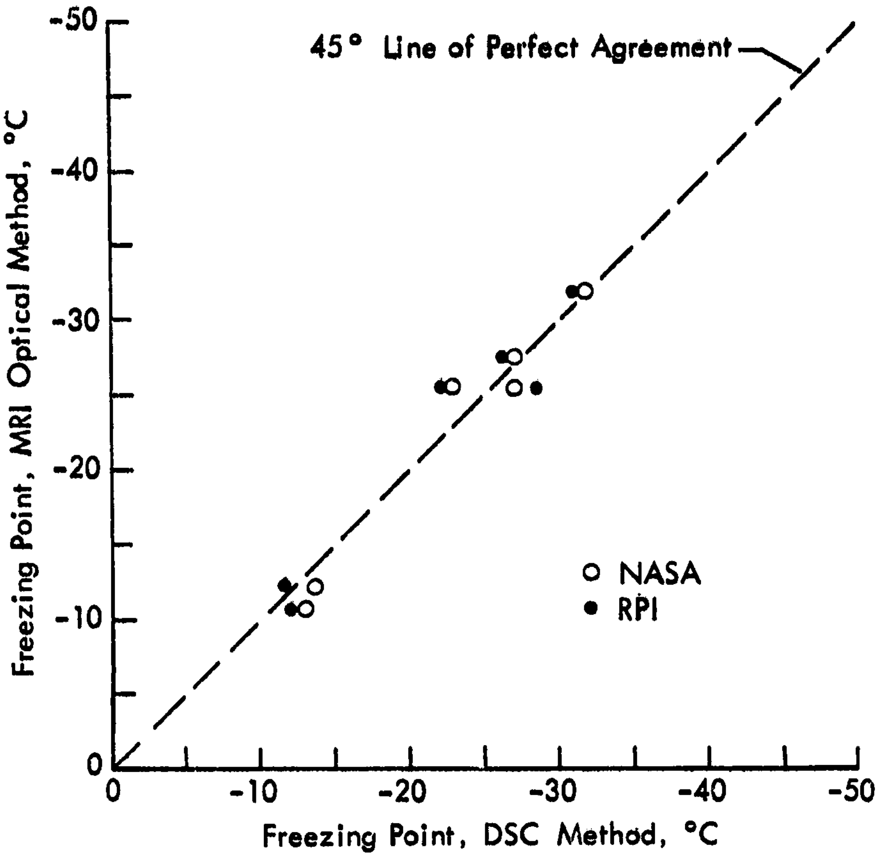


Figure 45 - Comparison of the Results of MRI Optical Method with Those Obtained by DSC Method

ested, the values predicted by the MRI thermal method falls in between the values obtained at NASA and RPI (using the ASTM method). Thermal technique also provides very good correlation with DSC, and therefore this technique is comparable to the standard DSC method as a tool for evaluating the freezing point. The thermal method - DTA - is expected to work only if the problem of secondary signals can be resolved.

Another observation made from the test results is that the freezing point measured in a test in which the fuel was cooled to about -15 to -20°C below its freezing point (see Figure 41) provides a more satisfactory result (very close to ASTM results). This suggests that the minimum cooling temperature should at least be about 15 to 20°C below the anticipated freezing point.

The optical technique is also capable of predicting the freezing point of aviation fuel very satisfactorily. However, the optical technique fails to predict satisfactory values for pure substances. These results are surprising because the technique did not fail for fuels which are complex mixtures of several species. Failure of the optical technique for pure substances remains unexplained.

F. Selection of Most Promising Method for the Design of Portable Unit

One of the two techniques, namely thermal and optical, was to be selected for the conceptual design of a portable, rapid freezing point apparatus. The following points were considered in the process of selection.

- Time required to complete a test.
- Ability of the technique to detect the freezing point of all aviation fuels tested.
- Size and simplicity of the test equipment that could be developed using the particular technique.
- Extent of care to be exercised by the user while testing.

The time required to complete a test is generally dependent on the rate at which the fuel is cooled and rewarmed and not on the particular technique employed to detect the freezing point. The time required to cool and rewarm the fuel depends on the freezing point of the test fuel and varies from 4 to 8 min. However, the first run in a day requires an additional time, if we employ the optical technique, to warm-up and stabilize the light source from the laser. This time is approximately 3 min for the laser used in our test setup. For field applications, this is an added time, and therefore we concluded that the thermal technique requires less time, and therefore is preferred to the optical technique.

With regard to the ability of the technique to detect the freezing point of all aviation fuels tested, we find that both thermal and optical techniques work satisfactorily for most of the fuels tested. However, the thermal technique works satisfactorily for all the fuels tested but the optical technique did not work satisfactorily for certain test samples, particularly pure species. In this respect also, we find that the thermal technique is superior to optical technique.

The thermal technique offers additional benefits of small-size test equipment and simplicity in construction and operation. The added components, in the optical technique, such as laser and its power source, detector and its power source make the test equipment relatively large and complex.

No excessive care need be exercised by the user to conduct the test using the thermal technique. In the optical system, preparation of the optical window, aligning the laser and detector, adjusting the exposed light, etc., require additional care, and therefore a skilled operator may be required to use the equipment.

Considering all the factors mentioned above, it was decided to select the thermal technique for designing concepts for a portable, rapid freezing point apparatus.

V. DESIGN OF PORTABLE UNIT

The results of the experimental evaluation (presented in the previous chapter) indicates that the thermal technique using the point of inflection method can be employed to conceptually design a self-contained, portable apparatus for the measurement of freezing point rapidly. This chapter presents the details of the design of a portable, rapid freezing point apparatus.

A. Thermoelectric Cooler

Figure 46 shows an isometric view of the TE cooler unit. The unit has a main housing which is made of 12.7 mm thick acrylic sheet. The interior of the housing accommodates other components. The arrangement of different components inside the housing is as follows. At the center is the cell holder which carries the test cell, and on each side of the test holder are three TE modules (forming a three stage cooler) which are bonded to each other. On the outside of each set of TE modules is bonded an ice-water box. A pressure plate is inserted between the right-side ice-water box and the right end wall of the housing. A clamp screw is provided in the right end wall of the housing and this screw extends up to the right face of the pressure plate.

The functions of the various components inside the housing are as follows:

Ice-water box: Ice-water boxes are filled with a mixture of ice and water during testing to serve as a heat sink (during cooling) or heat source (during rewarming).

Three-stage TE coolers: TE coolers are used in the unit which will, during testing, pump the heat either from the test fuel to the ice-water mixture (cooling mode) or vice versa (rewarming mode) with the aid of DC electric power.

Cell holder: The cell holder carries the test cell and during the test, the cell holder is inserted in the space in between the TE coolers to keep the test cell at the right position. A small hole provided at the top of the cell holder accommodates the thermocouple for the measurement of fuel temperature.

Test cell: The test cell is a small container that can be filled with fuel sample whenever a test is to be carried out. The cell holds about 4 ml of fuel sample.

Clamp screw: The clamp screw is used to tighten the test cell in between the two coolers.

Pressure plate: The pressure plate receives the point thrust developed by the clamp screw and distributes this thrust uniformly over the face of the ice-water box.

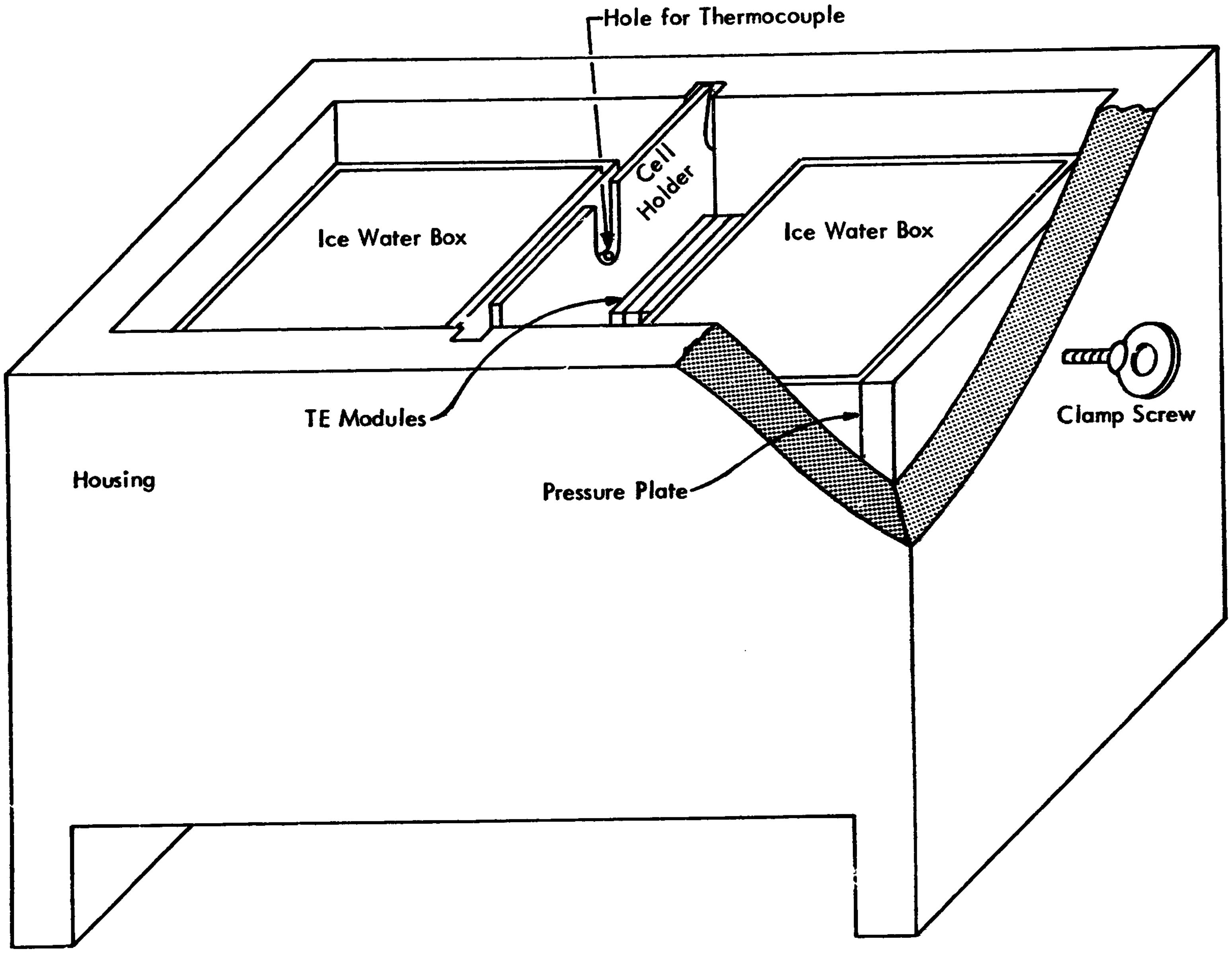


Figure 46 - Isometric View of the TE Cooler Unit

In addition to the components shown in Figure 46, other components that are required in the unit are: (a) one support block that will be kept below the TE modules, and that will support the modules and provide a seat to the cell holder; and (b) two cover plates that will be used to close the top during the performance of tests. In addition, the housing may be insulated using a 25 mm thick styrofoam sheet.

The dimensions and other specifications of all the components are shown in Figures 47, 48, and 49.

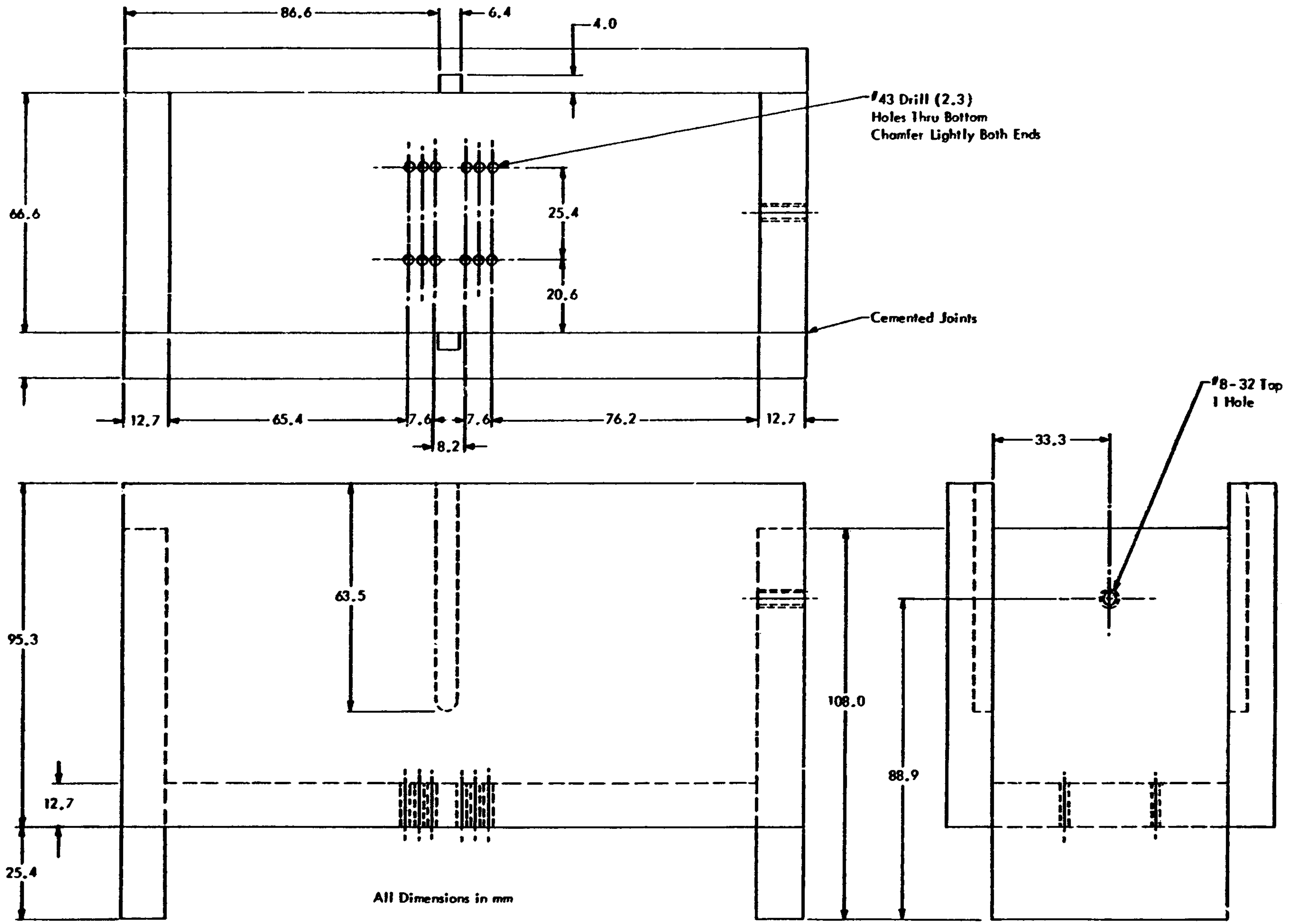
B. <u>Other Accessories</u>

The additional accessories that are required in the freezing point apparatus are: (a) a 12 V DC battery; and (b) an electrical microprocessor and temperature indicator (see Figure 50).

1. <u>The battery</u>: The apparatus requires DC power for the operation of TE modules during cooling and rewarming. A 12 V DC battery, capable of delivering current in the 10 to 20 amps range will be adequate for this purpose. The processor and indicator unit can also be operated using the same power source.

2. <u>Processor and temperature indicator</u>: This unit is intended to receive the temperature signal from the thermocouple, process the signal through certain analog circuits to identify the freezing point and indicate the temperature after making an analog to digital conversion. Primarily, there will be two analog circuits to process the temperature signal. A differentiating function circuit will first receive the millivolt signal of the thermocouple and outputs the time derivative of this signal. This derivate signal will then be fed to another circuit which will have peak-hold function. This circuit will hold the temperature signal when its input signal (which is the time derivate of temperature) attains a peak. In addition to the two analog circuits, there will also be a small A to D converter (analog to digital) that digitizes the temperature signal with readout on a LED display. This display will be made to "hold" when the peak-hold function finds a maximum in the time derivative signal. The display will then read the freezing point.

The unit, in addition to processing the data and indicating the temperature, will also control the cooling mode supply voltage and the rewarming mode supply voltage. In a more sophisticated unit, controls can also be arranged such that constant cooling rate and/or constant rewarming rate can be achieved.



Housing - 1 Req'd
Material: 12.7 thick Acrylic

Figure 47 - Components of TE Cooler Unit.

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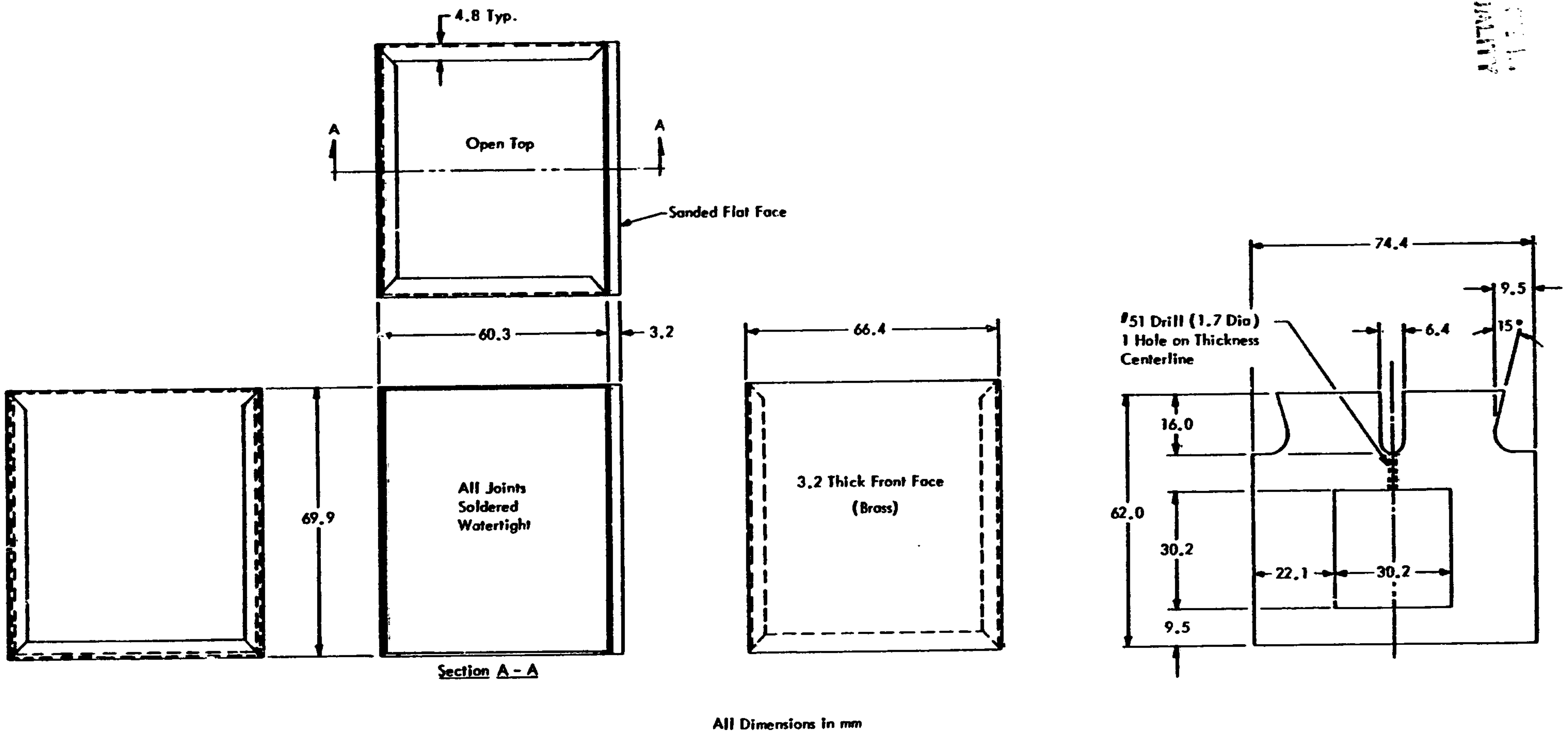

Ice Water Box - 2 Req'd
Material: 0.5 Brass Sheet & as Noted

Cell Holder - 1 Req'd
Material: 3.2 thick Acrylic

Figure 48 - Components of TE Cooler Unit (cont)

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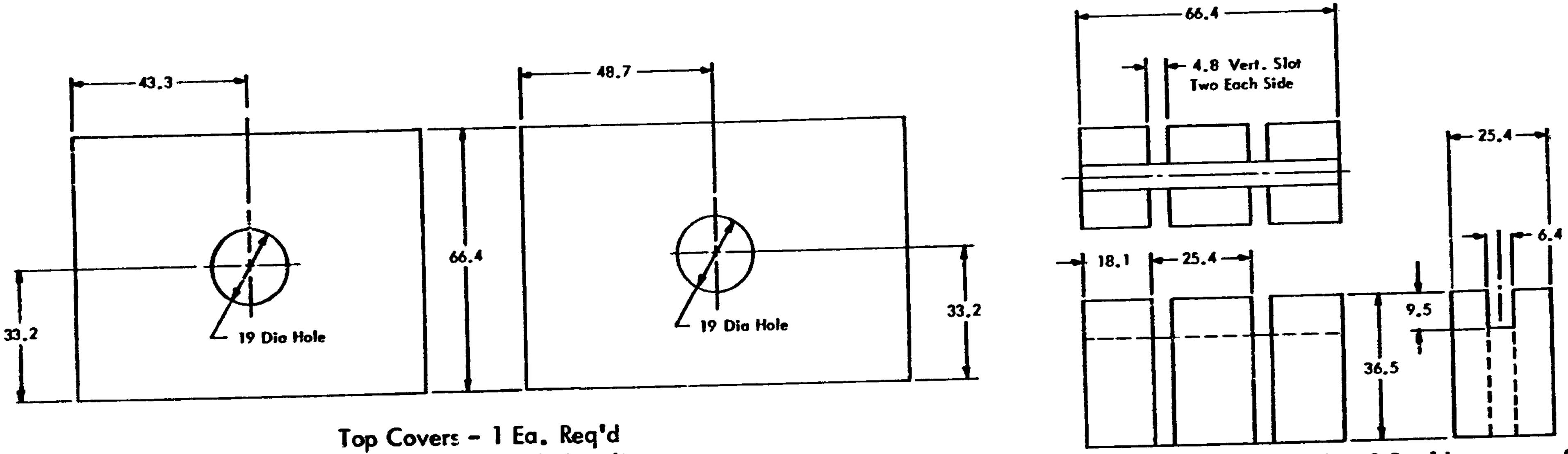
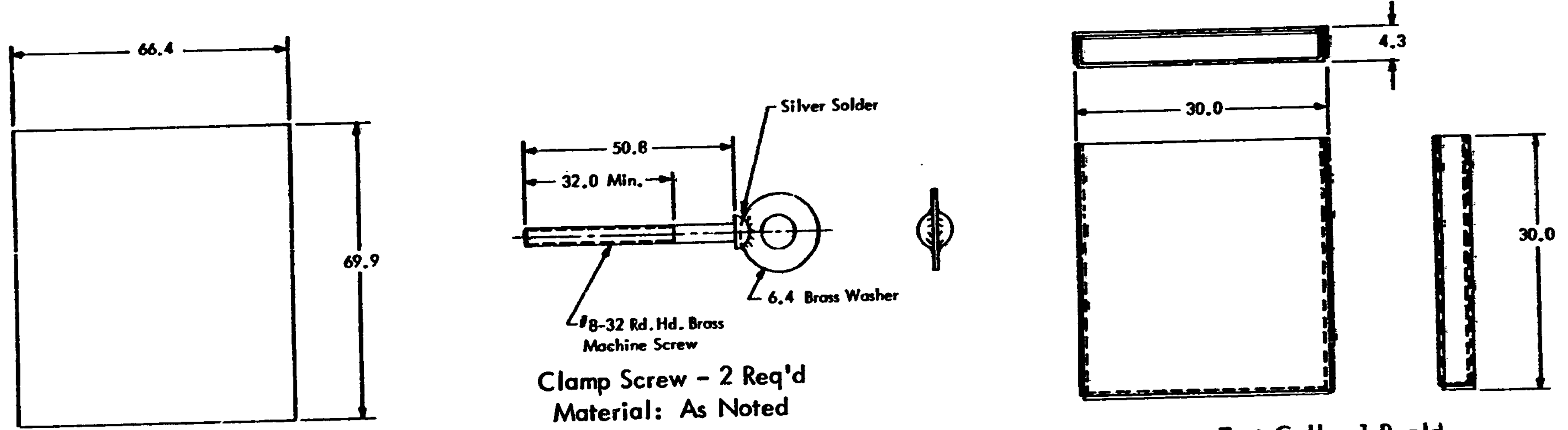


Top Covers - 1 Ea. Req'd
Material: i2.7 thick Acrylic

Support Block - 1 Req'd
Material: 25.4 thick Acrylic



Pressure Plate - 1 Req'd
Material: 6.4 thick Acrylic

Clamp Screw - 2 Req'd
Material: As Noted

All Dimensions in mm

Test Cell - 1 Req'd
Material: 0.5 thick Stainless Steel

Figure 49 - Components of TE Cooler Unit (conc)

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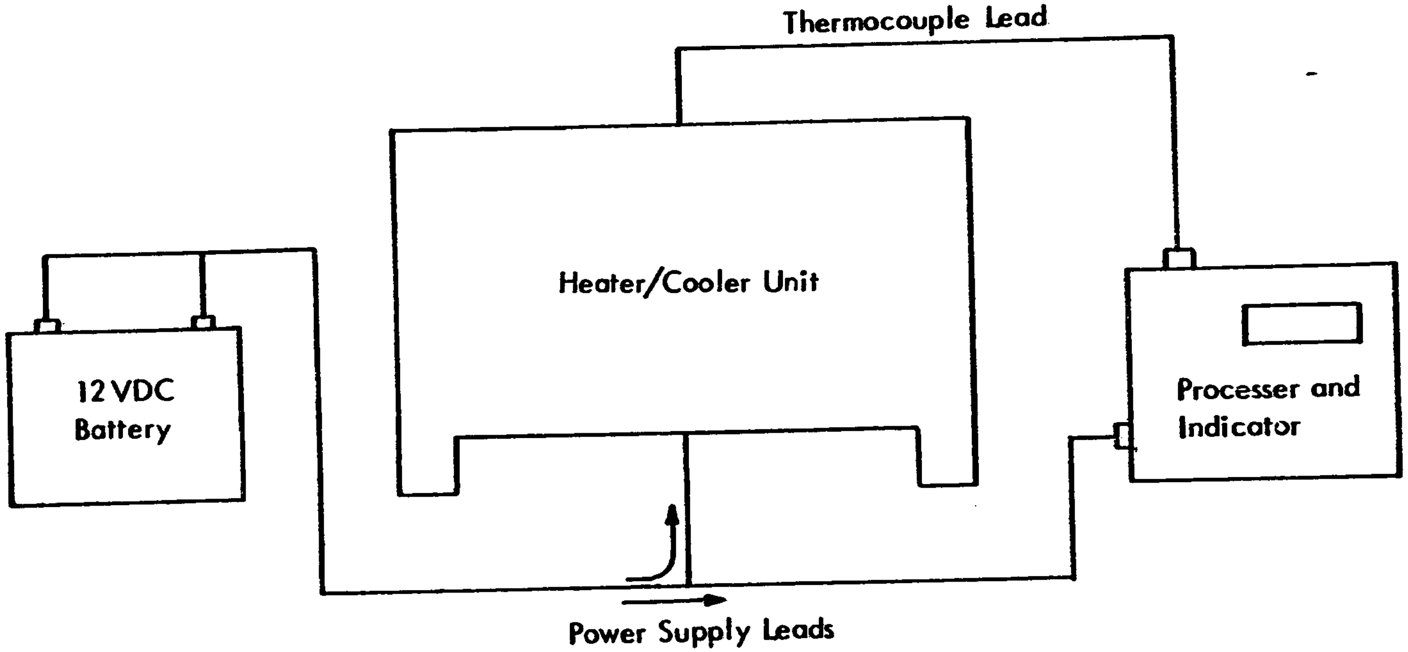

Figure 50 - Components of Freezing Point Apparatus

VI. CONCLUSIONS AND RECOMMENDATIONS

This chapter discusses the conclusions and recommendations based on our efforts in this study. The conclusions are presented first and the recommendations follow.

A. Conclusions

1. Portable devices for measuring the freezing point of aviation fuels having simple, compact construction and that are easy to operate can be designed and fabricated. A small 12 V DC battery is the only power source required to operate the device.

2. In the testing device which was built, the freezing point is measured rapidly; the time required to complete a single test is as low as 3 to 5 min and, in no case, exceeds 10 min.

3. Concepts selected for experimental evaluation included thermal and optical techniques. In all methods, both the sample and reference materials were cooled by thermoelectric modules. In one thermal method, the temperature difference between the test fuel and a reference was used to identify the freezing point. In another thermal method, the point of inflection observed in the temperature-time history was used to determine the freezing point. In the optical method, the detection of light scattered by the frozen fuel was used to measure the freezing point. All these methods were found to be capable of measuring the freezing point of aviation fuels.

4. A number of interesting observations were noted in these thermal and optical techniques. First, in the differential thermal method, the differential signal was found to be composed of a main latent heat signal and a secondary unwanted signal. For pure substances, the latent heat signal was very predominant and the effect of secondary signal was usually negligible. For aviation fuels, the secondary signals were of the same order of magnitude as the main signal and thus affected the measured freezing point. The secondary signals were generated at the time of switching from the cooling mode to the rewarming mode, and the temperature of the fuel at the time of switching was found to influence the measured freezing point. Several changes and modifications were incorporated into the test unit which helped to minimize the secondary signals but did not eliminate them completely.

5. The point of inflection method was used successfully in measuring the freezing point of both pure substances and aviation fuels. The measured values of the freezing points of eight different aviation fuels compared very well with reported values. There were no secondary signals generated in this test method. The best results were obtained when the supply voltage during rewarming was set so that the rewarming rate at the time of crossing the freezing point was at an optimum value. This suggests that a constant rewarming rate (heat added to the fuel in watts does not change

C-2

with time) is desirable in this technique. It is expected that very accurate measurements can be made if, in addition to having a constant rewarming rate, provision is made for the unit to operate at a constant cooling rate and to hold the low temperature for a finite period before switching from cooling to rewarming mode.

6. The secondary signals observed in the differential thermal method can probably be eliminated completely if the test and reference sample sizes are made small. The use of small samples were not explored in this program. Small samples may also measure the freezing point more accurately in the point of inflection method. Additional work is required to confirm this.

7. In the optical method, freezing points of several aviation fuels were measured accurately. In addition to detecting the freezing point, this technique can also be used to detect the wax appearance point (the temperature at which first few crystals are formed during cooling). When pure substances are tested, the optical technique measures the wax appearance point accurately while there is some error in the measured value of freezing point. The reason why this method could be used to measure the freezing point of aviation fuel but not that of pure substances is not known. More research is needed to understand the changes occurring in the light transmission properties of pure substances and aviation fuels. The optical method was found to be not as simple (both in construction and in operation) as the thermal method, because of added components such as a laser power source and a sensitive light detector. The optical scheme can be simplified, however, by using fiber optics and a small photovoltaic cell. With the introduction of fiber optics, it may be possible to develop a combined freezing point and wax appearance point apparatus.

B. Recommendations

Based on the results of this study, it is recommended that the following additional work be performed so that the overall objectives of developing a portable freezing point apparatus can be more exactly met.

1. The point of inflection method is expected to yield very accurate values of freezing point, if the TE cooler is equipped with controls to achieve a constant rewarming rate; it is recommended that suitable electric/electronic controls be added to the power supply circuit of the TE cooler. These controls should provide both constant cooling and rewarming rates. In addition, the controls should provide a fixed predetermined hold-up period at the end of cooling whenever necessary. After incorporating these controls, the point of inflection method should be evaluated further by conducting several tests on pure substances and on aviation fuels. These are necessary to verify the accuracy and repeatability of the test method. From the results of these tests, the optimum cooling and rewarming rates needed to improve the accuracy of the method could be established.

2. In the present test device the test and reference sample holders were sized to hold upto 2.5 ml of sample material in each. The

thickness of the sample holder in the direction of heat transfer is around 4 mm. It is suspected that during both cooling and rewarming, a nonuniform temperature field across this thickness exists. The temperature of the samples can, however, be made more uniform if the sample volume is reduced to a volume of about 0.02 to 0.03 ml. This could be done by using metal blocks with suitably sized holes to accommodate the test and reference samples. Small samples could then be used in a TE cooler which is equipped with controls for constant rate cooling and rewarming. Tests in this new configuration using both the differential thermal method and the point of inflection method could then be made. The differential thermal method would not be likely to exhibit secondary signals in this arrangement since it is more similar to the standard DTA apparatus. The point of inflection method is expected to measure the freezing point accurately with small samples, since the generation of secondary samples can be avoided.

The thermal conductivity of the material to be used in fabricating the sample holders of the small sample size system can have a significant effect on the peak ΔT value obtained in the differential thermal method. With a high thermal conductivity material, the peak ΔT obtained will be very small whereas with a low thermal conductivity material, the peak ΔT obtained will be much higher. In this respect, the low conductivity material may be preferable when one attempts to determine the latent heat evolved during melting through the process of integration of the area under the ΔT curve. However, low thermal conductivity material is expected to exhibit a peak which is spread out over a large temperature range, making it difficult to accurately correlate time-temperature behavior with freezing point. When high thermal conductivity material is used, the ΔT peak will be very sharp, accurately indicating the freezing point. These fundamental characteristics must be examined by performing several tests on aviation fuels using sample holders made of different materials having a wide range of thermal conductivity values.

3. In characterizing the aviation fuel, the total latent heat evolved during the process of melting for an aviation fuel is also an important parameter to fuel fundamental researchers. The same concepts developed for the freezing point determination can be employed to determine the latent heat evolved as a function of fuel temperature in its melting range. The area under a ΔT curve generated by the differential thermal scheme using controlled TE coolers and small samples can be correlated to determine this latent heat. As mentioned earlier, the thermal conductivity of the material of sample holder will play a significant role in these tests also. Several tests should be conducted to evaluate these concepts in the determination of the latent heat of fusion of aviation fuels. In the case of the point of inflection method, no means of relating the time-temperature history to the latent heat of fusion has been reported. Both theoretical and experimental efforts are needed to show the possibility of using the point of inflection method to determine the latent heat of melting.

4. The optical method evaluated in this program may have both some advantages and some disadvantages over the thermal method. The main advantage of the optical method is that this method is capable of predicting both the freezing point and wax appearance point in a single test.

Thus, the concepts involved in the optical method can be utilized to develop a combined freezing point and wax appearance point apparatus. There are a number of potential problems, however, yet to be resolved. The fundamental process that changes the light transmission properties during freezing and melting is not understood well enough to answer the question of why this method will successfully measure the freezing point of multicomponent substances like aviation fuels, but fails in the case of pure substances. The optical method in the configuration developed as of now is not as simple as the thermal methods both in terms of construction and operation. Therefore, we recommend that the unit be equipped with simple optical components such as optical fibers, photovoltaic cell and LED in the place of metal optical tubes, integrated detector, and laser light source. The resulting system will then be as simple as the thermal system. Tests need to be conducted to study the possibility of using this new optical system to determine the wax appearance point and the freezing point.

VII. REFERENCES

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