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ORGANOSILOXANE WORKING FLUIDS FOR THE LIQUID DROPLET RADIATOR

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I, II

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SUMMARY

The objective of the work reported here was to evaluate siloxane-based fluids as working fluids for the Liquid Droplet Radiator. Over an operating temperature range from 255 to 394K, working media need to have viscosities below about 25×10^{-6} m²/sec, and vapor pressures less than 10^{-7} Pascals. These properties and the heat transfer properties of the fluids must be retained during long missions in the environment at the orbital altitude of the Space Station. The environmental factors include vacuum of about 10^{-6} Pascals, collisions (5 eV) with atomic oxygen, and energetic radiation, both particulate and solar.

Five candidate fluids were recovered by vacuum distillation from existing siloxane polymers. Candidates included a polydimethylsiloxane, three phenyl-containing siloxanes, and a methylhexylsiloxane. Vapor pressures were approximated from evaporation rates in TGA under vacuum, using Dow Corning® 704 Fluid as a reference standard.

Polydimethylsiloxane (PDMS) and polymethylphenylsiloxane (PMPS) were selected for further characterization. Both fluids consisted of narrow molecular weight distributions with average molecular weights of about 2500 for PDMS and 1300 for PMPS.

The fluids were characterized by IR, Si²⁹ NMR, GPC, and LC. Properties measured as a function of temperature included viscosity, viscosity/shear dependence, vapor pressure, density, surface tension, specific heat, thermal conductivity, and electrical conductivity. Pour points, flash points and fire points were measured. Heats of vaporization were calculated from the vapor pressure/temperature relation. IR emittance and transmittance of thin films were determined.

A search of siloxane literature provided the basis for discussion of the thermal, oxidative, and radiation stability of the siloxane families. Flammability and toxicity are also discussed. Routes for adjusting viscosity, vapor pressure, and stability against elements of the LDR environment are suggested.

The requirement for low viscosity combined with low vapor pressure has been met in these siloxane fluids. Lighter fractions may optimize viscosity for operations in the lower end of the temperature range. Existing information on the reactions of atomic oxygen with siloxane fluids is probably inadequate for predicting service life in the unique combined environment of the LDR, or for directing further development of stabilized versions, if necessary.

INTRODUCTION

The Liquid Droplet Radiator (LDR) (Ref. 1) is a new approach to rejecting heat in space, in which waste heat collected in a space system by a circulating fluid is radiated into space directly from the surface of liquid droplets. An unusual fluid or family of fluids is required to perform this function. Temperature of the fluid may be 255 to 394K (0 to 250°F). Vapor pressure at the operating temperature must be extremely low to minimize contamination of the space system or loss of fluid by evaporation when exposed to the space environment. Viscosity must be low to facilitate pumping at low power cost and collection of droplets. The fluid must survive years of exposure to the space environment at orbital altitude without significant change in physical and thermal properties. Environmental factors include vacuum of about 10^6 Pascals, collisions (5 eV) with atomic oxygen, and energetic radiation, both particulate and solar.

In the first stages of the joint Air Force Rocket Propulsion Lab/NASA-Lewis Research Center program on the LDR, phenyl-containing siloxanes [tetramethyltetraphenyltrisiloxane (1) and trimethylpentaphenyltrisiloxane (2)] were considered as candidate fluids, having low vapor pressures and resistance to oxidation and radiation.

It was the objective of the work described here to evaluate other existing siloxane-based fluids as working fluids for the Liquid Droplet Radiator. First, five candidate silicone fluids were identified for screening on the basis of vapor pressure and viscosity (Task I). Following review of the results of Task I, two of these fluids were selected for further characterization (Task II). Measurement methods and properties are described in this report.

Following the exploration and measurement phases (Tasks I and II), recommendations are made concerning silicone fluids that might be synthesized or formulated to optimize performance in the LDR.

Operating life of the fluid in the LDR environment is affected by thermal stability, oxidative stability, and resistance to radiation. A search of the technical literature related to these subjects was carried out.

- (1) Dow Corning 704 Fluid
- (2) Dow Corning 705 Fluid

TASK I. SCREENING CANDIDATE FLUIDS

Selection of five candidates for screening.

Requirements for the initial candidate fluids were:

Silicon-based

Available

Viscosity - preferred 1×10^{-6} to 25×10^{-6} m²/sec
(1-25 cs) at 255-394K or over a substantial
segment of that temperature range.

Vapor Pressure - less than or equal to 10^{-7} Pa ($\sim 10^{-9}$ torr)
at 394K.

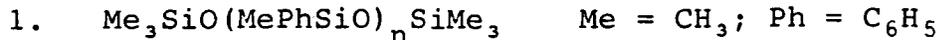
Ideally a single fluid should satisfy the full operating range of 255-394K. However, since low vapor pressure and low viscosity tend to be incompatible properties, an alternative would be to use two or more fluids, each suited to a segment of the temperature range.

An estimate of the allowable vapor pressure was made from the Knudsen model for evaporation at conditions of molecular flow (Appendix I). Droplets having diameters of approximately 0.1mm are proposed. The resulting high ratio of surface to volume maximizes the fraction evaporating. Fractional evaporation rate is inversely proportional to diameter of the drop. For a vapor pressure of 10^{-7} Pa, evaporative loss might be 10% or more per year, assuming that 10% of the fluid volume is exposed as droplets. Figure 1 shows the target vapor pressure in relation to the vapor pressure of 704 and 705 fluids. It should be noted that for materials of this molecular size, vapor pressure varies sharply with temperature. Lowering temperature by 10-15K reduces vapor pressure tenfold.

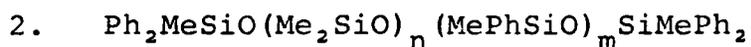
Projecting from vapor pressures of known siloxane products and compounds, it was clear that the necessary vapor pressure would occur in material with molecular weight over 1000 for the case of methylphenylsiloxane and over 2500 for dimethylsiloxane. Review of current products and materials being developed identified no compositions of these sizes except as they occurred as members of homologous series constituting polymeric products. In these polymers, either vapor pressures or viscosity would be high, depending on their distribution of molecular weights.

It was concluded that the most probable ready source for LDR fluid candidates would be distilled fractions from polymeric fluids. As recovered by a single stage vacuum distillation, the fluid fraction would be of narrow molecular weight distribution (low dispersity). For a given vapor pressure, the narrow distribution approaches the lowest viscosity possible for the specific polymer family. A single compound would be ideal. Again projecting from the vapor pressure/temperature relations known for more volatile members of siloxane homologous series, it appeared that the desired polymer fractions would distill in the range of 573 to 623K at 13 Pascal (0.1 torr).

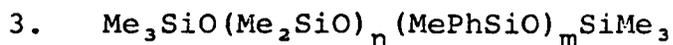
The following polymer families were selected for distillation:



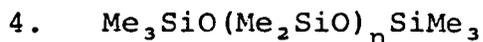
Phenyl sidegroups improve the resistance of siloxanes to oxidation and radiation. The ratio of phenyl to methyl constituents here is similar to that of 704 fluid. Viscosity would be higher than desired at low temperature.



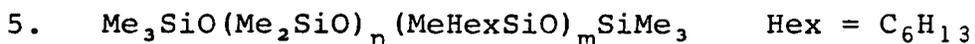
This polymer exists in the high-boiling residue of the process used to make 704 fluid. The presence of phenyl as end groups has the possibility of raising surface tension and/or showing a different relationship between viscosity and vapor pressure from that in (1) above.



The commercial source for this polymer has n approximately equal to m . It is expected that the narrow distillation cut would retain this ratio. This fluid, because of its lower phenyl content, would show less oxidative stability than (1) above, but lower viscosity.



Polydimethylsiloxane (PDMS) would have the highest chain length and molecular weight for a given vapor pressure, but lower viscosity, especially at the lower end of the LDR temperature range. While it is more susceptible to oxidation and damage by particle radiation, it is more transparent to ultraviolet radiation and possibly less affected.



The hexyl ligand offered the possibility of lower viscosity than in PDMS having the same vapor pressure. With the hexyl ligand, the chain length will be shorter, and consequently of lower viscosity. It would be necessary that the contribution of hexyl to viscosity be less than that of phenyl. A penalty in oxidation resistance, compared to PDMS, would be expected.

Branched methylsiloxane polymer was considered as the fifth candidate rather than the hexylmethylmethylsiloxane chosen. For polymers of the same molecular weight, branched structure is frequently found to give lower viscosity. Inspection of specific pairs of branched and linear compounds with molecular weight somewhat less than the LDR range showed the opposite effect, so this approach was abandoned.

Isolation of Task I Fluids

A fraction having narrow molecular-weight distribution was isolated by vacuum strip distillation from each of the five polymeric systems.

Equipment:

Conventional Pyrex® laboratory glass apparatus
1-liter three-neck strip pot, air-cooled pear-head
condenser, demountable connectors with taper or
spherical glass joints, sealed with silicone-
based vacuum grease
Electric heating mantle with Variac control
Magnetic stirrer
Pyrex receiver, 500 mL
Oil-sealed mechanical vacuum pump, 2-stage, capable of
blank-off pressure <1 Pascal (~0.01 torr)
Pressure measurement by tilt-McLeod mercury gauge,
connected by vacuum hose at the strip pot
Temperature measurement by mercury thermometers

Procedure:

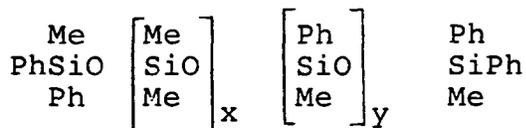
The source fluid was weighed to the strip pot. The system was assembled and vacuum was applied. Heat was regulated to give moderate rate of distillation. The pot temperature was taken to 631-653K (358-380°C) at 12-26 Pascal (0.1-0.2 Torr), (114 Pascals in one case), carrying the LDR fraction and the more volatile species overhead. The pot was cleaned and the distillate reloaded for topping. Volatiles were stripped to 548-582K (275-309°C), at 12-18 Pascals. The LDR cut remaining as bottoms was filtered through 0.45-micrometer paper. Insoluble dimethylsiloxane polymer from the vacuum grease made the phenyl-containing fluids hazy. Haze was removed by adding filteraid before filtering. Table I shows specific cut conditions and distribution of fractions for each fluid.

The first fluid stripped was polymethylphenylsiloxane. Gas chromatography was used with an internal standard ($\text{Me}_3\text{SiO}(\text{MePhSiO})_3\text{SiMe}_3$) to estimate the molecular sizes recovered with the selected strip conditions. Compounds through $\text{Me}_3\text{SiO}(\text{MePhSiO})_7\text{SiMe}_3$ were eluted. Species with $n = 6$ and 7 were major in the topping volatiles and were present in the LDR cut. This suggested that the bulk of the LDR cut would have $n = 8-10$.

Fluid Description

The general formulas for the five Task I fluids selected for vapor pressure and viscosity characterization are:

Ph₂Me

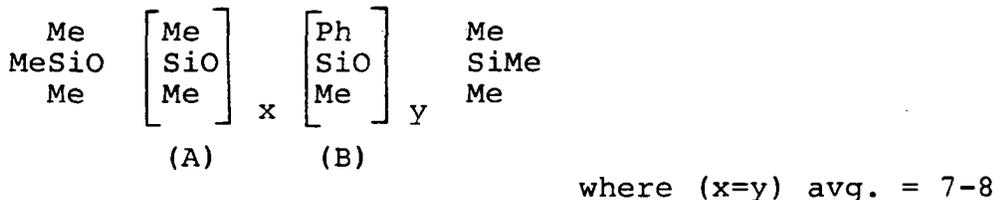


x and y were not determined for this fluid.

MePh



Me₂/MePh



The A and B units are not necessarily regularly repeating units since this material results from a random copolymerization. The structural formula refers to an average molecular composition.

Me₂



Hex Me/Me₂



The A and B units are not necessarily regularly repeating units since this material results from a random copolymerization. The structural formula refers to an average molecular composition.

Molecular weights and size distribution of these fluids were measured using gel permeation chromatography (GPC). GPC calibration data relating molecular weight to retention time are given in Figure 2. GPC calibration was accomplished using either pure compounds or narrow distribution standards of known molecular weight. Number average (\bar{M}_n)¹ and weight average (\bar{M}_w)² molecular weights and dispersity indices (\bar{M}_w/\bar{M}_n) are summarized in Table II. A typical chromatogram is given in Figure 3. The estimated accuracy of these molecular weight values is $\pm 10\%$.

The Ph₂Me and MePh fluids were also characterized in terms of molecular composition using reverse-phase liquid chromatography (LC). These materials consist of three to five major molecular entities, each differing by a single "mer" unit. Chromatograms of these two fluids are given in Figure 4.

A description of the GPC and LC units is given in Appendix II.

Measurements

Viscosity and vapor pressure of each fluid were measured. Kinematic viscosity was measured as a function of temperature over the range 255 to 394K (0° to 250°F) using Ubbelohde glass capillary viscometers. Viscometers were calibrated using oils certified by the National Bureau of Standards (obtained from Cannon Instrument Co., State College, PA.). Measurement procedures followed those described in Corporate Test Method (CTM) 0004 (Appendix II). CTM(s) are generally based on a corresponding ASTM Method. Minor deviations between our test procedure and the ASTM Method do occur, e.g. - frequency of calibration. Both accuracy and precision for these viscosity data are estimated to be $\pm 2\%$. Viscosity data are summarized in Table III and Figure 5.

A correlation is evident between fluid structure and the effect of temperature on viscosity. Those fluids with phenyl substituents on either the end groups or the polymer backbone exhibit a substantially greater viscosity-temperature dependence, especially at low temperatures. Furthermore, the influence of a permethylated mer unit on viscosity is evident from a comparison of the MePh fluid to the Me₂/MePh fluid, and the Me₂/MePh to the Me₂ fluid. Although the Me₂ fluid has the highest molecular weight and longest polymer chain length, it is the lowest viscosity fluid and exhibits the lowest dependence of viscosity on temperature.

Measurement of the vapor pressures of these fluids posed a formidable problem for two reasons. First, all of the fluids were distillation cuts from polymeric materials and as such consisted of a distribution of molecular species of similar chemical structures but different molecular chain lengths.

$$1. \quad \bar{M}_n = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

$$2. \quad \bar{M}_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$$

While extensive care and effort was expended to obtain as narrow a distribution of chain lengths as possible, the lowest molecular weight components still significantly influence the measured vapor pressure and fluid composition changes during measurement. Second, the measurement of vapor pressure in the targeted pressure range, 10^{-7} Pa, is difficult. A number of methods using sophisticated thermal analytical techniques have been reported (Ref. 2, 3). However, methods useful below about 10^{-3} Pa require a high degree of sophistication, such as the use of radioactively tagged materials. A recently developed technique, thermal evolution analysis (Ref. 4), has been demonstrated to be effective in our range of interest. However, considerable time and effort would be required to establish this technique.

Most of the cited methods are based on the Knudsen effusion equation (Ref. 5):

$$P = \frac{\Delta m}{\Delta t} \cdot \frac{1}{q} \left(\frac{2\pi RT}{M} \right)^{1/2} \quad (1)$$

Where: P = vapor pressure

R = ideal gas constant

q = orifice area

$\frac{\Delta m}{\Delta t}$ = mass loss rate

T = temperature (K)

M = molecular weight

In our approach, mass loss rates (evaporation rates) were obtained using a DuPont 1090 thermogravimetric analysis (TGA) system (Appendix II). However, the Knudsen equation did not apply directly. In our apparatus the requirement of thermal equilibrium between liquid and vapor phases of the evaporating sample was not necessarily met. In the Knudsen method this is accomplished by severely limiting the evaporation rate. The area of the vapor orifice is small compared to the sample surface. In our TGA approach, evaporation from the sample surface area (0.785 cm²) was not restricted in this way. However, deviations from thermal equilibrium were minimized by using very low evaporation rates. The Knudsen equation (1) also requires uninhibited molecular flow, i.e. operation at pressures $<10^{-2}$ Pa (10^{-4} torr). In our TGA apparatus, pressures of approximately 60 Pa (0.45 torr) could be conveniently maintained. The deviation from the requirement of unrestricted molecular flow was overcome by using an appropriate low vapor pressure standard fluid. For this standard, Dow Corning 704 Fluid was selected because of its low volatility and the availability of reliable vapor pressure data.

The Knudsen equation was applied as follows. Combining all constants in equation (1), together with a constant to represent the departure from uninhibited molecular flow, we obtain

$$P = \frac{\Delta m}{\Delta t} \cdot K \left(T/M \right)^{1/2} \quad (2)$$

or the evaporation rate is given by

$$\frac{\Delta m}{\Delta t} = \dot{m} = \frac{P}{K} \left(M/T \right)^{1/2} \quad (3)$$

For the standard fluid (DC-704),

$$\dot{m}_{704} = \frac{P_{704,T}}{K} \left(\frac{M_{704}}{T} \right)^{1/2} \quad (4)$$

Similarly, for the test fluid,

$$\dot{m}_{x,T} = \frac{P_{x,T}}{K} \left(\frac{M_x}{T} \right)^{1/2} \quad (5)$$

Dividing (4) by (5) and solving for the vapor pressure of the test fluid at temperature T, we obtain

$$P_{x,T} = \frac{\dot{m}_x}{\dot{m}_{704, T}} \left(P_{704,T} \right) \left(\frac{M_{704}}{M_x} \right)^{1/2} \quad (6)$$

With this relation, vapor pressures were measured as follows:

1. Obtain dynamic programmed TGA of the test fluid to establish the range of temperatures for evaporation rate measurements.
2. Perform isothermal evaporation rate measurements at constant pressure and several temperatures over this range.
3. Using a least-squares method, fit mass-loss for the test fluid and for the reference fluid DC-704 to the equation

$$\log_{10} \dot{m} = A - B/T \quad (7)$$

4. Calculate from equation (6) the vapor pressure at each test temperature for the test fluid. The vapor pressure (torr) for 704 is given by

$$\log_{10} P_{704} = \frac{7380}{T} - 10.07 \log T + 42.05 \quad (8)$$

The experimental set-up and procedures were as follows:

1. Load 80 to 90 mg. of the test fluid into the circular sample pan suspended from the lever arm of the TGA unit.
2. Clamp the glass envelope of the TGA unit securely into position.
3. Commence evacuation of the TGA sample chamber. A conventional mechanical vacuum pump is capable of providing the required working pressure of 0.45 torr. Pressure was regulated by air bleed through a micro-metering valve. Vacuum was monitored with a McLeod gauge.
4. Following evacuation of the TGA unit to a pressure of 0.45 torr, an initial devolatilization of the fluid was accomplished by heating the sample at a moderate constant temperature so as to evaporate 8-10 mg in 30 to 60 minutes of heating. This was intended to remove any adventitious low molecular weight decomposition products in the fluid which may have resulted from the stringent distillation conditions.
5. The TGA chamber was allowed to cool and the microprocessor was programmed for a series of mass loss measurements at selected constant temperatures.
6. The mass loss measurements commenced; mass of the samples was tracked by the microprocessor data unit. A typical series of mass loss measurements is given in Figure 6.
7. Evaporation rates were calculated for each temperature. The computer graphics system was used to expand each mass loss increment. The procedure is illustrated in Figure 7.

In Figure 8 the experimental evaporation rates for 704 Fluid are compared with the calculated mass loss curve for 704 under Knudsen effusion conditions, i.e. unrestricted molecular flow and liquid-vapor equilibrium. The difference in rates is of the order expected for the system pressure. The consistent systematic shift at all temperatures suggests that deviations from vapor-liquid equilibrium were minor or at least consistent.

To test the sensitivity of evaporation rate to system pressure, the evaporation rates for the 704 reference fluid were measured at 60 and 100 Pa (0.45 torr and 0.75 torr). The slight shift in two rate curves (also in Figure 8) suggest that control of system pressure to ± 0.05 torr is adequate.

In Figure 9, three series of measured mass loss rates are given for a single fluid. Run 1 was measured at higher temperatures than Runs 2 and 3. At high temperature, loss rate slowed appreciably during each temperature step as the composition of the sample and possibly that of the sample surface with respect to the bulk changed. Also, the temperature of the sample surface may fall below the indicated temperature when the rate of evaporation is excessive. Runs 2 and 3 demonstrate the repeatability of the mass loss rate measurements at lower temperatures and lower loss rates.

Mass loss rates for the five Task I fluids are given in Table IV and plotted in Figures 10a through 10e. For each fluid two series of mass loss rates were measured, as for example in Figure 10d, Series 1 and 2. In Series 1, loss rates were measured at progressively higher temperatures. After completing this series, the measurements were repeated on the same sample beginning at the low temperatures of the previous series. The difference in loss rates and slope between Series 1 and 2 is the result of changing composition of the fluid during Series 1. Series 2 better represents a fluid of constant composition, although somewhat heavier than the original fluid. The slope of the Series 2 data is appropriate for calculation of heat of vaporization of the fluid or extrapolation of the derived vapor pressure curve to lower temperature, i.e. those anticipated in the LDR. Typically, 25 to 30% of the initial fluid charge was evaporated in the first series of measurements.

The evaporation rate data for each fluid were fit to equation (7). The results of these data correlations are as follows:

704 Reference Fluid

$$\log_{10} \dot{m} = 8.47972 - \frac{5528}{T} \quad (\text{Correlation Coefficient} = 0.9980) \text{ (6 data points)}$$

Me₂/MePh

(Series 2)

$$\log_{10} \dot{m} = 12.98668 - \frac{9739}{T} \quad (\text{Correlation Coefficient} = 0.9978) \text{ (5 data points)}$$

Me₂

(Series 2)

$$\log_{10} \dot{m} = 13.81766 - \frac{10197}{T} \quad (\text{Correlation Coefficient} = 0.9977) \text{ (5 data points)}$$

HexMe/Me₂

(Series 2)

$$\log_{10} \dot{m} = 12.75908 - \frac{9350}{T} \quad (\text{Correlation Coefficient} = 0.9977) \text{ (6 data points)}$$

MePh

$$\begin{aligned} & \text{(Series 2)} \\ \log_{10} \dot{m} &= 12.85558 - \frac{9545}{T} \end{aligned} \quad \begin{aligned} & \text{(Correlation Coefficient =} \\ & 0.9993) \text{ (3 data points)} \end{aligned}$$

Ph₂Me

$$\begin{aligned} & \text{(Series 2)} \\ \log_{10} \dot{m} &= 12.16102 - \frac{9171}{T} \end{aligned} \quad \begin{aligned} & \text{(Correlation Coefficient =} \\ & 0.9951) \text{ (7 data points)} \end{aligned}$$

Using these relationships for mass loss rates versus temperature and the vapor pressure of the reference fluid (equation 8), the vapor pressure for each fluid was calculated. The vapor pressures for each fluid are given in Figures 11a to 11e. Figure 12 shows the vapor pressure curves derived from the Series 2 evaporation rates for all five fluids. These data reflect the estimated vapor pressure of each fluid after the removal of 20-30% of lower molecular weight species. A line of similar slope (not shown) through the first points determined in Series 1 would better represent the vapor pressure of the original fluid. The extrapolated vapor pressures of the five Task I fluids range from 8×10^{-7} to 7×10^{-8} Pa at 394K (250°F). The difference in vapor pressures between Series 1 and Series 2 show the great extent to which each fluid can be tailored by the selection of distillation parameters.

TASK II. EVALUATION OF TWO FLUIDS

Selection of Fluids

Two of five fluid structures of Task I were selected for further characterization. Vapor pressures and viscosities of the five are shown as a function of temperature in Figures 12 and 5, respectively. These data are combined in Figure 13 to show the working temperature window for each fluid as defined by the assigned targets for vapor pressure and viscosity. The solid bar for each fluid extends between viscosity of 25×10^{-6} m²/sec (25 cSt) as the low temperature end and vapor pressure of 10^{-7} Pa at the high. For Me₂/MePh fluid (polydimethylmethylphenylsiloxane), for example, as temperature rises, viscosity falls to 25×10^{-6} m²/sec at 333K (140°F) and vapor pressure remains below 10^{-7} Pa until 397K (255°F). Operating windows for all five fluids reach nearly to 394K (250°F), the target upper limit. Topping to a slightly stronger condition can lower vapor pressure sharply with moderate effect on viscosity. Near 394K, with species of this size, each MePhSiO- group (or three Me₂SiO- groups) reduces vapor pressure by about ten times.

The widest operating temperature windows occur for Me₂ fluid and HexMe/Me₂ fluid, (polydimethylsiloxane and polyhexylmethyldimethylsiloxane), with target viscosity near 298K. Phenyl substitution in the other three fluids raises viscosity, yielding a lower temperature boundary of 333-350K (140-170°F). A lighter fraction from any of these polymers can complete a two-fluid system covering most of the desired temperature range.

Also shown for comparison on Figure 13 is 704 Fluid. No operating window exists for 704 because as temperature rises, the limit on the vapor pressure is reached before viscosity falls to 25×10^{-6} m²/sec.

Since all five polymer systems provide a choice of vapor pressures by adjusting conditions in distillation, and since all five show acceptable viscosities, at least in two-fluid modes, the opportunity arose to consider stability as a criterion in selection of the two Task II fluids. Potentially significant stresses in the orbital environment are 5-electron-volt encounters with atomic oxygen, solar ultraviolet, and particle radiation. Original attention in the LDR program to phenylsiloxane fluids was partly in recognition of their relatively high resistance to particle radiation and conventional oxidation. MePh fluid (methylphenylpolysiloxane) has the highest phenyl content of the five candidates and was selected for Task II on that basis.

It was not possible to ascertain whether oxidation by atomic oxygen is a significant concern. Numbers of encounters will be far less than would be important for oxidation with air or oxygen. Higher reactivity of atomic oxygen in collisions that cause some ionization (5 eV) will greatly increase cross-linking

efficiency. On the other hand, rapid escape of volatile reaction fragments is reported to reduce oxidation effects, again under more conventional conditions. With the possibility that high phenyl content would not be called upon, it was decided to keep Me₂ fluid (dimethylpolysiloxane) in Task II for its low viscosity. Its viscosity is likely to be more stable under ultraviolet radiation than that of phenyl systems. Finally, should oxygen be the primary threat, additive technology may provide a substitute for the stabilizing role of phenyl on silicon.

Isolation of Task II Fluids

Polydimethylsiloxane and polymethylphenylsiloxane fractions for Task II characterization were recovered in essentially the same way as the Task I screening samples. Approximately 0.5 kilogram of each was isolated from eight and six liters of feedstocks, respectively. The use of a larger strip pot (3 liters), thermal rearrangement during strip, and different sources of feedstock complicated the effort to duplicate or improve upon the screening samples. At low pressure, vapor flow creates back pressure which became significant in the larger system. At 623K, traces of oxygen, water, or silanol groups catalyze rearrangement of siloxanes to volatile cyclics. These cyclics act as a vapor carrier, making the strip of heavier species more effective. A first attempt to recover polydimethylsiloxane was abandoned when a trace air leak produced cyclics that severely affected the product distribution. Polymethylphenylsiloxane was isolated from Dow Corning 710 fluid rather than from the developmental source of the screening case. The desired species were found near the lighter end of the polymer distribution, as opposed to the heavier end as in the earlier strip. These are variables which can be controlled with further development of the strip process.

Fluids recovered for characterization are:

	<u>Polydimethylsiloxane</u>	<u>Polymethylphenylsiloxane</u>
Reference	6758-23	6758-27
Source	Dow Corning 200 Lot MA091196	Dow Corning 710 Lot MA044423
Strip Conditions		
Pressure	26 Pa (0.2 torr)	29-45 Pa (.22- .35 torr)
Pot temp.	653K (380°C)	643-653K (370-380°C)
Vapor temp.	605K (332°C)	587-597K (314-324°C)

Topping conditions		
Pressure	39 Pa (0.3 torr)	52 Pa (0.4 torr)
Pot temp.	613K (340°C)	600K (327°C)
Vapor temp.	575K (302°C)	568K (295°C)
Cut yields, %		
Volatiles	82	17
LDR Cut	6	8
Bottoms	12	74

Fluid Characterization

Infra-red spectra of the Task II fluids are given in Figures 14 and 15. Si^{29} NMR spectra were obtained using a Varian XL-200 Multi-Nuclear NMR Spectrometer. The subject fluid was dissolved in deuterated chloroform 50% (V/V). This solution was doped with paramagnetic chromium-acetylacetonate to ensure quantitiveness.

The NMR spectra, Figures 16 and 17, provide molecular weights and unequivocal confirmation of molecular structure for each fluid. Chemical shift data derived from model compounds confirms the identification of both mer- and end-groups for each fluid. Absorption intensity provides a direct quantitative measure of both mer- and end-groups. From these data, the average chain length, including end-groups, for the fluids was determined to be 30 (± 3) units (i.e. Si-O) and 11 (± 1) units for the Me₂ and MePh fluids, respectively.

Polymer size distributions were obtained using GPC. MePh fluid was also characterized by LC. The average molecular weight ($\bar{M}_n \approx 2450$) of the Me₂ Task II fluid is lower than its counterpart in Task I ($\bar{M}_n \approx 2700$).

The liquid chromatograph of the MePh is given in Figure 18 along with that for MePh (Task I). The major components of MePh (II) and MePh (I) are nearly identical. Small amounts of more volatile lower molecular weight species are evident in the Task II fluid. This occurs mainly as a result of the two different source fluids used in obtaining the desired distilled fraction.

Density

Fluid densities were measured using a Mettler/Parar Digital Density Meter. Procedures are given in Appendix II. Water and air provided convenient calibration media. Accuracy of ± 0.5 kg/m³ ($\pm 5 \times 10^{-4}$ g/cm³) is specified by the instrument manufacturer. Data for the two Task II fluids are given in Figure 19 and Table V.

Densities vary with temperature according to the following equations:

$$\text{(MePh)} \quad \rho \text{ (kg/m}^3\text{)} = 1311 - 0.772 T \text{ (K)} \quad (9)$$

$$\text{(Me}_2\text{)} \quad \rho \text{ (kg/m}^3\text{)} = 1221 - 0.8878 T \text{ (K)} \quad (10)$$

Surface Tension

Surface tension measurements were obtained using a Wilhelmy-plate surface tensiometer (Ref. 6, 7). Tension on the suspended plate was measured with a Cahn Electrobalance with 1×10^{-10} kg (1×10^{-7} g) sensitivity. Accuracy of this technique is estimated to be $\pm 5 \times 10^{-4}$ N/m (0.5 dynes/cm). These data are summarized in Figure 20 and Table VI. The surface tension of the fluids vary with temperature according to the following equations:

$$\text{MePh} \quad \gamma \text{ (N/m)} = 0.0397 - 5.35 \times 10^{-5} T \text{ (K)} \quad (11)$$

$$\text{(Me}_2\text{)} \quad \gamma \text{ (N/m)} = 0.0411 - 6.94 \times 10^{-5} T \text{ (K)} \quad (12)$$

Heat Capacity

Heat capacity measurements were made using a Dupont 910 Differential Scanning Calorimeter (DSC). Procedures followed those provided by the instrument manufacturer (Appendix II). Instrument performance was verified by measuring the heat capacity of a standard reference fluid for which heat capacity data are available from earlier studies using a Bunsen ice-calorimeter. The ice calorimeter data are accurate to $\pm 0.5\%$. Agreement within $\pm 3\%$ between ice calorimeter data and DSC data is required for acceptance of the DSC results. An accuracy of $\pm 5\%$ is estimated for the DSC heat capacity results.

Heat capacity data for the two Task II fluids are given in Figure 21. Temperature dependence of the heat capacity is as follows:

$$\text{(MePh)} \quad C_p \text{ (J/kg-K)} = 901 + 1.93 T \quad (13)$$

$$\text{(Me}_2\text{)} \quad C_p \text{ (J/kg-K)} = 1058 + 1.66 T \quad (14)$$

Thermal Conductivity

Thermal conductivity measurements were obtained through the services of the Dow Thermal Research Laboratory. Their method utilizes a hot-wire transient technique which is reported to have excellent precision and accuracy (Ref. 8). Verification of their method and apparatus is based on thermal conductivity measurements of standard fluids (toluene, diphenyl ether). Good agreement with literature data (Ref. 9) confirmed the technique for liquids. The complete report is contained in Appendix III.

Thermal conductivity data are summarized in Figure 22 for the Task II fluids. The dependence of thermal conductivity on temperature follows the equations:

$$(\text{MePh}) \quad \lambda (\text{W/m-K}) = 0.1237 + 1.5858 \times 10^{-4} T - 3.66 \times 10^{-7} T^2 \quad (15)$$

$$(\text{Me}_2) \quad \lambda (\text{W/m-K}) = 0.1904 - 8.023 \times 10^{-5} T - 1.54 \times 10^{-7} T^2 \quad (16)$$

Over the years, a number of investigators skilled in thermal measurements have reported thermal conductivity data on low viscosity PDMS fluids. These data are summarized in Figure 23. It is evident that although numerous laboratories show reasonable precision in their results, accurate thermal conductivity measurements remain elusive. Uncertainties of $\pm 15\%$ are inherent in these data at the present time.

Electrical Conductivity

Silicones are excellent electrical insulators. A considerable number of silicone-based products are applied in electrically demanding applications based on their dielectric properties. Volume resistivity for each fluid over a range of temperatures was measured according to CTM 0272 (Appendix II). The test procedure is based on ASTM D-1169.

The data are summarized in Figure 24. The values reported for the Task II fluids are somewhat lower than values typically obtained for these types of materials. Volume resistivity measurements on dielectric materials are subject to some variability generally attributed to trace levels of contaminants arising from residual catalysts, absorbed/adsorbed water, and silanol (SiOH) sites on the fluid.

Manufacturing procedures typically used for dielectric-grade fluids would provide materials with significantly higher volume resistivity.

Pour Point

Pour points for the two Task II fluids were measured according to CTM 0133 (Appendix II) and reported to be less than 188K (-85°C) for the Me_2 fluid and 240K (-33°C) for the MePh fluid. The values are typical for these types of fluids.

Polymeric liquids are especially susceptible to supercooling effects and this is typically observed with silicone fluids. In view of this characteristic, pour point data must be viewed with caution when used to infer flow properties at low temperatures. This is of concern only with the MePh fluid since the melting point of the Me_2 fluid [233K (-50°C)] is well below the lowest temperature anticipated in this application.

Flash Point (Pensky-Martin Closed Cup)

Closed-cup flash points were measured according to CTM 0021A (Appendix II) which is based on ASTM D93. The flash points were 572K (570°F) and 544K (520°F) for the Me₂ and MePh fluids, respectively.

Fire Point

Fire points were measured according to CTM 0052 (Appendix II) which is based on ASTM D-92. In this test, the fluids were heated to temperatures of 616K (650°F) and 603K (625°F) for the Me₂ and MePh fluids, respectively, with no evidence of a sustained flame. Measurements at higher temperatures are not recommended since significant fluid decomposition may occur. The exceptionally high fire points recorded for the Task II fluids are expected in view of the low volatility of these fluids.

Viscosity - Temperature

Kinematic viscosities as a function of temperature were measured as described previously in the Task I phase of this effort. Data for the Task II fluids are summarized in Table VII and Figure 25, together with the data for their Task I counterparts.

The Task II Me₂ fluid has a slightly lower viscosity than the Task I sample. This finding is consistent with both GPC and vapor pressure data which indicate the molecular weight of the Task II fluid slightly lower.

The viscosity of MePh (Task II) is in good agreement with its counterpart in Task I except at the lowest temperature (-18°C), where higher viscosity was noted for the Task II fluid.

Viscosity - Shear Dependence

The viscosity - shear dependence of the Task II fluids was investigated by Savant, Inc., Midland Michigan. The complete report from Savant, Inc., together with descriptive literature on the Tapered Bearing Simulator Viscosimeter (TBS) is included in Appendix III.

Several techniques and apparatus were required to provide measurements over the range of temperatures, viscosities, shear stress and shear rates of interest. Some methods, [Scanning Brookfield Viscometer Technique (SBT) and Ubbelohde Suspended Level Capillary Viscometer (USLCV)], utilized conventional viscometric equipment with minor adaptations, while others, [Tapered Bearing Simulator Viscometer (TBS), and Cold

Cranking Simulator (CCS)] were either developed or adapted in the Savant Laboratory. A standard calibration fluid (S-3, available from Cannon Instrument Company) was used to calibrate the instruments.

The combination of methods available in this facility provided a special capability for characterization of the shear dependence of these fluids. Results are summarized in Table VIII.

A major objective in these measurements was to learn whether the fluids show non-Newtonian behavior. With the Me₂ fluid, shear rates as high as 600,000 sec⁻¹ were achieved with no discernible reduction in fluid viscosity. These findings are in agreement with those reported by Ito and Shishido (Ref. 10) in which somewhat higher shear rates were realized with no viscosity reduction for polydimethylsiloxane fluids of similar viscosity. For the MePh fluid at low temperatures (268 to 258K) with shear stresses of 10⁵ N/m² (10⁶ dynes/cm²) and shear rates ranging from 140 to 62,000 sec⁻¹, a slight non-Newtonian behavior was observed. At higher temperatures (423K) and shear rates of 10⁶ sec⁻¹, no evidence of non-Newtonian behavior was noted.

Vapor Pressure

Vapor pressure data were obtained using the same procedure as in Task I. Mass loss rates for the Me₂ (II) fluid are summarized in Table IX. Loss rates for Me₂ (II) and Me₂ (I) are plotted in Figure 26. It is evident from the first rates measured for each fluid (Series 1, low temperatures), that the Me₂ (II) fluid is somewhat more volatile than its counterpart in Task I. This is consistent with results of characterizations by GPC, which show that Me₂ (II) fluid, as distilled, includes species of lower molecular weight than does Me₂ (I) (2450 vs. 2700).

GPC analyses (Figure 27) also show virtually identical molecular weight distribution for Me₂ (I), as distilled, and Me₂ (II) fluid at the completion of its mass loss measurements. Again, characterization by GPC is consistent with evaporation rates, which are nearly alike for these two samples.

Mass loss rates for MePh (II) are given in Table IX. In Figure 28, loss rates for MePh (II) and MePh (I) are plotted as a function of temperature. LC data are given in Figure 18. The significant concentrations of several lower molecular weight components result in significantly higher loss rates for MePh (II). These findings demonstrate the need for care in the removal of low molecular weight species in the distillation procedures necessary to obtain these fluids.

Mass loss rate data for each Task II fluid were fitted to equation (7) using least squares.

Me₂ Task II

$$\text{(Series 2) } \log_{10} \dot{m} = 14.086 - \frac{10108}{T} \quad (\text{Corr. Coeff.} = 0.9989) \\ \text{(6 data points)}$$

MePh (Task II)

$$\text{(Series 2) } \log_{10} \dot{m} = 12.186 - \frac{8523}{T} \quad (\text{Corr. Coeff.} = 1.0000) \\ \text{(5 data points)}$$

Using the same data treatment as in Task I, these results were converted to vapor pressure curves using equations (6) and (8). The resulting vapor pressures along with those from Task I are given in Figures 29 and 30 for the Me₂ and MePh fluids.

The vapor pressure for the Task II fluids are given by:

$$\text{Me}_2 \text{ (II) Fluid: } \log_{10} P = 16.7247 - \frac{10087}{T} \quad (17)$$

$$\text{MePh (II) Fluid: } \log_{10} P = 14.8254 - \frac{8502}{T} \quad (18)$$

Vapor pressures for the Task II fluids were found to be higher than was intended in selecting conditions for isolating the fluids. The effect of distilling a further 20-30% is shown by comparing the mass loss rates of the fluids as distilled (Series 1), against those after test (Series 2). Vapor pressures at or below 10^{-7} Pa at 394K can be achieved in fluid fractions only slightly heavier than the Task I and II samples. The GPC and LC results discussed above show that these methods can provide control for isolating required fractions.

Heat of Vaporization, Temperature for $P_v = 1.3 \times 10^{-6}$ Pa
(10^{-8} torr)

Using the vapor pressure relationships, Equations 17 and 18, the temperature at which the fluid's vapor pressure equals 1.3×10^{-6} Pa (10^{-8} torr) was calculated. The heat of vaporization was calculated using the Clausius-Clapeyron equation. These parameters are summarized in Table X.

Emittance and Transmittance

A detailed report on the radiative characteristics of the two Task II fluids is included in Appendix III. All measurements were performed with a Nicolet 60SX Fourier-Transform infrared spectrophotometer. The methodology follows that of Kember, et. al. (Ref. 11). Software provided by the instrument manufacturer facilitated the subtraction of background spectra and calculation of fluid emittance, i.e. ratioing the radiant flux of the sample fluid to that of a blackbody under identical conditions.

Emissivity data for the two Task II fluids are given in Figures 31 and 32. Both materials approximate the emittance of a blackbody over the range of 5.6 to 25 microns. Flux from both samples in this range slightly exceeded that from the powdered graphite reference used, presumably because emittance of the graphite was less than 1.0. Because of detector limitations, emissivity measurements were limited to the 3 to 25 micron range. A relatively minor portion of the energy is radiated between 25 and 55 microns.

Transmittance data for the Task II fluids between 2.5 and 25 microns are given in Figures 33a, b, c. Data at fluid thicknesses of 0.2 mm and 0.02 mm were obtained at room temperature. For the latter thickness, spectra were run as 20% (w/v) solutions in 0.1 mm cells. Carbon tetrachloride was used for dilution between 2.5 and 7.25 microns; carbon bisulfide was used from 7.25 to 25 microns. Both fluids exhibit similar transmission characteristics. Figures 33d and 33e show the transmittance of 0.01 and 0.1mm films, respectively, in the far infrared (20 to 100 microns).

Thermal Stability, Oxidative Stability, Stability Against Radiation, and Operating Lifetime

The experimental activities reported above relate to the two critical areas of flow and evaporation and to properties affecting heat transfer in the LDR application. The third critical concern is the ability of the working fluid to retain its properties in service. Viscosity, mass loss by evaporation of reaction products, contamination of surfaces by volatile condensibles and heat transfer properties must be controlled.

The working fluid of the LDR at an altitude of 500 km will be exposed to an environment involving high vacuum (10^{-6} Pa), solar ultraviolet photon radiation, atomic oxygen at a particle density of $10^7/\text{cm}^3$, and energetic protons, electrons, and neutrons. (Ref. 12). The velocity of the liquid droplets in orbit will result in approximately 5 eV collisions with the oxygen atoms (O[3p]). The threshold energy for ionizing chemical bonds is on the same order. The energetic encounters will increase the already high reactivity of atomic oxygen.

There is a rich background of research describing the effects of the several components of the LDR environment, excepting atomic oxygen, on the polymer families of the candidate siloxane fluids. Splitting of the Si-C bond is discussed at length by Chvalovsky (Ref 12, 520 references.) Baney reviewed the literature through 1967 on thermal and oxidative reactions (R.H. Baney, "Thermal and Oxidative Behavior of Silicones", Dow Corning publication, 1967, 113 references).

In an effort to locate data closely applicable to selection or development of fluids for the LDR, a new search was made of the Dow Corning Technical Document Data Base, consisting of over 100,000 citations on organosilicon compounds. Focusing on thermal and oxidative reactions of siloxanes and on the effects of radiation, some 200 references from the published literature and a similar number of internal reports were listed. Abstracts were reviewed. While there is a great deal of useful information on mechanisms and kinetics of reactions, no prediction of lifetime for fluids in the LDR application is possible within the scope of this work. The scarcity of information on reactions of atomic oxygen with siloxanes precludes prediction, especially with the combined effects of energetic collisions, vacuum, and UV photons.

A sampling of the effects of the key environmental factors on polysiloxanes is given below, to suggest directions for selection or further development of LDR fluids. An intensive synthesis from this background literature could add rough quantitative guidance. The bibliography of published work described above can be made available for such an effort.

Thermal Effects

Thermal reactions of polydimethylsiloxanes and polymethylphenylsiloxanes below 523-573K in the absence of air, moisture, or catalysts are negligible in relation to required service life.

Extensive information available on reaction mechanisms may be useful, however, for predicting effects in the LDR environment. PDMS and PMPS behave quite differently in that the first reaction evident in PDMS is rearrangement of siloxane bonds, while for PMPS, crosslinking through cleavage of SiC or CH bonds dominates. Siloxane rearrangement predominates for PDMS to 673K or above. Volatile cyclosiloxanes result, and the molecular weight distribution of the linear nonvolatile portion broadens. The activation energy for siloxane rearrangement has been measured most commonly at about 42 kcal/mol, well below the SiO bond strength (108 kcal/mol). Ions and silanol are common but controllable species that greatly accelerate siloxane rearrangement. Oxygen at only 0.02-0.03% in the inert gas blanket is highly catalytic, perhaps through production of $-\text{SiOH}$. This effect is believed to have been present in preparing the Me_2 fluid for Task II, at 623K. Even the effects of the typical ions

and silanol are probably insignificant at 394K. The silylmethylene ($-\text{SiCH}_2\text{Si}-$) bond provides a way to strengthen the polymer chain against formation of cyclics. The activation energy for silylmethylene is reported to approach the bond strength for SiC .

Thermal crosslinking of PMPS also is unimportant at 394K. DC 704 gelled in 400 hours at 673K. But the rate of reaction (disappearance of the parent 704 molecule) at 623K was only 0.003% per hour (R. Halm, A. Huntress, unpublished work). Gel times and viscosity of higher molecular weight polymer can be expected to respond more strongly to crosslinking than do those of 704, but on the same order. There are indications that crosslinking may be less in a $\text{Me}_2\text{-Ph}_2$ configuration than in MePh having like proportions of Me and Ph ligands. Silphenylene/siloxane polymers have also been studied extensively, but usually in elastomeric compositions, and with crystalline alignment of the silphenylene groups as an objective.

A number of agents have been described that inhibit siloxane rearrangement, perhaps only for the case of catalyzed reactions. Various metals (Zr, Fe, Hf, Ce, Ti, B, P, Cu, Co) are reported, usually introduced as alkoxy, acetylacetonate, acetate, or other carboxylic acid salt. The SiH group has been found effective in PDMS, in conjunction with metal additive. These additives are often more effective for PDMS than for PMPS.

Oxidative Effects

Oxidation in conventional environments causes both depolymerization to cyclosiloxanes and crosslinking. Formaldehyde is the principal gaseous product, even in PMPS. Phenyl groups reduce crosslinking rates appreciably, through their greater stability and by protecting the Me group. It has been reported that a small amount of phenyl relative to Me is optimum, although specific circumstances may have produced this result. Formaldehyde from oxidation of PDMS in air becomes detectable by 423K. Activation energy for the oxidation of PDMS has been reported as 30 kcal/mol. The exotherm began at 513K in one set of DTA measurements. The presence of methylphenyl groups raised the exotherm to 548K for 7 mol percent MePh, and to 573K for 100 mol percent MePh (unpublished work). As in the thermal case, there are instances where performance of the Ph_2 group is found to be better than that of the MePh group.

Rates of oxidation measured as a function of film thickness have been interpreted as showing autocatalytic effects, particularly in relation to volatiles produced. Reactive species were believed to be removed by evaporation, so that thinner films reacted more slowly. In other work, crosslinked resinous films appeared on metal surface at 363-373K and grew to a limit of about 100 nanometers in 5-6 days (Ref. 14).

There has been extensive work on the effects of antioxidants in siloxanes. Gas evolution, gel times, viscoelastic properties, and intrinsic viscosity are most often followed. Many of the same metal salts reported for thermal stabilization are effective against oxidative reactions. Heat treatments to incorporate the metal atom into the siloxane chain are frequently employed. Polymers containing the heteroatoms are synthesized directly with the same effect. In PDMS, gel times at 573K and above are extended by from 30 to 500 times. In the DTA work noted above, Ce and Fe salts both raised the temperature of the exotherm 95K above that of the untreated PDMS, and 35K above that of PMPS. Inhibiting effects are generally not as pronounced for PMPS, but are observed. A partial listing of antioxidants other than the metal salts follows. Many of these are recognized free radical scavengers in organic chemistry:

- Ferrocene compounds
- Phenyl-alpha-naphthylamine
- Tricarbonyl Chromium
- Mn cyclopentadienyltricarbonyl
- Diethylamine
- Anthracene; 1,2-benzanthracene
- Pyrene
- Fluoranthene
- Beta,beta'dinaphthyl-p-phenylenediamine

Reactions of atomic oxygen with SiH_4 and Me_3SiH were reported (Ref. 15, 16, 17). No references to atomic oxygen with PDMS or PMPS were found. Heicklen (Ref. 18) has assembled reaction rate coefficients for $\text{O}(3p)$ in organic reactions. Rate coefficients are as much as a million times those for O_2 . The reactivity of $\text{O}(3p)$ with CH_4 is less than 10^{-5} that with $n\text{C}_4\text{H}_{10}$. This difference may suggest the magnitude of the possible advantage for PDMS or PMPS over organic polymers, but it also emphasizes the futility of estimating effects without careful experimentation.

Effects of Radiation

The effects of energetic radiation on PDMS, PMPS, and other polysiloxanes have been studied extensively. Rittenhouse and Singletary (Ref. 12) reviewed space-related effects. Approximately 60 citations were highlighted in the present search. Studies include exposures to electrons, protons, neutrons, and gamma, ultraviolet, and laser radiation.

The principal effect of radiation is crosslinking through the formation of $-\text{SiSi}-$, $-\text{SiCH}_2\text{Si}-$ or $-\text{SiCH}_2\text{CH}_2\text{Si}-$, accompanied by release of CH_4 and H_2 . Ions and free radicals are intermediates, as in organic radiation chemistry. Radiation in air produces unstable silicon-based peroxides and hydroperoxides which are, like radicals, detectable only at reduced temperature. Siloxane rearrangement is also reported in radiation chemistry.

Radiation induced reactions are capable of producing siloxane species smaller than the parent polymer. In gamma-radiation of DC 704, at a dose of several hundred megarads, the amounts of more volatile species formed was not detrimental to continued performance of the fluid in a diffusion pump.

Increase in the viscosity of PDMS fluids is seen with a radiation dose on the order of 10^6 J/kg. The viscosity of 50-100 cs PDMS may be doubled by a dose of 100 megarads. (For a relatively low molecular-weight polymer, doubling viscosity requires approximately one crosslink per two polymer chains, doubling molecular weight.) Hence, for a given dose (a given number of crosslinks) the viscosity of shorter chains will rise less than that of long chains.

Phenyl side groups or phenylene linkages in the polymer backbone improve the radiation resistance over PDMS. Rates of gas formation for PDMS are about 100 times those for PMPS. CH_4 and H_2 remain the principal gaseous products. The $-\text{Ph}_2\text{SiO}-$ group is seen to be more effective than $-\text{MePhSiO}-$ against both gamma radiation and protons.

Much work with ultraviolet radiation has been focused on thermal control coatings and the absorption of ultraviolet wavelengths. With ultraviolet the absorption bands of the phenyl group are detrimental. Aromatic impurities also are said to promote degradation of PDMS under ultraviolet exposure. Other workers report less gassing with phenyl present.

Stabilizers have been applied successfully to retard reactions under radiation. Again, free radical scavengers are favored. For illustration, di-tertbutyl-p-cresol, quinone, and 4-tert-butylanthraquinone are reported favorably against electrons; agents against gamma include copper phthalocyanine, n-butylmercaptan, acenaphthene, diphenylselenide, and heteroatoms (B, P, Ti) in the polymer chain.

Flammability

The unique low vapor pressures of the Me_2 and MePh fluid fractions isolated as candidates for the LDR assures that combustible vapor mixtures cannot occur except by thermal or oxidative degradation. The lower limit of combustible concentrations in air or oxygen involves a vapor partial pressure on the order of 100 Pascals or more. Distillation temperature for these fluids was approximately 573K at 13 Pascals. Temperature higher than this would be required to produce a partial pressure of the parent species in the combustible range.

Combustion can occur with the application of sufficient heat to cause degradation, and under conditions allowing accumulation of the degradation products. Significant degradation begins in air

above 523-573K. Spontaneous ignition temperature for low molecular weight siloxane products of degradation vary with composition and conditions, but should not be less than 650K. Combustion of low-volatility PDMS in pools tends to be self extinguishing because of the formation of a coating composed of silica and gel over the surface.

Background on the flammability characteristics of polysiloxanes will be found in References 19, 20, 21, and 22.

Toxicity

The two polysiloxane families represented by the LDR fluids are recognized as showing a very low order of toxicity, based on all testing reported. PDMS species larger than 8-10 mer units are not absorbed from the intestinal tract. Smaller species that are absorbed and metabolized show no toxic effects, in acute or long term oral studies. PDMS is approved for use in contact with foods and is a component in antacids where doses of 40-500 mg/day are typical. There is no absorption through the skin and no irritation. Direct contact with the eye may cause temporary conjunctival redness. References 23, 24, and 25 illustrate test results. Acute effects of PMPS (Dow Corning 710 Fluid) are summarized in Appendix IV.

TASK III. FURTHER DEVELOPMENT OF FLUIDS

The means for preparing fluids of the necessary low vapor pressure for the LDR has been demonstrated with the siloxane polymers isolated. Some further development of the vacuum strip process will be required to refine control, and possibly to produce moderately heavier fluid, with still lower vapor pressure. The viscosities of the fluids recovered are reasonable. Several directions might be taken to further reduce viscosity:

The copolymer Me₂/MePh might replace MePh fluid if the full stabilizing effect of the phenyl ligand is not required.

Structural effects on the viscosity of methylphenyl siloxanes can be explored. Me₂/MePh copolymer endblocked with MePh₂ may duplicate the vapor pressure and Me/Ph ratio of MePh fluid, with moderately lower viscosity.

Chemical routes exist by which either MePh or Me₂ fluid can be made nearly monodisperse. Eliminating the higher molecular weight members will reduce viscosity, especially for MePh fluid.

Further activity with respect to fluid lifetime probably should await more definite understanding of the effect of the unusual environment at the altitude of the Space Station. Both testing in the simulated environment and detailed study of known reaction mechanisms and kinetics will be needed. Stabilization may be useful either through additives, as discussed briefly above, or through altered polymers. Some alternative polymers include:

Polydimethyldiphenylsiloxane. Several studies show stability superior to methylphenyl structure.

Silmethylenesiloxane. Siloxane rearrangement is reduced by substituting (-SiCH₂Si-) for some of the siloxane bonds in the polymer backbone.

Silazane (-SiNHSi-) in the MePh siloxane chain is reported to resist proton radiation.

Siloxanes with metal atoms along the chain, as frequently described in literature.

Fluorinated siloxanes or fluorocarbon siloxanes. Special resistance to atomic oxygen is suggested in a concurrent program for structural coatings for the Space Station.

CONCLUDING REMARKS

Siloxane fluids combining the low vapor pressure and low viscosity needed in a working fluid for the Liquid Droplet Radiator have been identified and characterized. Lighter fractions of these fluids may optimize viscosity for operation in the lower end of the anticipated temperature range. Service lifetime in the unique combined environment of the LDR probably cannot be predicted from available data. Stabilizers or modified polymers probably can extend lifetime if greater stability is found to be necessary.

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TABLE I
SCREENING CANDIDATE FLUIDS

<u>Dow Corning Reference</u>	<u>Fluid</u>	<u>Source</u>
6138-42-2	$\text{Me}_3\text{SiO}(\text{MePhSiO})_n \text{SiMe}_3$	Bottoms from Developmental Fluid (also present in Dow Corning® 710 Fluid)
6758-8C	$\text{Ph}_2\text{MeSiO}(\text{Me}_2\text{SiO})_n (\text{MePhSiO})_m \text{SiMePh}_2$	Bottoms from Dow Corning 704®
6758-10B	$\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_n (\text{MePhSiO})_m \text{SiMe}_3$	Dow Corning® 550 Fluid
6758-12C	$\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_n \text{SiMe}_3$	Dow Corning® 200 Fluid/20 cst
6758-13B	$\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_n (\text{HexMeSiO})_m \text{SiMe}_3$	Developmental Fluid Ref. 6513-62-4

	<u>Initial Strip Conditions (T/P)</u>		<u>Topping Strip Conditions (T/P)</u>		<u>Weight Percent in Fractions</u>		
	<u>Pot</u>	<u>Vapor</u>	<u>Pot</u>	<u>Vapor</u>	<u>Volatiles</u>	<u>LDR Cut</u>	<u>Bottoms</u>
MePh	638	575/26	583	548/10	66	17	15
Ph ₂ Me	631	605/12	580	553/10	73	11	11
Me ₂ /MePh	653	601/26	589	578/12	22	5.6	71
Me ₂	653	624/26	604	582/18	64	13	21
HexMe/ Me ₂	653	625/114	590	575/12	41	10	47

TABLE II
MOLECULAR WEIGHTS BY GPC
TASK I FLUIDS

<u>Fluid</u>	\bar{M}_n	\bar{M}_w	<u>Dispersity Index</u>
Ph ₂ Me	1180	1390	1.17
MePh	1240	1280	1.03
Me ₂ /MePh	1690	1770	1.05
Me ₂	2670	2720	1.02
HexMe/Me ₂	2500	2700	1.08

TABLE III
 VISCOSITY
 TASK I FLUIDS

Fluid	Kinematic Viscosity [m ² /sec] ¹			
	255K(0°F/-18°C)	297K(75°F/24°C)	339K(150°F/66°C)	394K(250°F/121°C)
Ph ₂ Me	1574 x 10 ⁻⁶	91.8 x 10 ⁻⁶	27.4 x 10 ⁻⁶	9.92 x 10 ⁻⁶
MePh	6450 x 10 ⁻⁶	145.4 x 10 ⁻⁶	31.9 x 10 ⁻⁶	10.4 x 10 ⁻⁶
Me ₂ /MePh	567.7 x 10 ⁻⁶	64.6 x 10 ⁻⁶	21.8 x 10 ⁻⁶	8.74 x 10 ⁻⁶
Me ₂	76.3 x 10 ⁻⁶	28.8 x 10 ⁻⁶	14.49 x 10 ⁻⁶	7.20 x 10 ⁻⁶
HexMe/Me ₂	116.8 x 10 ⁻⁶	34.2 x 10 ⁻⁶	15.53 x 10 ⁻⁶	7.35 x 10 ⁻⁶

1. $\nu(\text{centistokes}) = \nu[\text{m}^2/\text{sec}] \times 10^6$

TABLE IV

TGA - EVAPORATIVE MASS LOSS DATA
TASK I

<u>Fluid</u>	<u>T(K)</u>	<u>Mass Loss Rate</u> <u>[kg/m²-sec]</u>	<u>1/T(K)</u>	<u>Time</u> <u>(Minutes)</u>
704 (0.45 Torr)	361	1.43000E-06	0.002766	900
	371	3.46000E-06	0.002693	300
	380	9.91000E-06	0.002631	150
	392	0.0000232	0.002550	100
	402	0.0000591	0.00249	60
	413	0.000112	0.002420	60
704 (0.75 Torr)	365	1.35000E-06	0.002735	540
	375	4.15000E-06	0.002662	240
	386	1.04000E-05	0.002590	150
	397	0.0000233	0.00252	90
MePh (0.45 Torr)	433	1.72000E-07	0.002313	720
	445	3.81000E-07	0.002246	540
	456	7.54000E-07	0.002190	360
	476	2.68000E-06	0.002097	360
	497	1.14000E-05	0.002016	120
	507	0.0000182	0.001971	60
	467	1.31500E-06	0.002143	60
	517	0.000028	0.001936	60
	527	0.0000494	0.001900	30
	466	2.31000E-07	0.002143	180
Ph ₂ Me (0.45 Torr) Run 1	545	0.0000243	0.001834	60
	536	0.0000178	0.001866	60
	525	1.18000E-05	0.001900	120
	515	7.95000E-06	0.001944	120
	506	5.17000E-06	0.001980	360
	496	3.55000E-06	0.002016	360
	486	2.29000E-06	0.002057	540
	478	1.82000E-06	0.002088	720
Ph ₂ Me (0.45 Torr) Run 2	448	3.25000E-07	0.002227	900
	458	5.38000E-07	0.002180	900
	466	9.60000E-07	0.002145	720
	478	1.74000E-06	0.002092	480
	487	2.77000E-06	0.002053	360
	497	4.71000E-06	0.002012	240
	507.5	8.08000E-06	0.001970	120

TABLE IV (continued)

<u>Fluid</u>	<u>T(K)</u>	<u>Mass Loss Rate</u> <u>[kg/m²-sec]</u>	<u>1/T(K)</u>	<u>Time</u> <u>(Minutes)</u>
Me ₂ /MePh (0.45 Torr)	447	9.05000E-08	0.002237	900
	458	1.81600E-07	0.002180	900
	468	4.01000E-07	0.002134	720
	486	1.63900E-06	0.002057	360
	497	3.04000E-06	0.002012	240
	508	5.67000E-06	0.001968	120
	458	5.44600E-08	0.002183	900
	468	1.45400E-07	0.002137	720
	478	3.78000E-07	0.002092	360
Me ₂ (0.45 Torr)	447	2.21500E-08	0.002237	900
	458	7.11000E-08	0.002180	900
	468	2.79000E-07	0.002137	720
	479	7.40600E-07	0.002087	480
	488	1.15400E-06	0.002049	360
	498	2.73000E-06	0.002007	240
	508	4.86500E-06	0.001968	120
	458	3.78500E-08	0.002183	900
	468	1.03100E-07	0.002137	720
479	2.98000E-07	0.002087	480	
HexMe/Me ₂ (0.45 Torr)	420	1.24600E-08	0.002381	900
	433	2.95400E-08	0.002309	900
	445	9.05000E-08	0.002246	720
	453	2.10000E-07	0.002207	720
	463	4.98000E-07	0.002159	360
	483	2.98000E-06	0.002070	120
	493	6.45000E-06	0.002028	120
	433	1.75000E-08	0.002309	360
	443	4.34000E-08	0.002257	240
	453	1.14000E-07	0.002207	200
463	2.95000E-07	0.002159	120	
Ph ₂ Me (0.45 Torr) Run 3	437	1.93000E-07	0.002288	720
	446	2.48000E-07	0.002242	720
	458	4.99000E-07	0.002183	480
	468	1.26000E-06	0.002137	360
	478	2.17000E-06	0.002092	180
	488	3.54000E-06	0.002049	180
	507	1.06000E-05	0.001972	120
	438	1.66000E-08	0.002283	720
	446	4.62000E-08	0.002242	720
	458	1.22000E-07	0.002183	480
	468	3.18000E-07	0.002137	360
	478	7.85000E-07	0.002092	150

TABLE IV (continued)

<u>Fluid</u>	<u>T(K)</u>	<u>Mass Loss Rate</u> <u>[kg/m²-sec]</u>	<u>1/T(K)</u>	<u>Time</u> <u>(Minutes)</u>
704	298	1.74000E-08	0.0033524	---
(Calculated)	373	0.000155	0.0026832	---
(Knudsen eq'n)	473	0.192	0.002116	---
	572	13.34	0.0017472	---
	675	199.9	0.0014822	---
	423	0.00892	0.0023619	---
	323	6.43000E-07	0.0030913	---
	348	1.22000E-05	0.0028729	---
	394	0.000983	0.0025401	---

TABLE V
DENSITY
TASK II FLUIDS

(Me ₂ Fluid)		
<u>Temperature K(°C)</u>	<u>Density¹</u>	
	<u>kg/m³</u>	
293 (20.0)	960.9	ρ (kg/m ³) = 1221-0.8878T
298 (25.0)	956.4	
303 (30.0)	951.8	
313 (40.0)	943.2	
323 (50.0)	934.2	
333.2 (60.2)	925.1	
343.3 (70.3)	916.2	

(MePh Fluid)		
<u>Temperature K(°C)</u>	<u>Density</u>	
	<u>kg/m³</u>	
293 (20.0)	1085.0	ρ (kg/m ³) = 1311-0.7723T
298 (25.0)	1081.0	
303 (30.0)	1077.3	
313 (40.0)	1069.7	
323 (50.0)	1061.8	
333.2 (60.2)	1053.8	
343.3 (70.3)	1046.2	

1. ρ (g/cm³) = ρ (kg/m³) x 10⁻³

TABLE VI
SURFACE TENSION
TASK II FLUIDS

<u>Fluid</u>	<u>Temperature K (°C)</u>	<u>Surface Tension¹ N/m</u>
Me ₂	295 (22.0)	0.0205
	295.1 (22.1)	0.0206
	301.5 (28.5)	0.0202
	305.0 (32.0)	0.0200
	308.0 (35.0)	0.0198
	310.0 (37.0)	0.0196
	313.0 (40.0)	0.0194
	315.5 (42.5)	0.0191
	323.0 (50.0)	0.0188
	329.7 (56.7)	0.0181
	334.4 (61.4)	0.0180
	347.5 (74.5)	0.0171
	366.0 (93.0)	0.0156
	373.0 (100.0)	0.0152

$$\gamma = 0.0411 - 6.9 \times 10^{-5} T$$

MePh	293.7 (20.7)	0.0240
	301.5 (28.5)	0.0236
	304.0 (31.0)	0.0236
	309.5 (36.5)	0.0232
	314.0 (41.0)	0.0228
	319.0 (46.0)	0.0226
	323.0 (50.0)	0.0223
	326.0 (53.0)	0.0222
	332.0 (59.0)	0.0219
	336.5 (63.5)	0.0216
	340.0 (67.0)	0.0215
	352.0 (79.0)	0.0208
	357.0 (84.0)	0.0205
	363.0 (88.0)	0.0204
	367.0 (92.0)	0.0202

$$\gamma = 0.0397 - 5.3 \times 10^{-5} T$$

1. γ (dynes/cm) = γ (N/m) $\times 10^3$

TABLE VII

KINEMATIC VISCOSITY VS. TEMPERATURE
TASK I & TASK II FLUIDS

Fluid	Kinematic Viscosity (m ² /sec.) ^{1.}			
	<u>255K (0°F/-18C)</u>	<u>297K (75°F/24C)</u>	<u>339K (150°F/66C)</u>	<u>394K (250°F/121C)</u>
MePh				
Task II	1438.0 x 10 ⁻⁵	14.8 x 10 ⁻⁵	2.96 x 10 ⁻⁵	----
Task I	645.0 x 10 ⁻⁵	14.54 x 10 ⁻⁵	3.19 x 10 ⁻⁵	1.04 x 10 ⁻⁵
Me ₂				
Task II	6.76 x 10 ⁻⁵	2.54 x 10 ⁻⁵	1.29 x 10 ⁻⁵	----
Task I	7.63 x 10 ⁻⁵	2.88 x 10 ⁻⁵	1.449 x 10 ⁻⁵	.720 x 10 ⁻⁵

1. $\nu(\text{centistokes}) = \nu(\text{m}^2/\text{sec}) \times 10^6$

TABLE VIII
 VISCOSITY-SHEAR DATA ¹
 TASK II FLUIDS

<u>Device/ Technique</u>	<u>°C Temp.</u>	<u>Shear Stress, Dyne/Sq. Cm.</u>	<u>Viscosity, cP.</u>		<u>Ratio²</u>	<u>(sec⁻¹) Shear Rate³</u>
			<u>Low Temp.</u>	<u>High Temp.</u>		
<u>Me₂ Fluid</u>						
Brookfield	-40	1,000	158			633
CCS	-40	1,000,000	165		0.96	606,000
USLCV	150	10		4.02		249
TBS	150	40,000		4.13	0.97	969,000
<u>MePh Fluid</u>						
Brookfield	-5	2,370	1700			139
CCS	-5	1,000,000	1610		1.06	62,100
Brookfield	-10	4,840	3230			150
CCS	-10	1,000,000	2940		1.10	34,000
Brookfield	-15	4,540	6820			66.6
CCS	-15	1,000,000	6200		1.10	16,100
USLCV	150	25		6.34		394
TBS	150	65,000		6.49	0.98	1,000,000

1. Savant, Inc., Midland, Michigan

2. Ratio = $\frac{\text{Low shear dynamic viscosity}}{\text{High shear dynamic viscosity}}$ (Temperature constant)

3. Shear rate (sec.⁻¹) = $\frac{\text{Shear stress}}{\text{Dynamic viscosity}}$

TABLE IX

TGA - EVAPORATIVE MASS LOSS DATA
TASK II FLUIDS

<u>Fluid</u>	<u>T(K)</u>	<u>Mass Loss Rate</u> <u>(kg/m²-sec)</u>	<u>1/T(K)</u>	<u>Time (Minutes)</u>	
Me ₂	448	1.35000E-07	0.002232	720	
	458	3.23000E-07	0.002183	720	
	465	6.14000E-07	0.002151	360	
	470	8.72000E-07	0.002128	360	
	479	1.65000E-06	0.002088	240	
	489	4.43000E-06	0.002045	180	
	499	6.12000E-06	0.002004	60	
	508	0.0000172	0.001969	60	
	460	1.37000E-07	0.002174	540	
	470	3.78000E-07	0.002128	360	
	479	8.86000E-07	0.002088	360	
	489	2.53000E-06	0.002045	120	
	MePh	463	1.20000E-05	0.00216	120
		417	1.72000E-07	0.002398	420
426		3.97000E-07	0.002347	420	
436		9.32000E-07	0.002294	240	
446		1.61000E-06	0.002242	240	
455		4.34000E-06	0.002198	90	
465		8.58000E-06	0.002151	90	
426		1.63000E-07	0.002347	420	
436		4.48000E-07	0.002294	240	
446		1.07000E-06	0.002242	240	
455		2.36000E-06	0.002198	90	

TABLE X

HEAT OF VAPORIZATION & TEMPERATURE ($P_v = 1.3 \times 10^{-6}$ Pa)
TASK II FLUIDS

<u>Fluid</u>	<u>Vapor Pressure Parameters</u> ¹		<u>ΔH_v (J/mole)</u> <u>(cal./g mole)</u>	<u>T [K]</u>
	<u>A</u>	<u>B</u>		
Me ₂	16.7247	-10087	195,000 (46,600)	408
MePh	14.8254	-8502	165,000 (39,400)	373

1. $\log_{10} P_v = A + \frac{B}{T}$

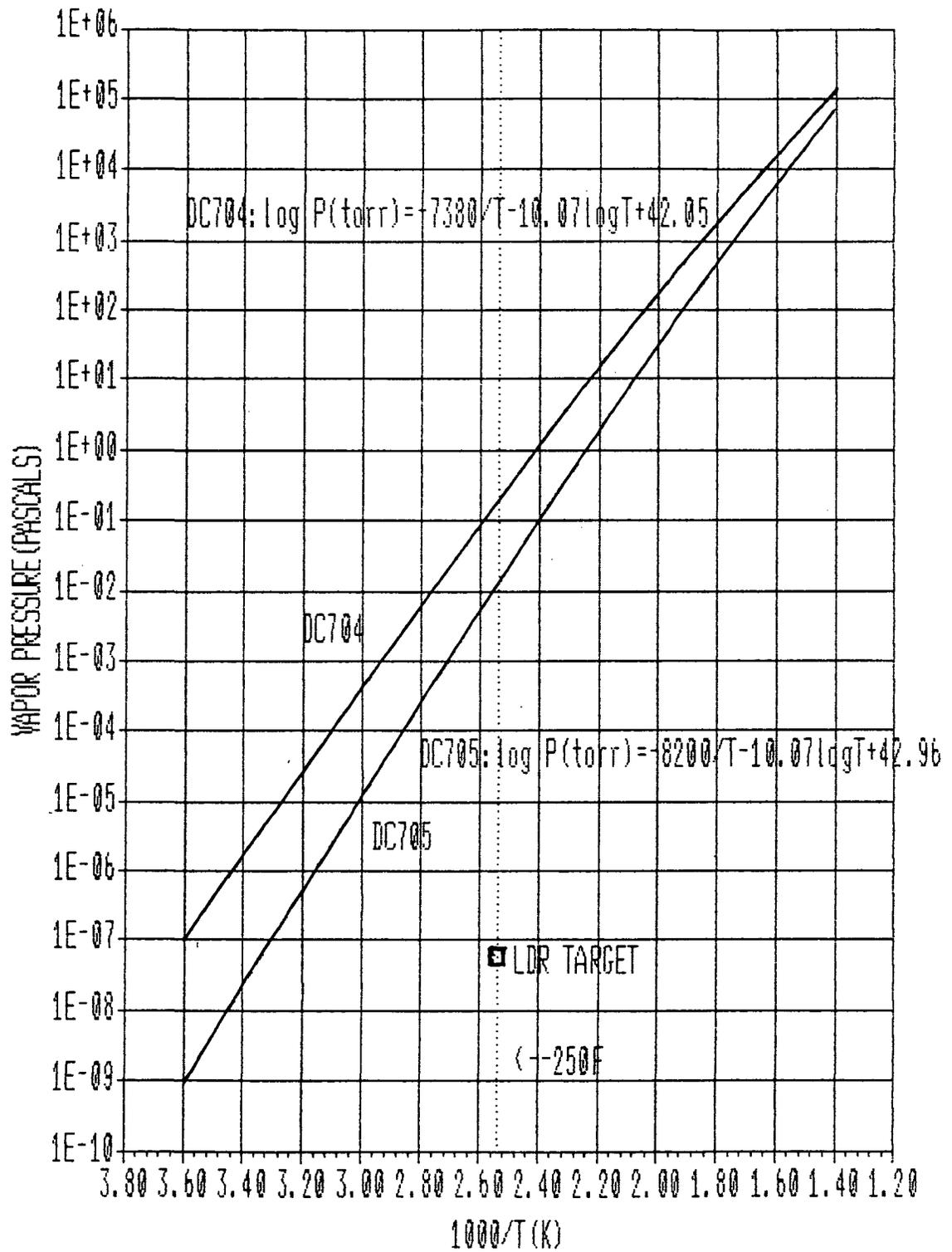


Figure 1. Vapor Pressure of DC 704, DC 705.

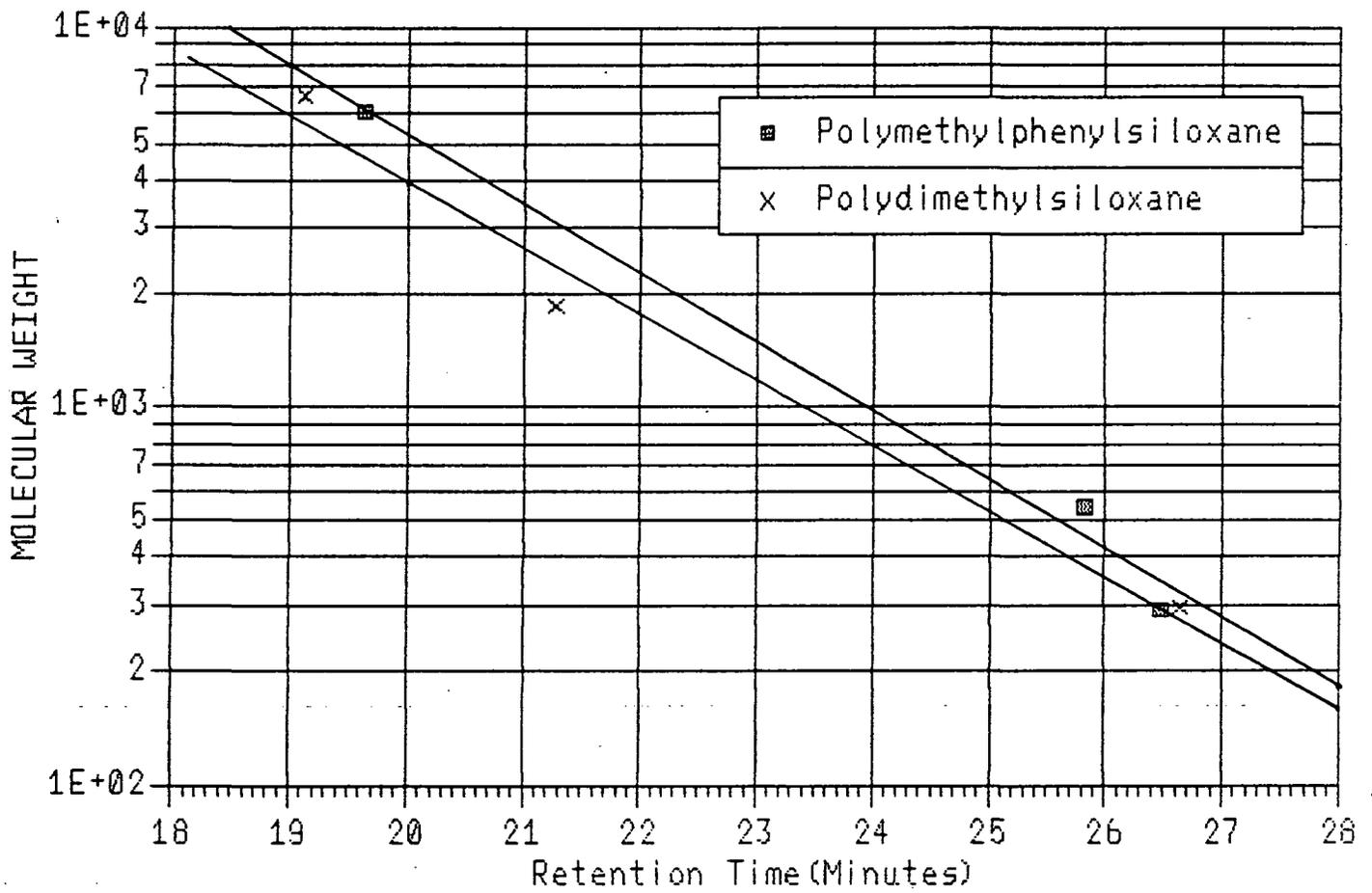


FIGURE 2. GPC Calibration

Number-Average MW = 1686

Weight-Average MW = 1773

Polydispersity Index $\left(\frac{M_w}{M_n}\right) = 1.05$

Peak Apex MW = 1689

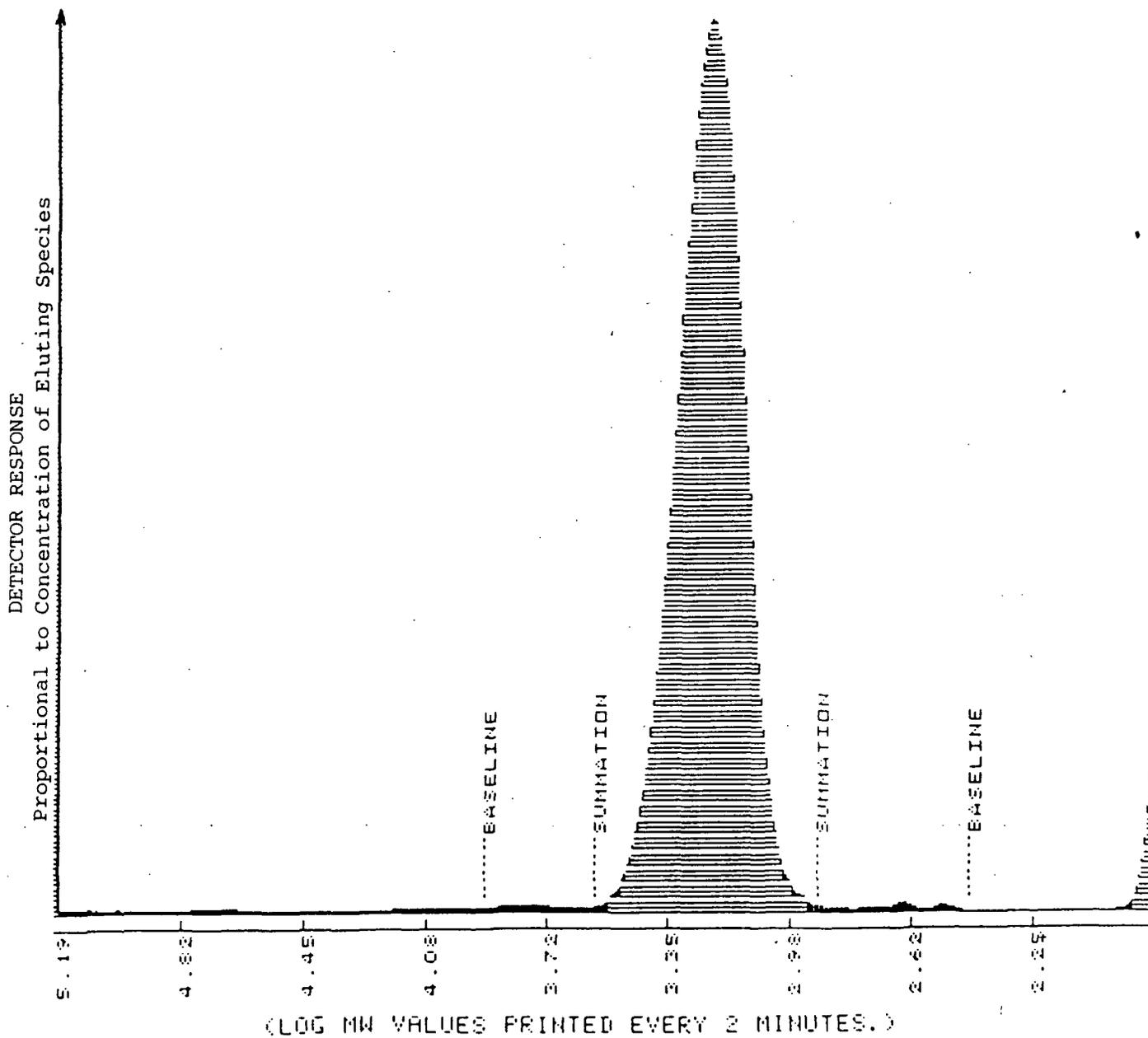


FIGURE 3. GPC Chromatogram of Me₂/McPh - (I)

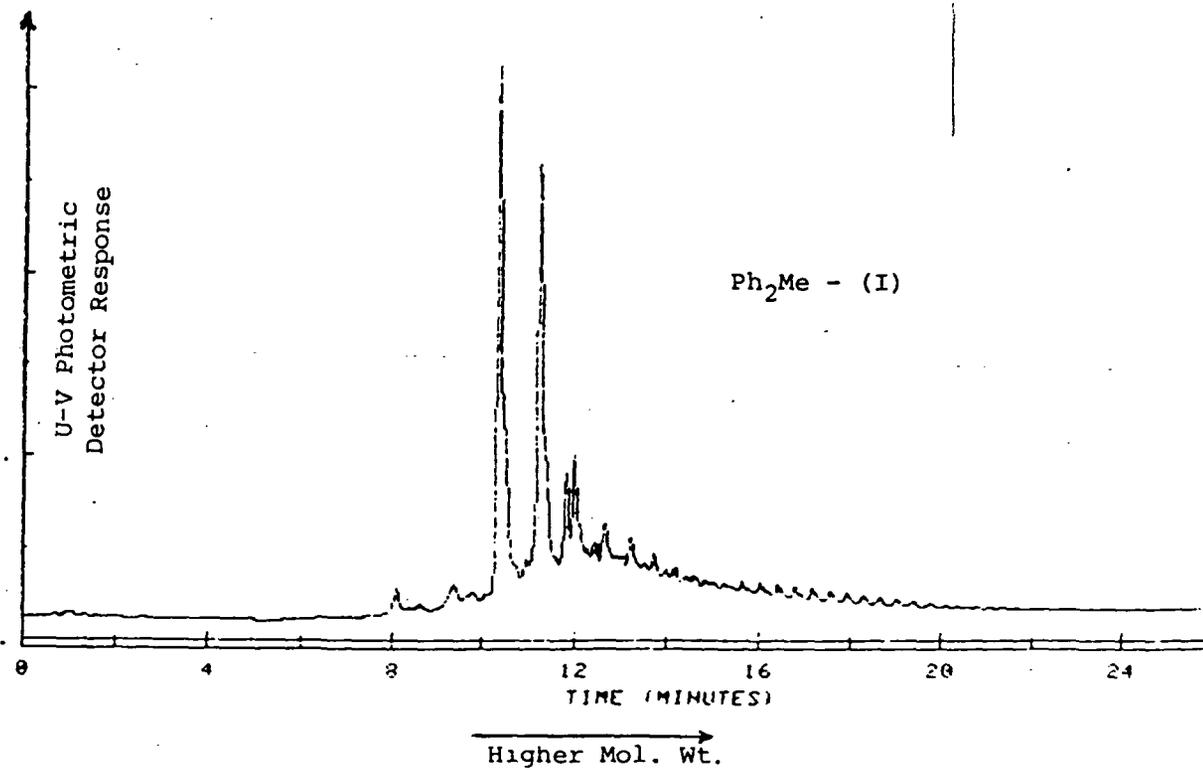
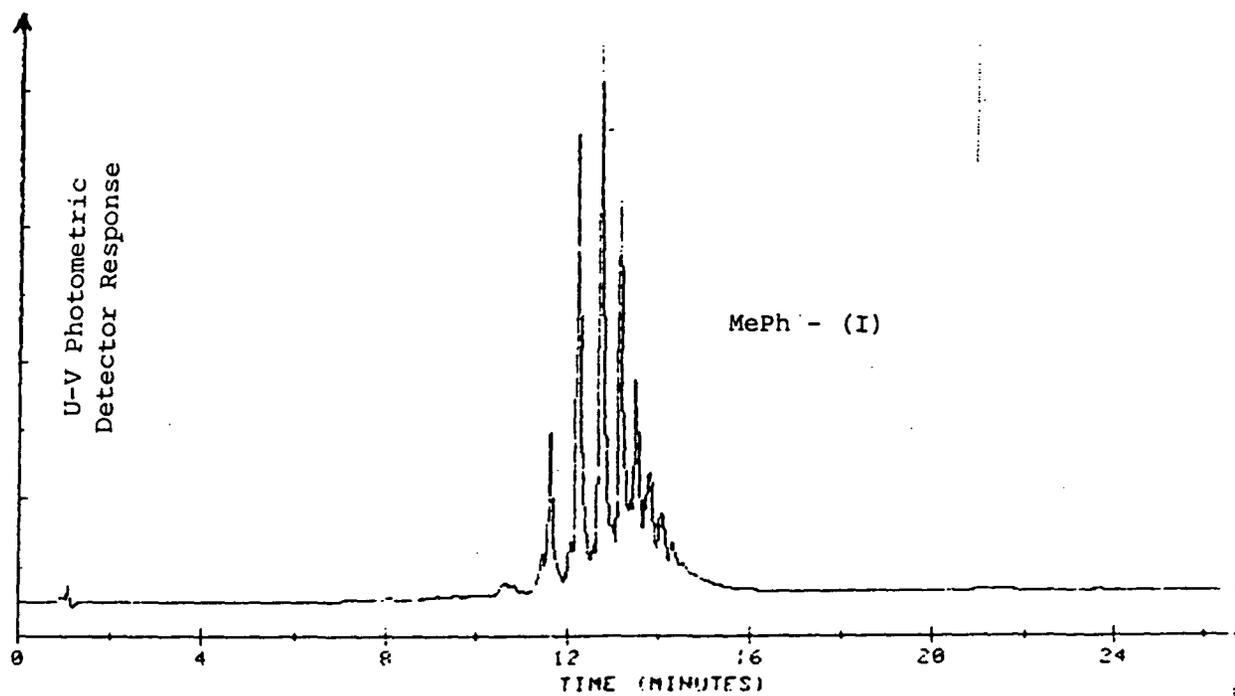


FIGURE 4. Reverse-Phase Liquid Chromatographic Analysis of MePh - (I) and Ph₂Me - (I)

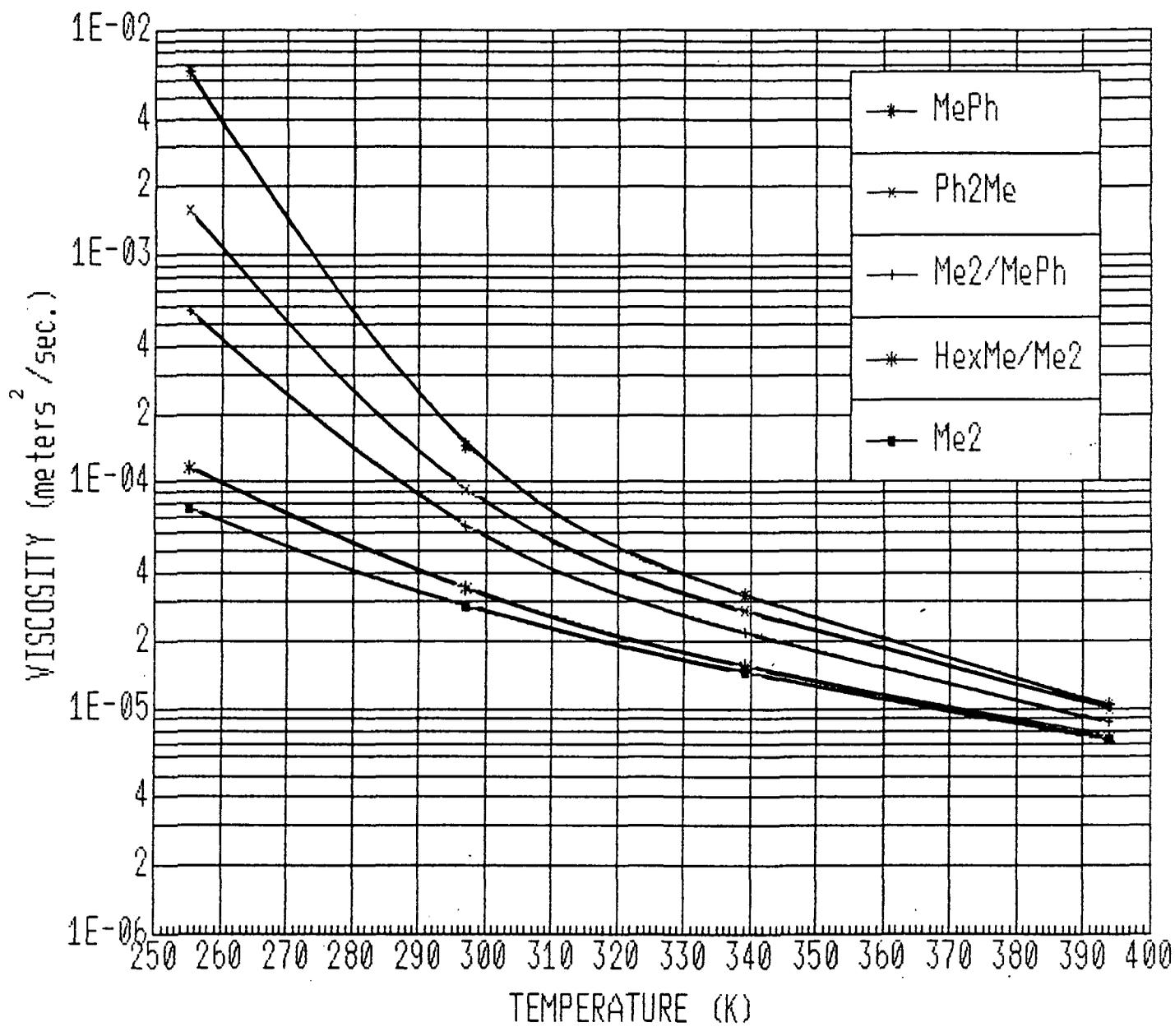


FIGURE 5. Kinematic Viscosity of Task I Fluids

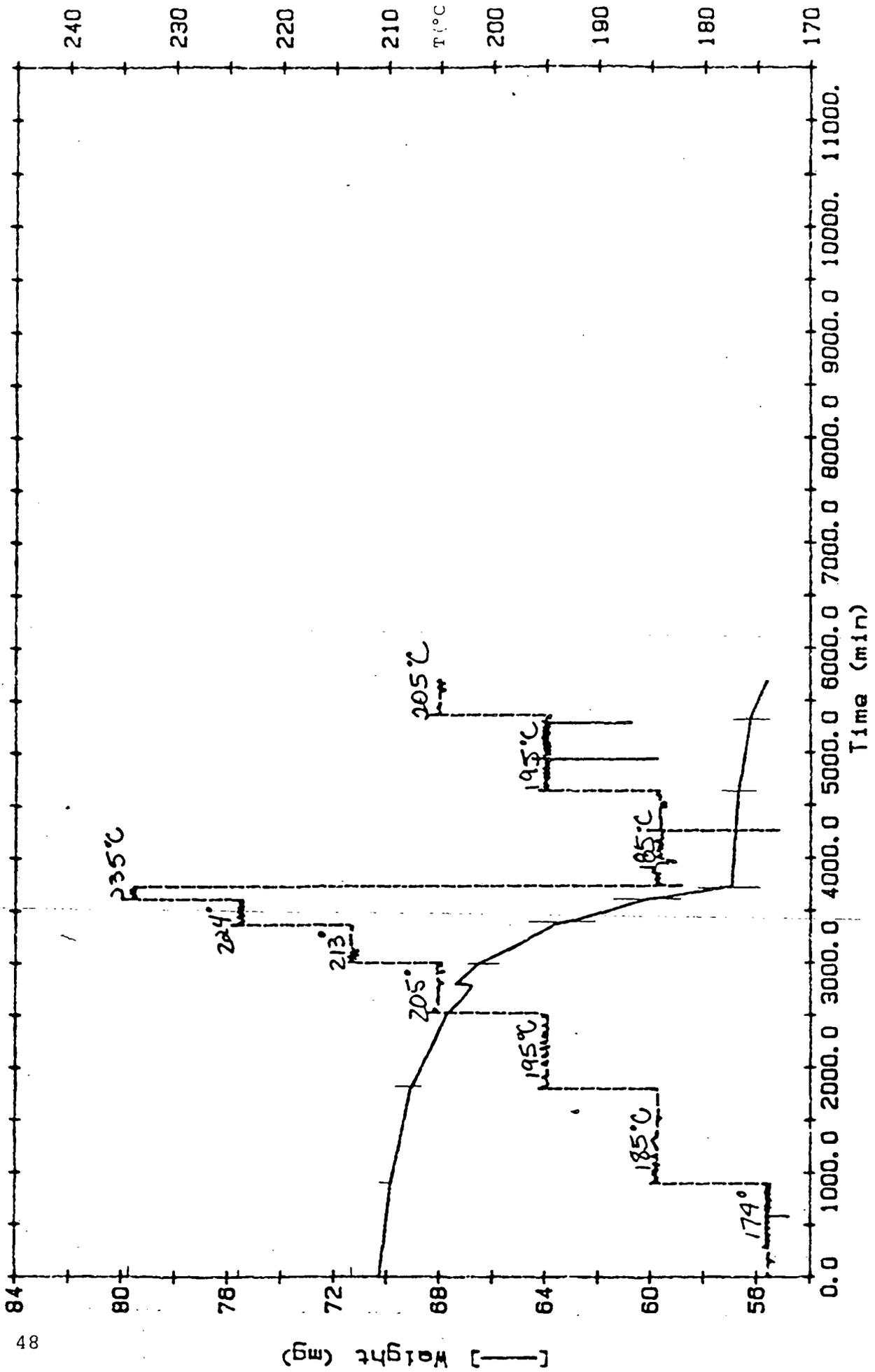
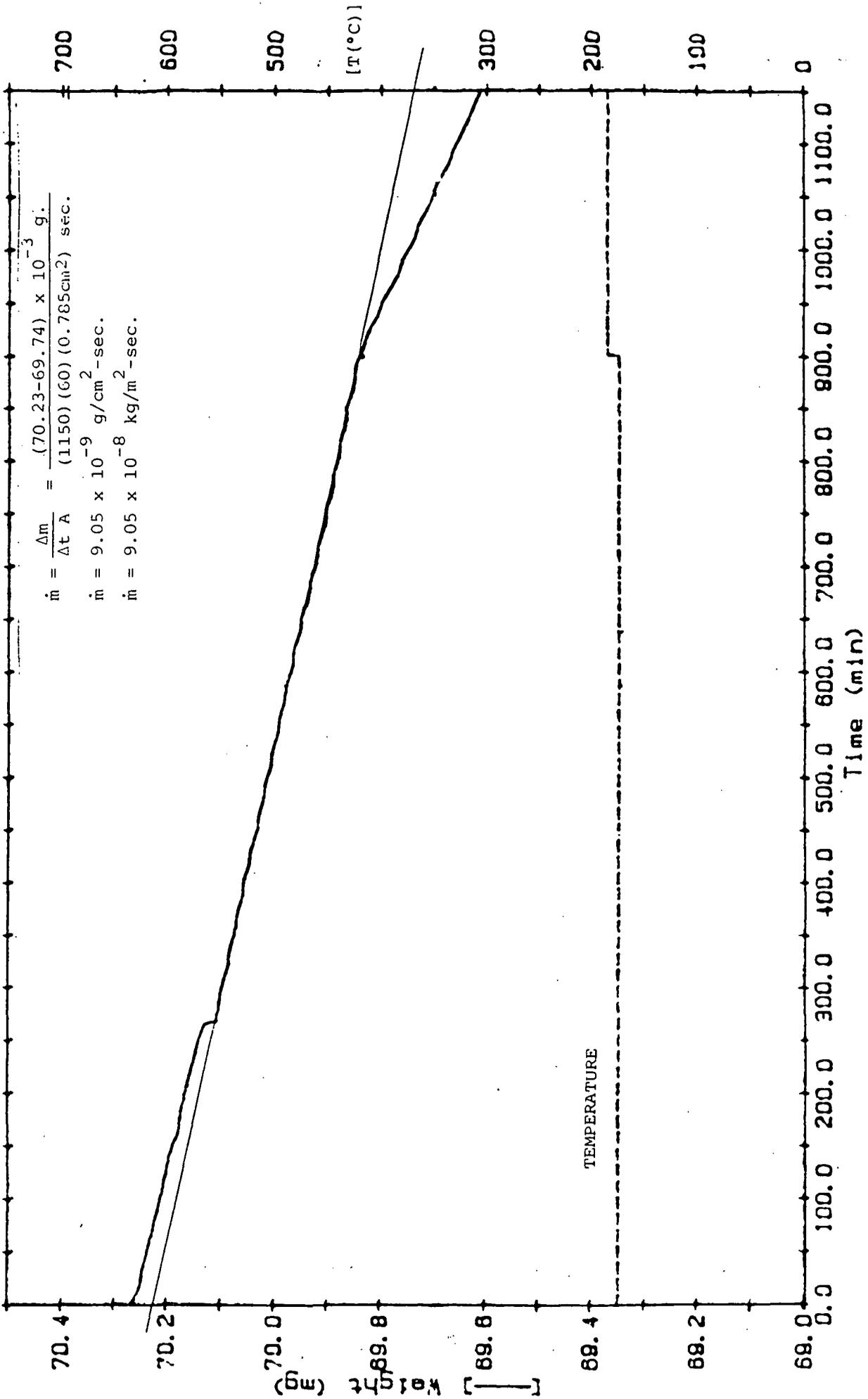


FIGURE 6. Typical evaporative mass loss profile - Me₂/Meph - (I)



49 FIGURE 7. Calculation of mass loss rate using TGA graphics system.
 Me₂/Meph Fluid at 174°C for 900 minutes.

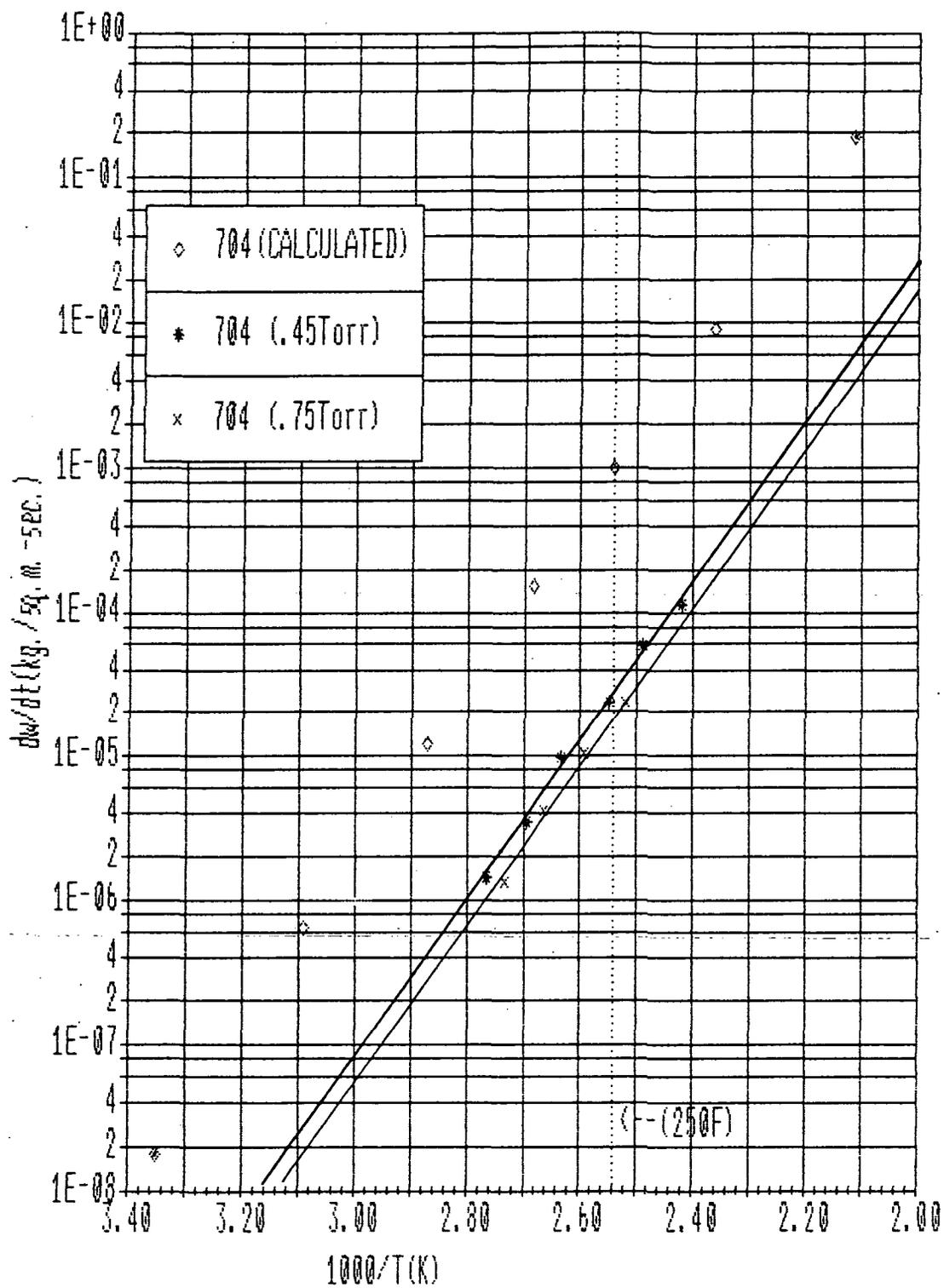


FIGURE 8. Mass Loss Rate Data of 704 Reference Fluid
 a) Calculated-Knudsen Equation
 b) Measured (0.45 Torr and 0.75 Torr)

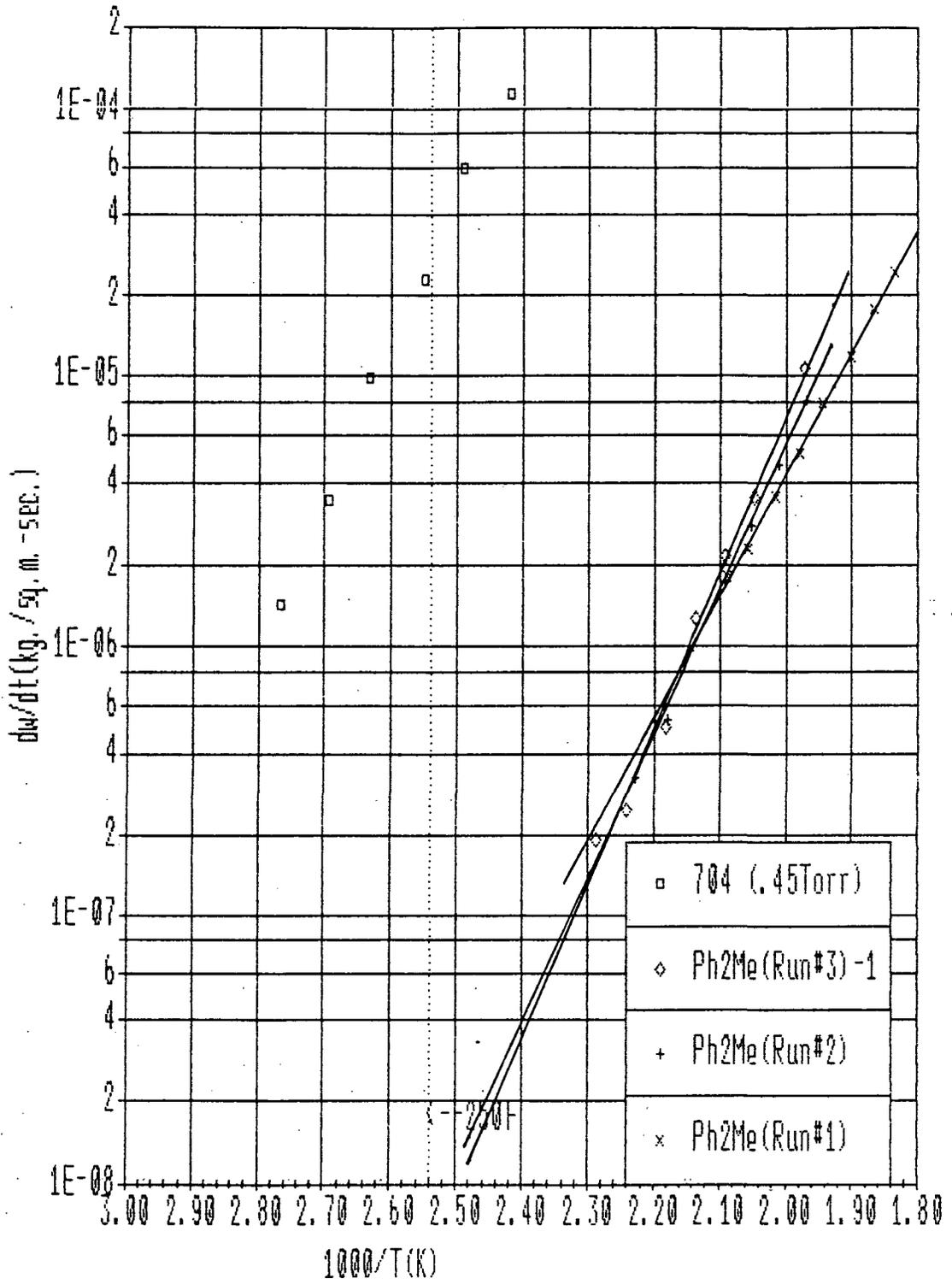


FIGURE 9. Measurements of Mass Loss Rates - Repeatability

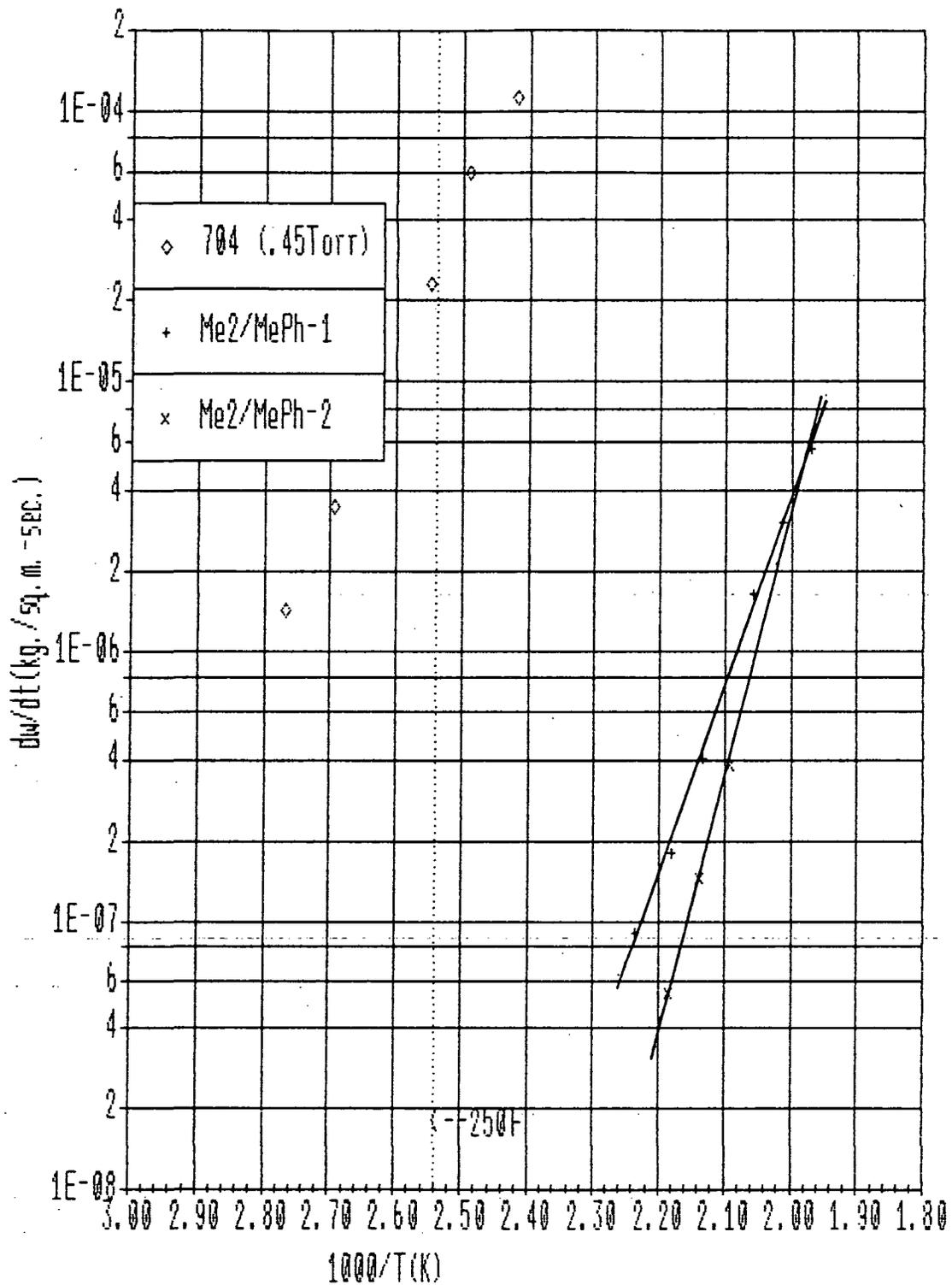


FIGURE 10a. Mass Loss Rates for Me₂/MePh - (I)

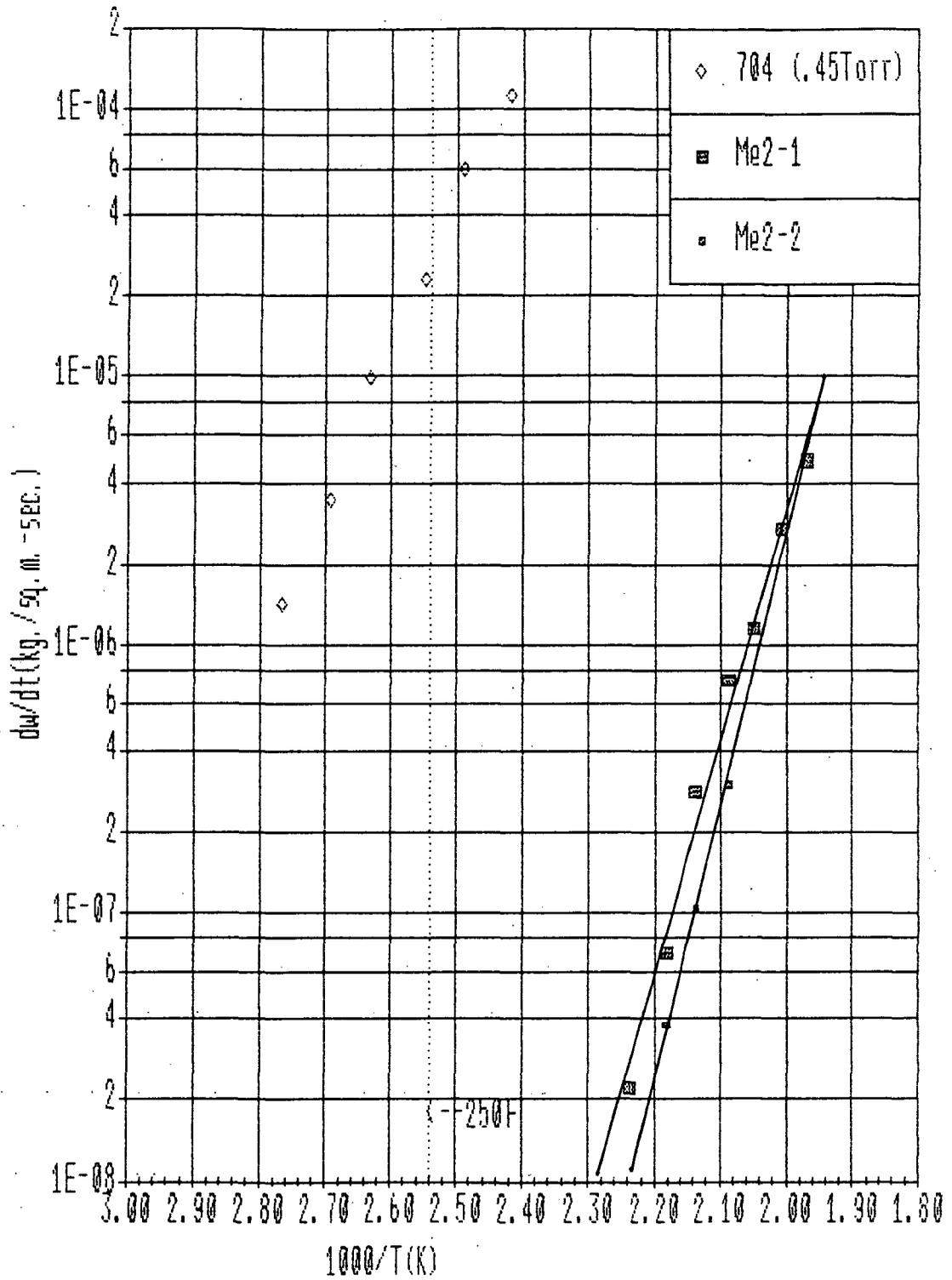


FIGURE 10b. Mass Loss Rates for Me₂ - (I)

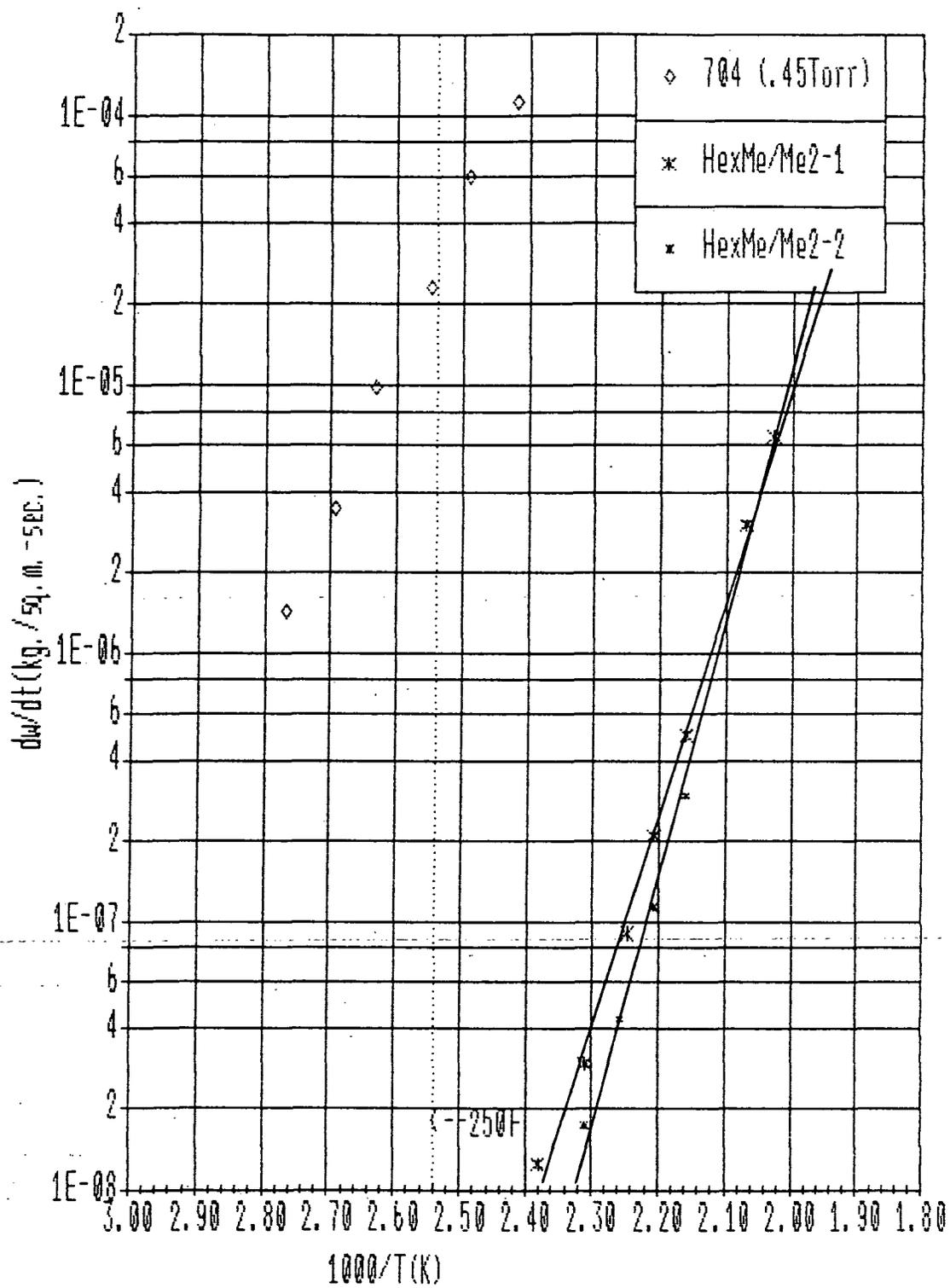


FIGURE 10c. Mass Loss Rates for HexMe/Me₂ - (I)

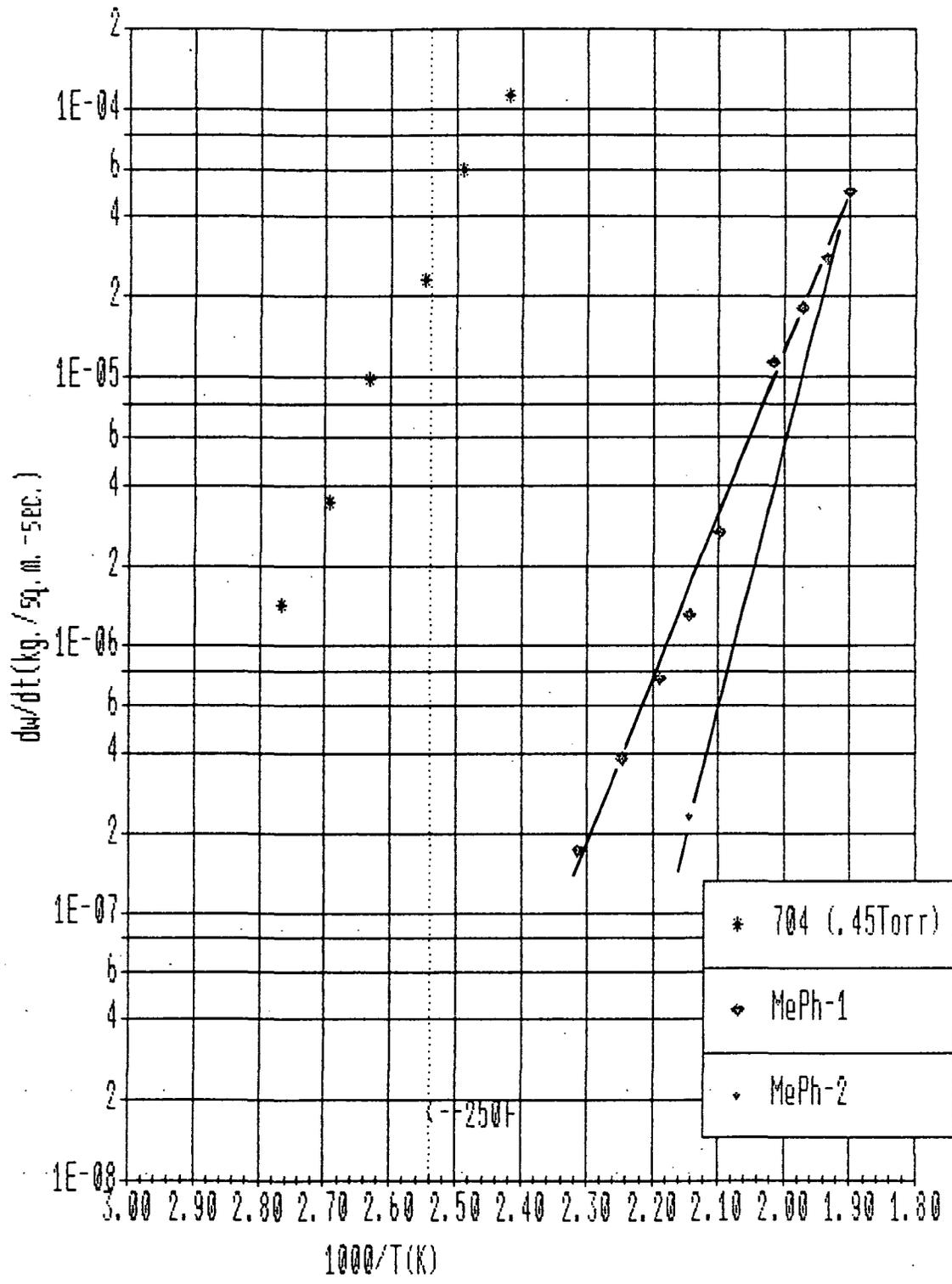


FIGURE 10d. Mass Loss Rates for MePh - (I)

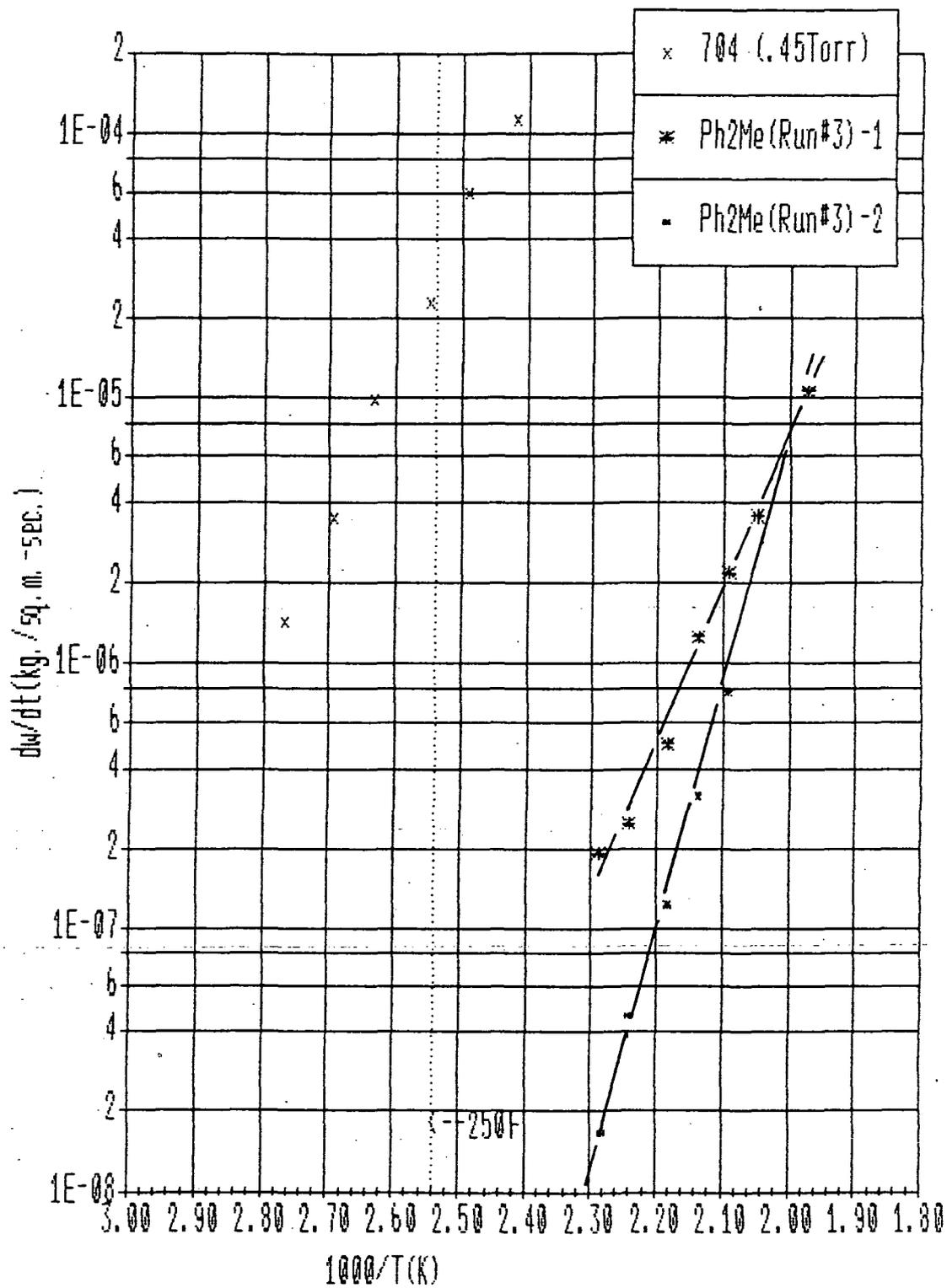


FIGURE 10e. Mass Loss Rates for Ph_2Me - (I)

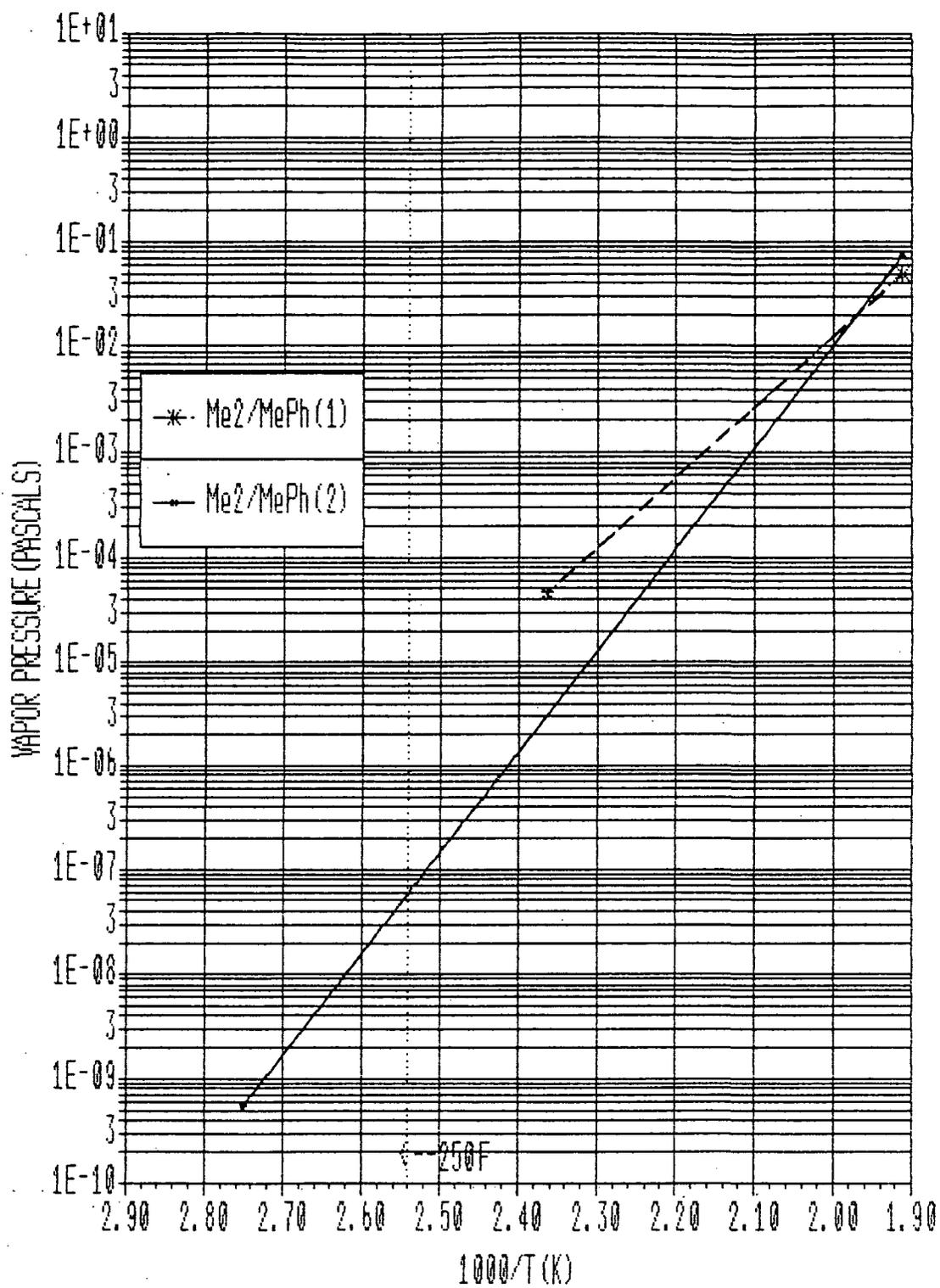


FIGURE 11a. Vapor Pressure of Me₂/MePh (1), Me₂/MePh (2)

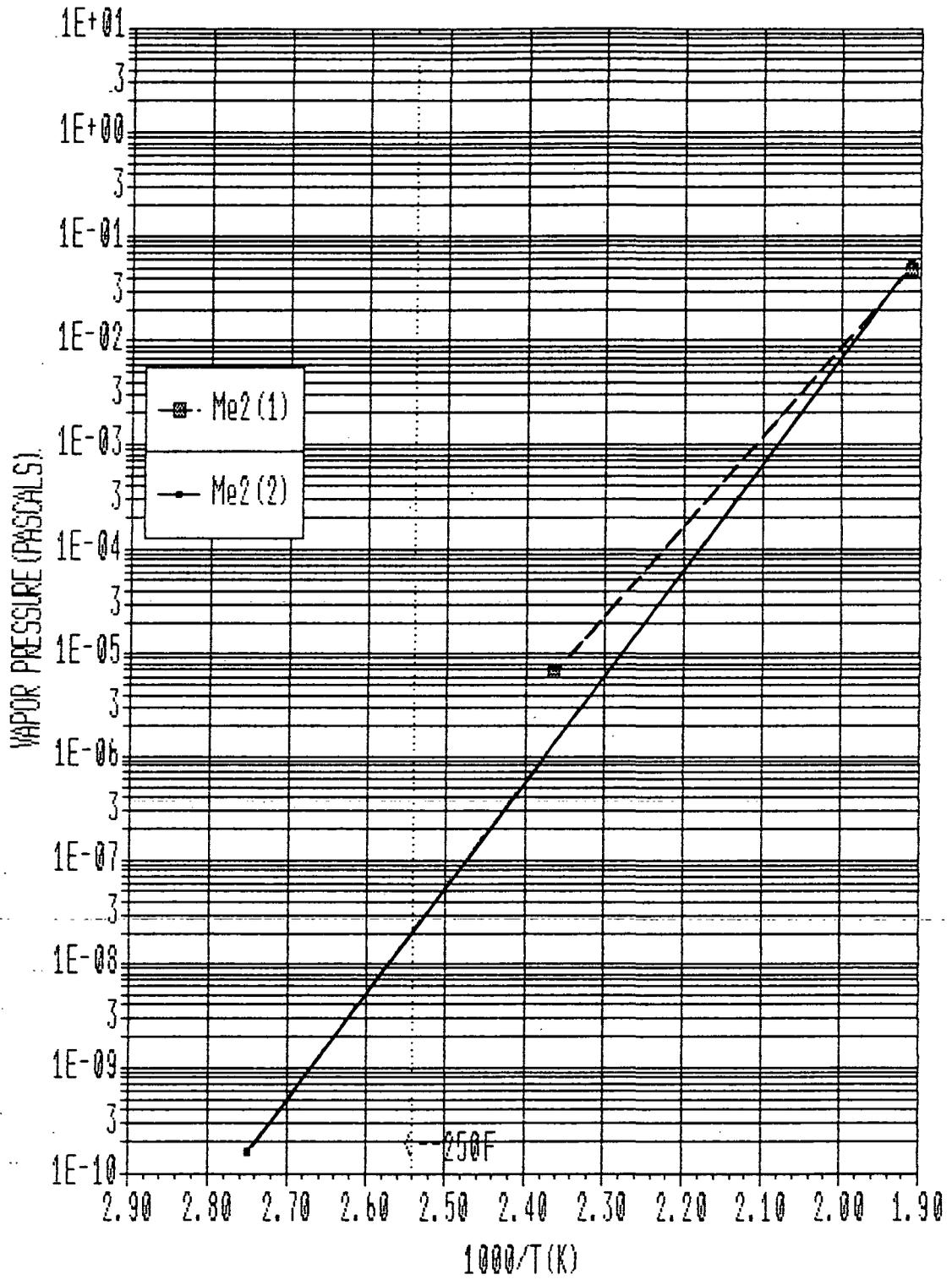


FIGURE 11b. Vapor Pressure of Me₂ (1), Me₂ (2)

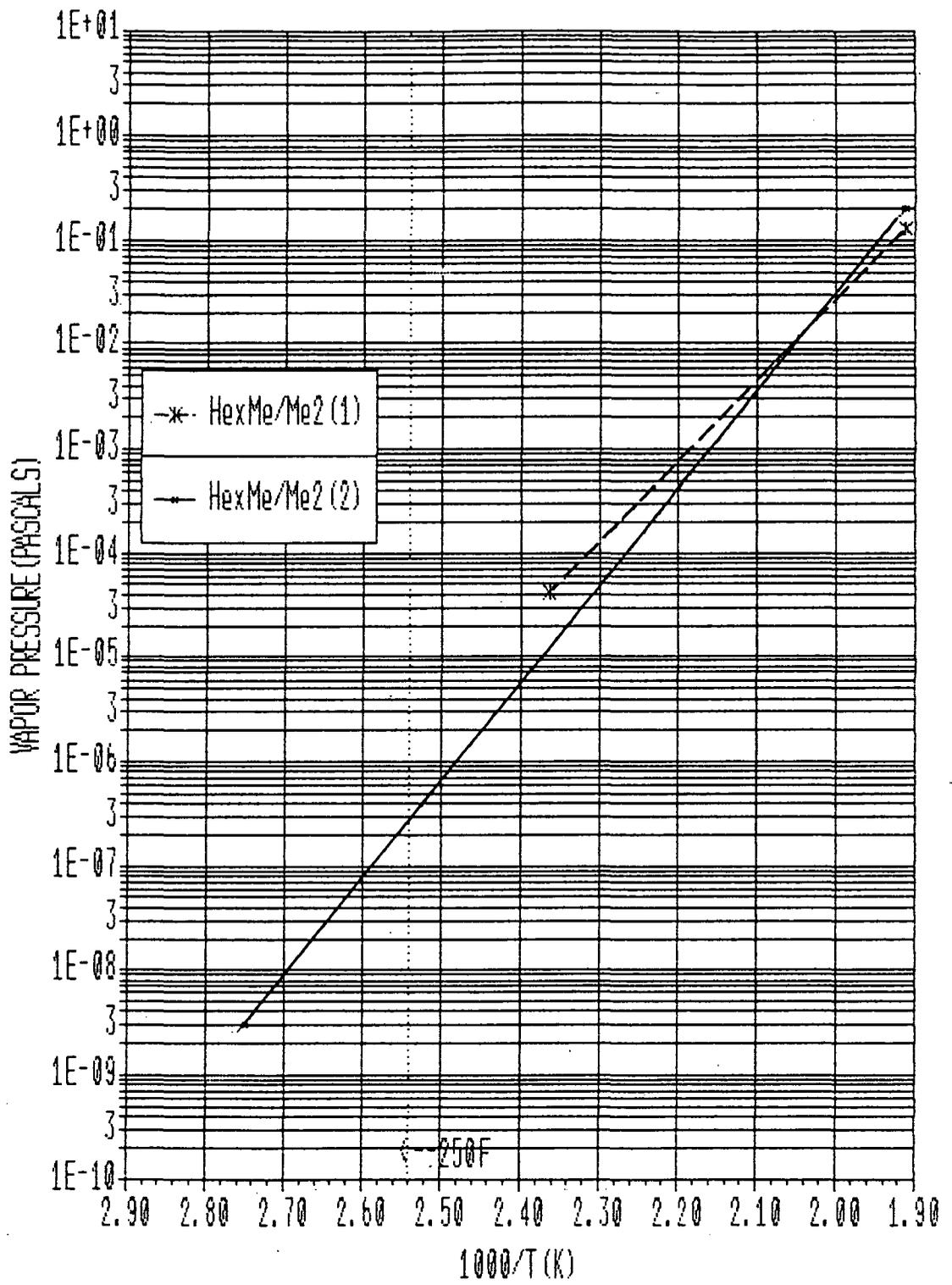


FIGURE 11c. Vapor Pressure of HexMe/Me₂ (1), HexMe/Me₂ (2)

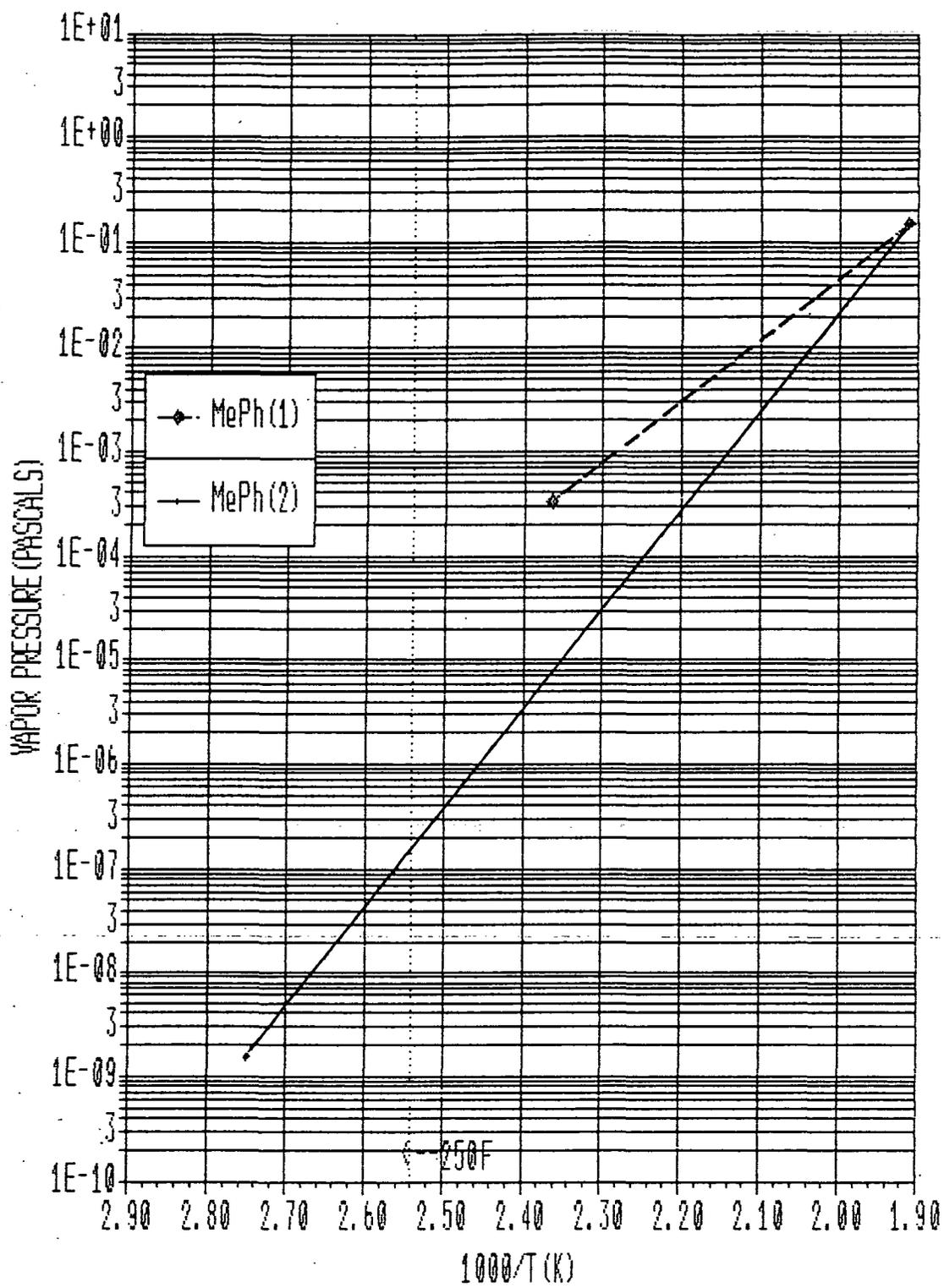


FIGURE 11d. Vapor Pressure of MePh (1), MePh (2)

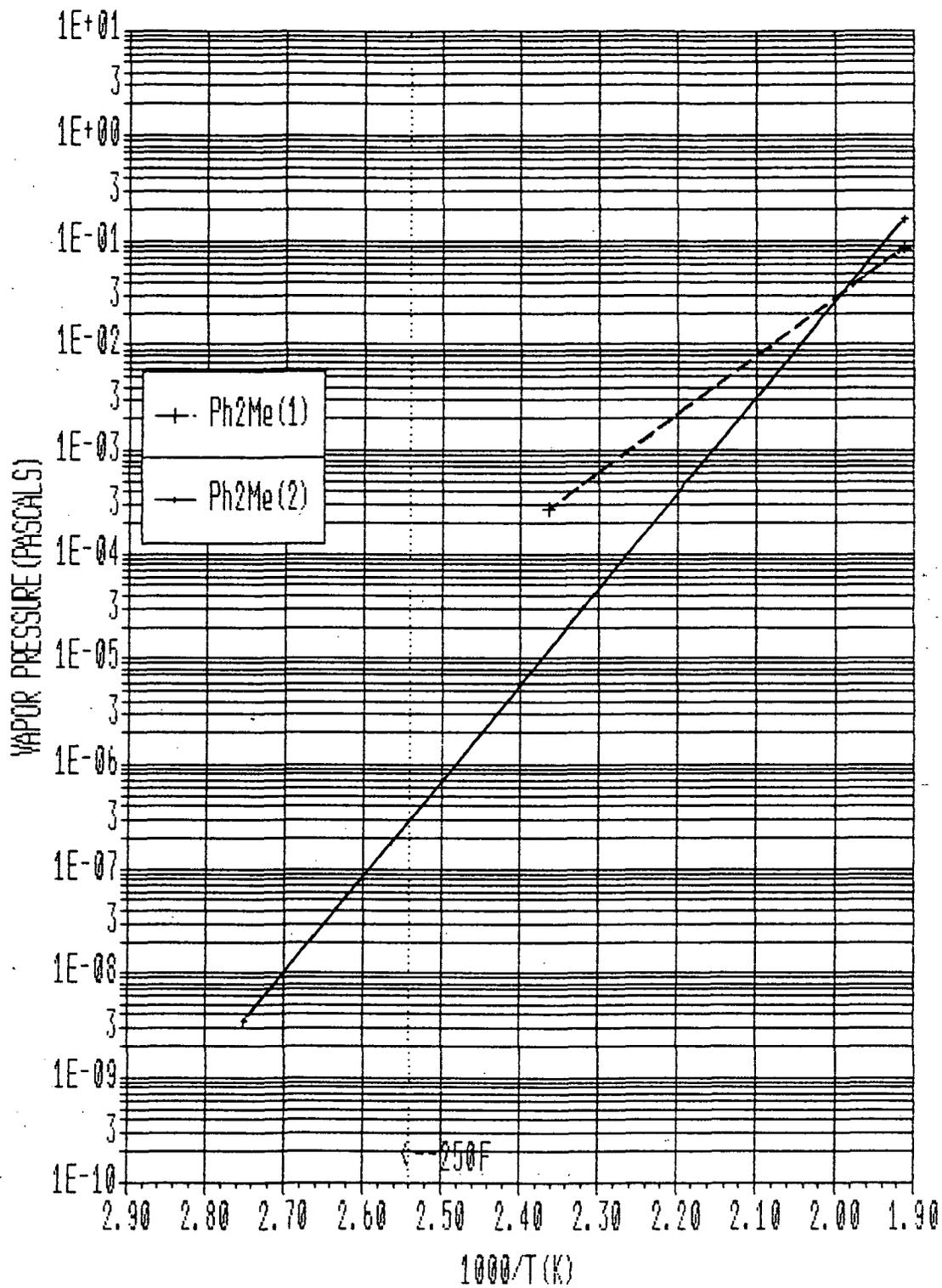


FIGURE 11e. Vapor Pressure of Ph₂Me (1), Ph₂Me (2)

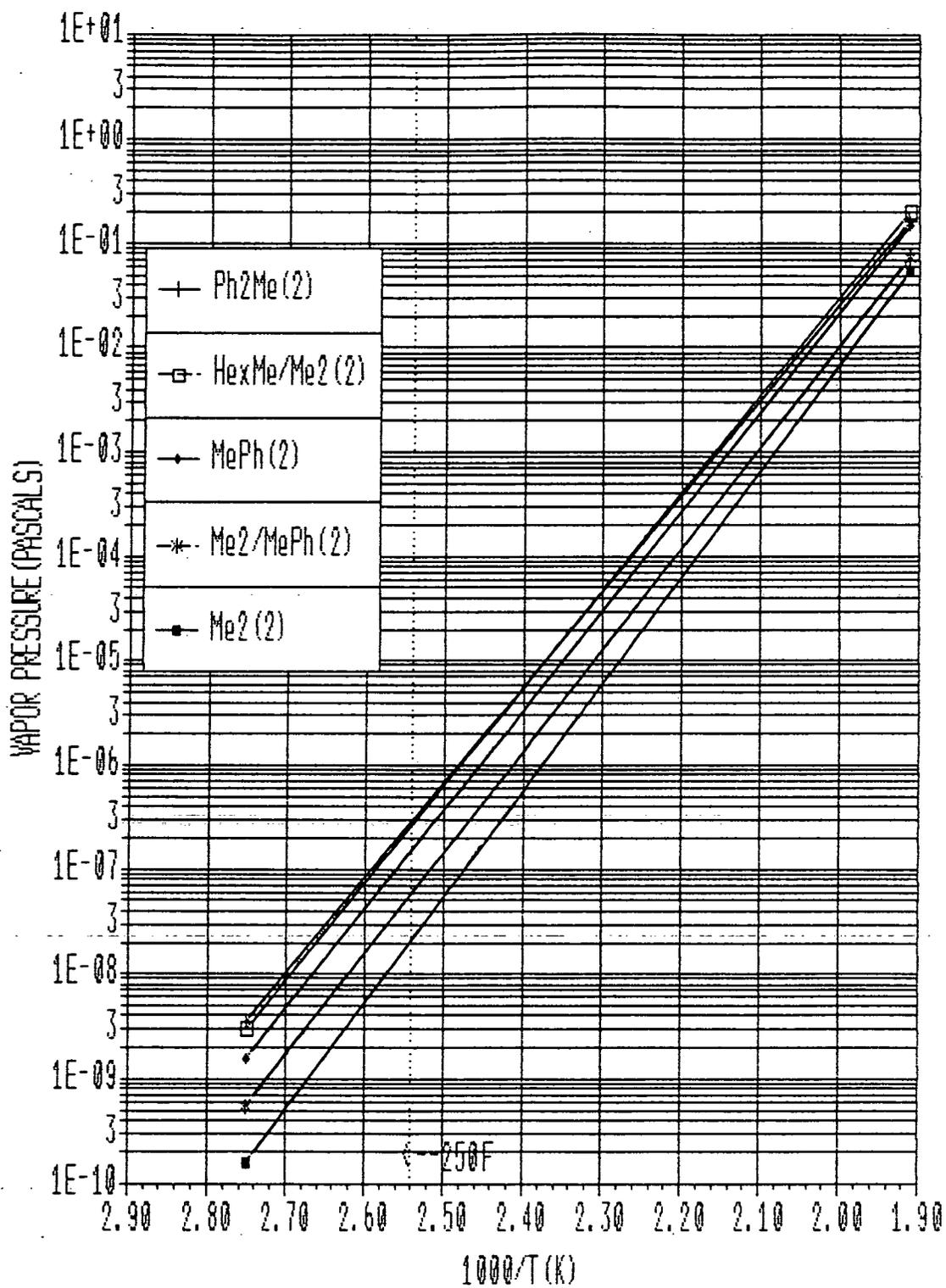


FIGURE 12. Vapor Pressures of Task I Fluids

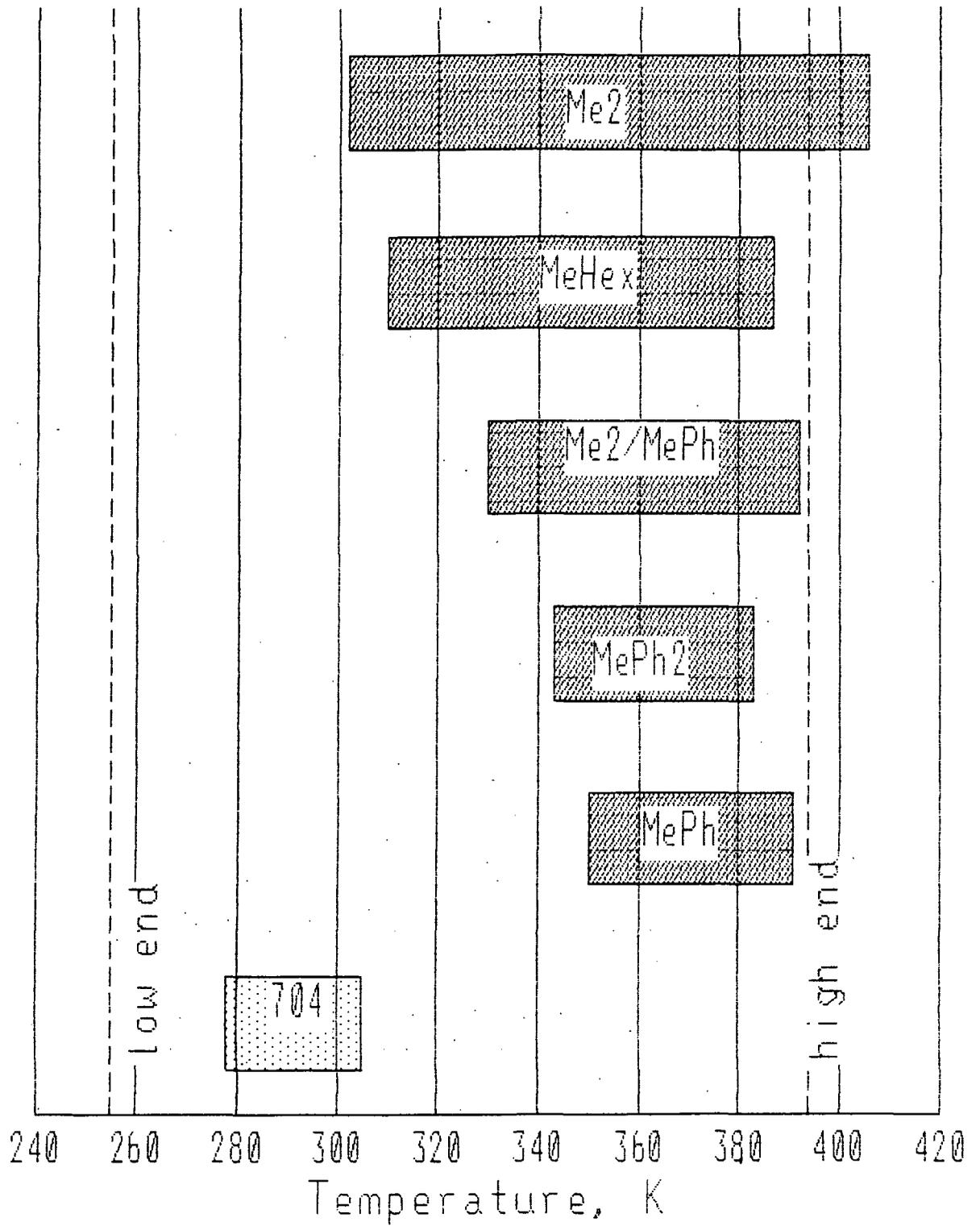
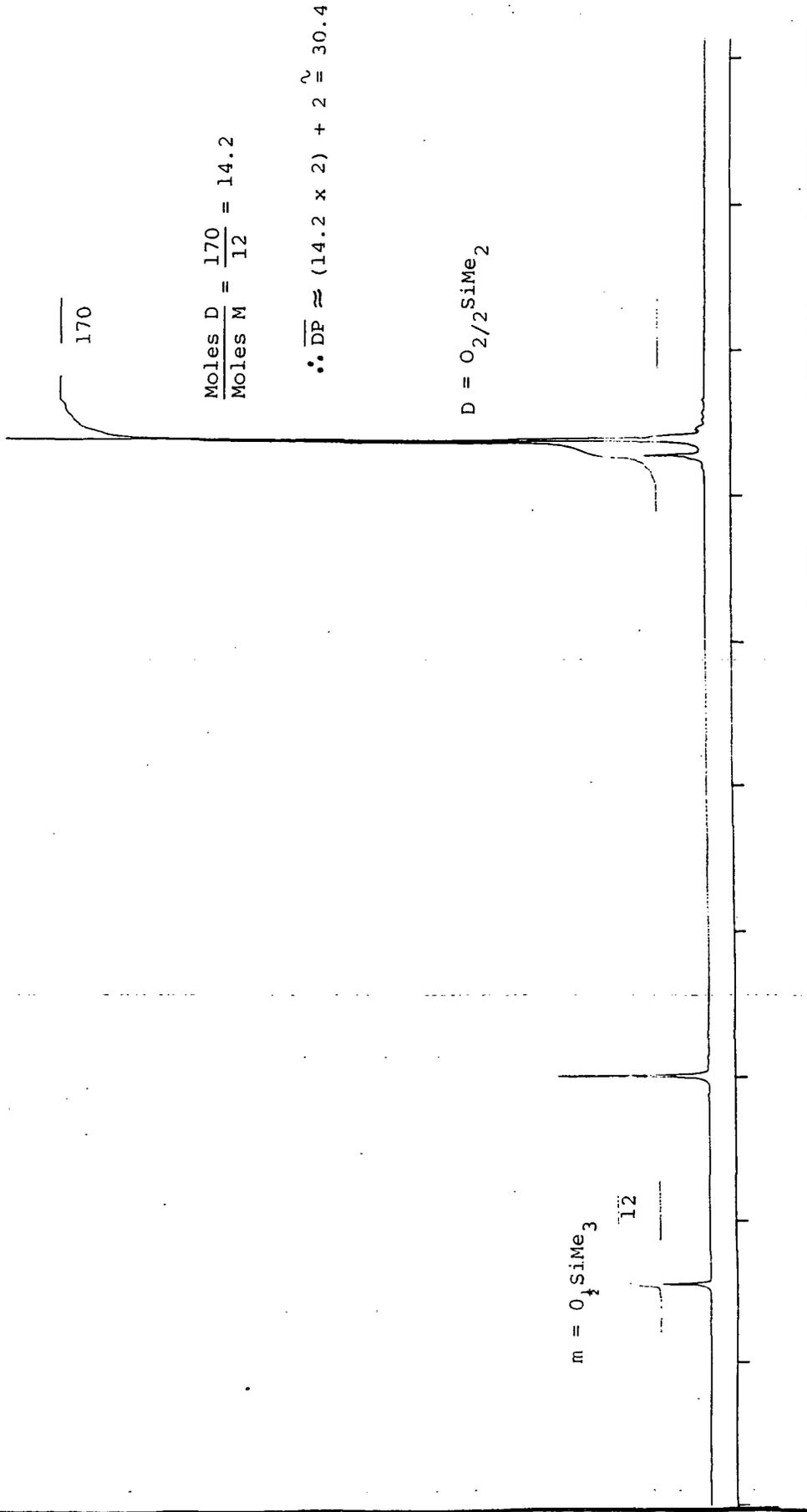


FIGURE 13. Working Temperature Ranges, Task I Fluids
 Range bars terminate at viscosity of
 $25 \times 10^{-6} \text{ m}^2/\text{sec}$ (low temperature) and
 10^{-7} Pa (high temperature)
 No working range exists for 704


 FIGURE 16. Si^{29} -NMR Spectra of Me_2 (II) Fluid

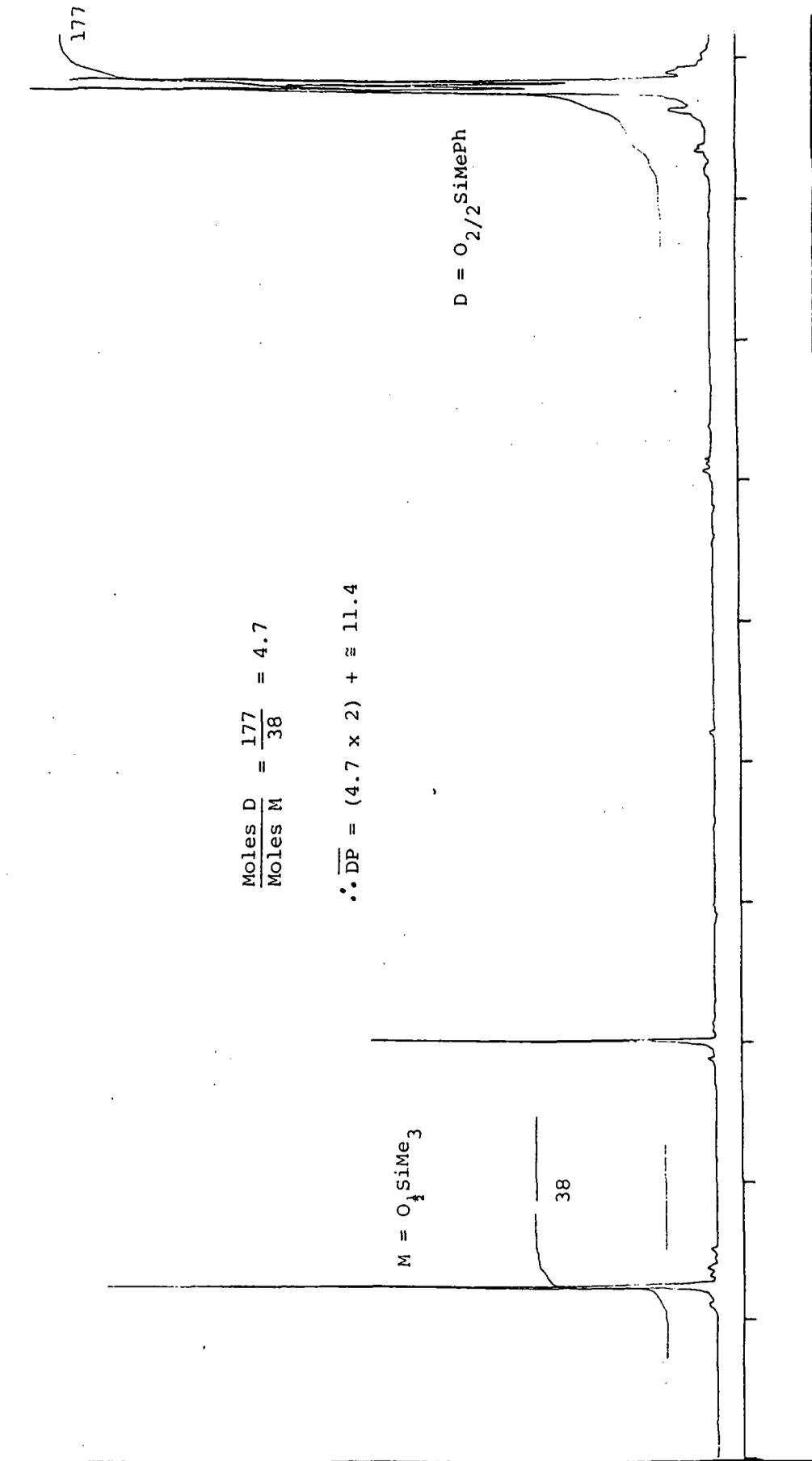


FIGURE 17. Si^{29} -NMR Spectra of MePh (II) Fluid

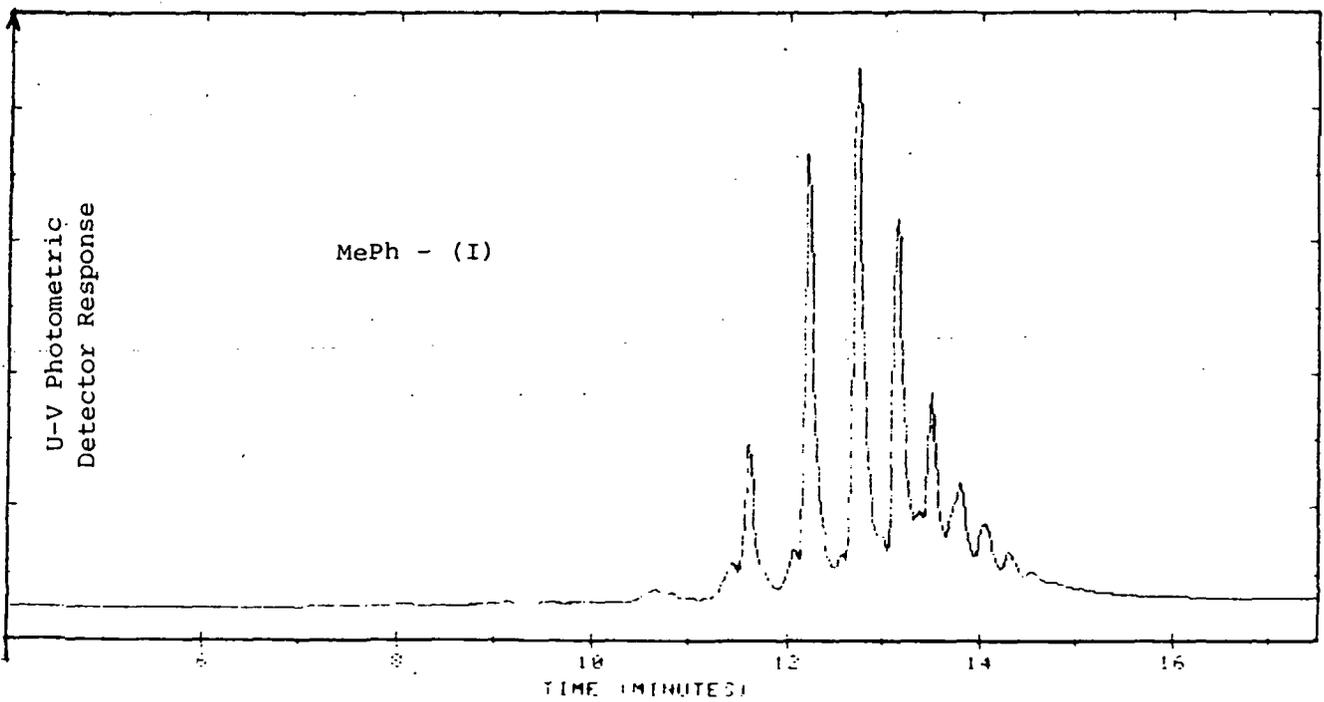
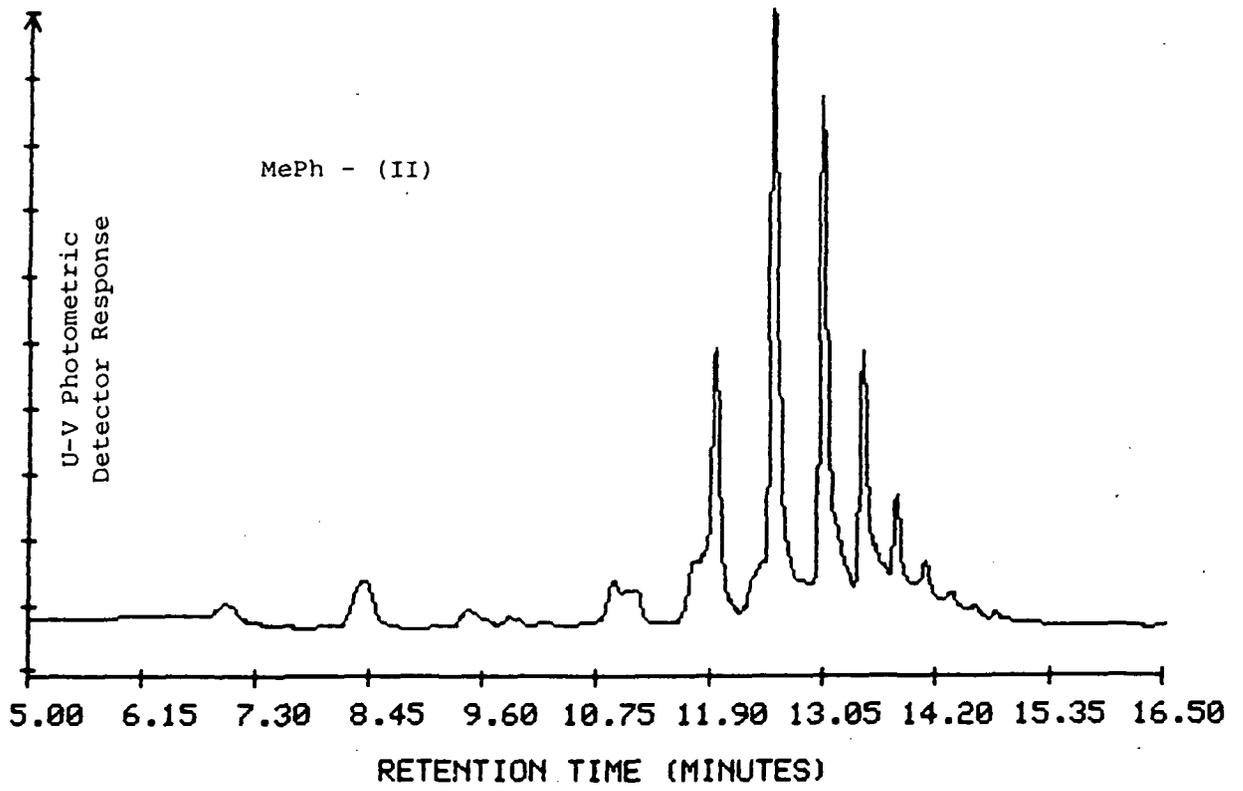


FIGURE 18. Reverse-Phase Liquid Chromatograms of MePh (I and II) Fluid

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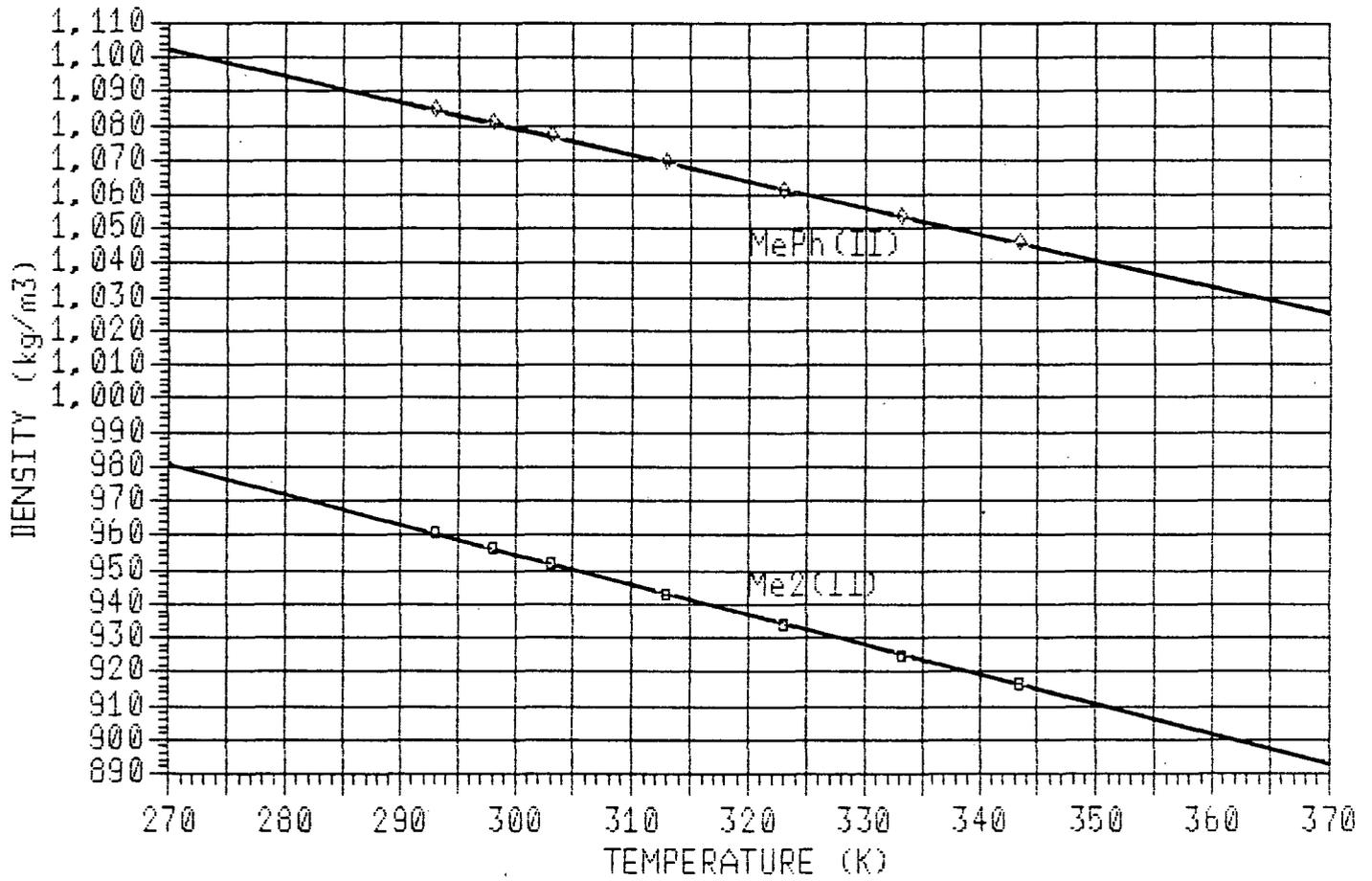


FIGURE 19. Density of Task II Fluids

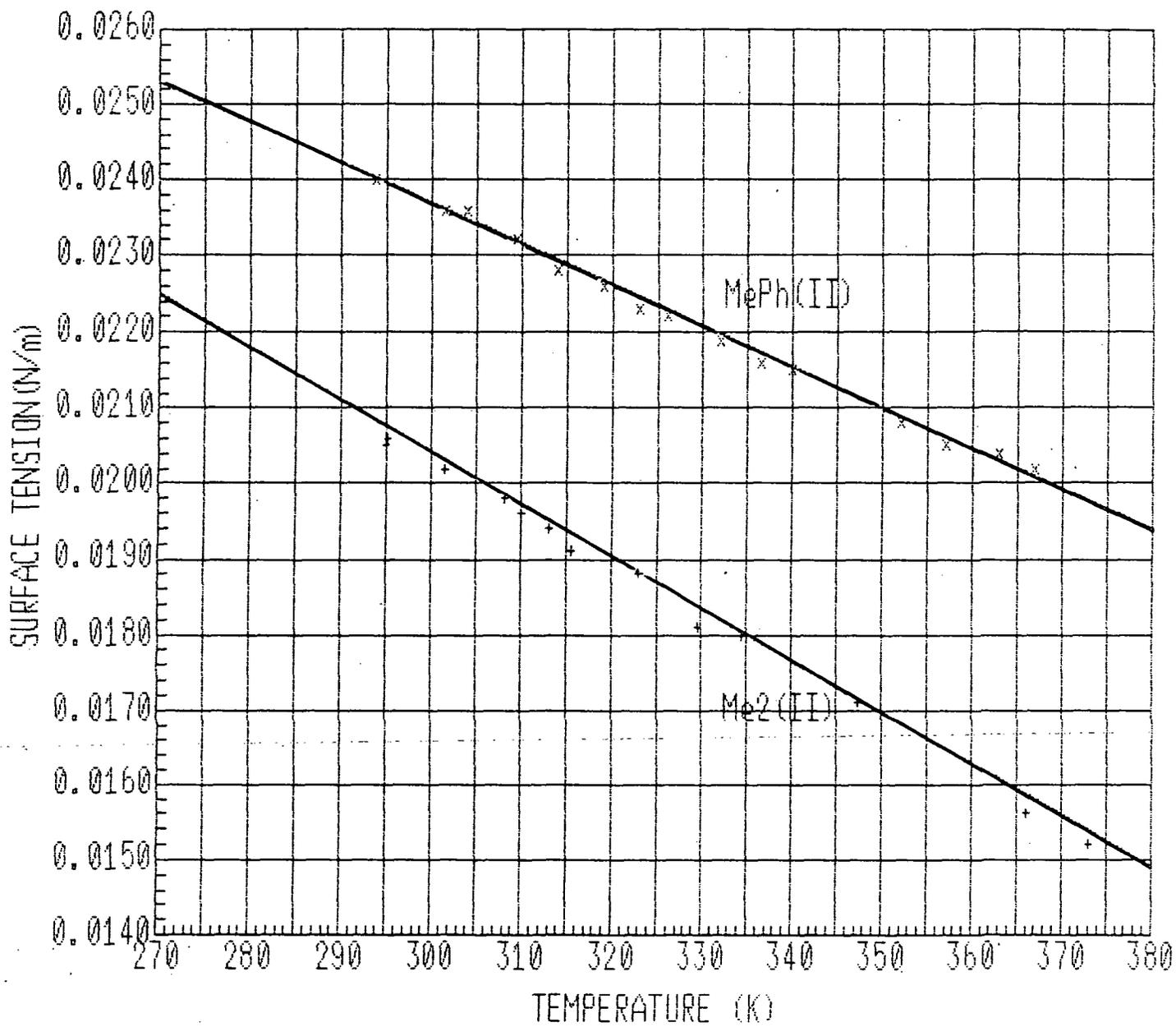


FIGURE 20. Surface Tension of Task II Fluids

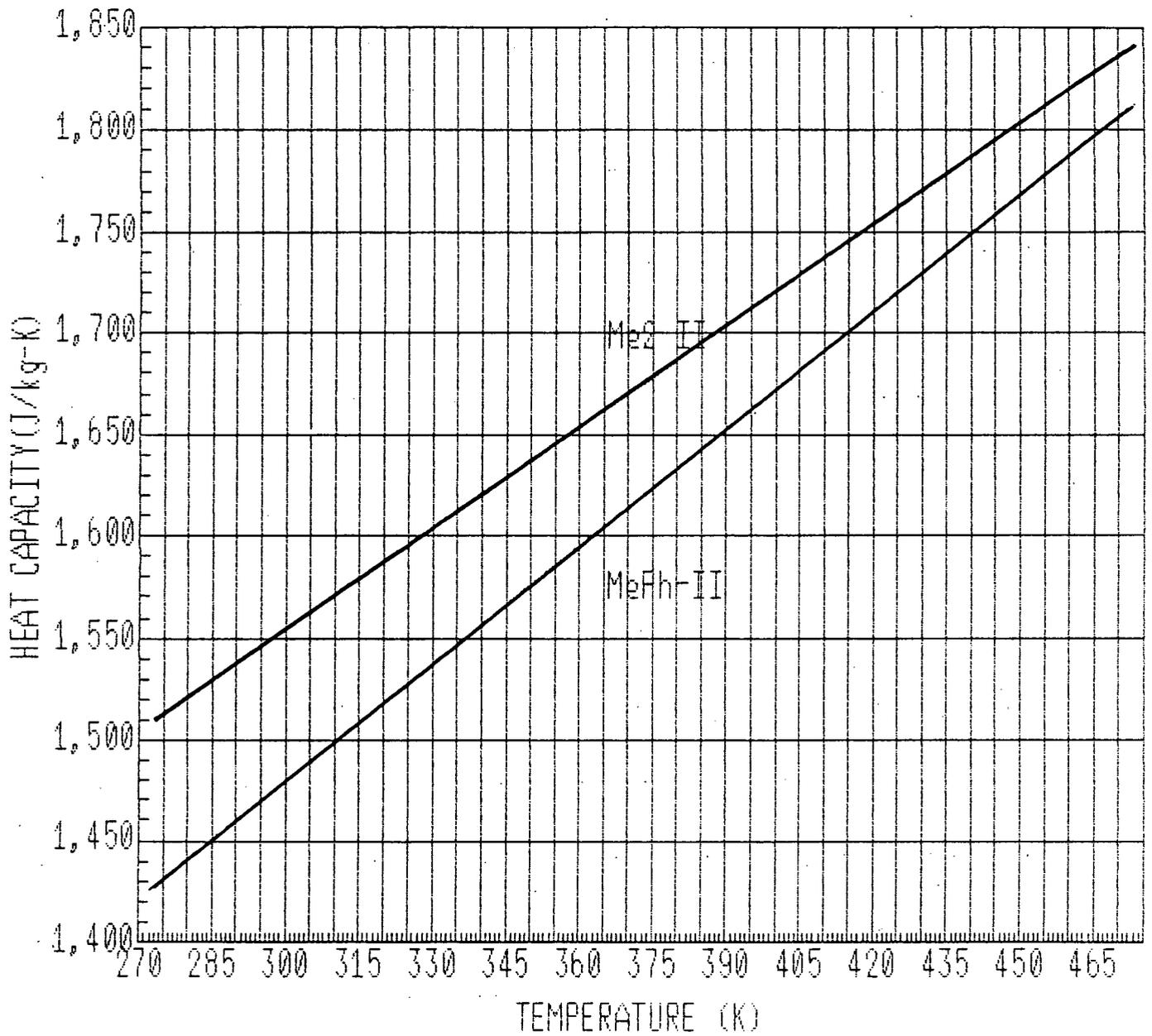


FIGURE 21. Heat Capacity of Task II Fluids

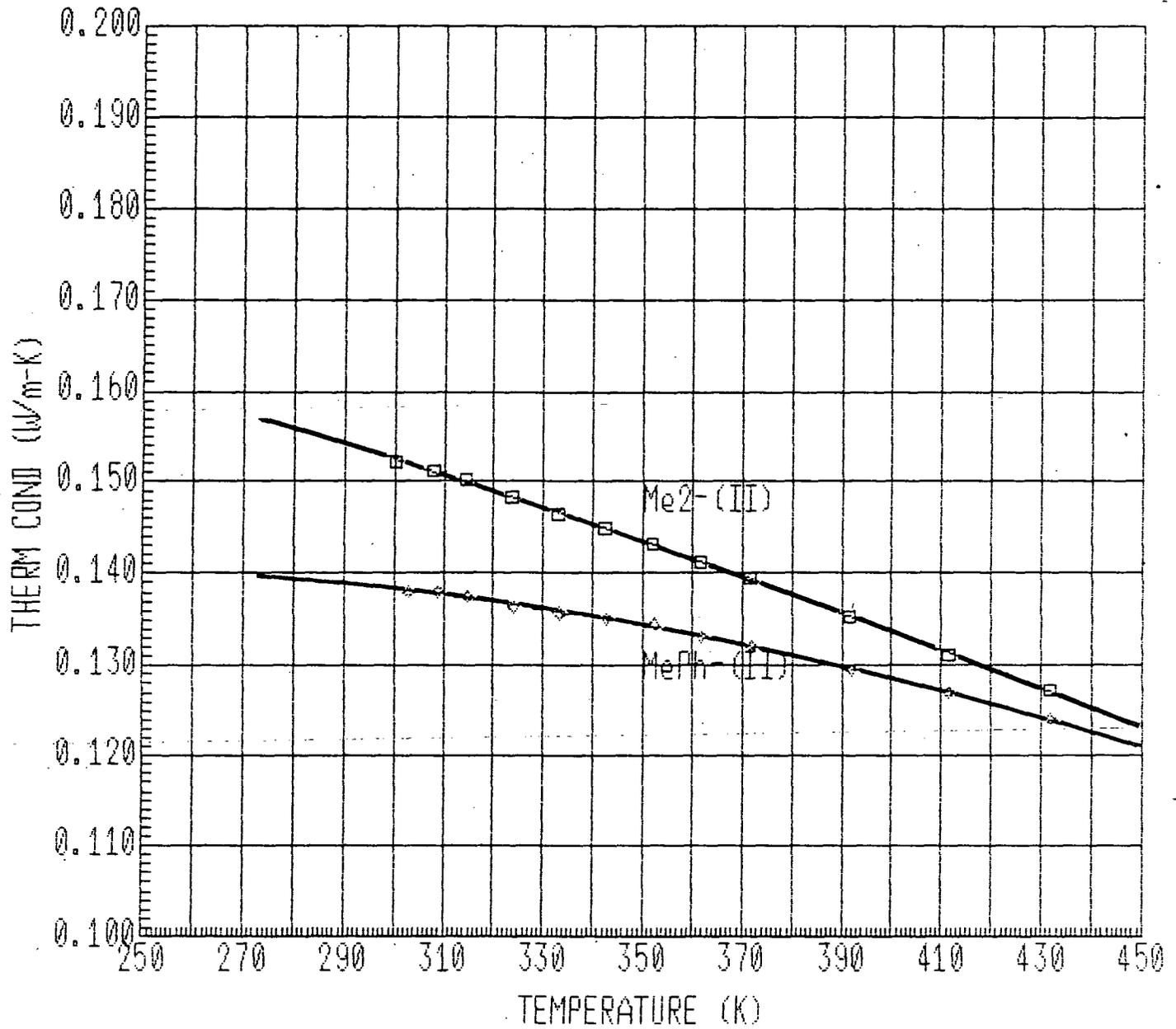


FIGURE 22. Thermal Conductivity of Task II Fluids

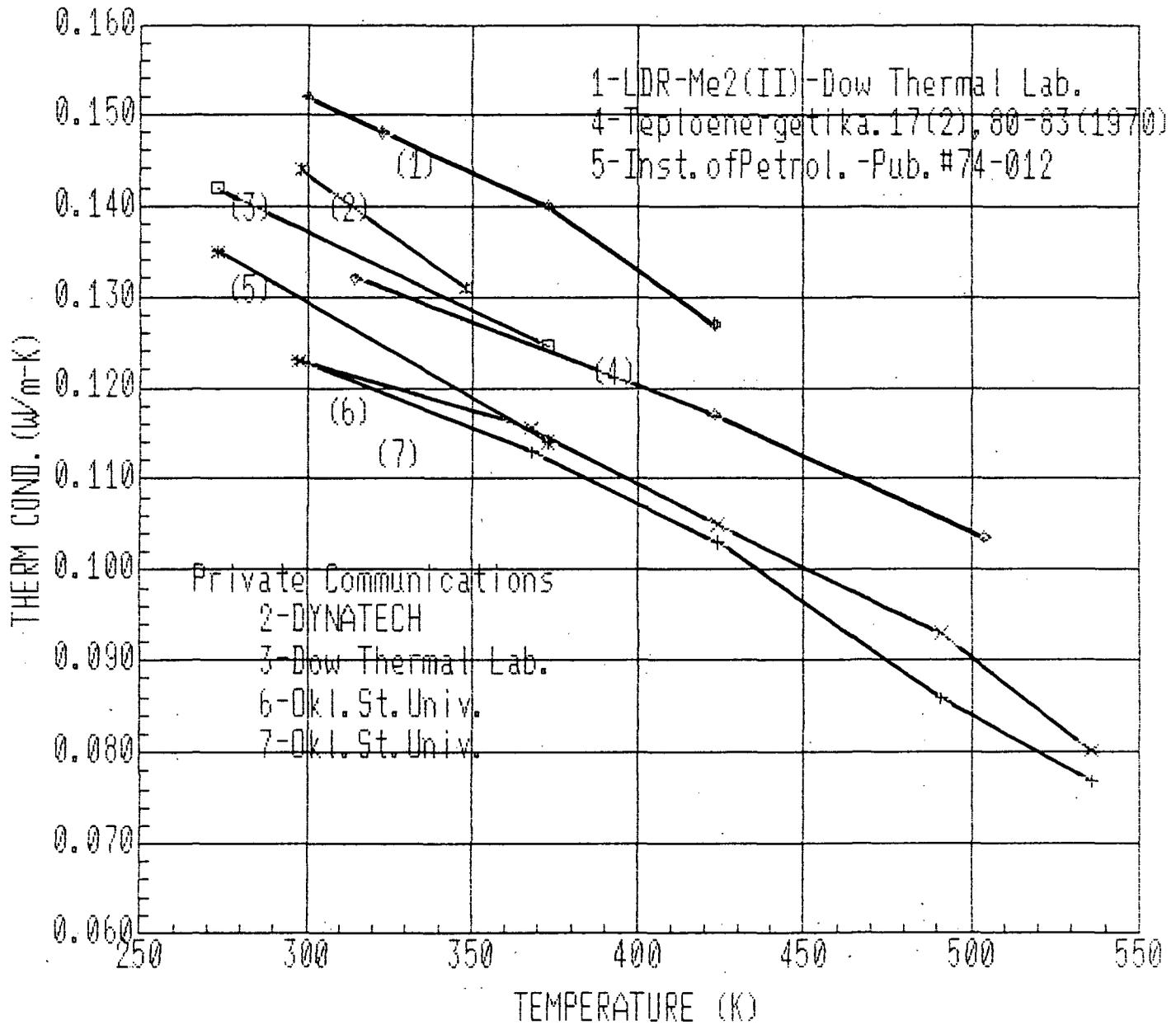


FIGURE 23. Thermal Conductivity of PDMS Fluids

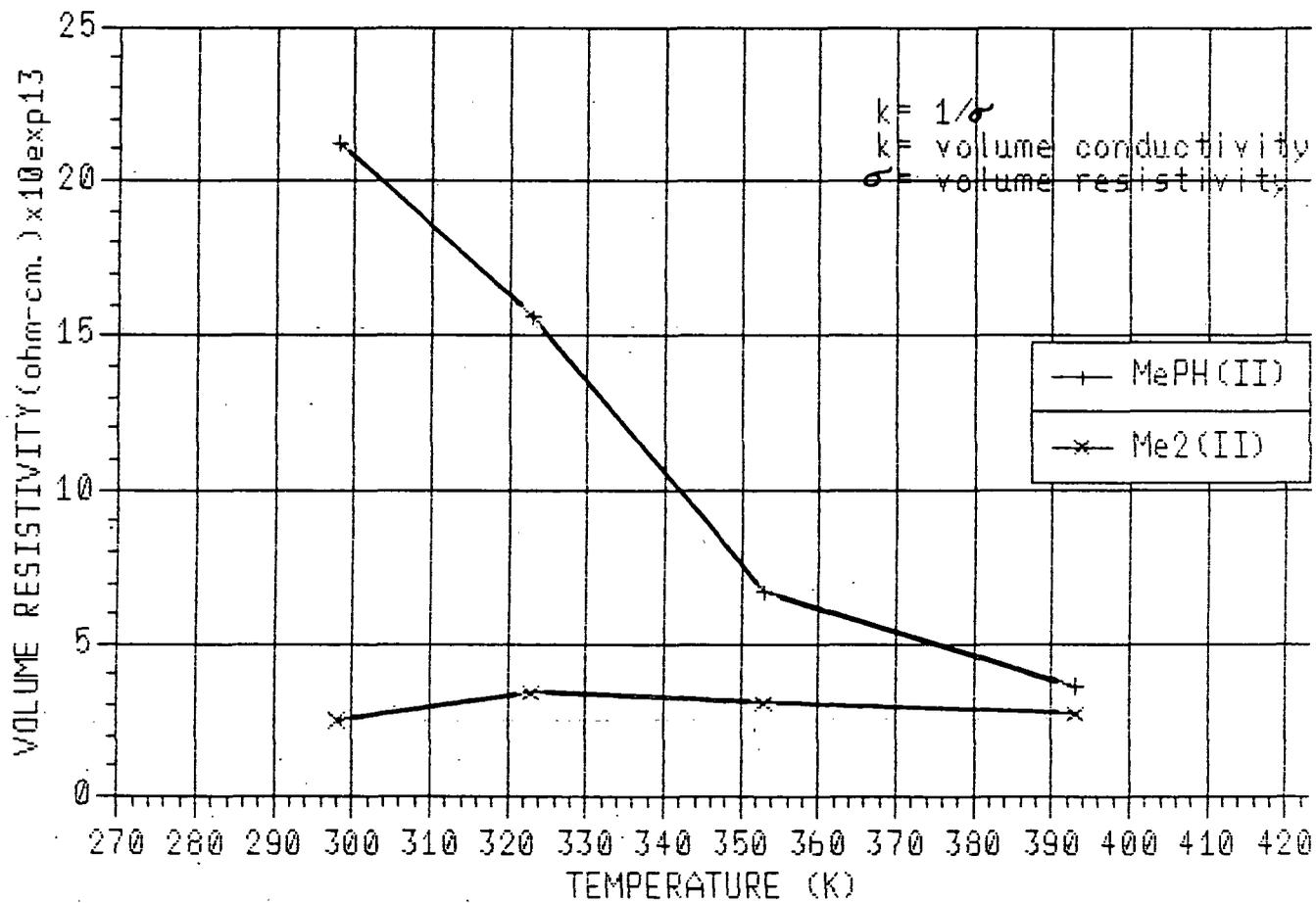


FIGURE 24. Volume Resistivity of Task II Fluids

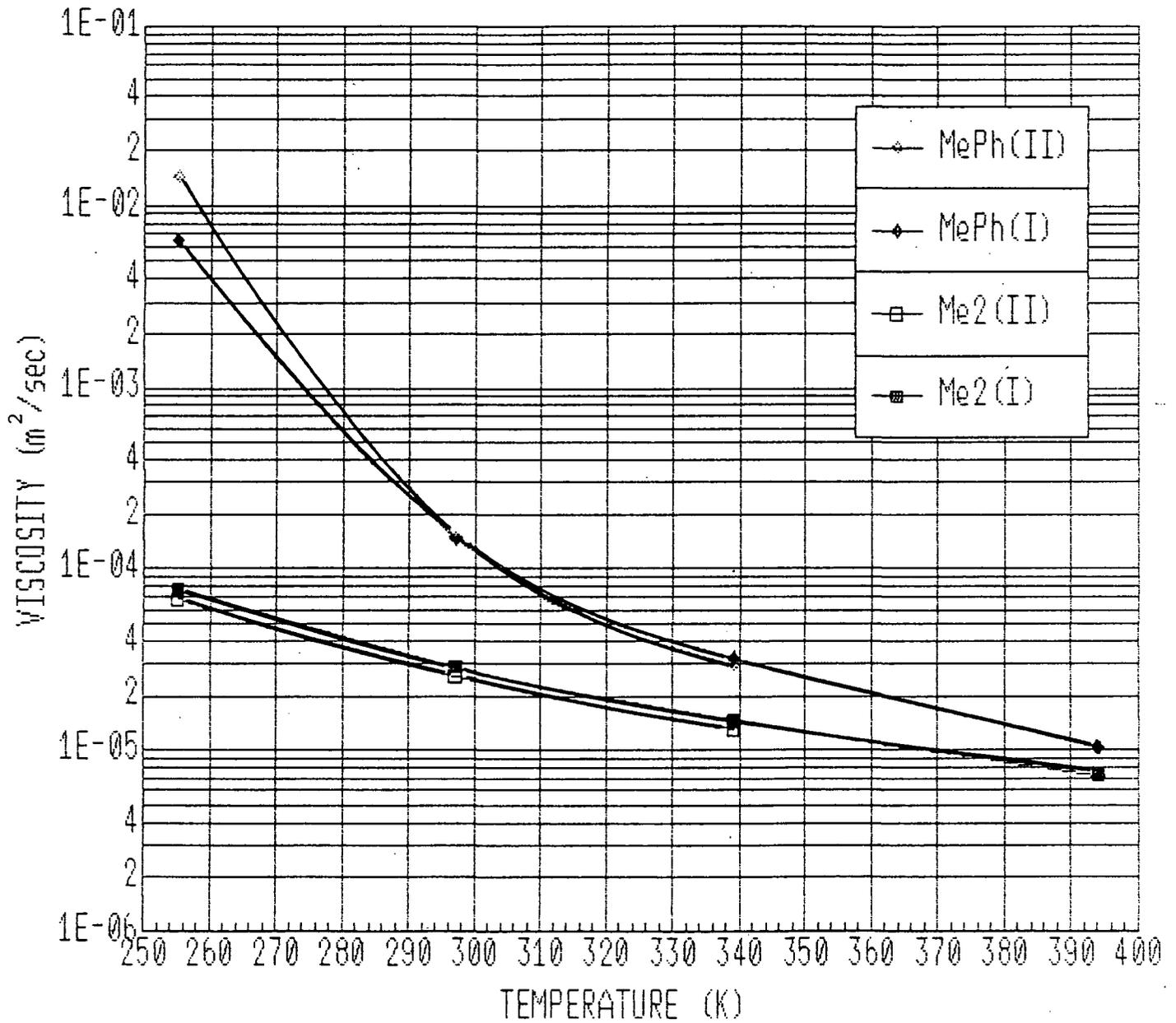


FIGURE 25. Kinematic Viscosity of Task (I and II) Fluids

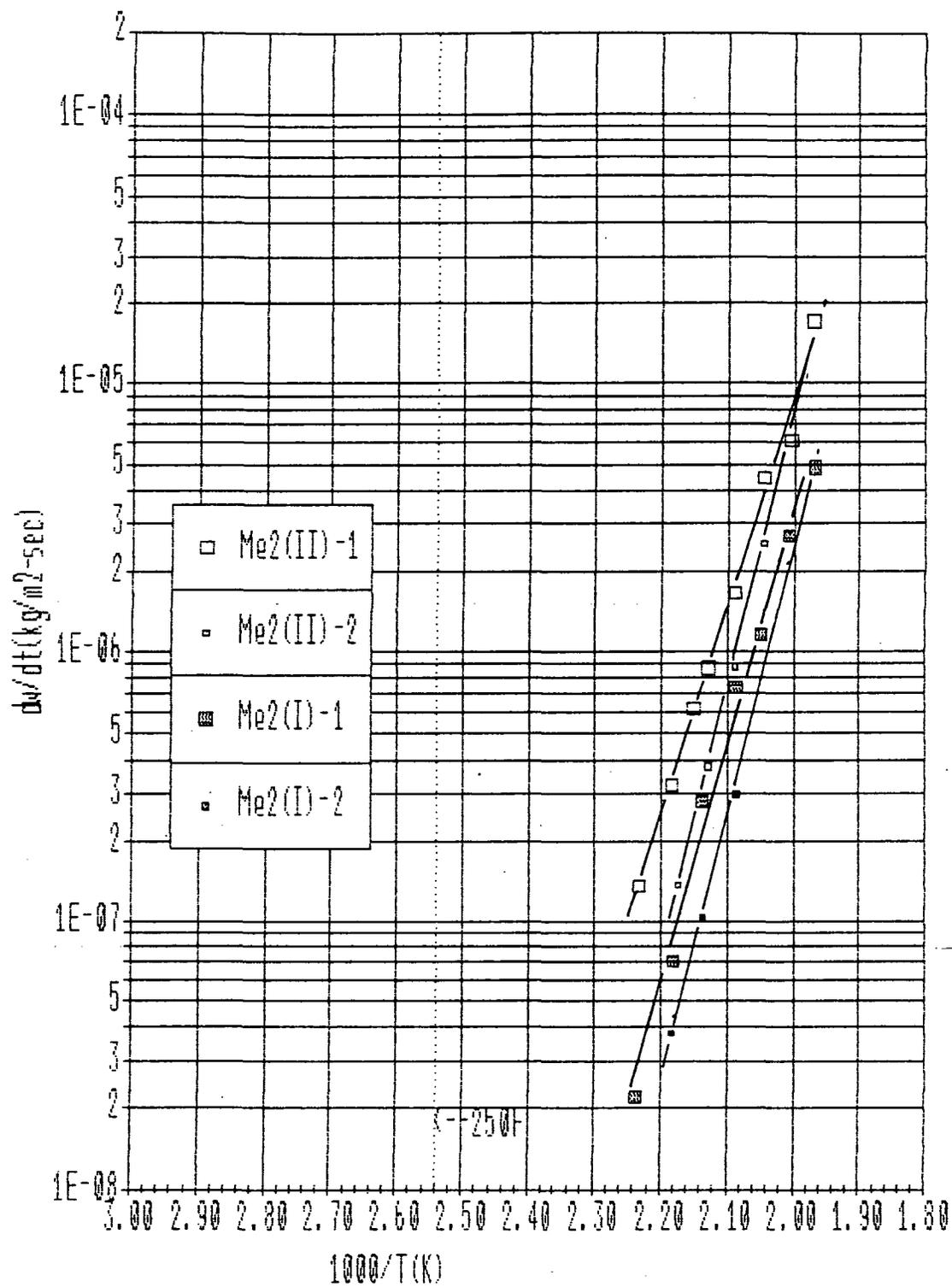


FIGURE 26. Mass Loss Rates for Me₂ (II) and Me₂ (I)

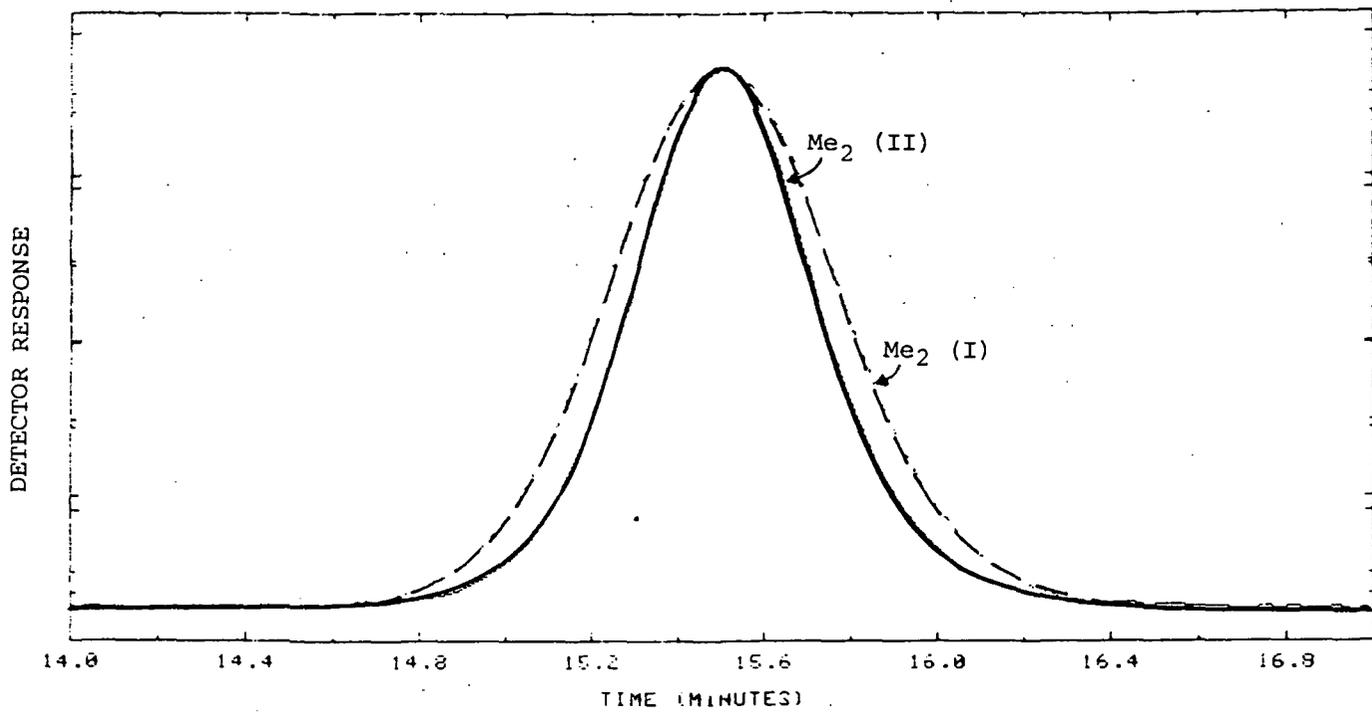


FIGURE 27. GPC Analysis - Me₂ (I) Before Mass Loss Measurements
- Me₂ (II) After Mass Loss Measurements

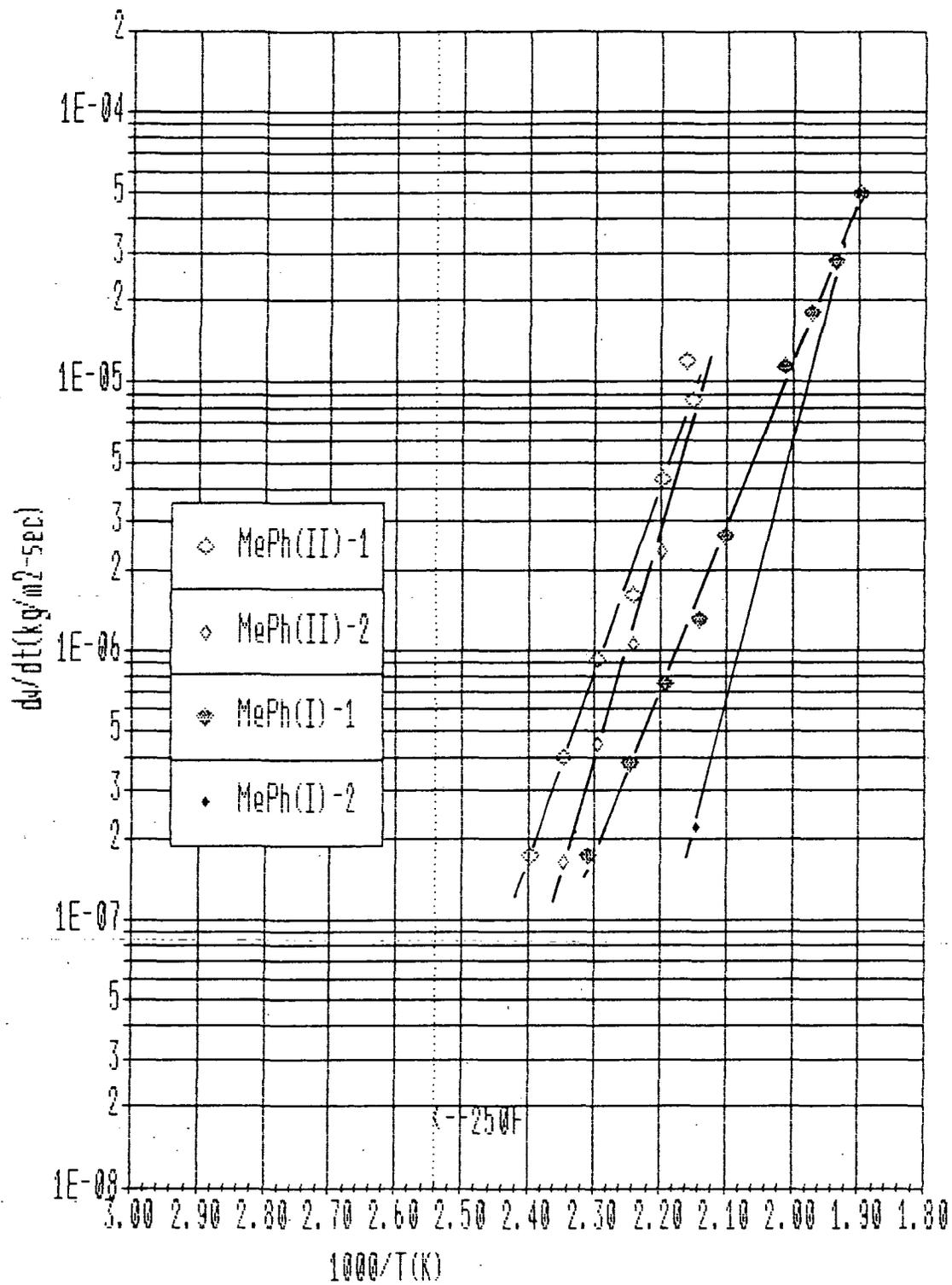


FIGURE 28. Mass Loss Rates for MePh (II) and MePh (I)

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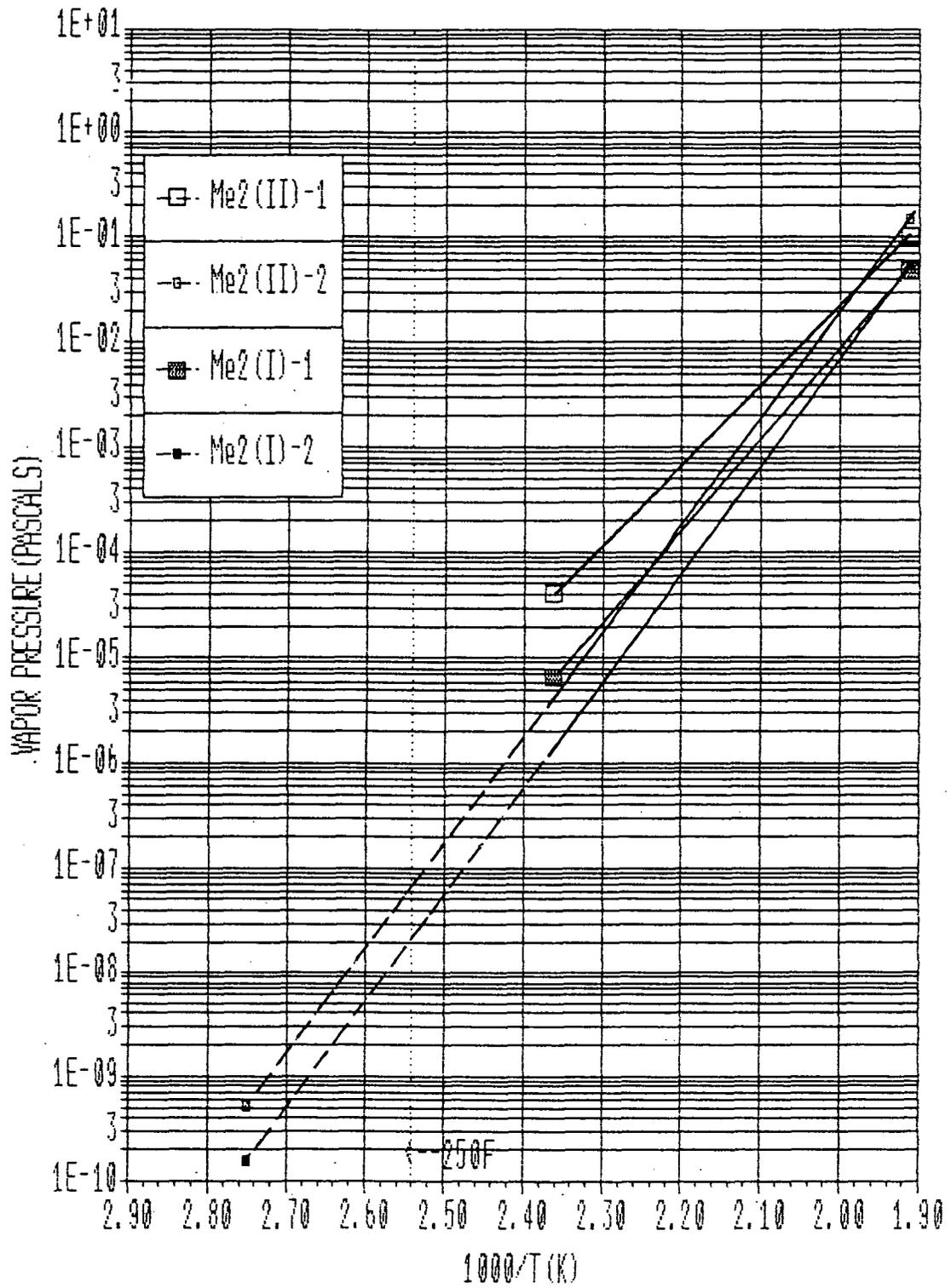


FIGURE 29. Vapor Pressure of Me₂ (II) and Me₂ (I)

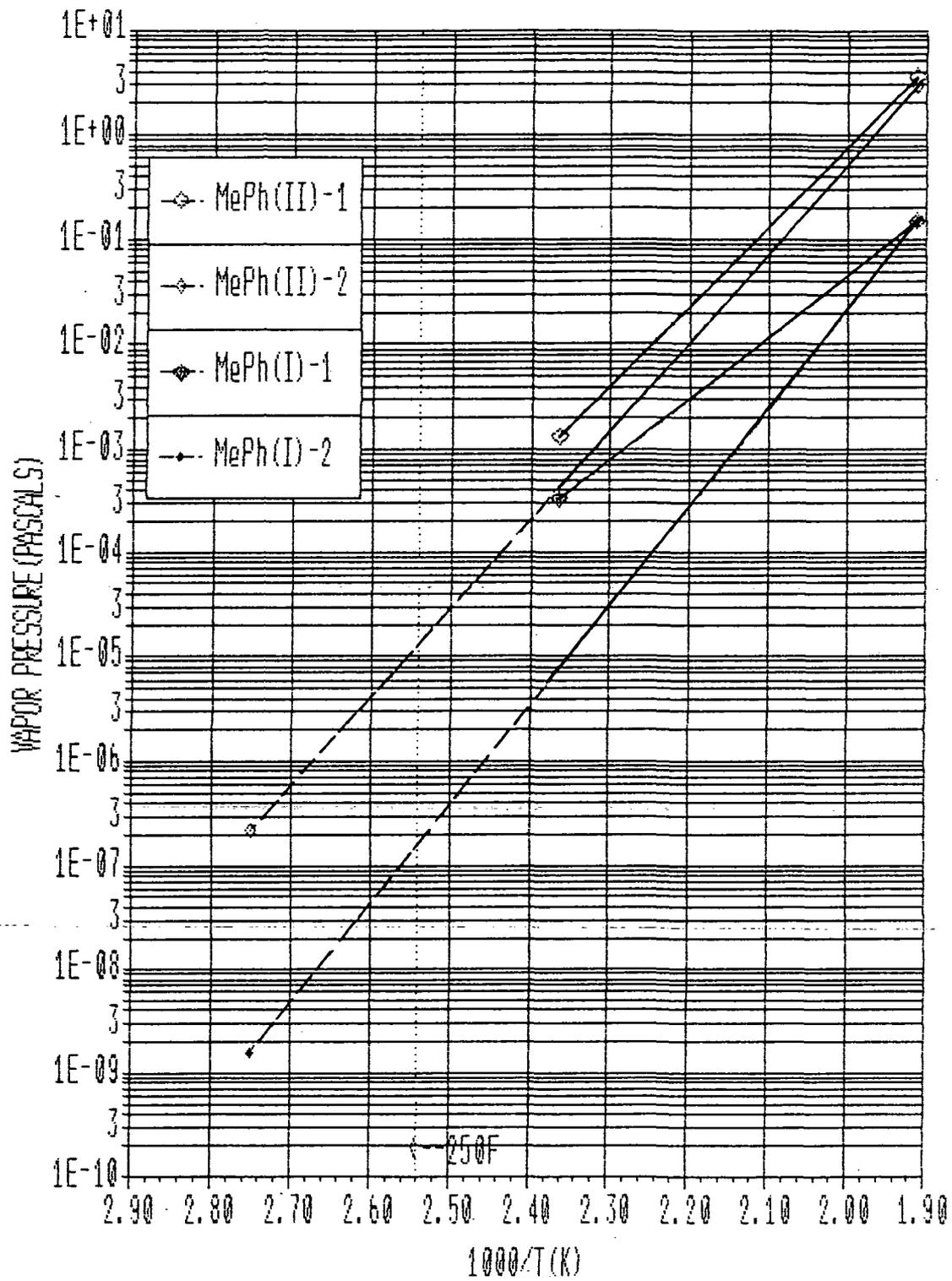
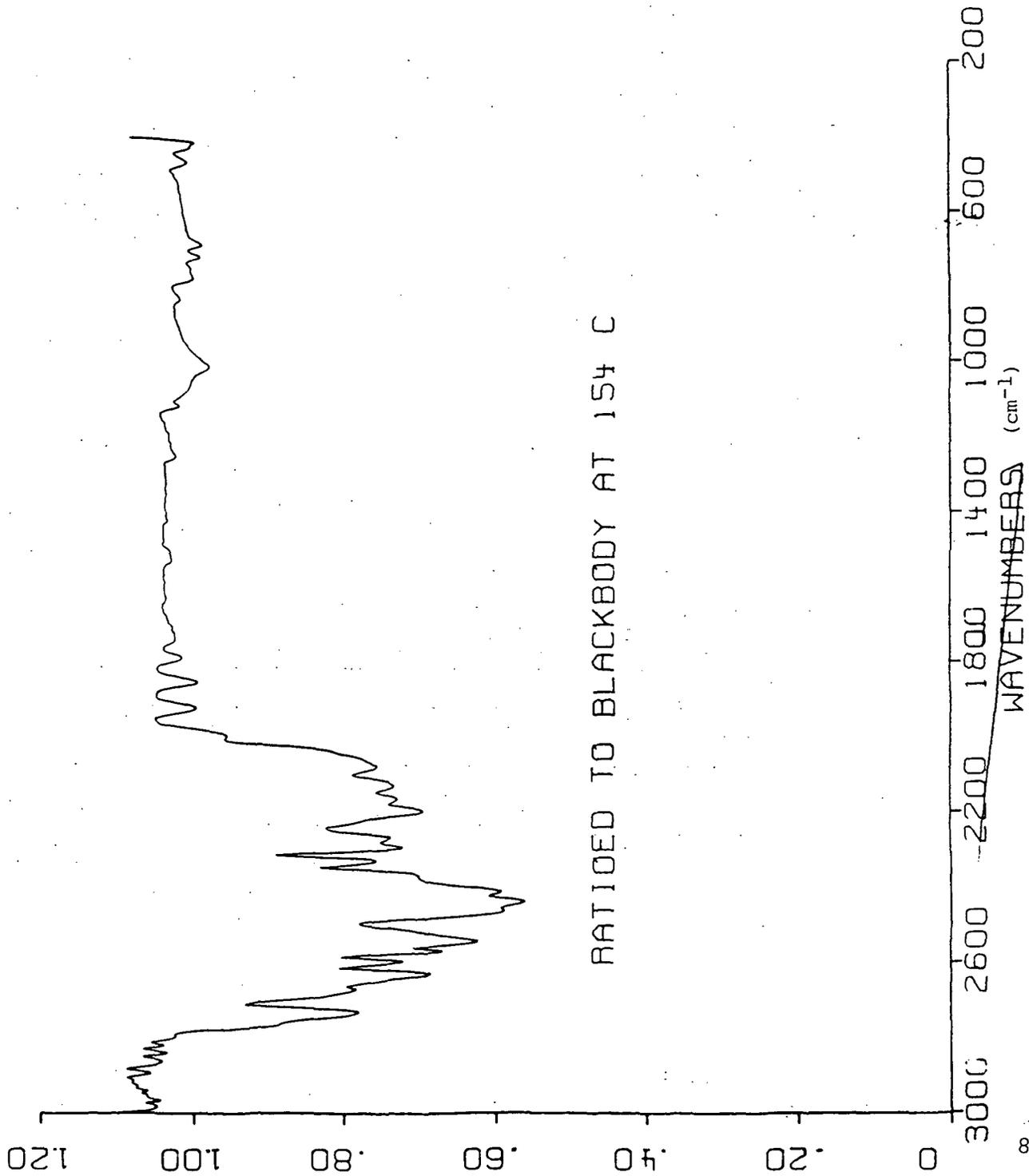


FIGURE 30. Vapor Pressure of MePh (II) and MePh (I)



RATIOED TO BLACKBODY AT 154 C

FIGURE 31. Emission Spectrum of a 0.5mm Layer of MePh (II) Fluid

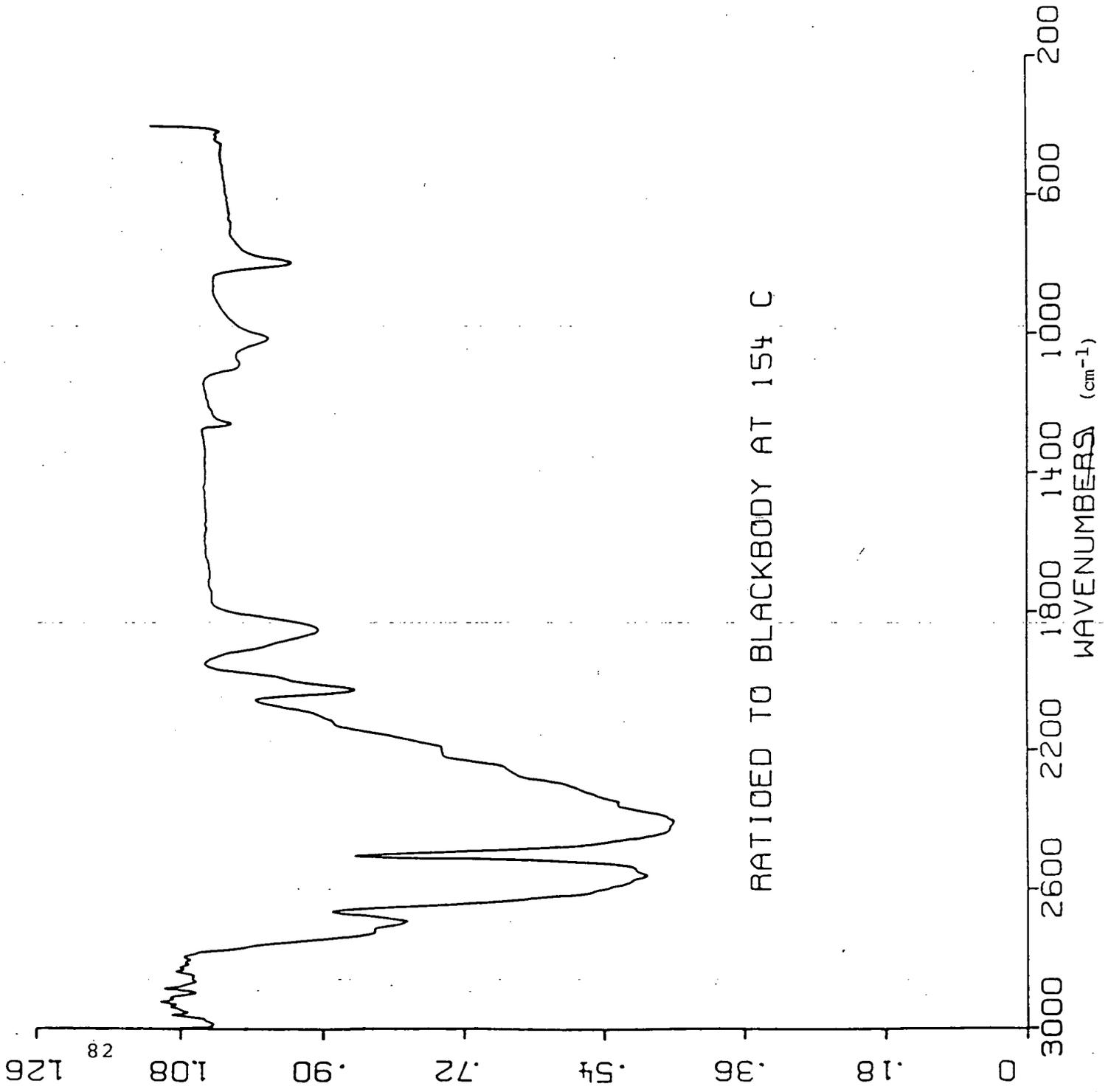


FIGURE 32. Emission Spectrum of a 0.5mm Layer of Me₂ (II) Fluid

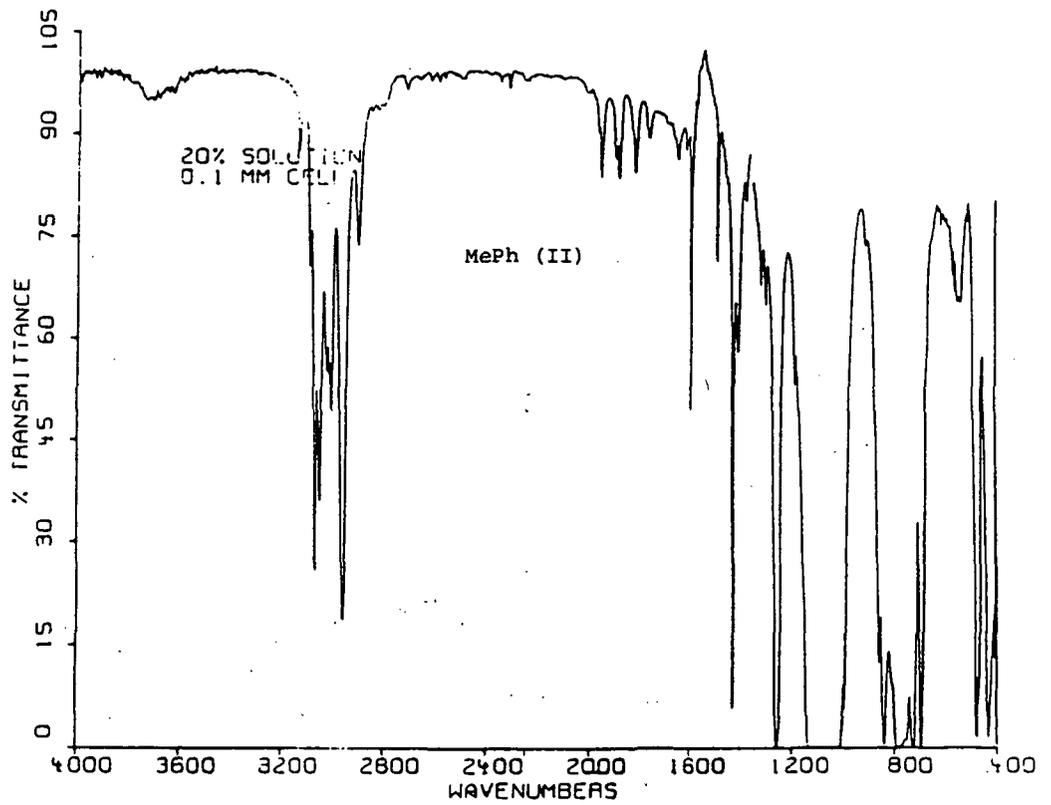
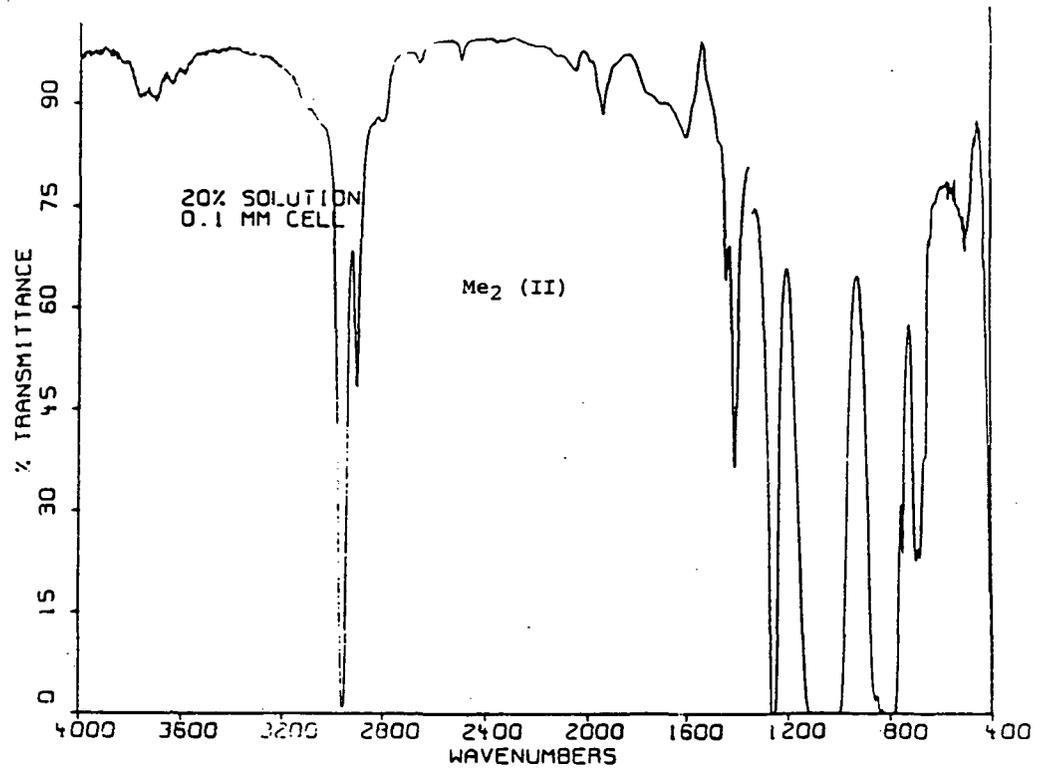


FIGURE 33a. Transmission Spectra of Task II Fluids in a 20% Solution in a 0.1mm Cell

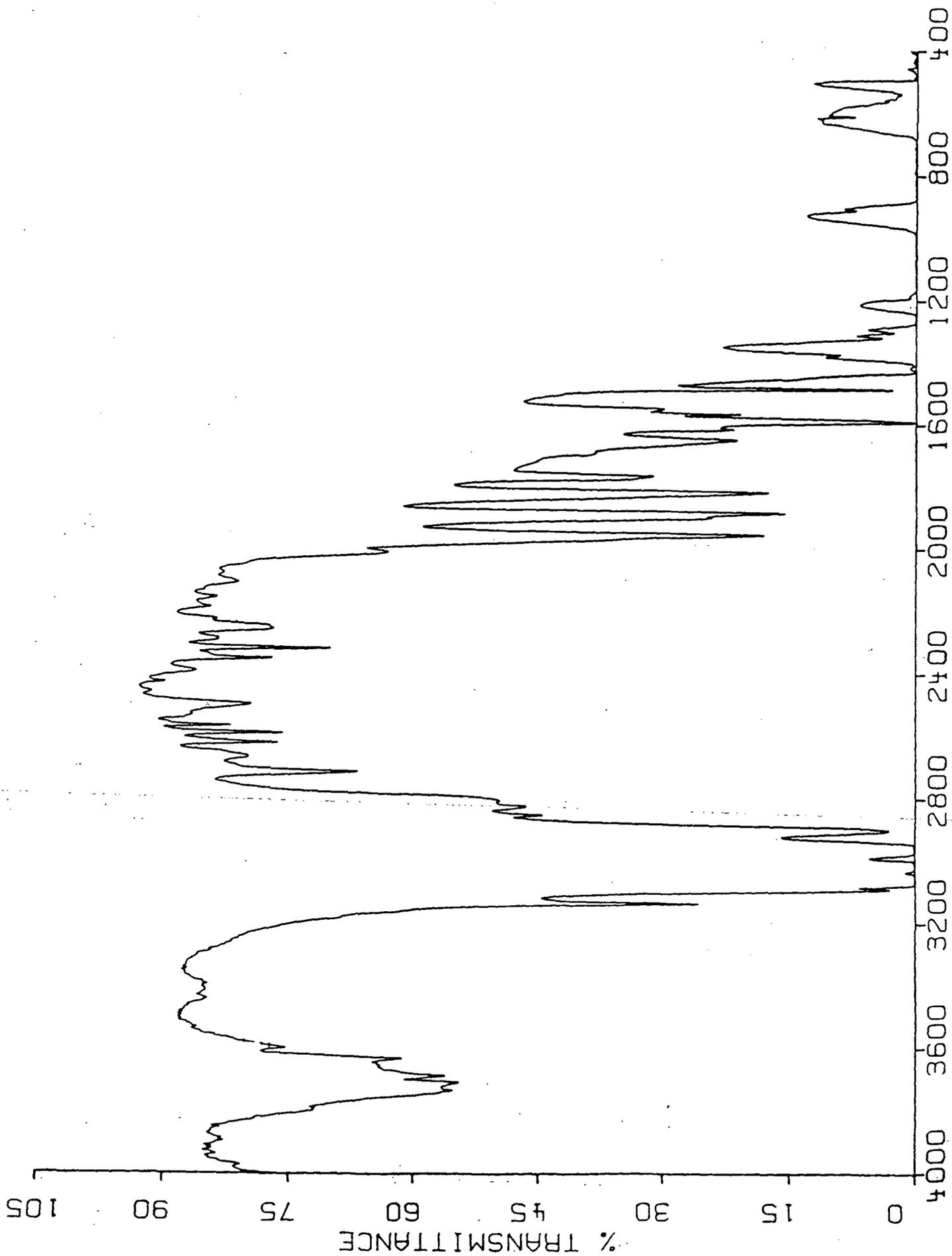


FIGURE 33b. Transmission Spectrum of a 0.2 mm Layer of MePh - (II)

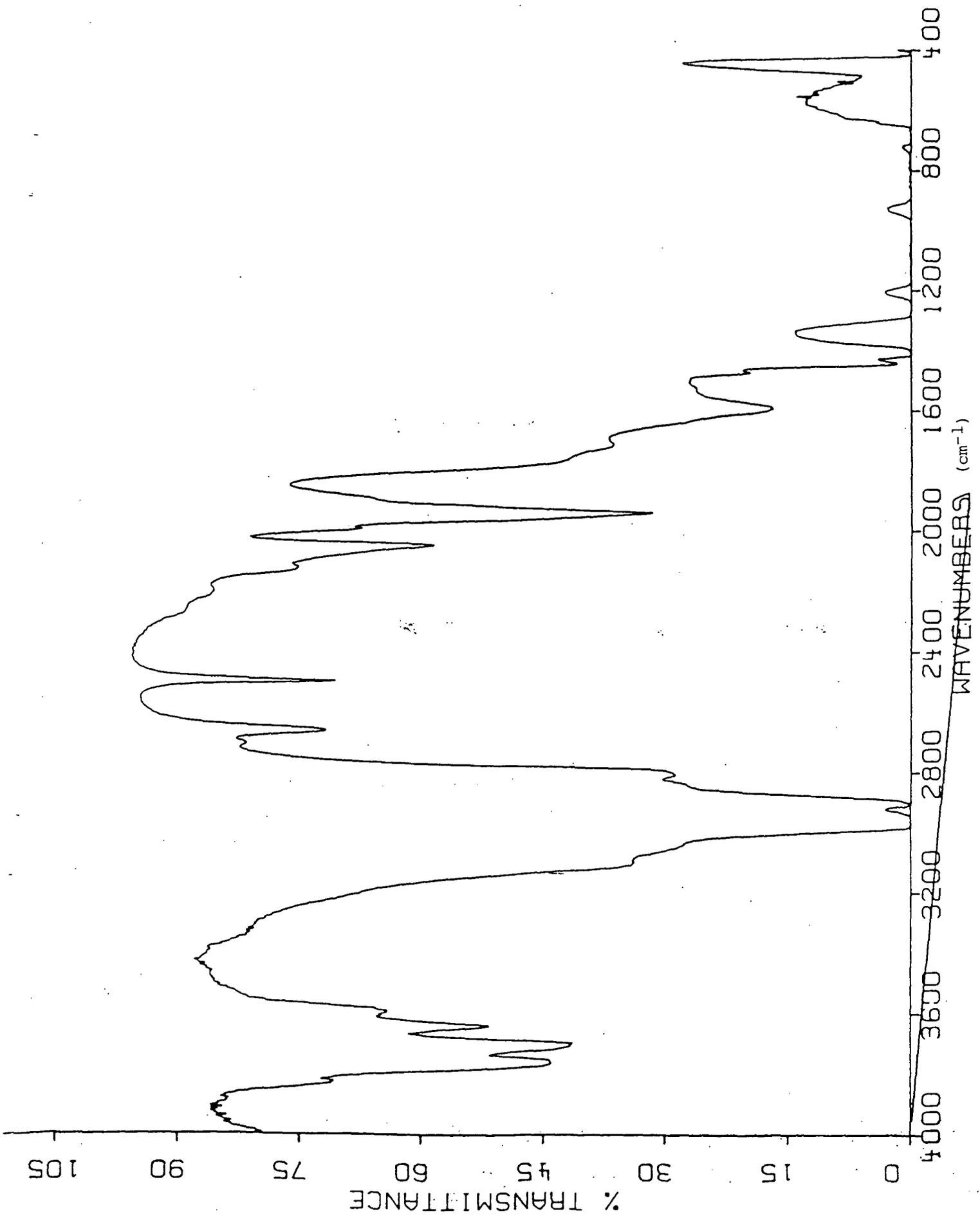


FIGURE 33c. Transmission Spectrum of a 0.2mm Layer of Me₂ - (II)

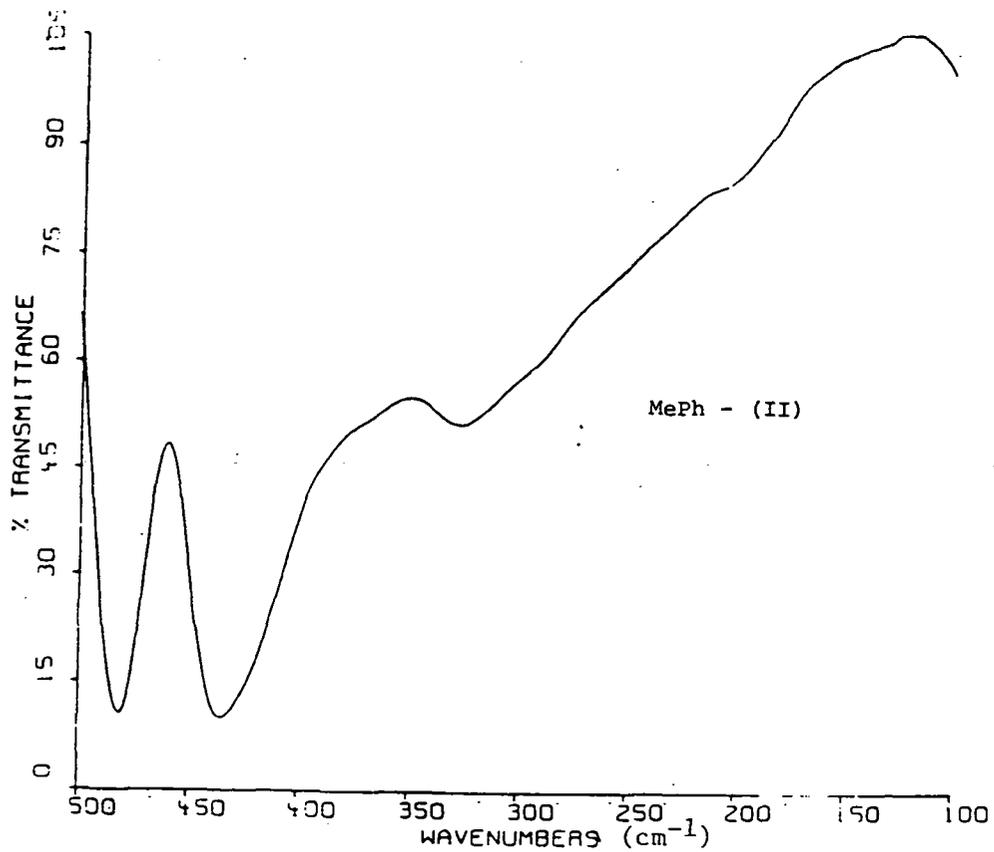
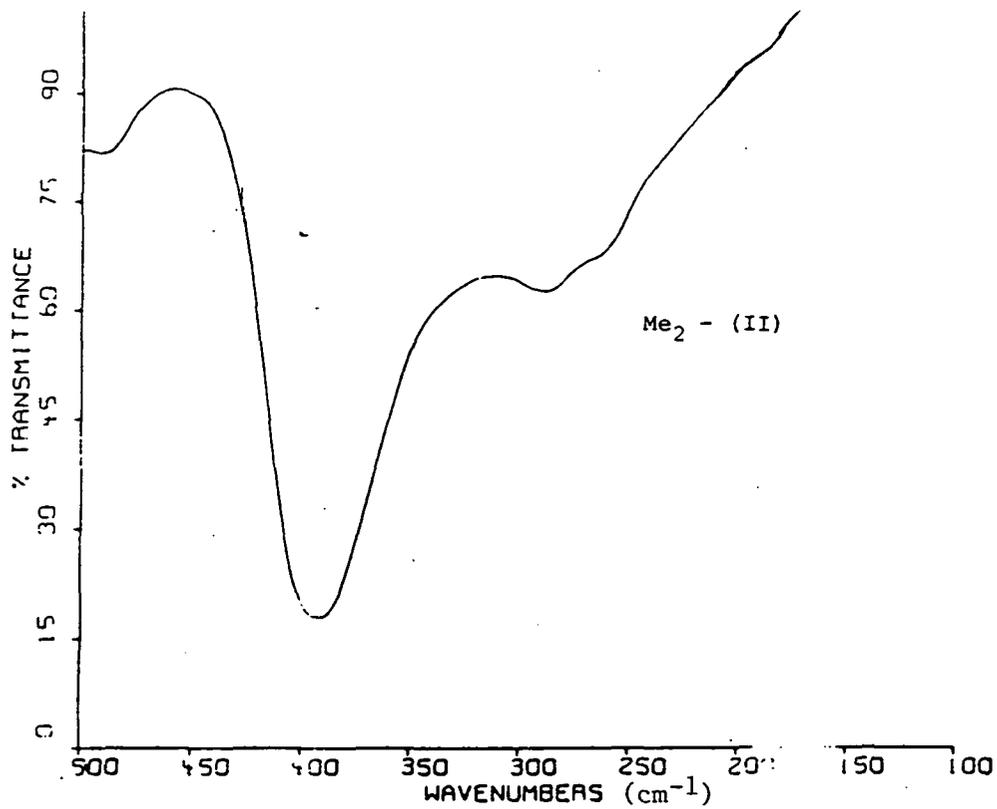


FIGURE 33d. Transmission Spectra of 0.01mm Films of Fluids in the far IR Region.

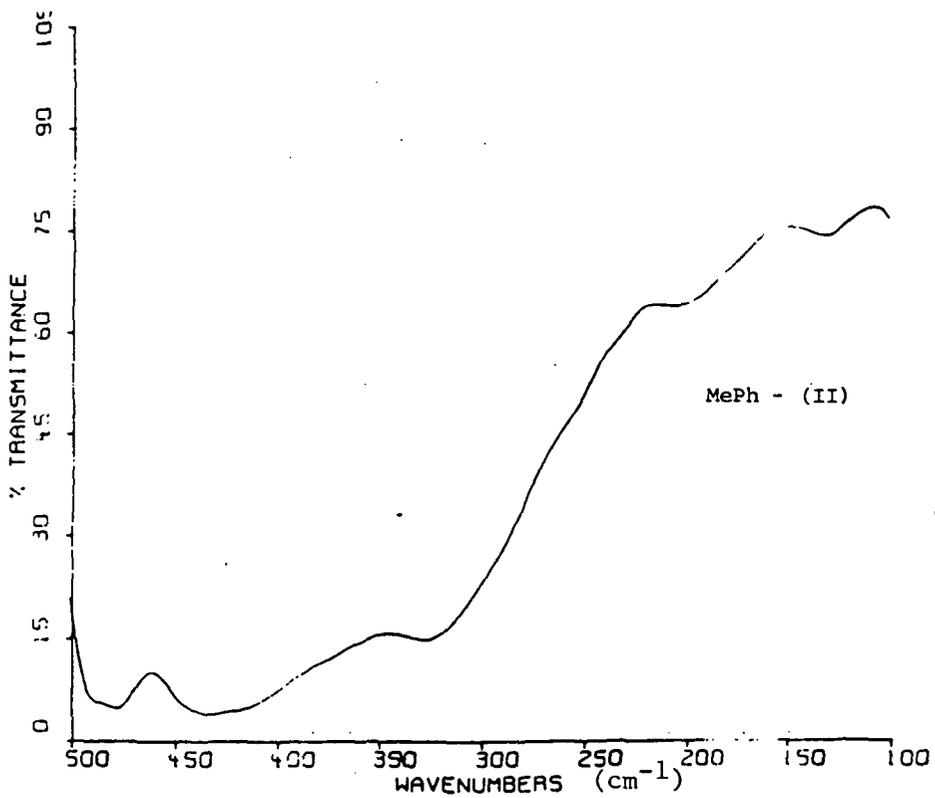
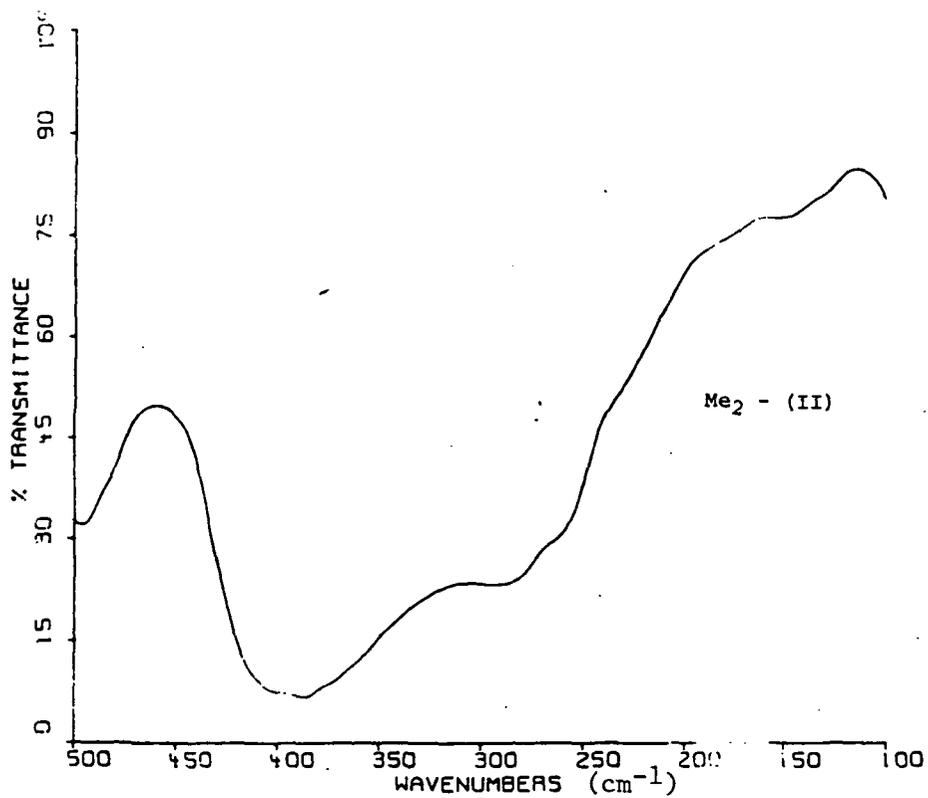


Figure 33e. Transmission Spectra of 0.1mm Films of Fluids in the far IR Region.

APPENDIX I

TARGET VAPOR PRESSURE FOR LDR FLUID

APPENDIX I

TARGET VAPOR PRESSURE FOR LDR FLUID

An estimate is made of the vapor pressure of an LDR fluid that results in mass loss by evaporation from droplets of 10% per year.

Assumed:

Drop diameter, $d = 0.01$ cm

Fraction of fluid charge exposed as droplets at all times = 10%

Temperature of droplets = 394K (250°F)

Molecular weight, $M = 1000$

Evaporation follows Knudsen (no correction here for surface tension or curvature of small drop):

$$\text{Then } \dot{m} = \frac{A P_v}{17.14} \left(\frac{M}{T} \right)^{1/2} \quad (\text{I} - 1)$$

Where: \dot{m} = mass loss rate, gm/sec

A = area of evaporating surface = πd^2

P_v = vapor pressure, torr

M = molecular weight

$$\text{Fractional loss rates, } F = \frac{\dot{m}}{m} \quad (\text{I} - 2)$$

$$m = V\rho \quad (\text{I} - 3)$$

Where: V = volume of drop, $\pi d^3/6$

ρ = density of fluid ~ 1 gm/cm³

Combining equations 1, 2, and 3, fractional loss per year (for 10% of charge exposed) is:

$$F = 1.76 \times 10^{-8} P_v$$

For 10% loss per year ($F = 0.1$)

$$P_v = 5.6 \times 10^{-10} \text{ torr}$$

$$\text{or } 7.5 \times 10^{-8} \text{ Pascal.}$$

APPENDIX II

DOW CORNING CTM'S AND EQUIPMENT LITERATURE

APPENDIX II

This appendix includes the Dow Corning Test Methods (CTM's) and equipment literature relevant to the physical property measurements reported herein.

Liquid Chromatograph (GPC)
Liquid Chromatograph (Reverse-Phase)
Kinematic Viscosity [CTM-0004]
951 Thermogravimetric Analyzer
Mettler Paar Digital Density Meter
Specific Heat - 910 Differential Scanning Calorimeter
FT-IR Spectrophotometer
Pour Point [CTM-0133]
Flash Point [CTM-0021A]
Fire Point [CTM-0052]
Volume Resistivity [CTM-0272]

Liquid Chromatograph - GPC

Pump: Perkin-Elmer Series 4
Column Set: TSK Gel Type H: 1 x 64000H, 1 x 62500H,
1 x 62000H
Injection Volume: 50 microliters
Detector: ERMA Differential Refractometer
Mobile Phase: Tetrahydrofuran (uninhibited)

Liquid Chromatograph - Reverse Phase

Pump: Perkin-Elmer Series 4
Column: Shandon C-18 4.6 x 100 mm 3 μ m particles
Injection Volume: 10 μ l, 0.7% solution
Detector: Waters Model 490 U-V, 260 nm

Gradient Conditions:

Sector	Time	Flow Rate ml/min.	% H ₂ O	% THF*	% ACN**	Gradient Shape
equil	12	1	30	40	30	
1	10	1	0	40	60	linear
2	10	1	0	40	60	
3	6	2	0	40	60	step
4	3	2	30	40	30	
5	5	1	30	40	30	

*Tetrahydrofuran, uninhibited

**Acetonitrile, HPLC grade

corporate test method

VISCOSITY - Glass Capillary Viscometer

July 29, 1970

CTM 0004

Abstract

The kinematic viscosity of liquids is determined by measuring the time required for a fixed volume of samples to pass through a calibrated glass capillary using "gravity-flow". The method is based on ASTM D-445, IP 71 and the results are reported in Stokes. A calculation for determining the absolute viscosity (dynamic viscosity) in Poise is given (Note 1).

Apparatus

Bath: Constant temperature to hold $25 \pm 0.2^{\circ}\text{C}$. Any suitable source.

Viscometer: A set of one of the following types (Note 2) to cover the desired range of viscosities.

1. Cannon Fenski: Fisher Scientific Co., Pittsburgh, PA, Cat. No. 13-616.
2. Ostwald: Fisher Scientific Co., Cat. No. 13-695.
3. Ubbelohde: Fisher Scientific Co., Cat. No. 13-614.

Reagents

Primary standard fluids: Various viscosities, Cannon Instrument Co., State College, PA.

Secondary standard fluids: Appropriate viscosity silicone oil standardized using calibrated master viscometers (ASTM D-2162).

Precautions

Safety: Normal safe laboratory practices.

Procedural: No unusual precautions.

Page 1 of 4

The method described has been adapted from either our investigations or literature procedures or both. The Dow Corning Corporation does not assume any liability in connection with the use of this method. Applicability to samples of interest must be ascertained by the user. This method should not be reproduced or published in whole or part without written permission of the Dow Corning Corporation.

Parameters

Viscosities may be determined at temperatures other than 25°C. Results will be in Stokes or centiStokes unless otherwise requested.

Procedure

Select a clean, dry calibrated viscometer that will yield a flow time of greater than 80 sec with the sample. Load the viscometer in the correct manner as dictated by the design (Note 3). Place the tube in the constant temperature bath and allow it to reach equilibrium (at least 15 min. at 25°C). Use suction or pressure (Note 4) to adjust the head level of the sample to a point about 5 mm above the first timing mark. Allow the sample to flow freely. Start a timer as the meniscus passes the first timing mark. Stop the timer as the meniscus passes the second timing mark. Record the time to the nearest 0.1 sec. Repeat the test without refilling the tube. If the two results do not agree to within 0.2 sec, repeat the procedure with a new sample. Use the average in calculating the viscosity. Report viscosity and temperature.

Standardization

→ Viscometers should be calibrated and given an identification mark upon receipt and then calibrated at least once every year or whenever cleaned with strong acid or base or after being repaired. Either primary or secondary standards may be used.

Follow the procedure and determine the flow time. Calculate the viscometer factor:

$$F = \frac{\text{Viscosity of Standard}}{\text{flow time, sec}} = \frac{\text{Stokes*}}{\text{sec}}$$

* CentiStokes may be used if preferred where:

$$1 \text{ St} = 100 \text{ cSt}$$

Viscometers should be thoroughly cleaned with appropriate cleaning mixtures. Viscometers used with silicone fluids should be retained exclusively for that purpose. They may require cleaning with hydrofluoric acid.

Calculations

Kinematic viscosity:

$$\text{Viscosity, St*} = F \times \text{flow time, sec}$$

* CentiStokes if preferred.

Absolute viscosity:

$$\text{Viscosity } P^* = (\text{kinematic viscosity, St}) (\text{density g/cm}^3)$$

* CentiPoise if preferred.

Precision and Accuracy

The relative error should be less than $\pm 1\%$ (Note 5).

Notes

1. In cgs units, viscosity is expressed in the following dimensions:

a. Stokes - cm^2/sec

b. Poise - g/cm/sec

2. The Ubbelohde viscometers are the preferred unit. They cover the range of 0.4 to 100,000 cSt. They are easy to fill and are free falling column viscometers.

The Cannon Fenski viscometers have one advantage. They require a smaller sample size. However, they require an exact fill. They cover the range of 0.4 to 16,000 cSt. Any of these viscometers may be used interchangeably, if properly standardized.

The Oswald viscometers are not preferred due to the extreme self-leveling effect of the fluid flow and consistent fill requirement. They cover the range of 0.4 to 16,000 cSt.

3. The Ubbelohde viscometers are filled by pouring the sample down the largest tube until the bulb is about $3/4$ full (the vent tube must be open). The amount is not critical. The other two must be filled by drawing the sample in to fill mark or by adding a specific volume.

4. Care must be taken in handling volatile samples.

5. A "quick and dirty" viscosity measurement with a precision of $\pm 5\%$ or better can be obtained using a calibrated volumetric pipet on as little as 1 ml of sample and following this basic procedure.

References

1. ASTM D-445
2. ASTM D-2162
3. ASTM D-2515
4. Institute of Petroleum 71/66

Figures, Graphs and Sketches

None

Ed. Corr.

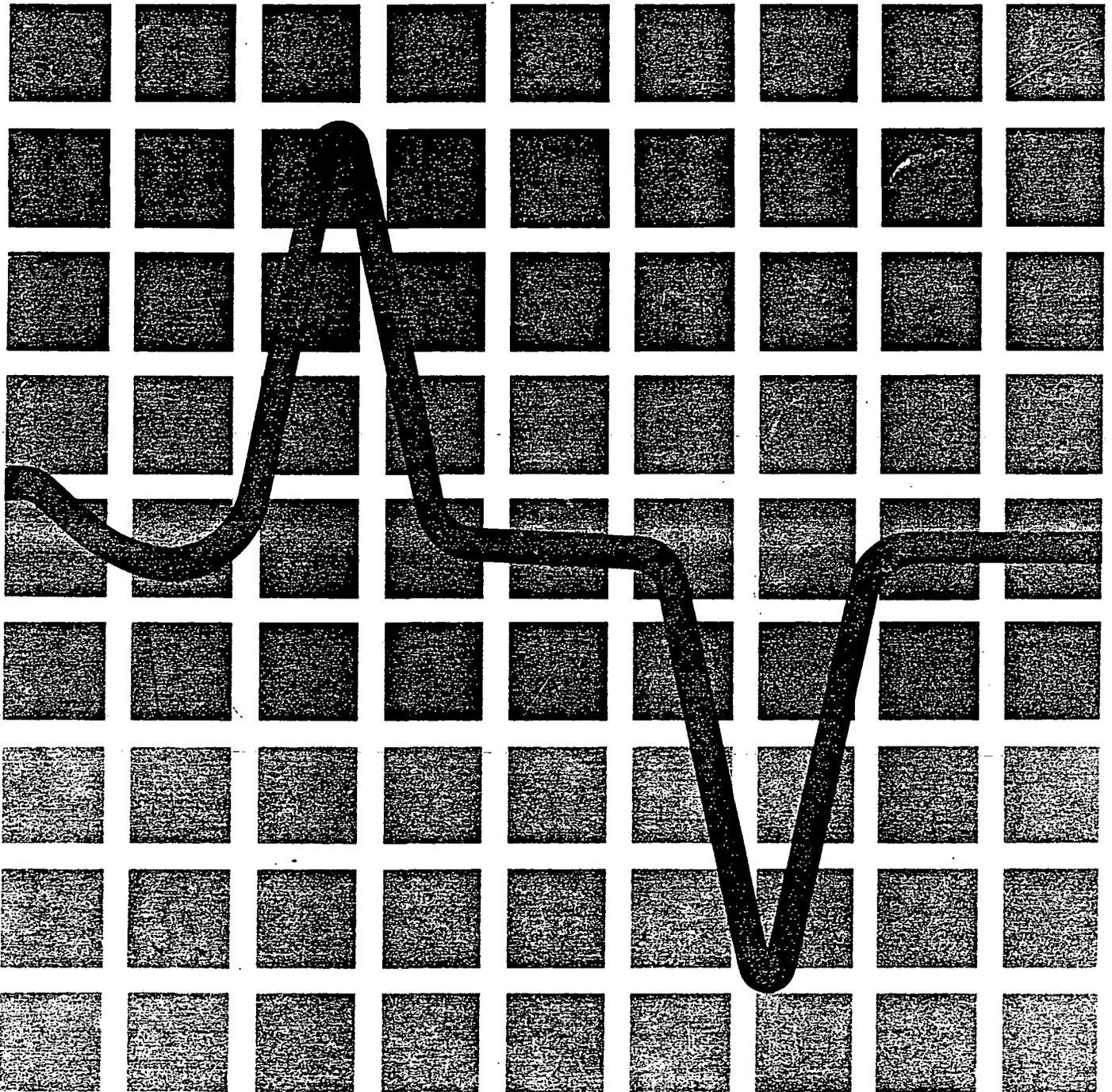
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951 TGA Thermogravimetric Analyzer

Operator's Manual



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Section 1. INTRODUCTION

1-1. PURPOSE OF MANUAL

This manual contains information necessary to understand, install, operate, maintain, and order parts for the Du Pont 951 Thermogravimetric Analyzer (figure 1-1). This section of the manual provides component description, principles of operation, and specifications.

1-2. INSTRUMENT FUNCTION

The 951 Thermogravimetric Analyzer (TGA) is a plug-in module for Du Pont Thermal Analyzers. It constantly measures the amount and rate of weight change of material, either as a

function of increasing temperature, or isothermally as a function of time, in a varied but controlled atmosphere. The TGA can be interfaced with other analytical instruments (such as a gas chromatograph or a mass spectrometer) for multiple measurements. Also, the TGA can be readily modified or isolated for special applications.

1-3. DESCRIPTION (figure 1-2)

The TGA consists of three major sections: a furnace assembly, a balance assembly, and a cabinet assembly.

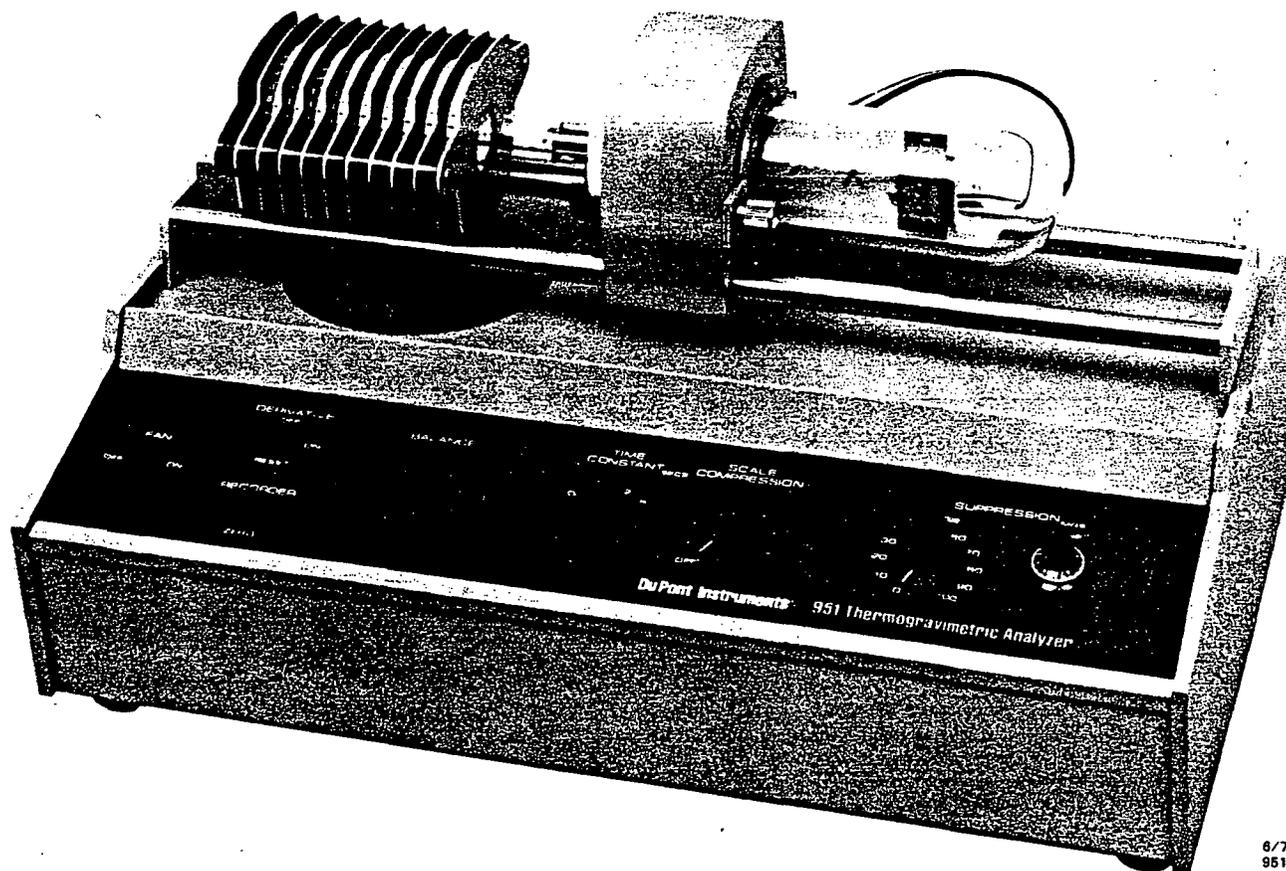
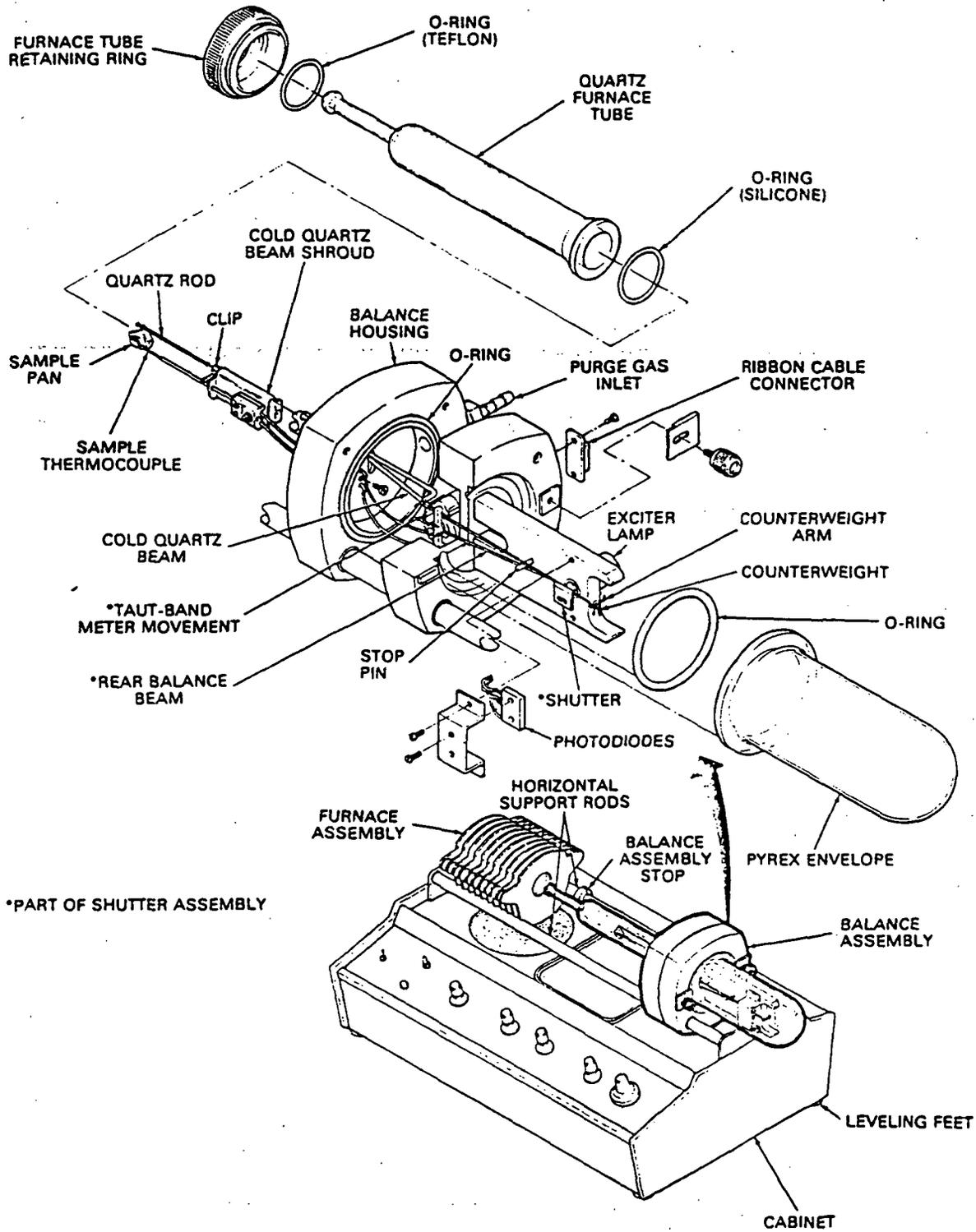
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Figure 1-1. 951 Thermogravimetric Analyzer



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951R/3

Figure 1-2. 951 TGA Location of Components

a. Furnace Assembly

The furnace assembly is a 500-W, resistance-wound plug-in unit of low thermal mass that can be heated and cooled rapidly. (Heating rates up to 100°C/min. can be obtained to an upper limit of 1000°C). A Platinel II control thermocouple, in the furnace wall, monitors furnace temperature. For rapid work involving consecutive analyses, two furnaces can be used alternately. The furnace can be rapidly cooled by a fan within the cabinet assembly.

b. Balance Assembly

The balance assembly consists of a balance housing, a control chamber, and a sample chamber. Mounted within the balance housing is a taut-band meter movement to which a balance beam is attached. The ends of this beam extend into the sample and control chambers. The control chamber contains a shutter assembly and a counterweight arm, mounted on the beam, and a beam stop pin; a lamp and photodiodes are mounted on a member extending from the balance housing. A Pyrex® envelope, held in place by two thumb-screw retainers and sealed by a silicone O-ring, encloses the control chamber. The sample chamber contains a quartz rod, which is attached to the beam, a sample pan suspended from the rod, and a sample thermocouple. A quartz furnace tube, held in place by a retaining ring and sealed by two O-rings, encloses the sample chamber. Both aluminum and platinum sample pans are available. Platinum pans are recommended for use above 500°C. Pyrex furnace tubes are available for operation below 500°C.

The balance assembly rides on horizontal support rods. This permits movement of the balance assembly for sample loading. A stop on one support rod positions the assembly so that the sample is in the center of the furnace.

Purge gas is admitted through a hose fitting on the rear of the balance housing, and exits through the opening in the furnace tube. Electrical connections to the balance assembly are made through a connector on the rear of the balance housing.

Nine weights are provided for counterbalancing the sample pan and for calibrating the instrument.

Quantity		Weight
1	—	5 mg
2	—	10 mg
2	—	20 mg
1	—	50 mg
1	—	100 mg
1	—	200 mg
1	—	50 mg (Precision)

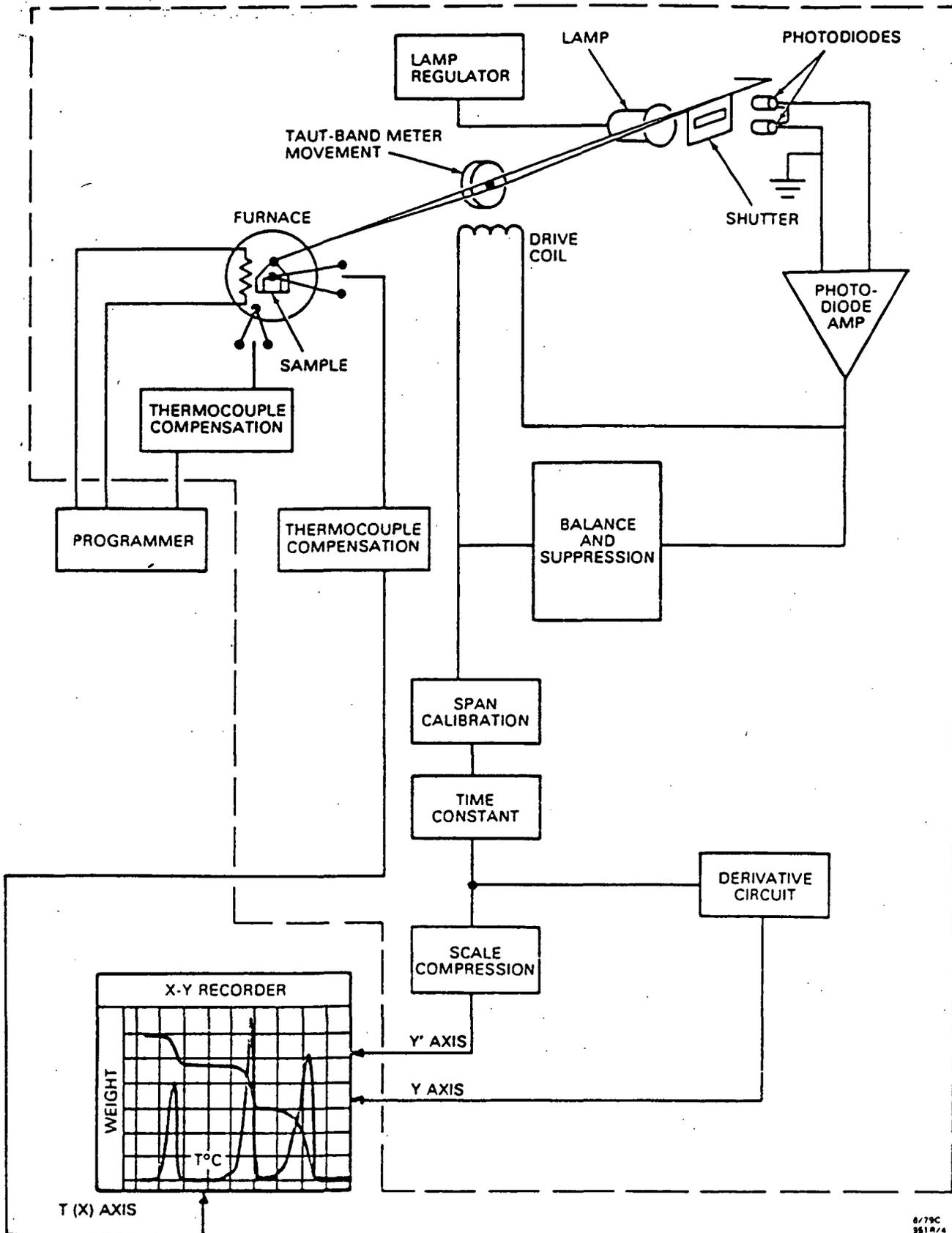
c. Cabinet Assembly

The cabinet assembly houses the balance control and associated electronic circuits and the cooling fan. Adjustment and calibration controls, an accessory connector, and a fuse are on the rear. Operator controls are on the front. Leveling feet are provided for leveling the unit in its operating position.

1-4. PRINCIPLES OF OPERATION

(figure 1-3)

The 951 TGA operates on a null-balance principle. Physically attached to a taut-band meter movement, the balance beam is maintained in a horizontal reference position by an optically actuated servo loop. Attached to the control end of the balance beam is a light shutter; a constant intensity lamp is focused through an aperture slit in the shutter to strike two vertically mounted photodiodes. When the balance beam is in a null position, the focused light strikes both photodiodes equally. As sample weight is lost or gained, however, the beam becomes unbalanced and moves from the null position, causing more light to strike one photodiode than the other. The voltage output from the photodiode receiving the most light increases and unbalances the photodiode amplifier, producing a current flow in the taut-band meter which acts as a restoring force on the balance beam, driving it back to its null position. The magnitude of the restoring current flow is directly proportional to the sample weight lost



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Figure 1-3. 951 TGA Block Diagram

(or gained). After being conditioned, the restoring current is displayed on the vertical axes of an X-Y recorder as either absolute sample weight loss/gain or weight percent loss/gain; the format is pre-selectable by the operator.

Balance and suppression controls are provided for adjusting the meter movement drive current. Small differences in weight (less than 5 mg) during initial nulling of an empty balance are compensated with the balance circuit. Fixed current offsets equivalent to weight (mass) are accomplished with the suppression circuit. A coarse control provides 10 steps of 10 mg each for a total of 100 mg. A fine control, consisting of a 10-turn potentiometer, provides 1 mg for each turn. Thus the combination of both coarse and fine controls allows for a total electronic weight suppression of 110 mg. For suppression above 110 mg, mechanical tare procedures are used by placing weights on the counter-weight arm in the control chamber.

A time constant circuit filters (smooths) the output signal to compensate for minor ambient vibration. It can be adjusted in four steps ranging from zero (no filtering) to 5 seconds (maximum filtering).

A scale compression (attenuation) circuit provides for the adjustment of the Y'-axis output signal to the recorder. In the off position of the control, there is no compression of the signal and the full output signal is applied to the Y' axis. When the control is rotated clockwise, a potentiometer is placed in the circuit which compresses the output signal. Full scale readings on the recorder may then be calibrated in weight percent.

A span calibration circuit provides a sensitivity adjustment which is used when calibrating the balance beam.

The sample temperature is obtained from the sample thermocouple located close to the

sample. The thermocouple output is electronically compensated and then displayed on the recorder.

During heating, the sample may undergo changes which liberate gases. To prevent these gases from back-diffusing and condensing on the meter movement, purge gas is admitted into the balance housing. The purge gas flows over the meter movement, fills the control chamber, and purges the sample chamber by exiting through the end of the furnace tube.

The heating rate and temperature of the furnace are set by the programmer. The control thermocouple in the furnace provides the necessary temperature information to the programmer for temperature control.

1-5. SPECIFICATIONS

- Capacity 500 mg including sample pan
- Weight Ranges 0.020 to 20 mg/cm (0.050 to 50 mg/in.)
- Temperature Range: Ambient to 1200°C
- Suppression 110 mg electronic tare, stepped and continuously variable; mechanical tare to 500 mg
- Suppression Accuracy ±0.4% of suppression
- Precision of Weight Measurement 0.4% of full scale
- Accuracy of Weight Measurement ± 1.0% of full scale
- Derivative Range 0.020 to 20 (mg/min)/cm [0.05-50 (mg/min)/in.]
- Time Constant 0 (direct), 1, 2, 5 seconds
- Pressure Atmospheric to 100Pa (1 torr)
- Purge Rate Up to 1 l/min
- Control Thermocouple Platinel II
- Sample Thermocouple Chromel-Alumel

Mettler Digital Density Meters from Mettler/Par

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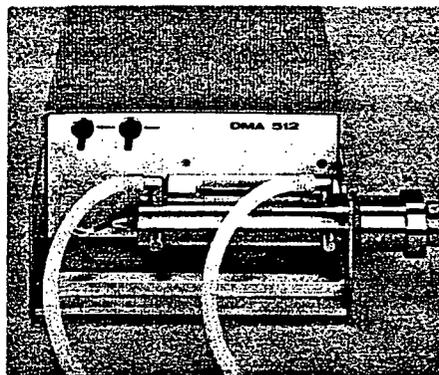
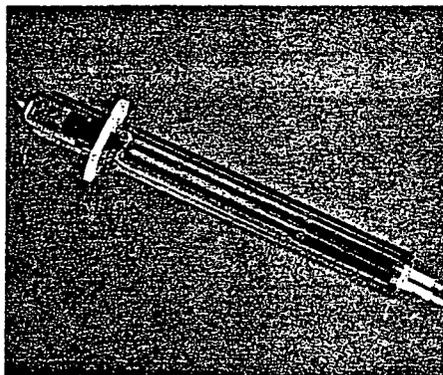
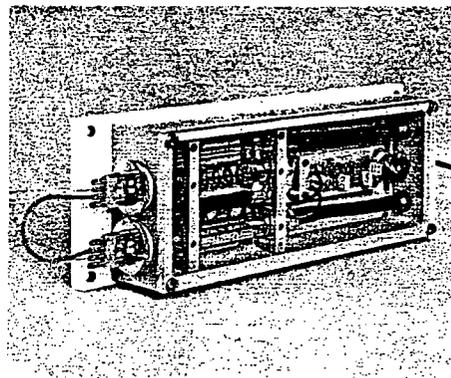
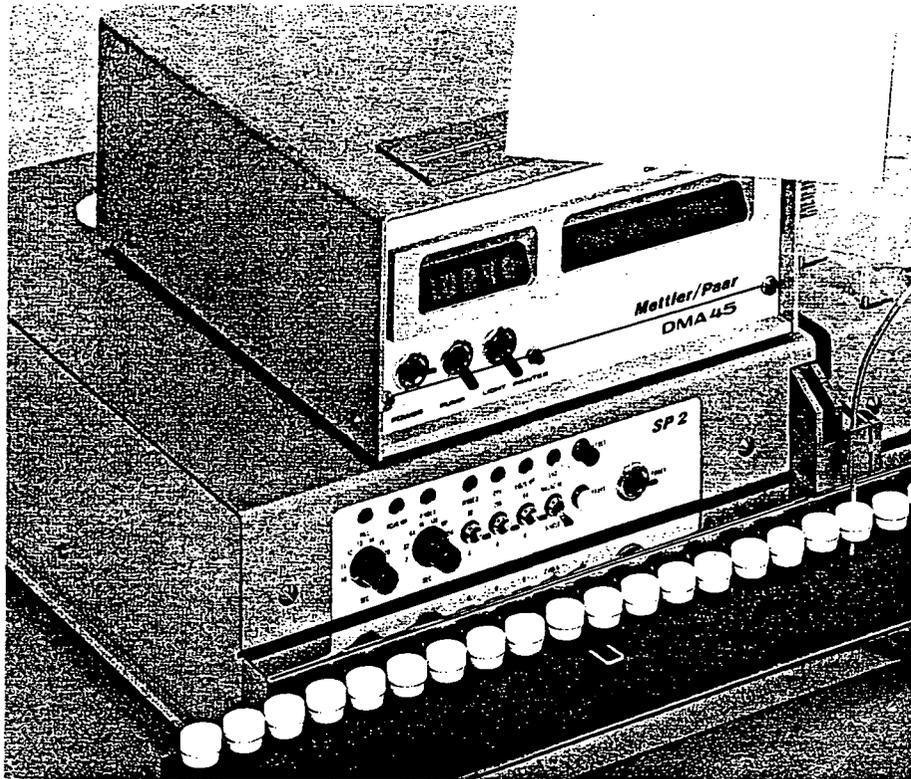
**Measuring specific gravity, density,
concentration and other density-related values**



METTLER

Mettler/Par Digital Density Mete

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Mettler/Par Digital Density Meters provide a fast, accurate means of measuring densities or specific gravities of liquids and gases, as well as concentration of solutions. Highly accurate results are obtained in seconds without the need for skilled technicians. And without time-consuming procedures such as pycnometer filling, waiting for temperature equilibrium, weighing. There's no need to determine weight, volume or temperature of samples — thereby eliminating inherent sources of error.

Wide range of applications

Fields of application range from both pure and clinical research to quality assurance and process control. Mettler/Par Digital Density Meters are ideally suited for identification, characterization

and purity of measurements. They are also used for concentration measurements (Brix, Plato, Balling, API, etc.), for determining densities of physiological fluids (protein content of serum, density of blood on continuous flow or single sample base), for the study of enzymes, proteins, polymerizations and macromolecules. These instruments are in wide use throughout the pharmaceutical, cosmetic, petrochemical, food, beverage and general chemical industries. There are also numerous research applications in universities and hospitals. Other uses are found in government (ERDA) and police laboratories.

A unique measuring method

The heart of each Density Meter is a U-shaped, oscillating sample tube. In

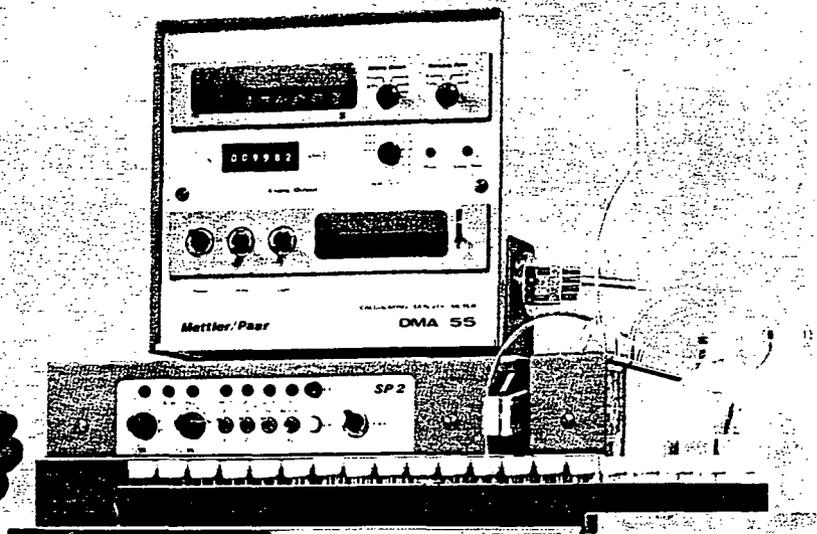
operation, this tube is completely filled with 0.7 ml of sample substance by injection with a hypodermic syringe, with a pump, with vacuum suction or by continuous flow. The sample tube is electromagnetically excited. Density, specific gravity, or concentration of the sample is determined precisely by the measurement of the period of oscillation of the sample tube. Accuracy is not affected by the liquid's viscosity, volatility and surface tension. As long as the sample is liquid or pasty enough to be injected and withdrawn, it can be measured.

This measuring method is most accurate and its versatility allows the study of many samples which cannot be measured precisely any other way.

Direct digital data

Most of the Mettler/Par density instruments are equipped with a built-in microcomputer, for direct display, in large digital numerals, of density, specific gravity, concentration or other density-related values such as Brix, Plato, Balling, API, etc. Some instruments have a built-in electronic Peltier-effect thermostat (no cooling water required). Some read a digital period value for external calculation of the density. Digital data then can be transmitted to a printer or computer for data storage or evaluation. Analog output signals, available in some instruments, can be used for continuous

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monitoring of density or concentration changes on flowing samples.

Special capabilities

The usefulness of Mettler/Par Digital Density Meters can be greatly extended through a wide range of accessories. For example, there are a variety of remote measuring cells for use at higher and lower sample temperatures, at high pressures, with 0.1 ml sample volume (instead of 0.7 ml) or for continuous flow measurements in hazardous areas and other conditions. An automatic sample changer can be used with the instrument for completely automatic measurement of up to 20 samples.

Choose the precision you need

DMA35 has a precision of 10^{-3} g/cm³, and is a battery-powered hand-held model for field, production line or lab work. DMA45 and DMA46 read density, specific gravity or concentration direct with a precision² of 10^{-4} g/cm³ and are ideal for routine use in quality control or in checking formulation accuracy. The DMA46 comes with a built-in Peltier-effect thermostat (no water thermostat required). A variation, the DMA40, comes without microcomputer and reads period values only to be converted to densities by an outside calculator.

The DMA55, equipped with a microcomputer, has five-place precision² and is recommended for use where higher ac-

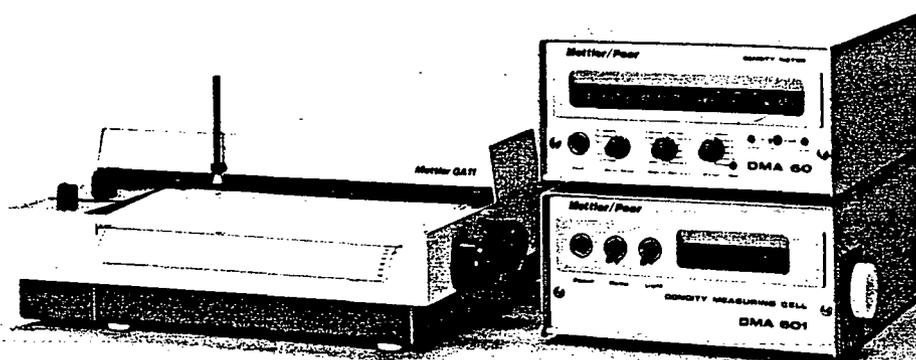
curacy and/or continuous flow measurement are required. The measuring time is selectable between 0.7 and 5.0 seconds. The microcomputer in the DMA55 can be supplied with customized programs. An analog output is also offered. The zero point of the analog output range can be set with a 10^{-5} g/cm³ precision within the whole density range and the span can be selected from 0.001 to 0.5 g/cm³. The resolution of the analog signal is 0.1 per cent. Printers and recorders are optional accessories.

DMA60 offers six-place precision², reads period values, has analog output for the two or three least significant digits of the period value. This unit will work with one or two DMA602 measuring cells and is ideally suited for research, for determining new literature values, for absolute

best accuracy and precision. A unique unconditionally stable, phase-locked loop frequency multiplier allows the use of the second DMA602 measuring cell as the time base in the period measurement. This results in highest precision due to minimizing or completely eliminating effects of sample temperature variation.

¹ O. Kratky, H. Leopold, H. Stabinger: The determination of the partial specific volume of proteins by the mechanical oscillator technique. In: Hirs, C. H. W., S. N. Timasheff (Eds): *Methods in Enzymology*, Vol. XXVII, Part D, Academic Press, New York-London 1973, 98-110, and H. Leopold, R. Jelinek, G. P. Tillz: The application of the mechanical oscillator technique for the determination of the density of physiological fluids. *Biomedizinische Technik*, 22 (1977), S. 231-235.

² After correct calibration, accuracy equals precision in a range of 0.5 to 1.5 g/cm³.



Density Meter Specifications

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Measuring units	3-place precision	4-place precision			5-place precision	6-place precision
Model numbers	DMA35	DMA 40D	DMA 45	DMA 46	DMA 55	DMA 60/602
Measuring range	0...1.999g/cm ³	0...3 g/cm ³	0...3 g/cm ³	0...3 g/cm ³	0...3 g/cm ³	0...3 g/cm ³
Precision ^{1,2}	±1 x 10 ⁻³ g/cm ³	±1 x 10 ⁻⁴ g/cm ³	±1 x 10 ⁻⁴ g/cm ³	±1 x 10 ⁻⁴ g/cm ³	±1 x 10 ⁻⁵ g/cm ³	1.5 x 10 ⁻⁶ g/cm ³ ⁹
Sample size (approximately)	2.0 ml	0.7 ml	0.7 ml	0.7 ml	0.7 ml	0.7 ml
Sample temperature range	0...+40°C	-10... +60 °C	-10... +60 °C	+15... +38 °C	-10... +60 °C	-10... +60 °C
Temperature equilibrium ³	-	0.5...1 min	0.5...1 min	0.5...3.5 min	0.5...4 min	1...5 min
Typ. test or cycling time ⁴	15...60 secs	1...5 min	1...5 min	1...8 min	2...6 min ⁸	2...8 min
Pressure ⁵	7 psi	up to 150 psi	up to 150 psi	up to 150 psi	up to 150 psi	up to 150 psi
Digital display reads	choice of true density, specific gravity, Brix	period of oscillation "T"	true density, concentration, specific gravity	true density, concentration, specific gravity	true density, specific gravity, concentration and other parameters related to density	period of oscillation "T"
Digital data output	-	5 decades BCD ⁶	5 decades BCD	5 decades BCD	6 decades BCD ⁶	8 decades BCD
Analog output	-	-	-	-	0...5 V ⁷ (lower voltages, e.g. 0...100 mV, available on request)	0...5 V (conversion of 2 or 3 least significant digits of T-value) ⁷ (lower voltages, e.g. 0...100 mV, available on request)
Required external thermostat precision	has built-in thermostat	±0.05 °C	±0.05 °C	has built-in thermostat	±0.01 °C	±0.01 °C
Dimensions	3.7 x 7 x 26.5 cm	250 x 300 x 130 mm	250 x 300 x 130 mm	250 x 425 x 130 mm	250 x 425 x 260 mm	250 x 425 x 130 mm, each
Weight	550g	11 kg	11 kg	15 kg	20 kg	8 kg / 21 kg

¹ The instruments are to be calibrated with air and a liquid of known density (usually bidistilled boiled water). The specification refers to a range of ±0.5 g/cm³ around calibration point and depends on the thermal coefficient of expansion of sample. If properly calibrated, the accuracy of each measurement can approach the precision of the instrument.

² If calibrated with air and water, DMA 40, DMA 45 and DMA 46 will show a deviation from true density less than ±5.10⁻⁴ g/cm³, DMA 50 and DMA 60 will show a deviation from true density less than ±1.10⁻⁴ over entire range of 0 to 3 g/cm³.

³ Depending on desired precision and the thermal preconditioning of the sample.

⁴ If applicable sample, changer SP 2 is used.

⁵ Given values apply to standard version. Higher pressure up to 700 psi upon request; up to 6000 psi on special remote cell.

⁶ Optional version excluding digital data output available.

⁷ ≥10 kΩ load; resolution better than 0.1%; for DMA 55 only: range from 0.001 to 0.5 g/cm³, selectable in nine steps.

⁸ For continuous flow a sampling rate from approximately 10 to 80 per min. can be selected.

⁹ Best accuracy and precision is achieved when using two remote cells in differential mode.

Type	Max. precision (g/cm ³)	Calibr. range (g/cm ³)	Sample size (ml)	Temp. range (°C)	Normal press. range	Dimensions (mm)	Weight (kg)
DMA401*	1 x 10 ⁻⁴	±0.5	0.7	-10 to +60	vac. to 150 psi	140 x 380 x 85	10
DMA401W*	1 x 10 ⁻⁴	±0.5	3.0	-10 to +60	vac. to 15 psi	140 x 380 x 85	10
DMA512	1 x 10 ⁻⁵	±0.1	1.0	-10 to +150	vac. to 6000 psi	250 x 425 x 130	20
	1 x 10 ⁻⁴	±0.5	1.0	-10 to +150	vac. to 6000 psi		
DMA602	1.5 x 10 ⁻⁴	±0.5	0.7	-10 to +60	vac. to 150 psi	250 x 425 x 130	21
DMA602T	1.5 x 10 ⁻⁴	±0.5	0.7	-200 to +60	vac. to 150 psi	250 x 425 x 130	21
DMA602H	1.5 x 10 ⁻⁴	±0.5	0.7	-10 to +150	vac. to 150 psi	250 x 425 x 130	21
DMA602M	1.5 x 10 ⁻⁴	±0.01	0.1 (0.3)	-10 to +60	vac. to 150 psi	250 x 425 x 130	21
	1 x 10 ⁻³	±0.1					
DMA602W	1.5 x 10 ⁻⁴	±0.5	0.7	-10 to +60	vac. to 15 psi	250 x 425 x 130	21
DMA602HT	1.5 x 10 ⁻⁴	±0.5	0.7	-200 to +150	vac. to 150 psi	250 x 425 x 130	21
DMA602MH	1.5 x 10 ⁻⁴	±0.01	0.1 (0.3)	-10 to +150	vac. to 150 psi	250 x 425 x 130	21
	1 x 10 ⁻³	±0.1					
DMA602MW	1.5 x 10 ⁻⁴	±0.01	0.1 (0.3)	-10 to +60	vac. to 15 psi	250 x 425 x 130	21
	1 x 10 ⁻³	±0.1					
DMA602HW	1.5 x 10 ⁻⁴	±0.5	0.7	-10 to +150	vac. to 15 psi	250 x 425 x 130	21

Note: The "W" designates cells with heat exchanger for continuous flow operation. Maximum flow rate is 8 ml/min. for temperature difference of ±5 °C and expected accuracy of 1 x 10⁻⁵ g/cm³ (DMA 602W) and accuracy of 1 x 10⁻⁶ g/cm³ (DMA 401W).

The letter "P" placed behind model designation specifies a cell for selected higher pressure range. Up to 700 psi on standard cells, up to 150 psi on "W" cells. Pressure range for "MP", "WMP", as well as 401P & 401WP cells on request.

* Comes with Adapter Box 49194. Dimensions are 145 x 190 x 65 mm; weight 1 kg.

Operator's Manual

910 Differential Scanning Calorimeter

Du Pont Company
Clinical and Instrument Systems Division
Concord Plaza — McKean Building
Wilmington, DE 19898

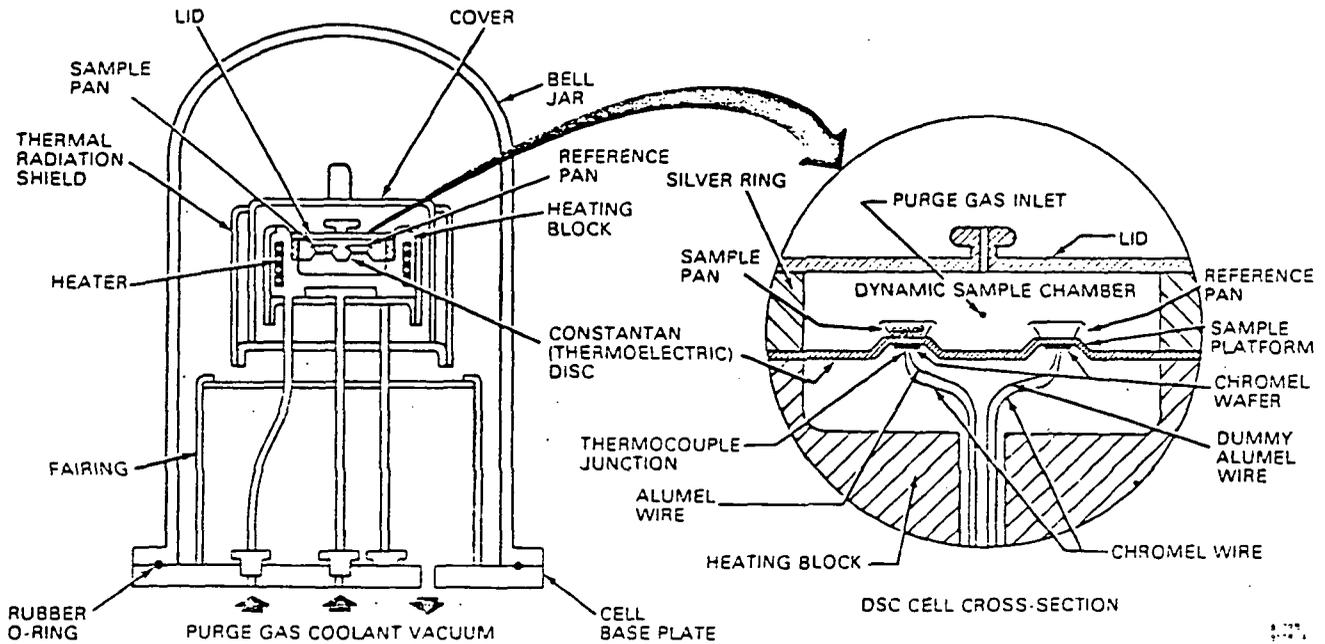
Thermal Analyzers
Clinical and Instrument Systems Division



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DSC Cell

The system's measuring unit is a plug-in DSC cell, which is used to measure differential heat flow. In the cell, the sample and an empty reference pan sit on raised platforms on a constantan disc. Heat is transferred through the disc to the sample and reference. Differential heat flow is monitored by thermocouples located beneath the disc.



Cross Section, DSC Cell

Pressure DSC Cell

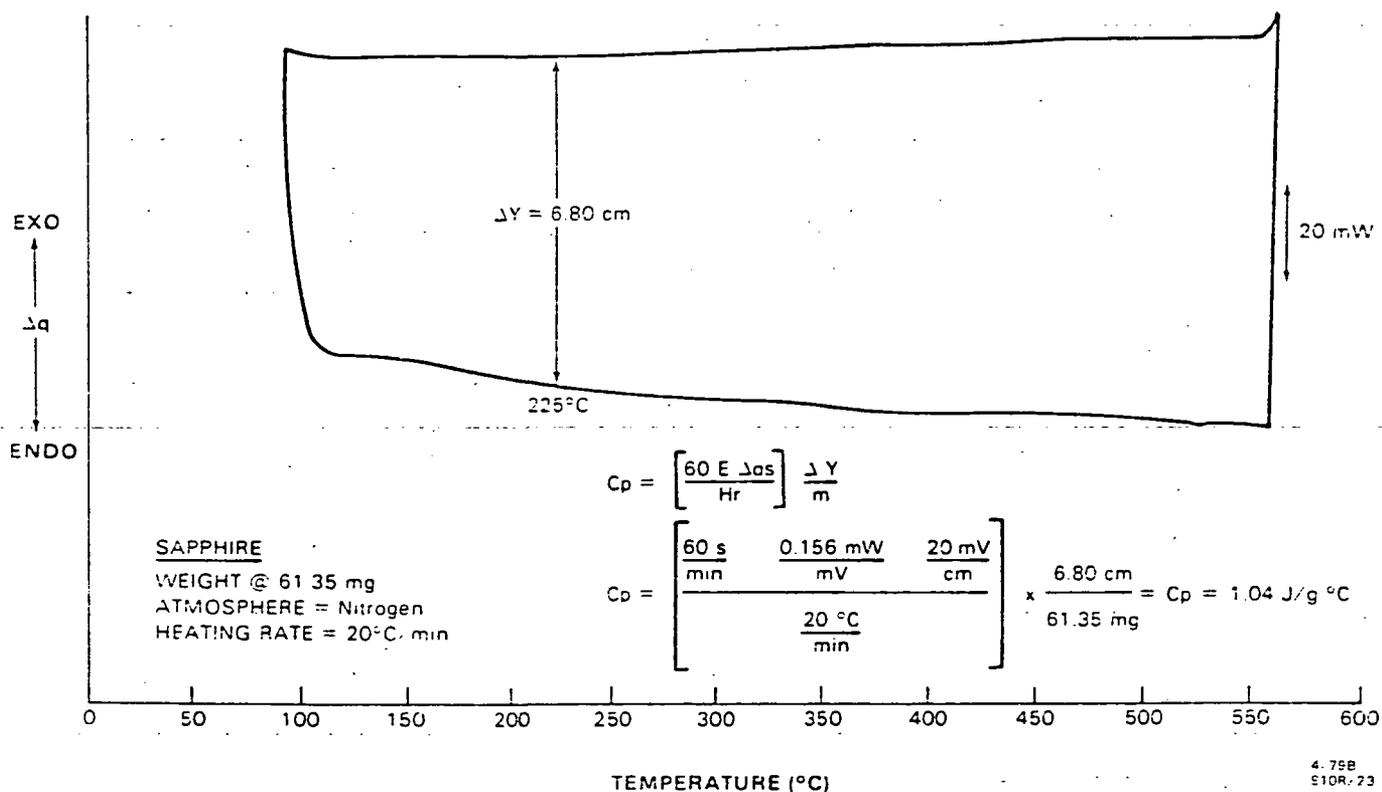
The pressure DSC cell is a DSC cell enclosed in a steel cylinder that can be pressurized to 7 MPa (1000 psig). This cell has two gas pressure control valves and a pressure gauge on the front; a pressure relief valve and gas pressure fittings are located on the rear. An 8.3 MPa (1200 psig) pressure relief valve is contained in the base.

Determining Heat Capacity

To determine the heat capacity of a test specimen, compare the heat flow difference between sample and reference under blank and sample conditions as follows:

- Load empty sample and reference pans.
- Set the starting and limit temperatures over the temperature range desired.
- Allow the system to equilibrate for 5 minutes.
- Position the pen near the top of the chart.
- Temperature-program the empty pans at an appropriate rate (e.g., 20°C/min). Deflection from the initial equilibrium point may be up or down depending on the heat capacity difference between the pans.
- Repeat this procedure under identical conditions with a weighed sample in the sample pan. Do not adjust pen position between blank and sample runs.
- Calculate heat capacity by measuring the difference in Y-axis displacement (calorimetric differential) between the sample and blank curves at any desired temperature. See the following figure.
- Substitute the difference into the following equation:

$$C_p = \left[\frac{60E \Delta qs}{Hr} \right] \frac{\Delta Y}{m}$$



Specific Heat of Sapphire

where E = Cell calibration coefficient at the temperature of interest in mW/mV (dimensionless)

Δqs = Y-axis RANGE setting in mV/cm ($\text{mcal}\cdot\text{s}^{-1}/\text{in}$)

Hr = Heating rate in $^{\circ}\text{C}/\text{min}$

ΔY = Difference in Y-axis deflection between sample and blank curves at temperature of interest in cm (in)

m = Sample mass in mg (mg)

Cp = Heat capacity in $\text{J/g } ^{\circ}\text{C}$ ($\text{mcal}/\text{mg } ^{\circ}\text{C}$)

NOTES

- The quantity $(60E \Delta qs/Hr)$ is constant under a given set of experimental conditions. It converts the ΔY measurement directly into units of heat capacity in $\text{J/g } ^{\circ}\text{C}$ ($\text{mcal}/\text{mg } ^{\circ}\text{C}$).
- For highest accuracy, determine the value of this constant (as an entity) by running a standard material of known specific heat under identical conditions as the unknown sample. Then substitute the values of ΔY , m , and Cp for the standard into the above equation at the temperature of interest.
- A sapphire (Al_2O_3) standard is provided in the accessory kit for this purpose.

PRESSURE DSC OPERATING PROCEDURES

A safety margin is designed into the pressure DSC cell. Nevertheless, you should pay attention to the following precautions.

WARNING

Any time the OUT or pressure relief valve is opened during operation, you may be applying full pressure to the external lines or components (flowmeter, vacuum pump, etc). These components may not be able to withstand full pressure.

Sample Loading

Do not use tools to open or close the cell. Use the following procedure to prepare the cell for a run:

- Open the pressure release valve and leave it open to ensure that the cell is at ambient temperature.
- Close the IN control valve.

WARNING

Excessive bolt friction is an almost sure sign that the cell is still under some pressure. Check the valves.

- Remove the top plate, cell cover, and silver lid.
- Load the sample and reference as you would in a normal DSC cell.

Nicolet 60SX: Setting new standards for research-grade FT-IR.

Uncompromising FT-IR Performance and Versatility

When choosing a research-grade FT-IR, you shouldn't settle for less than Nicolet's 60SX. While others make promises and offer compromises, Nicolet *delivers* proven performance and versatility that no other FT-IR can match.

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In evaluating a research-grade FT-IR, your first consideration is the quality of the fundamental spectral data and the spectrometer's overall performance. The uncompromising design of the 60SX interferometer and electronics provides the ultimate in speed, sensitivity, and accuracy.

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Fastest spectra in FT-IR! 60SX rapid scanning (up to 50 scans/second) lets you study dynamic processes such as reaction kinetics and catalysis.

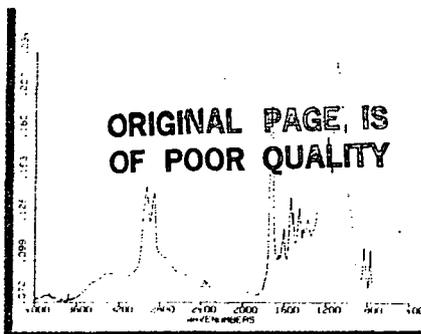
Unmatched microsampling capabilities. The 60SX computer-controlled microsampling accessory provides best performance for:

- Samples as small as 12 microns.
- Surface analysis of small samples with Nicolet's exclusive micro-ATR.
- Automated sample positioning and mapping.

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Micro-ATR measurement of a small, coated fiber optic sample shows superb sensitivity.

- Experiment modules let you set up experiments away from the optical bench.
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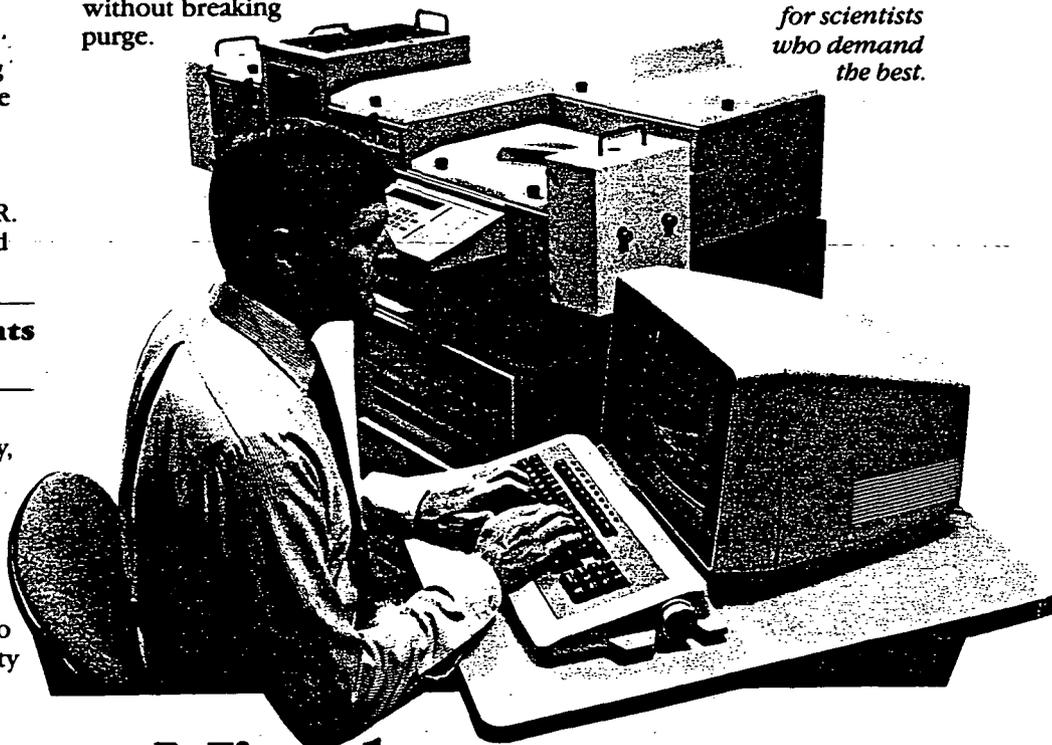
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1.0 60SX PHYSICAL LAYOUT

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The 60SX is a complete research-grade FT-IR system offering a resolution of 0.25 cm^{-1} throughout the standard range of $5000 - 400 \text{ cm}^{-1}$. The system components can be arranged into two main groups: the data system including the computer, disk drives, and terminal, and the spectrometer including the optical bench and master control. See figure 1 for a typical 60SX system configuration.

1.1 OPTICAL BENCH

The standard optical bench offers a resolution of 0.25 cm^{-1} throughout the standard range of $5000 - 400 \text{ cm}^{-1}$. The range is extendable from $25,000 - 10 \text{ cm}^{-1}$ with the appropriate combination of source, beamsplitter, and detector. Applications intensive options such as automatic beamsplitter changer, computer-aided alignment, and microbeam are available. Additional software and hardware features will be released from time to time.

The system includes a continuous scan Michelson interferometer with maximum retardation of 4.0 cm , variable mirror drive rates, and a nominal aperture of $2''$ diameter. A laser reference interferometer is included for wavelength accuracy. A unique system for monitoring absolute mirror position during the scan is also included. The system has the capabilities for multiple detectors and multiple sources selectable under computer control. Many of the common bench functions can be controlled through the bench control panel without the data system. Special firmware for custom options can be accessed through this panel. Figure 2 shows the optical layout of the 60SX bench.

1.2 MASTER CONTROL

The master control contains the electronics to control the 60SX bench. The master control is microprocessor based which allows flexibility in programming and operation. A number of important signals are available at the master control for troubleshooting the system.

1.3 POWER SUPPLY

The power supply assembly contains the various DC power supplies for the 60SX bench. These power the entire bench including the sources, laser, and electronics. It also indicates the presence of power to the laser in the system.

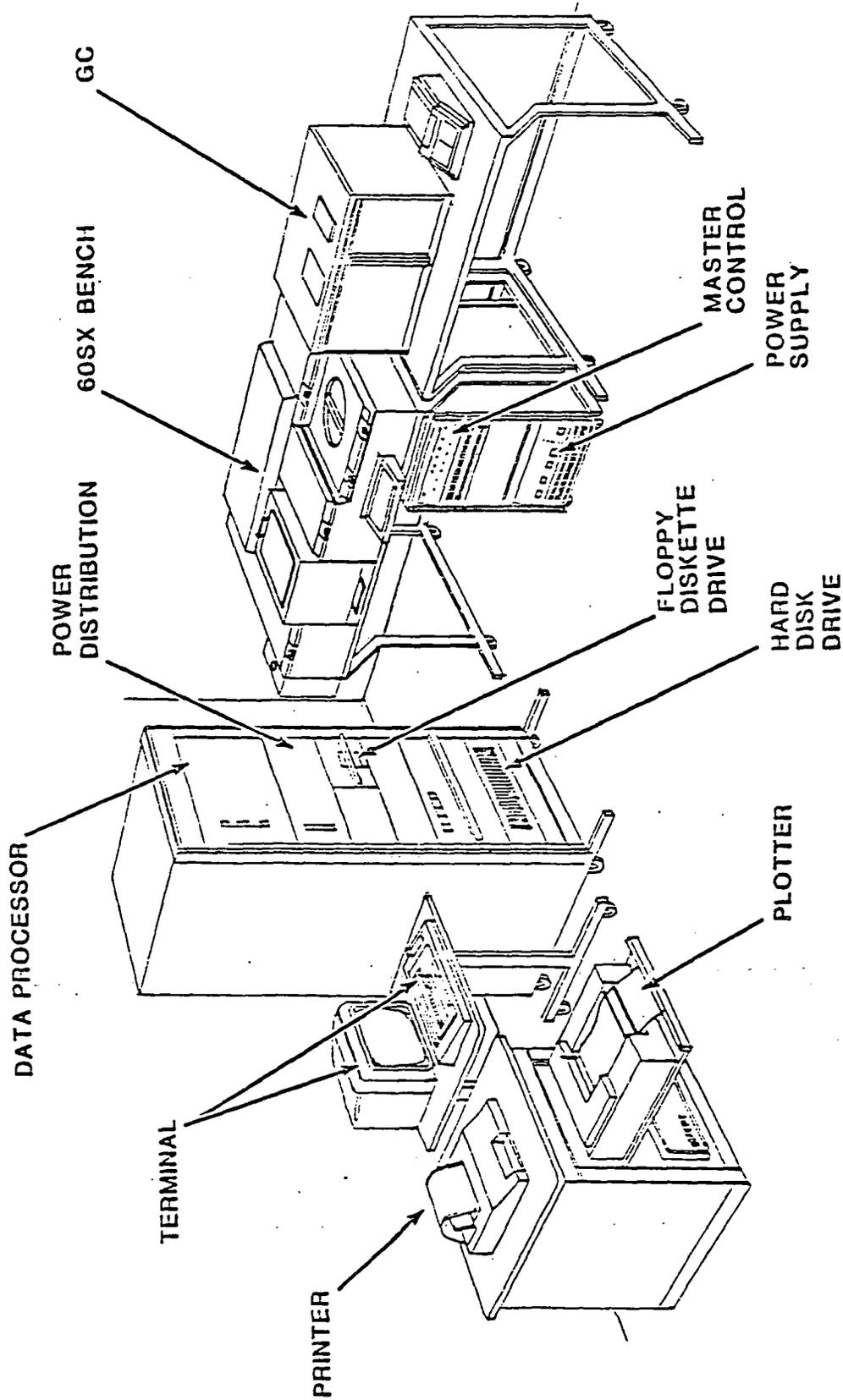


Figure 1 TYPICAL 60SX SYSTEM LAYOUT

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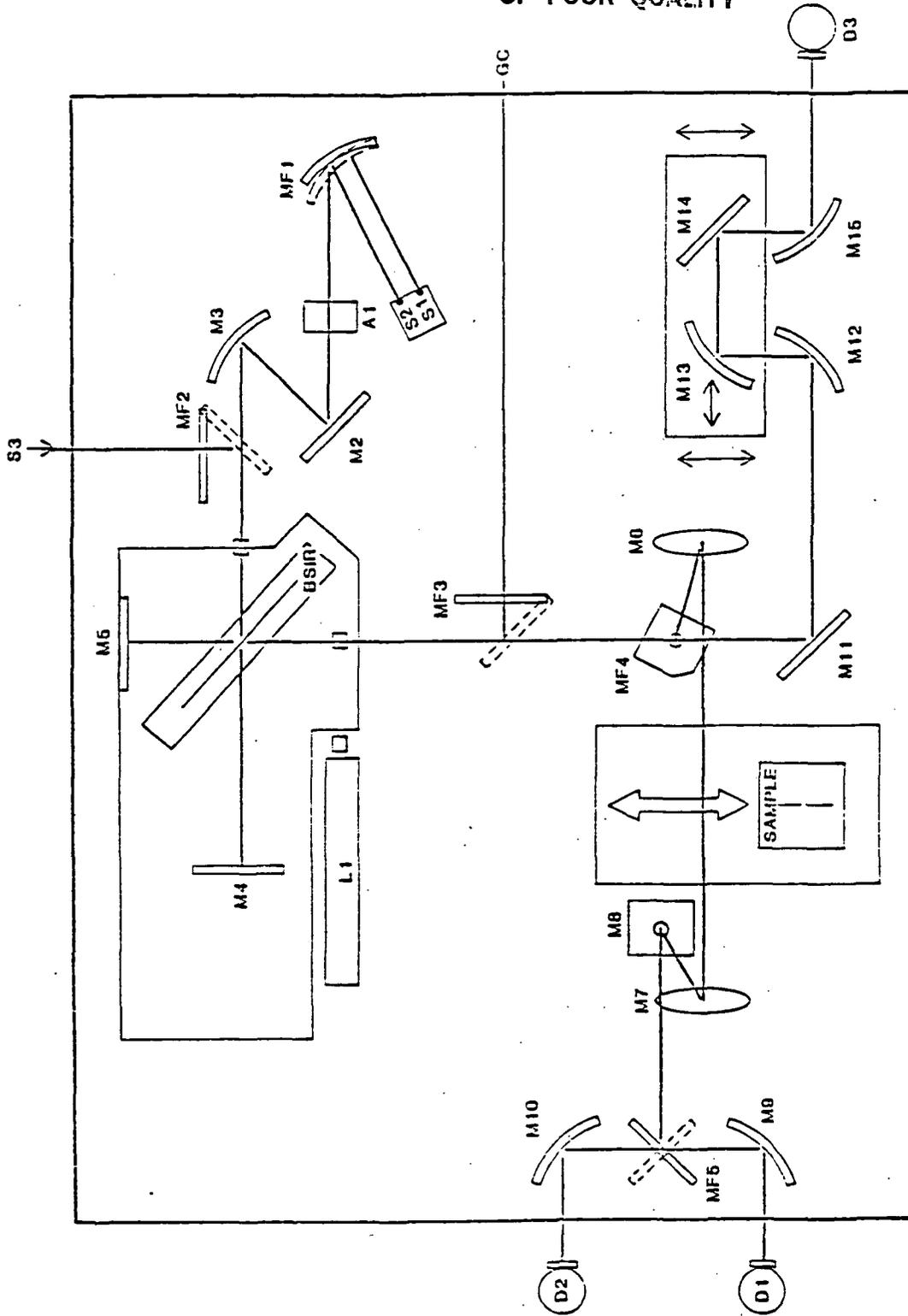


Figure 2 60SX OPTICAL BENCH LAYOUT

corporate test method

POUR POINT

January 28, 1971

CTM 0133

Abstract

The Pour Point of a liquid is determined by cooling the material under controlled conditions (Note 1) and observing the temperature at which the material will not flow when the container is held at an angle. The primary method uses one cooling bath and does not comply with ASTM D-97. Compliance with ASTM D-97 must be specified (Note 2). The results are reported in degrees Fahrenheit to the nearest five degrees.

Apparatus

Bath: Any suitable container for holding the required cooling solution and having a support to hold the jacket in a vertical position (Note 2).

Flask: Dewar, stainless steel, 4 in. (10.2 cm) ID and 7-1/2 in. (17 cm) high. Any suitable source.

Flask: Glass, 1.2 in. (3.1 cm) ID and 5 in. (12.7 cm) high with a flat bottom. Any suitable source.

Place a mark on the flask 2-1/8 in. (5.4 cm) above the bottom of the inside.

Jacket: Brass, 1.6 in. (4.1 cm) ID and 4.5 in. (11.5 cm) high, equipped with a cork disk in the bottom and a support ring to allow the glass flask to be inserted and moved easily but held in a vertical position. Any suitable source.

Reagents

Normally equipped laboratory (Note 2).

Precautions

Safety: Use extreme care in handling the cooling mixture(s) and the cold tubes to avoid frost burns.

Procedural: No unusual precautions.

Page 1 of 3

The method described has been adapted from either our investigations or literature procedures or both. The Dow Corning Corporation does not assume any liability in connection with the use of this method. Applicability to samples of interest must be ascertained by the user. This method should not be reproduced or published in whole or part without written permission of the Dow Corning Corporation.

Parameters

If compliance with ASTM D-97 is specified, the estimated Pour Point must be known to allow for proper sample handling. For single temperature cooling, a mixture of dry ice and acetone will be used unless otherwise specified.

Procedure

Stabilize the liquid to be tested for at least 24 h at room temperature. Pour the liquid into the glass flask up to the 2-1/8 in. mark. Close the flask with the cork which supports the thermometer vertically in the center of the flask with the bulb $1/8 \pm 1/32$ in. (3 mm) below the surface of the material. Place the glass flask in the brass jacket and carefully lower the brass jacket into the Dewar flask (Note 2) containing a mixture of dry ice and acetone. Periodically remove the glass flask and tip it, observing the surface of the liquid. If the material does not flow, read and record the temperature. Add 5°F to that value and report the number as the Pour Point (Note 3).

If the temperature of the liquid reaches -40°F (-40°C), transfer (Note 4) the brass jacket to a new Dewar flask containing liquid nitrogen and continue the observations until the material does not flow or the temperature stabilizes and report the value as Pour Point.

If the material crystallizes at any point, stop the test and report "Crystallized at _____ °F".

Standardization

The thermometers should be standardized at least once every three months.

Calculations

None required.

Precision and Accuracy

The repeatability of the value reported (the maximum expected difference between two independent results) should not exceed 5°F, the 95% confidence level.

Notes

1. The values obtained by this method do not relate to other storage or cooling conditions. For example, a material may have a Pour Point of -80°F as determined by this method and be found to be completely unmoving after storage at -40°F for 24 h. No precautions are taken to prevent supercooling.

2. Compliance with ASTM D-97 requires the use of a series of baths, each cooler than the preceding one. Suggested baths are:
 - A. Water and ice.
 - B. Water, ice and NaCl or CaCl₂.
 - C. Acetone and dry ice (the amount of dry ice may be varied to achieve the desired temperature).
 - D. Liquid nitrogen.

It also requires preheating of the liquid and controlled cooling. The transfers from bath to bath are dictated by the temperature of the liquid approaching the temperature of the bath.

The same reporting and observation conditions apply.

3. If the observed Pour Point is -38°F, then the reported value will be -33°F (-38 + 5 = -33).
4. For materials expected to have Pour Points below -40°F, place the jacket directly into the Dewar flask containing liquid nitrogen.

References

ASTM D-97
IP 15
BS 4452

Figures, Graphs, and Sketches

None.

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corporate test method

FLASH POINT--Pensky Marten Closed Cup

July 1, 1975

CTM 0021A

→ Abstract

This procedure should be used on materials similar to fuel oils, lube oils, suspensions of solids, liquids that tend to form a surface film under test conditions, and other liquids (Note 1). The material is placed in a Pensky Marten Closed Cup flash apparatus. Periodically during a controlled temperature rise, a flame is placed into the confined air space over the sample. The temperature at which the material will flash, but does not continue to burn, is recorded. This procedure is based on ASTM D93, E134, and IP34 and the results are reported in degrees fahrenheit.

Apparatus

Tester: Pensky Marten Closed Cup to meet ASTM E134. Fisher Scientific, Pittsburgh, PA, Cat. No. 13-493.

Thermometer: ASTM Specification as listed, Fisher Scientific

ASTM	Range, F	Cat. No.
9F	20-230	13-500
10F	200-700	13-505

Reagents

Normally equipped laboratory.

Precautions

Safety: The possibility of fire and explosion exists. The nature of the material under test should be known.

Procedural: No unusual precautions.

Parameters

The approximate flash point should be known to allow for proper heating rate and selection of thermometer. Flash point is reported in °F unless otherwise specified.

→ Procedure

The nature of the material being tested dictates which of the following procedures to use.

Page 1 of 3

The method described has been adapted from either our investigations or literature procedures or both. The Dow Corning Corporation does not assume any liability in connection with the use of this method. Applicability to samples of interest must be ascertained by the user. This method should not be reproduced or published in whole or part without written permission of the Dow Corning Corporation.

Solutions or clear liquids: Fill the cup to the fill mark with sample. Place the lid on the cup. If the material flashes at or below room temperature, cool to at least 30°F below the expected flash point. Place the cup in the holder and lock in position. Put the thermometer (Note 2) in place. Turn on the stirrer to 105 + 15 rpm with the action in a downward direction. Light the test flame and adjust to a 5/32 + 1/32 in. diameter. Begin heating the sample at 10 ± 1°F/min. At about 30°F below the expected flash point, begin applying the test flame as follows:

1. Flash below 220°F once every 2°F
2. Flash above 220°F once every 5°F

The flame should be lowered in about 0.5 sec., left in the lowered position for about 1 sec., and quickly raised. Discontinue stirring when applying the flame. Record the lowest temperature at which the test flame causes a distinct flash in the interior of the cup (Note 3). Report the temperature to the nearest degree (Note 4).

Materials containing suspended solids: Follow the above procedure except for the following:

1. Initially adjust the temperature to at least 20°F below the expected flash point.
2. For flash points below 150°F, fill the air space between the cup and the interior of the air bath with water at the initial temperature of the test equipment and sample.
3. The stirring will be at 250 + 10 rpm.
4. The temperature rise throughout the test will be not less than 2 nor more than 3°F/min.

Standardization

The thermometer should be standardized or replaced at least once every month.

Calculation

None required.

Precision and Accuracy

The precision of this method should be as follows:

	<u>Below 200°F</u>	<u>Above 200°F</u>
Repeatability	+ 4	+ 10
Reproducibility	± 6	± 15

Notes

1. This method should be used for those liquids which have a viscosity of 45 SUS (6 cSt) or more at 100°F (37.8°C) or that contain suspended solids, or have a tendency to form a surface film while under test.
2. Choose the correct thermometer for the temperature range.
3. Do not confuse the true flash with the bluish halo that sometimes surrounds the test flame.
4. Observe and record barometric pressure at the time of test. When pressure differs from 760 mm Hg, correct the flash point by means of the following equation:

$$\text{Corrected flash point} = ^\circ\text{F} + 0.06(760 - P)$$

$$\text{Corrected flash point} = ^\circ\text{C} + 0.03(760 - P)$$

F = Observed flash point °F

C = Observed flash point °C

P = Barometric pressure, mm Hg

Record flash point to nearest °F or 0.5°C.

Reference

ASTM D93, E134

Institute of Petroleum 34

Figures, Graphs, and Sketches

None

+ Denotes change

corporate test method

FIRE POINT - Liquids - Cleveland Open Cup

September 29, 1970

CTM 0052

Abstract

The temperature at which a liquid will sustain a fire for at least five seconds in a Cleveland open cup test apparatus is determined and reported as the Fire Point. After the Flash Point of the material is reached, the heating is continued at the same rate until the application of the flame results in a sustained fire. The procedure is based on ASTM D-92 and the results are reported in degrees Fahrenheit.

Apparatus

Burner: Meeker, Central Scientific Co., Chicago, IL, Cat. No. 11043.

Cup: Cleveland Open Cup Flash Tester with heating plate. Fisher Scientific Co., Pittsburgh, PA, Cat. No. 13-529 (Note 1).

Thermometer: ASTM open flash, graduated in 5°F intervals from 20 to 760°F. Fisher Scientific Co., Cat. No. 13-535 (ASTM 11F). The thermometers must be a low immersion style.

Reagents

Normally equipped laboratory.

Precautions

Safety: The possibility of a continuing fire or explosion exists. The nature of the material under test should be known. Adequate precautions must be made for the protection of the operator and for the removal of toxic vapors and products of combustion. A fire extinguisher should be available.

Procedural: No unusual precautions.

Page 1 of 3

Parameters

The approximate flash point should be known to allow for proper flame regulation. Other types of flash point apparatus may be specified. The results may be reported as degrees Centigrade.

Procedure

Fill the cup with material so that the surface level is at the filling line at room temperature. Place the thermometer vertically in the sample so that the bottom of the bulb is $1/4 \pm 1/16$ in. (6.4 mm) above the bottom of the cup. Turn on the Meeker burner and adjust the flame so the rate of heating does not exceed $30^{\circ}\text{F}/\text{min}$. At 50°F below the expected flash point, reduce the rate of heating to $10 \pm 1^{\circ}\text{F}/\text{min}$.

Adjust the test flame to a $5/32 \pm 1/32$ in. (4.0 mm) diameter.

If the flash point is also being determined, start flame application at least 50°F below the expected flash point (Note 2). Pass the flame over the material at 5°F intervals. Continue the application past the initial flash point until the material continues to burn for at least 5 sec. Record and report this temperature as the Fire Point (Note 3).

Standardization

The thermometer should be standardized or replaced once every month.

Calculations

None.

Precision and Accuracy

The repeatability of the value reported (the maximum difference between two independent results) should not exceed 15°F at the 95% confidence level.

Notes

1. Other types of flash point testers may be specified. In the case of a dispute, when an automatic flash point tester is used for determination of Fire Point, the manual method shall be considered the referee method.

2. The test flame must pass horizontally across the center of the cup with a smooth continuous motion not more than 5/64 in. (2 mm) above the upper edge of the cup. The pass should be first in one direction and then in the opposite direction. The time consumed in a pass should be about 1 sec.
3. Variations in barometric pressure affect the Fire Point. A correction should be applied, as required:

<u>PRESSURE</u> <u>mm of Hg</u>	<u>ADD CORRECTION</u> <u>Degrees Fahrenheit</u>
715-635	5
635-550	10

References

ASTM D-92.

Institute of Petroleum 36.

DIN 51 376.

Figures, Graphs, and Sketches

None.

Ed. Form.

9/79

JEW

4:B

corporate test method

VOLUME RESISTIVITY--Liquid and Semi-Solid Insulating Materials

July 20, 1972

CTM 0272

Abstract

The volume resistivity of liquid insulating materials is measured in a Balzbaugh cell and that of semi-solids in a special cell. The measurement is made with a commercial ohmmeter and the method is based on ASTM D 1169.

Volume resistivity is defined as the ratio of the potential gradient parallel to the current in the material to the current density. In the metric system the volume resistivity of an electrical insulating material in ohm-cm is numerically equal to the volume resistance in ohms between opposite faces of a 1 cm cube of material.

Apparatus

Capacitance bridge: Type 716C (Schering type), General Radio Co., West Concord, Mass.

Cell: Balzbaugh, two-terminal, 100 μ f, Balzbaugh Laboratories, Inc., South Hingham, Mass. Use for materials 1000 cS or less unless otherwise specified.

Reference standards: Comparison resistors, type CR, nominally 10^4 , 10^6 , and 10^7 megohms. Rhode and Schwarz Sales Co., Passaic, N.J. Calibrated, certified, and traceable to the National Bureau of Standards.

Semi-solid sample holder: See Figure 1.

Tera-Ohmmeter: Type h 4/10, Rhode and Schwarz Sales Co.

Reagents

Normally equipped laboratory.

Precautions

Safety: Normal safe laboratory practices.

Procedural: No unusual precautions.

Page 1 of 5

The method described has been adapted from either our investigations or literature procedures or both. The Dow Corning Corporation does not assume any liability in connection with the use of this method. Applicability to samples of interest must be ascertained by the user. This method should not be reproduced or published in whole or part without written permission of the Dow Corning Corporation.

Parameters

Other potentials and electrification periods may be specified. Other temperatures and sample conditioning may be specified.

Procedure

Condition the material at 23 ± 2 C and make all determinations under the same conditions, unless otherwise specified. Add a sufficient amount of material to be tested to the correct clean dry test cell (Note 1) to cover the capacitor plates (Note 2). Attach the leads from the ohmmeter to the test cell with the positive lead to the inner electrode and the negative lead to the outer electrode. Adjust the applied voltage to 500 volts and measure the resistance (R) (Note 3) after 60 sec of electrification. Calculate the volume resistivity (VR) and report the value.

Standardization

The equipment should be calibrated and adjusted every three months to produce the certified values of the reference standards.

The Balzbaugh cell should be calibrated at least once every six months as follows: Fill the cell with reagent grade cyclohexane (other pure materials of known dielectric constant may be used--cyclohexane is used because of its extremely low electrical loss) and connect the leads to the capacitance bridge. Set the bridge capacitance dial at 100 μ f and balance the bridge using the external capacitor. Disconnect the leads from the cell and rebalance the bridge using the bridge capacitor. Read and record the bridge capacitor (C_c). Remove the cyclohexane and dry the cell. Repeat the above with the empty cell and record the bridge capacitor reading as the air capacitance (C_a). Calculate the cell factor (C_f).

The semi-solid sample holder (Fig 1) should be calibrated at least once every six months as follows:

Assemble the cell completely. Connect the cell to the bridge and screw the micrometer adjustment down until the top electrode just touches the base. Record the micrometer dial reading. Move the top electrode up to produce a spacing of 0.025 in. and lock the spindle. Fill the cup in the base with reagent grade cyclohexane using an eye dropper and proceed as outlined above for the Balzbaugh cell.

$$C_f = 3.6\pi C_v$$

$$C_v = \frac{C_c - C_a}{K_c - K_a}$$

C_c = capacitance of cyclohexane

C_a = capacitance of air

K_c = DK of cyclohexane (2.0150)

K_a = DK of air (1.0006)

Calculations

$$VR = (C_f)(R) = \text{ohm-cm}$$

C_f = cell factor

R = resistance measured in ohms

Precision and Accuracy

The precision of the reported results should be in the range of + 5 %.

Notes

1. The semi-solid sample holder (Fig 1) is used for materials which have a viscosity greater than 1000 cS, unless otherwise specified. The upper electrode is adjusted to give a spacing of 0.025 in. and the spindle is locked. The cup in the base is filled with material to be tested and the cell carefully assembled until the Teflon® sleeve is fully seated on the base and the upper electrode forced into the material to be tested.

Both cells must be cleaned using a dry low-boiling hydrocarbon. After a final rinse, the cell should be heated at 110 C for about 10 min or placed in a vacuum chamber to remove the last traces of solvent and prevent moisture condensation.

2. When both dielectric constant and volume resistivity measurements are required on the same material, fill the cell and make the dielectric constant measurement first.
3. The measured value (R) is frequently reported directly as Insulation Resistance. The number is of limited value since it is dependent upon the cell configuration and the electrode spacing.

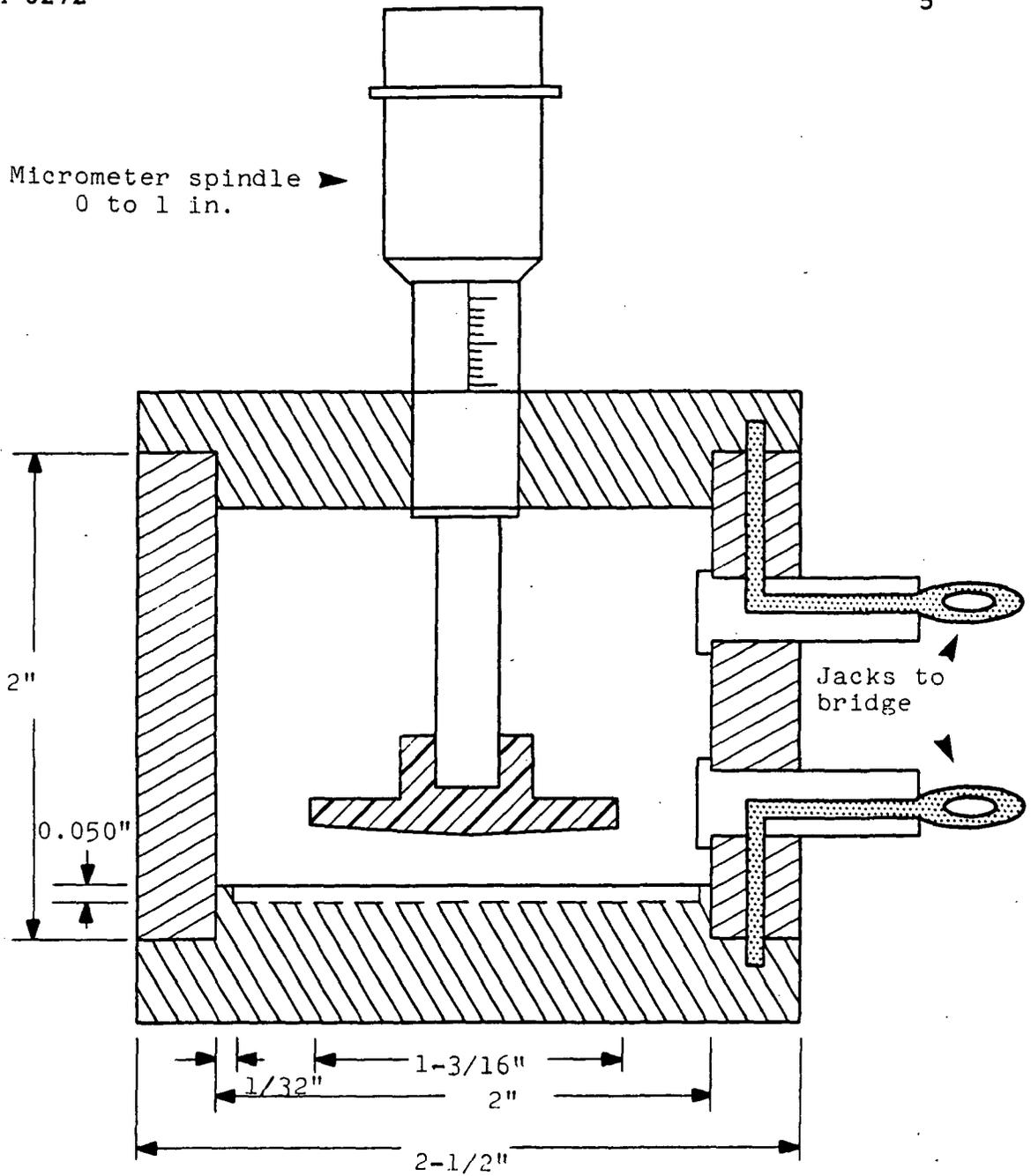
References

ASTM D 1169

Figures, Graphs, and Sketches

1 Figure

MCL x
CTL x



 2 in. ID, 2-1/2 in. OD Teflon® tube with an opening about 1-1/2 in. wide and 3/4 in. high on the bottom edge to allow observation of the electrode and sample.

 Brass electrode with base bevelled about 1 to 2° to prevent air entrapment

 Stainless steel

 Stiff copper wire to complete electrical circuit. Slip fit into base.

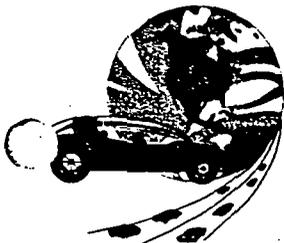
Liquid and Semi-Solid Cell

APPENDIX III

APPENDIX III

This appendix contains complete reports of shear viscosity, thermal conductivity, and emittance/transmittance measurements on Task II fluids.

Shear Viscosity	Savant, Inc., Midland, MI
Thermal Conductivity	Dow Thermal Laboratory Midland, MI
Emittance/Transmittance	Analytical Research, Dow Corning



SAVANT, INC.

234 E. LARKIN STREET

MIDLAND, MICHIGAN 48640-0111

1985 September 16

Dr. Robert Buch
Dow Corning U.S.A.
Mail #108
Midland, MI 48640-0994

Dear Dr. Buch:

We have, as you know from our phone conversation of August 28th, completed the high and low temperature, high and low shear stress analyses of the two samples you sent us, using the Newtonian calibration fluid S-3 from Cannon Instrument Company for reference at low temperatures. In the written report on the subject, you requested that we note the shear stresses obtained.

The attached report presents the desired information. If you need further input, please let me know. It has been good working with you on this interesting assignment and I hope we may serve you and your associates again.

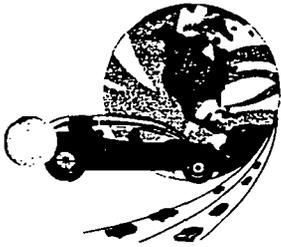
Yours very truly,

A handwritten signature in cursive script, appearing to read "Ted Selby". The signature is written in black ink and is positioned above the typed name of the sender.

Theodore W. Selby, Director
Research & Development

TWS/cp
Attachment

cc: Mr. Thomas J. Tolton, Manager, Savant Laboratories



Report DCC-2-1

to

Dow Corning Corporation

High/Low, Temperature/Shear Analysis of Coolants

by

Savant Laboratories
Midland, Michigan

1985 September 11

INTRODUCTION

A meeting between Dr. Robert Buch of Dow Corning Corporation and Messrs. Thomas Tolton and Theodore Selby of Savant, Inc. on July 17th, 1985, was held at the Savant offices to define Dow Corning Corporation's needs for viscometric analysis of two fluids being prepared as special coolants. The critical questions raised were whether or not the fluids were Newtonian or not and whether the Savant Laboratories could perform the necessary measurements. The answer to the latter question was affirmative with the understanding that Savant would have to develop the necessary procedure in the process. It was explained that much of Savant work is in the area of advanced materials studies where original techniques and equipment must be developed.

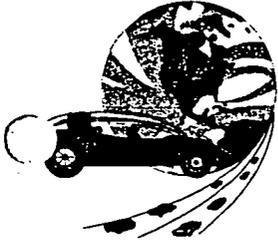
In the ensuing technical discussion it was noted by the Savant representatives that the degree of non-Newtonian behavior, while usually associated with the difference in viscosity determined at widely different shear rates, really is dependent on shear stress -- the force per laminar area of shear. Thus, the critical element at both low and high temperatures in determining non-Newtonian behavior was in applying a wide range of shear stress to the fluids.

SUMMARY

Applying widely differing shear stresses (varying by a factor of up to 4,000), neither coolant gave evidence of being markedly non-Newtonian.

The precision of the viscometric analyses allows the statement that Coolant EC 721-38-7 is probably slightly non-Newtonian at low temperatures.

Coolant EC 721-38-17 seems completely Newtonian



FLUIDS

Two fluids were submitted with the code identifications EC 721-38-7 and EC 721-38-17. Two more fluids of known Newtonian viscometric properties were also included for reference and procedural development purposes. These latter fluids were S-3 from Cannon Instrument Company and DC 705 from the Dow Corning Company. The former, S-3, was used to calibrate the two low-temperature viscometers and the latter was used to develop all the test procedures since the experimental fluids were available in relatively limited volumes.

EQUIPMENT

Four viscometric instruments were used two of which were either totally or partially developed at Savant Laboratories. Of the six techniques used to generate the data, four were totally developed at the Savant Laboratories and, of the remaining two, both were modifications of other procedures used by the ASTM.

Tapered Bearing Simulator Viscometer (TBS) -

A world-class, very high shear rate instrument invented at Savant, developed by the Savant Laboratories and manufactured and marketed by Tannas Co. of Midland, Michigan, the instrument is capable of

1. shear rates from 100,000 to values in excess of 3,000,000 1/sec,
2. shear stresses from less than 1000 to more than 1,000,000 dynes/sq.cm,
3. viscosities from less than 1 to more than 100 centipoise at full shear, and
4. temperatures from room temperature to over 200 C.

Over 70 units are presently used world-wide.

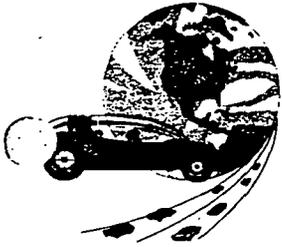
Scanning Brookfield Viscometer Technique (SBT) -

A world-class instrument and low-temperature, low-shear technique utilizing the Siverso Programmable Cold-bath and the Brookfield LVTD Recording Rotational Viscometer. The technique, developed by the Savant Laboratories is under round-robin evaluation by the ASTM and is a required analysis for multi-grade engine oils used in Ford vehicles around the world.

Shear rates range from 12.4 to 2480 1/sec with shear stresses up to 5000 dynes/sq.cm.

Cold-Cranking Simulator (CCS) -

A world-class instrument and technique developed by the Cannon Instrument Company. The technique has been modified by the ASTM and a special version developed and applied by the Savant Laboratories. The temperature range covered by the CCS is above 0 C to below -40 C. Shear rate and stress must be calculated from dimensions and rotor speed; essentially, the shear rate is variable between 15,000 and 300,000 1/sec while the shear stress is constant at about 1,000,000 dynes/sq.cm.



Ubbelohde Suspended Level Capillary Viscometer (USLCV) -

A world-class instrument used for very accurate lower shear capillary viscometry, particularly at a variety of temperatures where the constant calibration constant of the instrument makes it superior to the more common Ostwald capillary viscometer (which is subject to calibration change with temperature because of the effect of temperature on the density of the fluid). The nominal capillary diameter of the USLCV instrument used was 0.63 mm, the bulb volume was 3.0 cubic cm, and the flow rates ranged from 286 to 382 seconds to empty the bulb. The average shear rate can be calculated from these values and the Kroepelin equation: The average shear rates ranged from about 260 to 360 1/sec. and the shear stresses from about 10 to 25 dynes/sq.cm.

Density -

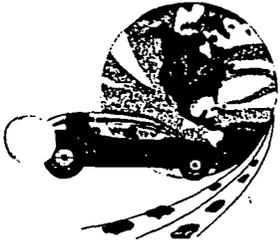
Work in the low-shear USLCV produced results in units of Kinematic Viscosity since the hydrostatic head is the force driving the fluid and the viscometric result is a consequence of both physical properties. These Kinematic values had to be converted to units of Absolute or Dynamic Viscosity in order to be compared to the high shear results (which, for obvious reasons associated with the absence of dependence on gravity to produce flow, are nearly always produced in units of Dynamic Viscosity). Since the Dynamic Viscosity can be found from the product of density multiplied by the Kinematic Viscosity, it was necessary to determine the density of the fluids at the temperature of viscometric test in the capillary. Savant Laboratories developed a method for determining density in the same high-temperature bath as used for capillary viscometry. This technique is known simply as the Savant Density Technique and it was used in the present evaluation.

RESULTS AND DISCUSSION

The raw results of the study are shown in Table 1. The wide viscosity differences in the two coolants made it necessary to develop special approaches including the use of reference fluids to specially calibrate the low temperature viscometers, particularly for the lowest viscosity coolant. In this case the Cannon Reference Fluid S-3 was applied to directly calibrate the CCS and the Brookfield viscometers at -40 C.

The Scanning Brookfield approach was not without problems since the low spindle speed used in this technique, 0.3 RPM, gave poor sensitivity at lowest viscosities. As a consequence, a further modification in the technique was made by running the viscometer at the highest speed which would keep the pen on the chart. The results of this technique are noted simply as Brookfield Technique.

The analyzed results taken from the raw data are given in Table 2. Here a quick perusal will show that neither of the fluids show marked departure from Newtonian behavior. This is evident in the similarities in viscosities taken at widely



different shear stresses. At the most, Coolant EC 721-38-7 shows a 10% decrease in viscosity at very high shear stresses in the CCS viscometer at low temperatures. This is almost within experimental error which latter is about 2% repeatability at the 95% confidence level with the Brookfield and about 3% repeatability at the 95% confidence level with the CCS for a combined error of 6% repeatability.

In special regard to the results with Coolant EC 721-38-7: of the two fluids examined, this latter coolant would be the one most expected to give non-Newtonian results principally because of its molecular configuration. Shear stresses of 1,000,000 dynes/sq.cm. show a marginally significant effect of shear stress on viscosity while shear stresses of less than 100,000 dynes/sq.cm. show none. A part of the difference in the results may also be attributed to the closer packing of the molecules at the lower temperature -- a condition which often leads to more shear dependence.

Within the different techniques tried at low temperature, the simple calibrated Brookfield gave the most dependable results and, as will be noted, these are the results used in the analyses presented in Table 2.

CONCLUSIONS

The study has shown that, to any meaningful degree, neither coolant study shows non-Newtonian behavior. Whether this fact is the most desirable situation or not has not been questioned. Conceivably, a strongly non-Newtonian coolant could give very desirable characteristics in reducing pumping losses.

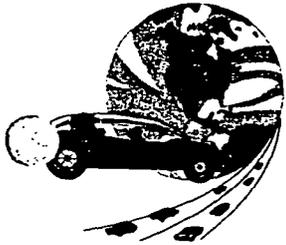
The study has also shown how state-of-the-art equipment and techniques give very acceptable results at both low and high temperatures and shear stresses/rates. Use of shear stress rather than shear rate as a measure of viscometric response is the best approach toward the distinction of non-Newtonian behavior.

Signed

Madame Kelly

Date

85-9-11



(TABLE 1)

Data Summary

PROJECT: DCC-02
DATE: 1985 August 30

High-Temperature Tests:

Sample	KV150	Dens@150	Calc@150	TBS150
S850802P	4.74 cSt.	0.8480 g./ml.	4.02 cP.	4.13 cP.
S850802Q	6.43 cSt.	0.9864 g./ml.	6.34 cP.	6.49 cP.

Low-Temperature Tests:

Sample	Temp., C.	CCS	SBT, #1	SBT, #2	Brkfld Visc.
S850802P	-40	165 cP.	-----	-----	158 cP.
S850802Q	0	940 cP.	-----	-----	-----
	-5	1610 cP.	1956 cP.	1298 cP.	1705 cP.
	-10	2940 cP.	3358 cP.	2775 cP.	3226 cP.
	-15	6200 cP.	6890 cP.	6429 cP.	6818 cP.
	-20	-----	17330 cP.	16920 cP.	17630 cP.

NOTE: Savant ID Dow Corning ID
S850802P EC 721-38-17
S850802Q EC 721-38-7

SIGNED: David A. Piasecki



TABLE 2

Comparison of Viscosities of Experimental Coolants
at Different Temperatures and Shear Conditions

Coolant	Savant ID#	Device/ Technique	Temp. C	Shear Stress, Dyne/sq.cm.	Viscosity, cP		Ratio
					Low Temp.	High Temp.	
EC 721-38-							
17	s 850802 p	Brookfield	-40	1,000	158		
17	"	CCS	-40	1,000,000	165		0.96
17	"	USLCV	150	10		4.02✓	
17	"	TBS	150	40,000		4.13✓	0.97
7	s 850802 q	Brookfield	-5	2,370	1700		
7	"	CCS	-5	1,000,000	1610		1.06
7	"	Brookfield	-10	4,840	3230		
7	"	CCS	-10	1,000,000	2940		1.10
7	"	Brookfield	-15	4,540	6820		
7	"	CCS	-15	1,000,000	6200		1.10
7	"	USLCV	150	25		6.34✓	
7	"	TBS	150	65,000		6.49✓	0.98



DOW CHEMICAL U.S.A.

MICHIGAN DIVISION
August 26, 1985

MIDLAND, MICHIGAN 48674

Robert R. Buch
Dow Corning Corporation
408 Building
Midland, MI 48686

Dear Bob:

The new hot-wire transient technique for the absolute determination of thermal conductivity of liquids was used to investigate the two silicone oil samples (Ref: E6721-38-8 and E6721-38-18). The theory of the transient technique is well discussed elsewhere; J. J. DeGroot, J. Kestin and H. Sookiazian, "Instrument to Measure the Thermal Conductivity of Gases," *Physica* 75, 454-482, 1974.

Numerous values at each of the twelve temperatures (27-159°C) were determined for each sample. Average values for each temperature of the two samples are given in the attached Tables I and IV, along with the temperature dependent quadratic equations (Tables II and V) obtained by a curve fitting of the observed data. The percent deviation of the experimental data from the derived quadratic equation is <0.5 for both samples. Caution: DO NOT use these equations to obtain data below 10°C or above 170°C.

The temperature dependence thermal conductivity is nonlinear for Ref: E6721-38-18, see attached Figure 1.

Sincerely,
8

George C. Karris

George C. Karris
Analytical Labs
Thermal Group
1707 Building

jw

Attachments

cc: T. W. McGee, 1707 Building
W. R. Kracht, 1707 Building

TABLE I

AUG 08, 1985 15:40:06 ---- PHYSICO-CHEMICAL STUDIES ---- DATASET 1 PAGE 3

'THERM. COND. OF SILICONE OIL E6721-38-8, G.C.KARRIS 8-10-85'

CURVE FITTING BY ORTHOGONAL POLYNOMIAL OF POWERS 0 BY 1 TO 2

NO.	SCALE X	ACT. X °C	Y (OBS.) $\lambda, W/(m-k)$	OBS-CALC	% DEV
1	-0.952381	29.9000	0.13800	-0.00017	-0.123
2	-0.862311	36.0000	0.13810	0.00033	0.238
3	-0.775194	41.9000	0.13750	0.00014	0.101
4	-0.639350	51.1000	0.13630	-0.00037	-0.272
5	-0.503507	60.3000	0.13570	-0.00022	-0.160
6	-0.361757	69.9000	0.13510	0.00003	0.026
7	-0.221484	79.4000	0.13450	0.00034	0.256
8	-0.079734	89.0000	0.13320	0.00003	0.022
9	0.066445	98.9000	0.13210	0.00002	0.013
10	0.361757	118.9000	0.12950	-0.00017	-0.130
11	0.652639	138.6000	0.12700	-0.00000	-0.003
12	0.952381	158.9000	0.12400	0.00004	0.031

TABLE II

AUG 08, 1985 15:40:06 ----- PHYSICOCHEMICAL STUDIES ----- DATASET 1 PAGE 1

'THERM. COND. OF SILICONE OIL E6721-38-8, G.C.KARRIS 8-10-85'
 CURVE FITTING BY ORTHOGONAL POLYNOMIAL OF POWERS 0 BY 1 TO 2

U = 4 WEIGHT = 1 PS = 0 PD = 1 FF = 2
 TL = 0.0 DT = 10.00 TH = 180.00000
 CP TOLERANCE = 1.00%
 SL = 0.0 HL = 0.0 TREF = 0.0

SCALE FACTOR LINEAR TRANSLATION A B FRAC ERR REDUC FAC
 67.7250000000 94.4000000000 -1.000 1.000 1.000D-09 1.00000

DIAGNOSTIC STATISTICS TABLE

PWR	DF	PCT	RMS % DEV	SUM DEVSQ/DF	RATIO	SUM WT*DEVSQ	RATIO
0	11	.122D-02	3.493	.204D-04	0.0000	.224D-03	0.0002
1	10	.229D-04	0.478	.399D-06	0.0196	.399D-05	0.0178
2	9	.295D-05	0.172	.545D-07	0.1367	.490D-06	0.1230

2TH POWER (FINAL) POLYNOMIAL COEFFICIENTS FOR Y = F(SCALED T)
 .132586499752 -7.45922661576D-03 -1.67683693761D-03

NON-SCALED POLYNOMIAL COEFFICIENTS FOR Y = F(T)
 .139725813951 -4.11167888049D-05 -3.65588734566D-07 ; 10-170°C*

* Caution: Do NOT use this equation to obtain data
 below 10°C or above 170°C

TABLE III

AUG 08, 1985 15:40:06 ---- PHYSICOCHEMICAL STUDIES ---- DATASET 1 PAGE 2

'THERM. COND. OF SILICONE OIL E6721-38-8, G.C.KARRIS 8-10-85'

CURVE FITTING BY ORTHOGONAL POLYNOMIAL OF POWERS 0 BY 1 TO 2

SCALE X	$^{\circ}\text{C}$ ACT. X	$\lambda, W/(m-k)$	DY/DX	D2Y/DX2
-1.393872	0	.13973	-4.1117D-05	-7.3118D-07
-1.246216	10.000	.13928	-4.8429D-05	-7.3118D-07
-1.098560	20.000	.13876	-5.5740D-05	-7.3118D-07
-0.950904	30.000	.13816	-6.3052D-05	-7.3118D-07
-0.803248	40.000	.13750	-7.0364D-05	-7.3118D-07
-0.655592	50.000	.13676	-7.7676D-05	-7.3118D-07
-0.507937	60.000	.13594	-8.4987D-05	-7.3118D-07
-0.360281	70.000	.13506	-9.2299D-05	-7.3118D-07
-0.212625	80.000	.13410	-9.9611D-05	-7.3118D-07
-0.064969	90.000	.13306	-1.0692D-04	-7.3118D-07
0.082687	100.00	.13196	-1.1423D-04	-7.3118D-07
0.230343	110.00	.13078	-1.2155D-04	-7.3118D-07
0.377999	120.00	.12953	-1.2886D-04	-7.3118D-07
0.525655	130.00	.12820	-1.3617D-04	-7.3118D-07
0.673311	140.00	.12680	-1.4348D-04	-7.3118D-07
0.820967	150.00	.12533	-1.5079D-04	-7.3118D-07
0.968623	160.00	.12379	-1.5811D-04	-7.3118D-07
1.116279	170.00	.12217	-1.6542D-04	-7.3118D-07
1.263935	180.00	.12048	-1.7273D-04	-7.3118D-07

20

TABLE IV

AUG 14, 1985 8:07:42 ---- PHYSICOCHEMICAL STUDIES ---- DATASET 1 PAGE 3

'THER. COND. OF SILICONE OIL E6721-38-18, G.C.KARRIS 8-14-85'

NO.	SCALE X	ACT. X	Y (OBS.)	OBS-CALC	% DEV
			$\lambda, W/(m-k)$		
1	-0.952381	27.2000	0.15220	-0.00025	-0.165
2	-0.840847	34.9000	0.15130	0.00019	0.123
3	-0.746696	41.4000	0.15030	0.00033	0.219
4	-0.611986	50.7000	0.14820	-0.00011	-0.076
5	-0.475828	60.1000	0.14640	-0.00021	-0.143
6	-0.339670	69.5000	0.14480	-0.00008	-0.055
7	-0.202064	79.0000	0.14320	0.00010	0.067
8	-0.060112	88.8000	0.14120	-0.00004	-0.030
9	0.083288	98.7000	0.13950	0.00017	0.120
10	0.371537	118.6000	0.13540	-0.00000	-0.001
11	0.658338	138.4000	0.13120	-0.00017	-0.130
12	0.952381	158.7000	0.12720	0.00009	0.069

TABLE V

AUG 14, 1985 8:07:42 ---- PHYSICOCHEMICAL STUDIES ---- DATASET 1 PAGE 1

'THER. COND. OF SILICONE OIL E6721-38-18, G.C.KARRIS 8-14-85'
 CURVE FITTING BY ORTHOGONAL POLYNOMIAL OF POWERS 0 BY 1 TO 2

U = 4 WEIGHT = 1 PS = 0 PD = 1 PF = 2
 TL = 0.0 DT = 10.00 TH = 180.00000
 CP TOLERANCE = 1.00%
 SL = 0.0 HL = 0.0 TREF = 0.0

SCALE FACTOR	LINEAR TRANSLATION	A	B	FRAC ERR	REDUC FAC
69.0375000000	92.9500000000	-1.000	1.000	1.000D-09	1.00000

DIAGNOSTIC STATISTICS TABLE

PWR	DF	PCT	RMS % DEV	SUM DEVSQ/DF	RATIO	SUM WT*DEVSQ	RATIO
0	11	.344D-02	5.867	.644D-04	0.0001	.709D-03	0.0007
1	10	.495D-05	0.223	.100D-06	0.0016	.100D-05	0.0014
2	9	.179D-05	0.134	.383D-07	0.3824	.345D-06	0.3441

2TH POWER (FINAL) POLYNOMIAL COEFFICIENTS FOR Y = F(SCALED T)
 .140445613340 -1.33029649111D-02 -7.32386763998D-04

NON-SCALED POLYNOMIAL COEFFICIENTS FOR Y = F(T)
 .157028715397 -1.64125848299D-04 -1.53663377427D-07 ; 10-170°C*

** Caution : Do NOT use this equation to obtain data
 below 10°C or above 170°C.*

TABLE VI

AUG 14, 1985 8:07:42 ---- PHYSICO-CHEMICAL STUDIES ---- DATASET 1 PAGE 2

'THER. COND. OF SILICONE OIL E6721-38-18, G.C.KARRIS 8-14-85'
 CURVE FITTING BY ORTHOGONAL POLYNOMIAL OF POWERS 0 BY 1 TO 2

SCALE X	ACT. X	$\lambda, W/(m-k)$	DY/DX	D2Y/DX2
-1.346370	0	.15703	-1.6413D-04	-3.0733D-07
-1.201521	10.000	.15537	-1.6720D-04	-3.0733D-07
-1.056672	20.000	.15368	-1.7027D-04	-3.0733D-07
-0.911823	30.000	.15197	-1.7335D-04	-3.0733D-07
-0.766974	40.000	.15022	-1.7642D-04	-3.0733D-07
-0.622126	50.000	.14844	-1.7949D-04	-3.0733D-07
-0.477277	60.000	.14663	-1.8257D-04	-3.0733D-07
-0.332428	70.000	.14479	-1.8564D-04	-3.0733D-07
-0.187579	80.000	.14292	-1.8871D-04	-3.0733D-07
-0.042730	90.000	.14101	-1.9179D-04	-3.0733D-07
0.102118	100.00	.13908	-1.9486D-04	-3.0733D-07
0.246967	110.00	.13712	-1.9793D-04	-3.0733D-07
0.391816	120.00	.13512	-2.0101D-04	-3.0733D-07
0.536665	130.00	.13310	-2.0408D-04	-3.0733D-07
0.681514	140.00	.13104	-2.0715D-04	-3.0733D-07
0.826362	150.00	.12895	-2.1022D-04	-3.0733D-07
0.971211	160.00	.12683	-2.1330D-04	-3.0733D-07
1.116060	170.00	.12469	-2.1637D-04	-3.0733D-07
1.260909	180.00	.12251	-2.1944D-04	-3.0733D-07

○ #18
△ #8

FIGURE 1

~~THERMAL CONDUCTIVITY VS. TEMPERATURE~~
OF

SILICONE OIL: E6721-38-8 (710)
SILICONE OIL: E6721-38-18 (200)

$$\lambda \left(\frac{W}{M^2K} \right) = A + BT + CT^2$$

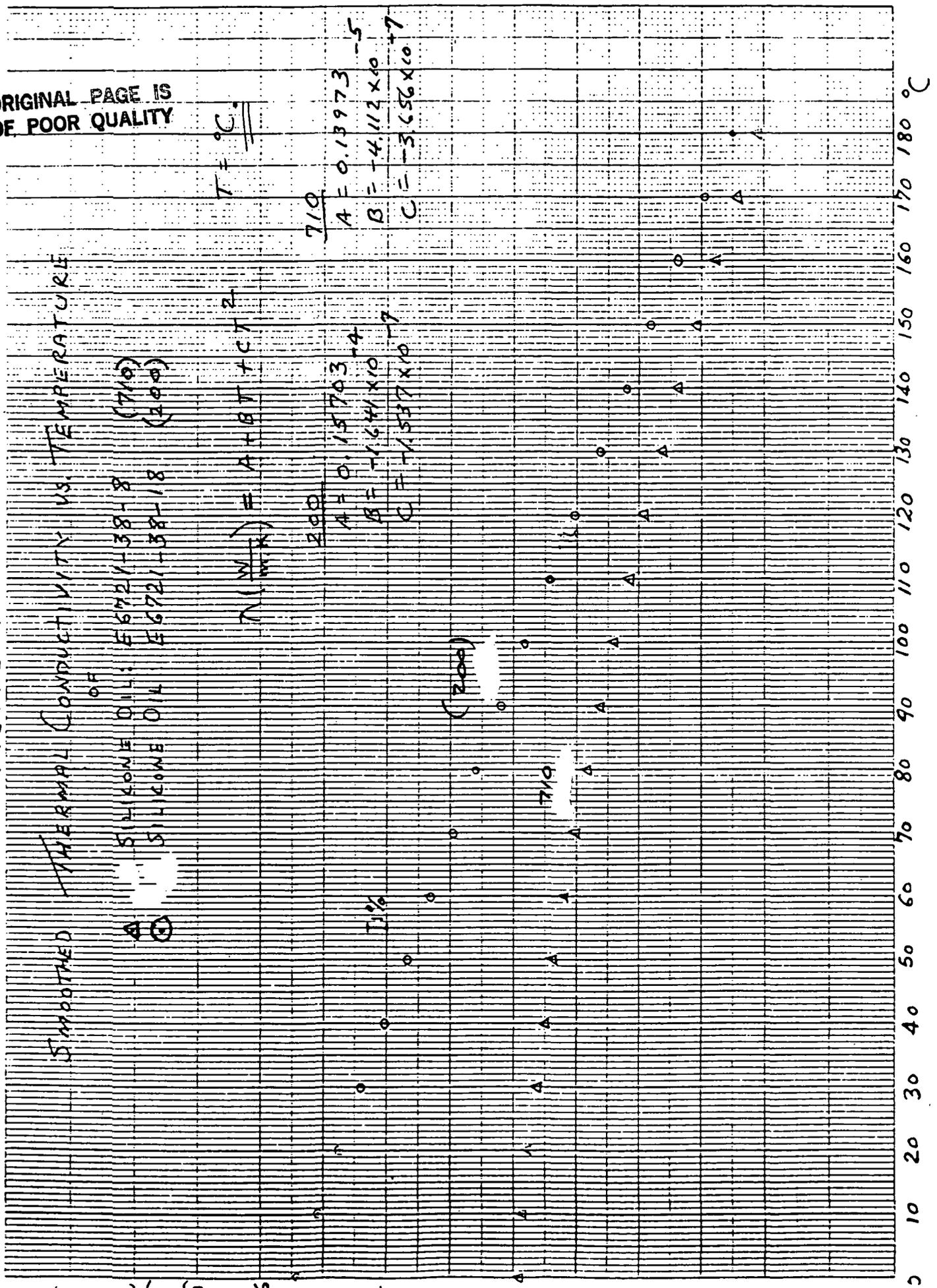
200

A = 0.15703 - 4
B = -1.641 x 10⁻⁷
C = -1.537 x 10⁻⁷

710

A = 0.13973 - 5
B = -4.112 x 10⁻⁷
C = -3.656 x 10⁻⁷

$$T = \text{°C}$$



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AUTHOR: A. L. SMITH
DEPARTMENT: ANALYTICAL RESEARCH
DATE: 19850828
TITLE: INFRARED EMISSION SPECTRA OF TWO SELECTED SILICONE FLUIDS

ABSTRACT

We were requested to measure the emissivity and transmittance of two candidate fluids over the wavelength range 3 to 55 micrometers. The emissivity was measured at 150C from 3 to 25 micrometers using the Nicolet FTIR spectrometer together with an external oven and first surface mirrors to direct the radiation into the spectrometer. Because of detector limitations, it was not possible to include the segment 25 to 55 μ ; however, this includes only a relatively small portion of the total energy. Both fluids act as quite good black bodies in thicknesses of ca. 0.5 mm.

Transmission was measured at two fluid thicknesses over the entire wavelength range.

INFORMATION RETRIEVAL INDEX

Infrared emission, Infrared emissivity, Fluid droplet emissivity, Liquid droplet radiator.

INTRODUCTION

As a part of contract NAS3-24400 between Dow Corning and NASA- Lewis Research Center entitled "Evaluation of Working Fluids for the Liquid Droplet Radiator" we were asked to measure:(1) the emissivity and (2) the fraction of energy transmitted as a function of wavelength through a nonopaque layer of fluid in the range 3-55 micrometers. The Nicolet 60SX FTIR spectrometer was utilized to make these measurements, although detector limitations precluded emission measurements in the 25-55 μ range.

Emissivity is defined as the emittance of a thick (optically opaque) layer. Emittance is defined in two ways: radiant flux per unit area; or as the ratio of radiant flux to the flux of a blackbody at the same temperature and viewing geometry. The latter definition was used in the work described here.

Transmission measurements were obtained in the usual manner, using liquid cells of appropriate thickness and also liquid films on thin polyethylene sheet.

RESULTS AND DISCUSSION

The two fluids tested are identified below.

Analytical Sample No.	Reference No.	Fluid Type	Fluid No.
71583	E6721-38-5	DC 710 Fluid cut (PhMeSiO)	5
71584	E6721-38-15	DC 200 Fluid cut (Me2SiO)	15

An initial run was made using the TGS (room temperature) detector in order to insure that the equipment was properly aligned and functioning. The emission spectrum of a thin film (ca. 0.01 mm) of fluid No. 5 was obtained and is shown in Fig. 1. The spectrum is quite recognizable and confirms that the system was working properly.

A trial run with the cooled detector (MCT) gave results which indicated that best results would be obtained with longer spectrum accumulation time--at least 5 min. Parameters were set to give the best results (Table 1). Spectra were then obtained for the two fluid samples at a thickness of ca. 0.5 mm, and for two "blackbody" samples.

One blackbody sample consisted of soot from a fuel-rich methane flame, deposited in an Al sample cup. This blackbody was visually nearly perfect, in that it absorbed nearly all the incident light. The second sample consisted of a thick (1 mm) layer of powdered graphite in an Al cup. Although it was not as absorbing of visible light as the soot specimen, it was a better blackbody emitter in the infrared (Fig. 2), probably because the methane soot sample was not thick enough. The graphite blackbody spectrum was therefore used for reference.

A calculated Planck function for 423 K is shown in Fig. 3, and may be compared with the observed blackbody curve. Dividing the blackbody curve by the Planck function curve gives the instrument function (Fig. 4).

Single beam spectra were obtained and ratioed as explained in the EXPERIMENTAL section. Results of the emission experiment are shown in Figs. 5 and 6. The ordinate indicates the percent of blackbody emission given off by the sample. It is observed that both fluids are excellent blackbodies, except in the 2000-3000 cm^{-1} region. It is well known, of course, that strong absorbers are also strong emitters, so it is no surprise that the silicone fluids, which absorb strongly in the infrared, are also good blackbodies.

Results of the transmission measurements are shown in Figs. 7-10. Because it is difficult to obtain a cell thickness of 0.02 mm with any accuracy, spectra were run as 20% (w/v) solutions in 0.1 mm cells. Spectra taken at 0.2 mm (Fig. 8) show very strong absorption. The far infrared (500-100 cm^{-1}) spectra were more difficult to obtain because of the intrinsically low energy in this region, and the lack of suitable cell materials. The approximate thicknesses of these samples were 0.1 and 0.01

mm. Results are shown in Figs. 9 and 10. Operating parameters are listed in Table 1.

EXPERIMENTAL

The Fourier transform infrared spectrometer was a Nicolet 60 SX, adapted for emission measurements by removing the external source cover and temporarily placing a 45 degree first-surface mirror, mounted on a heavy base, in the instrument in such a position as to direct external radiation into the interferometer. A temporary aluminum shield was placed in front of the source to prevent any radiation from leaking around the 2 7/8 x 3 3/4 in. diagonal mirror. For the initial range-finding experiments, the TGS detector was used, but for the final work, the cooled MCT detector, which is a factor of 5 more sensitive, was used.

The use of a cooled detector introduces some special problems, since the detector picks up radiation from the beam splitter and other room-temperature components of the spectrometer. To correct for these effects, it is necessary to make four measurements: sample at 150 C and at room temperature (21 C); and blackbody at 150 C and 21 C (1). The interferograms for the measurements at the two temperatures are subtracted, transformed to give single beam spectra, and then ratioed to give a percent of blackbody emission.

The oven was adapted from the oven used for chemiluminescence measurements, and has been described (2). The photomultiplier was removed from the top, and replaced with a clamp arrangement which carried another 2 7/8 x 3 3/4 in. mirror to direct the sample radiation into the spectrometer (Fig. 11). Samples were placed into 2 in. aluminum foil cups, which in turn fit into the sample carrier in the interior of the oven. The temperature was regulated using a thermocouple imbedded in the metal wall of the sample carrier, and the heating elements were also imbedded in the box surrounding the sample. The temperature of the air in the sample compartment was monitored with another thermocouple to 1 degree C, and was

taken as the sample temperature after time for equilibration.

Data manipulation is easily accomplished with existing software. To subtract interferograms, the specific commands are: CLS, CLB, BKS (SAM - BKG), to SAM. FPS gives the single beam spectrum. Ratio using RAS with sample in SAM and blackbody in BKG. Mathematically,

$$\epsilon = \frac{E(\text{sample}) \text{ corr.}}{E(\text{blackbody}) \text{ corr.}}$$

where E corr. = transform{IG(T2) - IG(T1)}

Interferograms and intermediate spectra are filed in destination files until needed and moved into the proper file using the OFN and MOX commands. To generate the Planck function, set TBB = 423 K and EMY = RN. Then use BBG to generate the Planck curve.

Table 1

Parameters used were:

Run No.	PFN	DET	GAN	NSS=NSB	NDP	NTP
1 Emiss.	5	TGS	1	128	2048	4096
2 "	6	MCT	8	256	2048	4096
3 "	6	MCT	8	2000	2048	4096
Trans.	1	TGS	1	32	8182	16384
Trans.	2	TGS-FIR	8	256	2048	4096

DOCUMENTATION

Documentation for this report is found in book 6369, pp. 86 through 95.

REFERENCES

1. D. Kember, D. H. Chenery, N. Sheppard and J. Fell, Spectrochim. Acta 35A, 455, (1979).
2. A. Lee Smith, Dow Corning Research Report I-0030-5728 (Dec. 31, 1984).

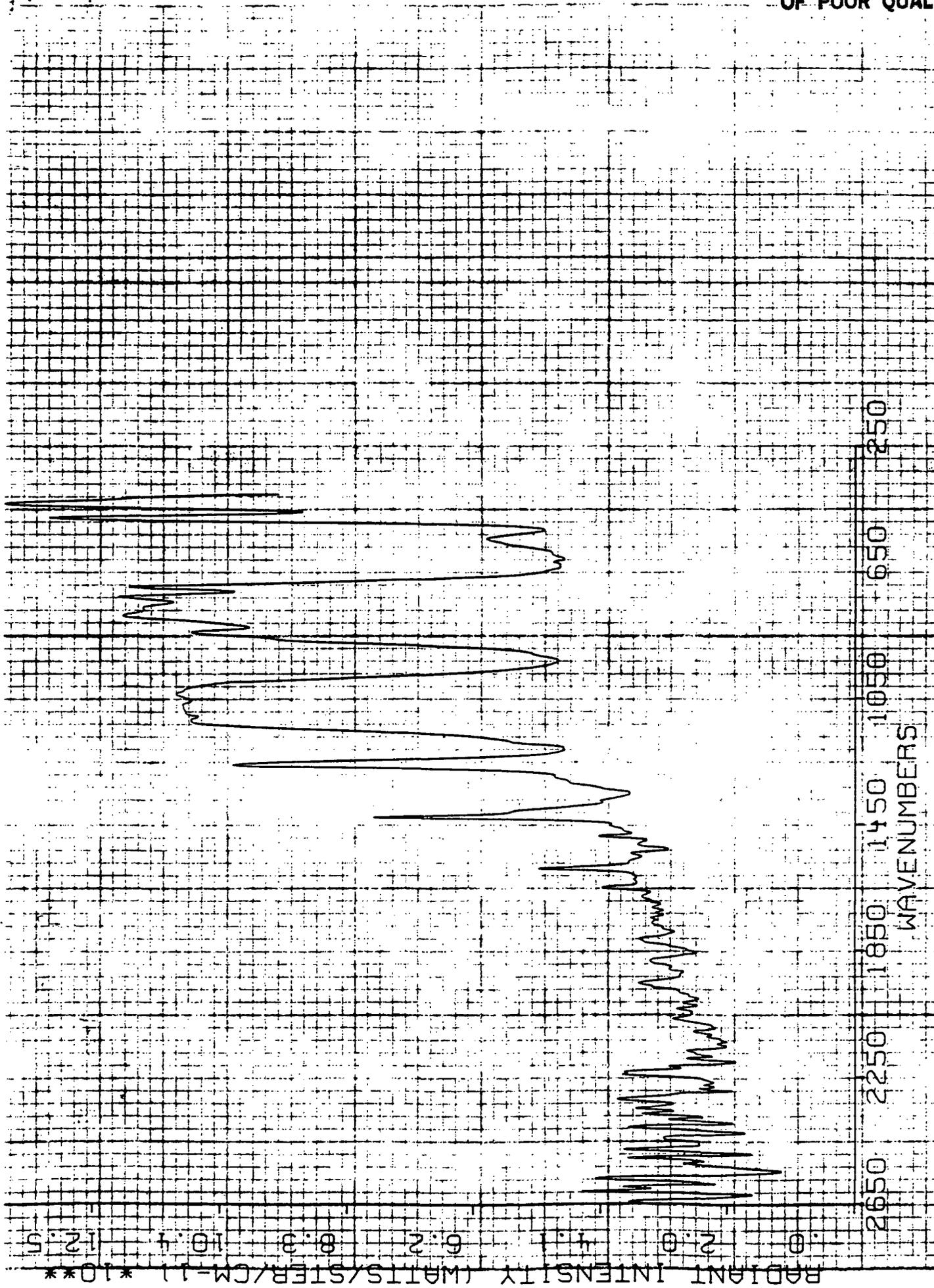
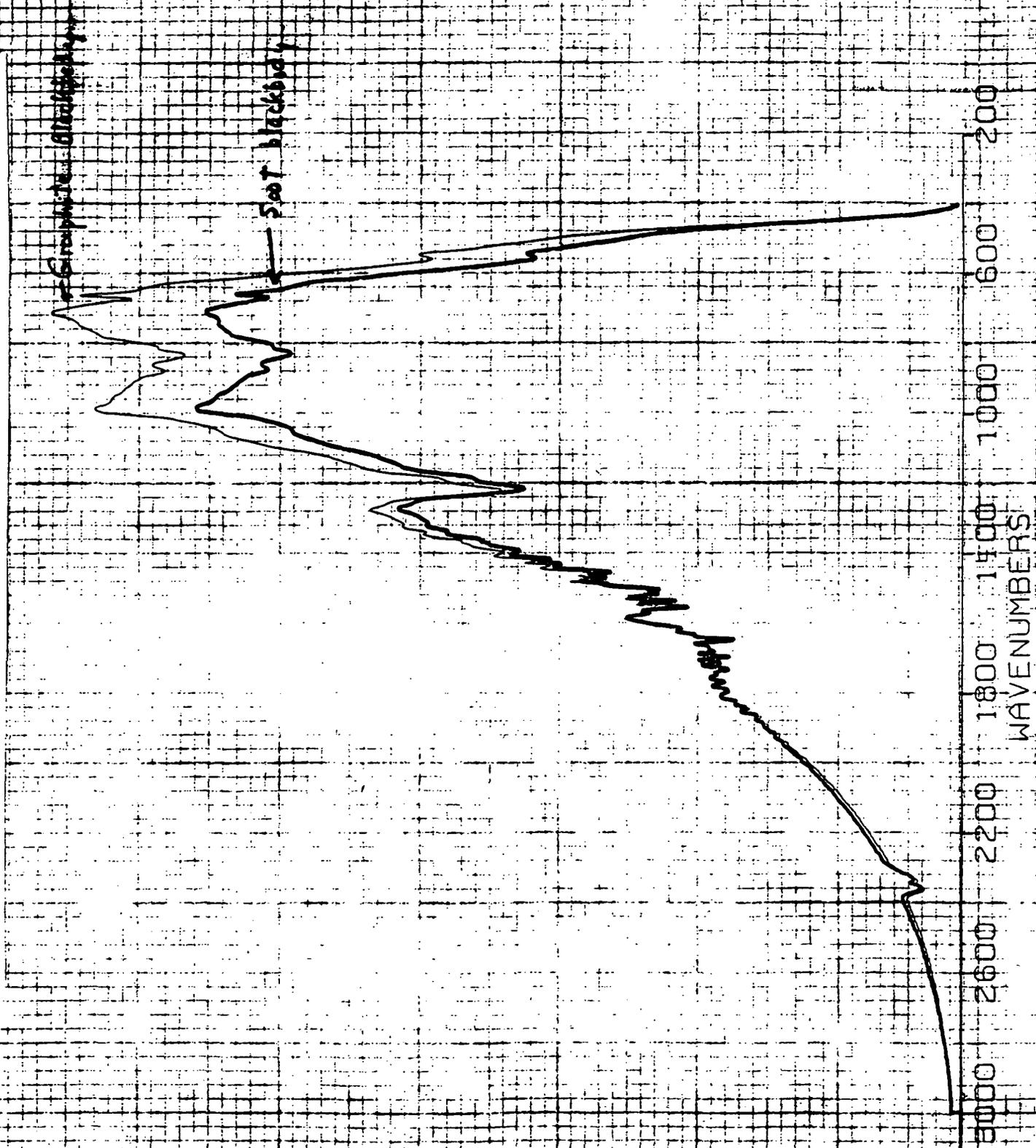


Fig. 1. Emission spectrum of a thin film of Sample No. 5 at 150 C.

Fig. 2. Emission spectra of soot and graphite blackbodies.



8-21-85

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Fig. 3. Planck function for 423 K.

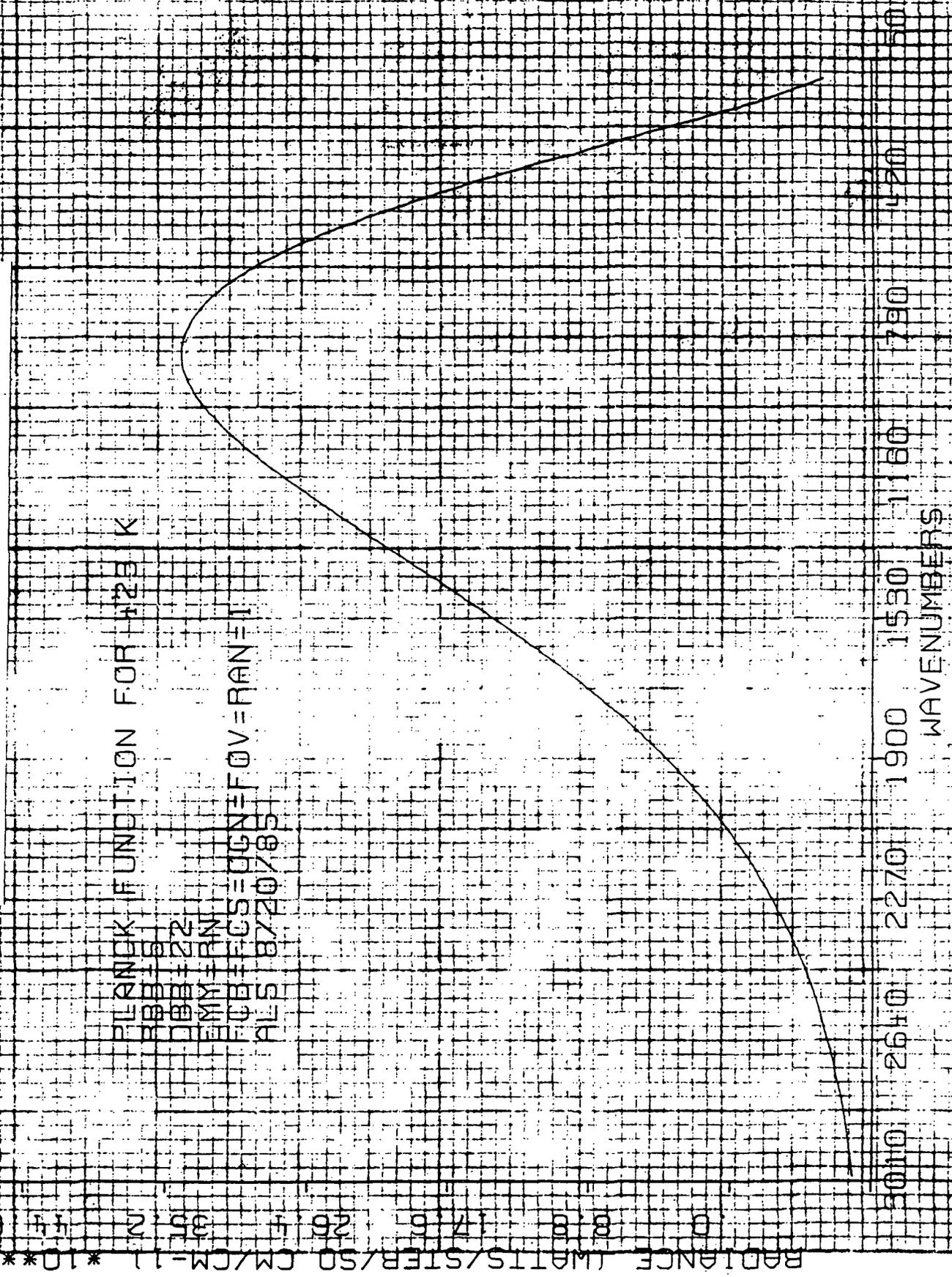


Fig. 4. Instrument response function for a blackbody at 423 K.

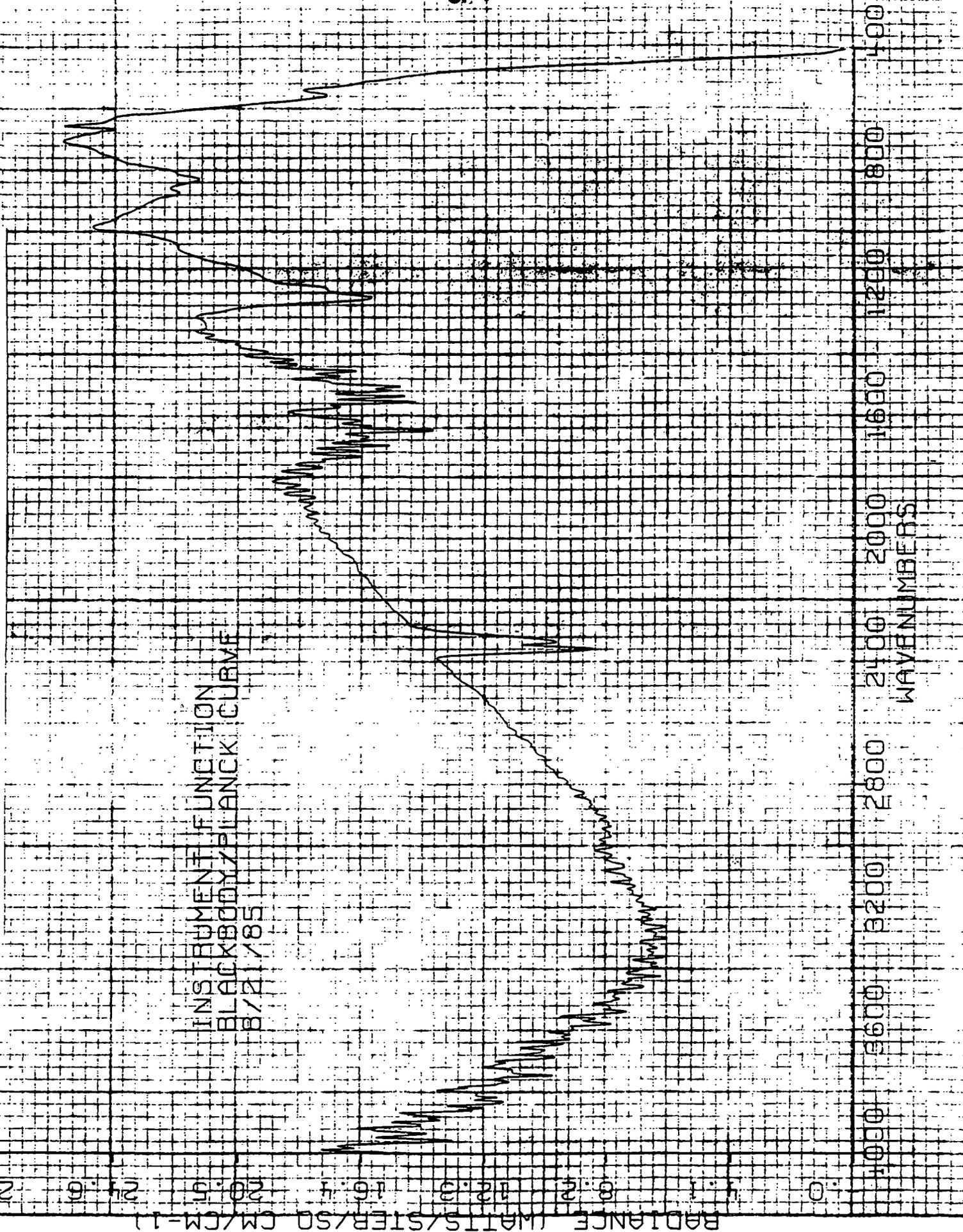


Fig. 5. Emission spectrum of a 0.5 mm layer of Sample No. 5.

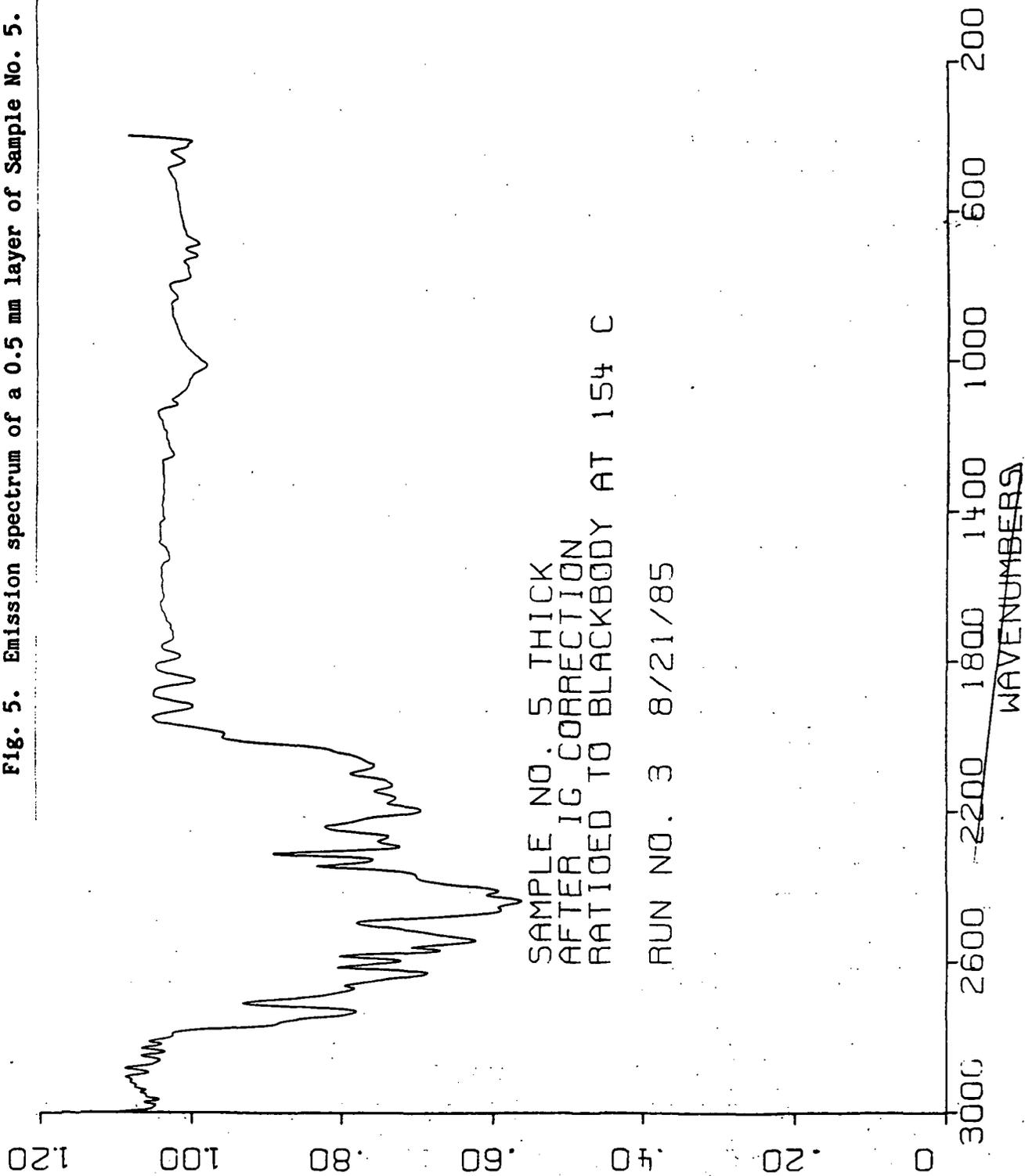
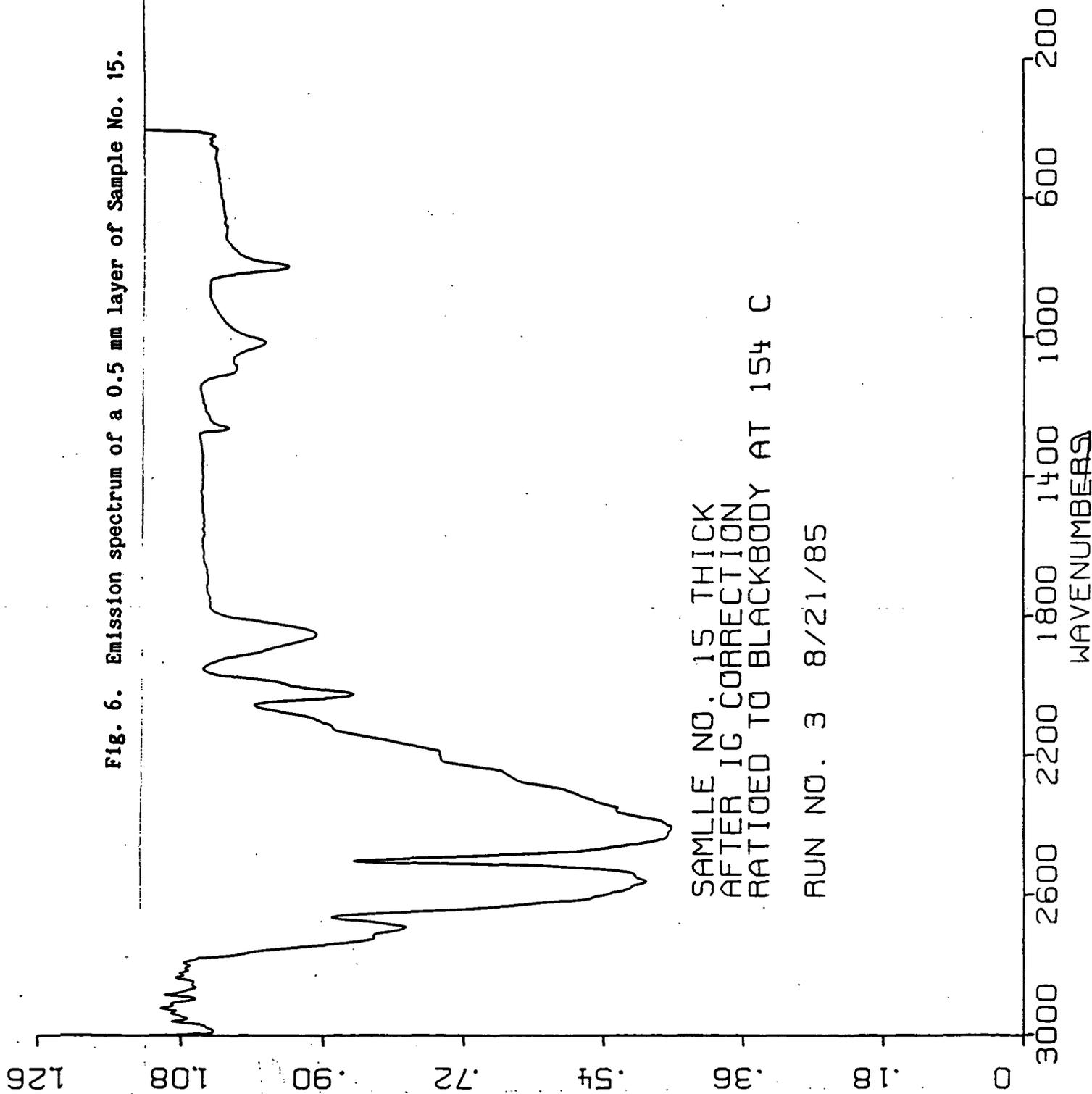


Fig. 6. Emission spectrum of a 0.5 mm layer of Sample No. 15.



SAMPLE NO. 15 THICK
AFTER 1G CORRECTION
RATIOED TO BLACKBODY AT 154 C

RUN NO. 3 8/21/85

Fig. 7. Transmission spectra of fluids in 20% solution in a 0.1 mm cell.

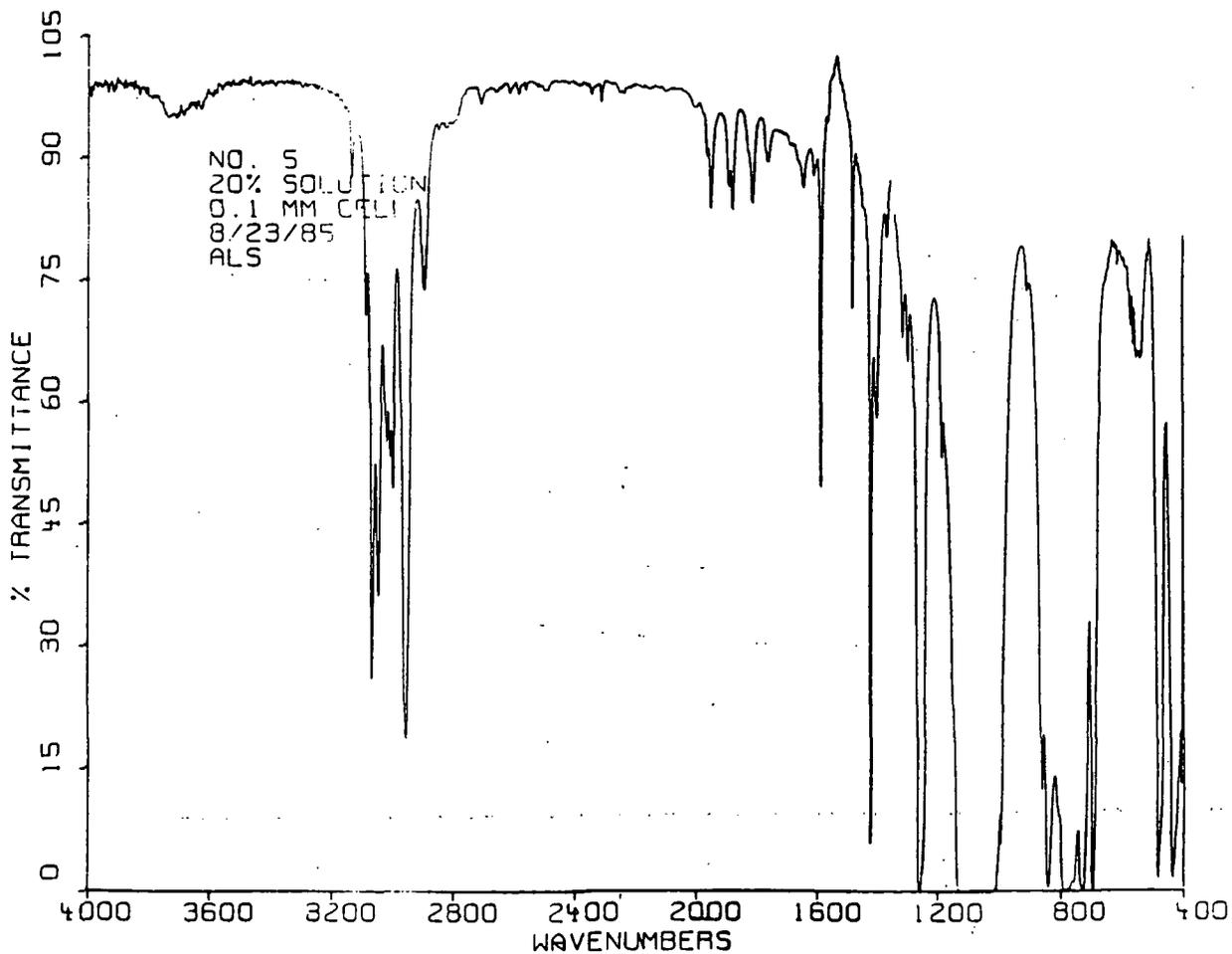
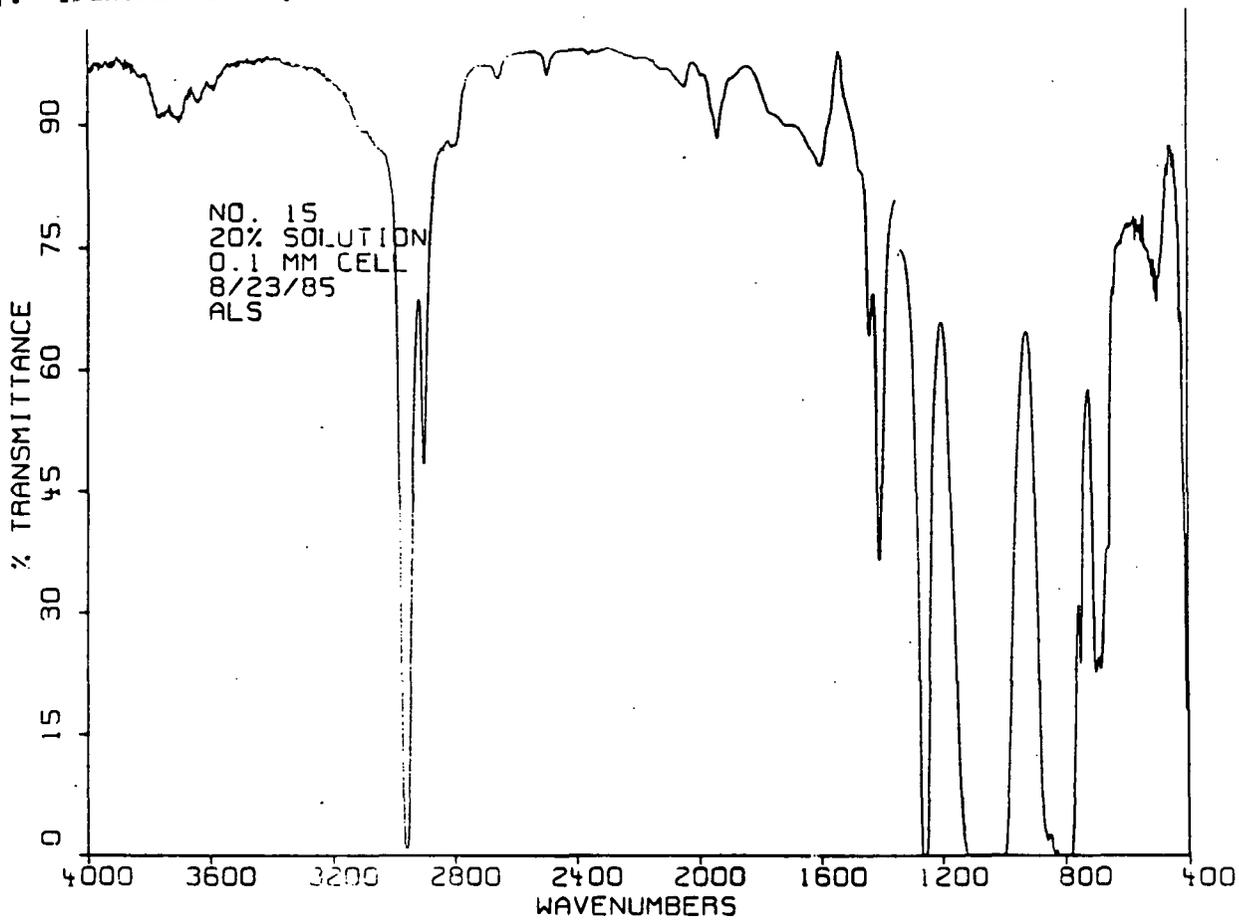


Fig. 8. Transmission spectrum of a 0.2 mm layer of Sample No. 5.

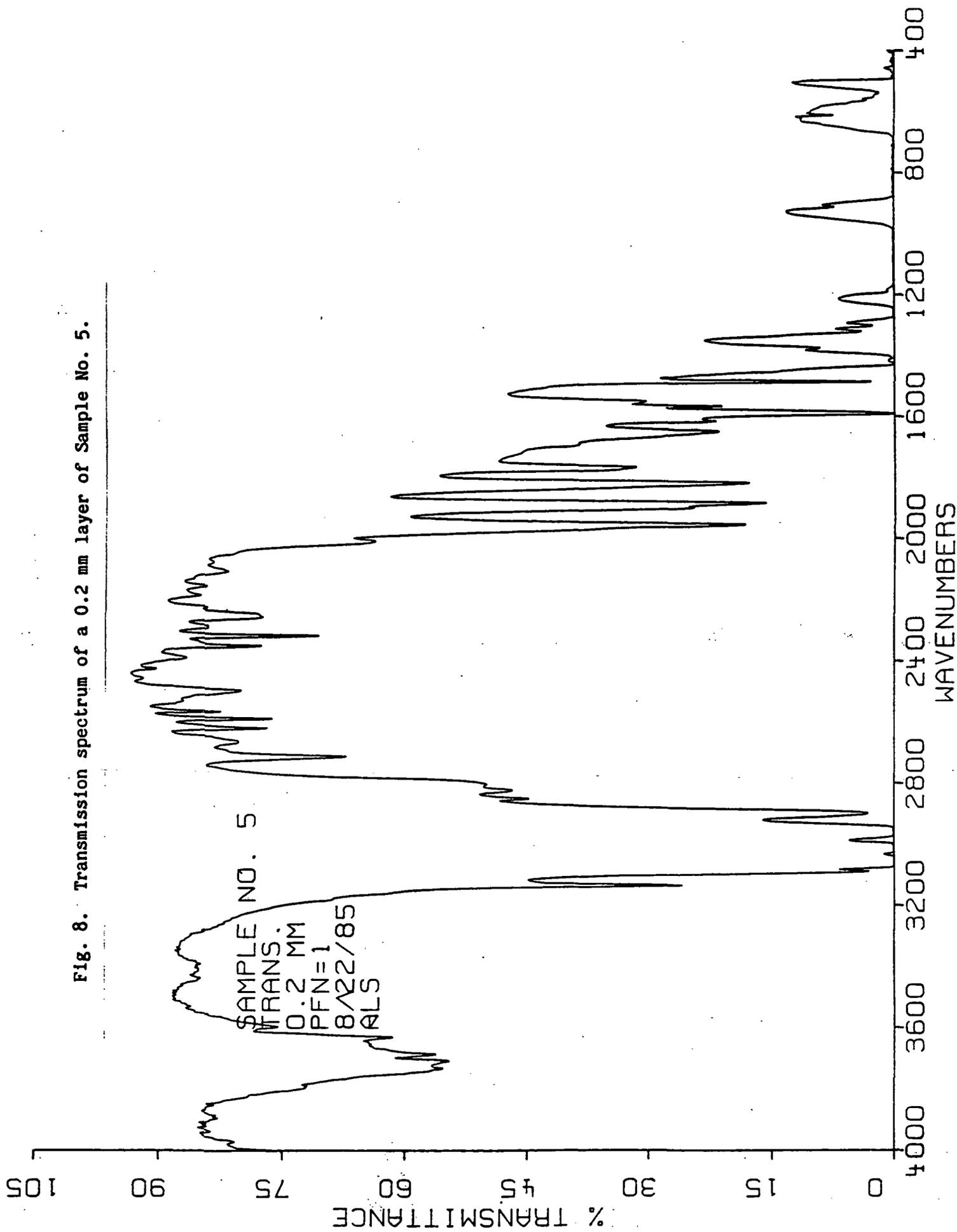
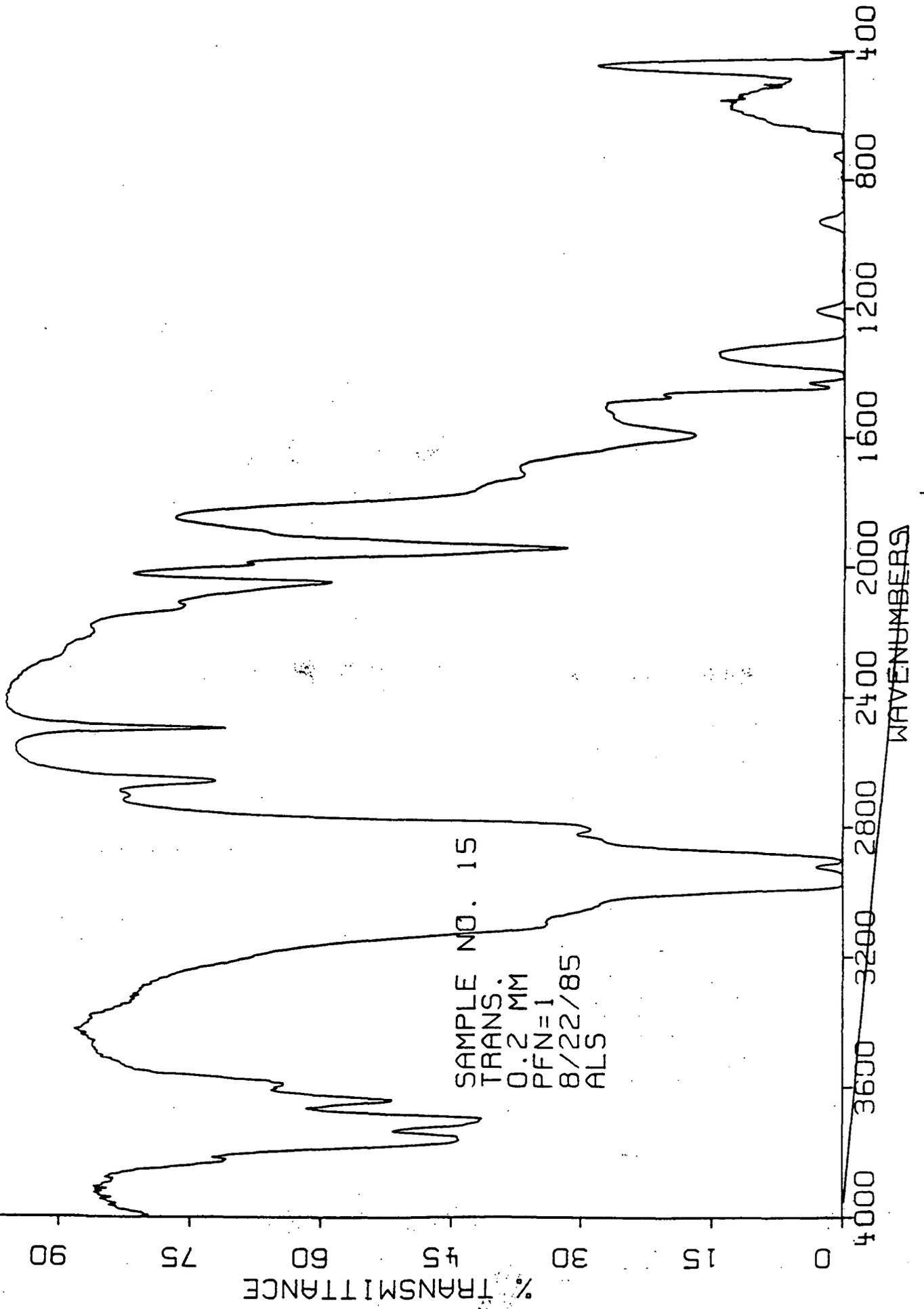


Fig. 9. Transmission spectrum of a 0.2 mm layer of Sample No. 15.



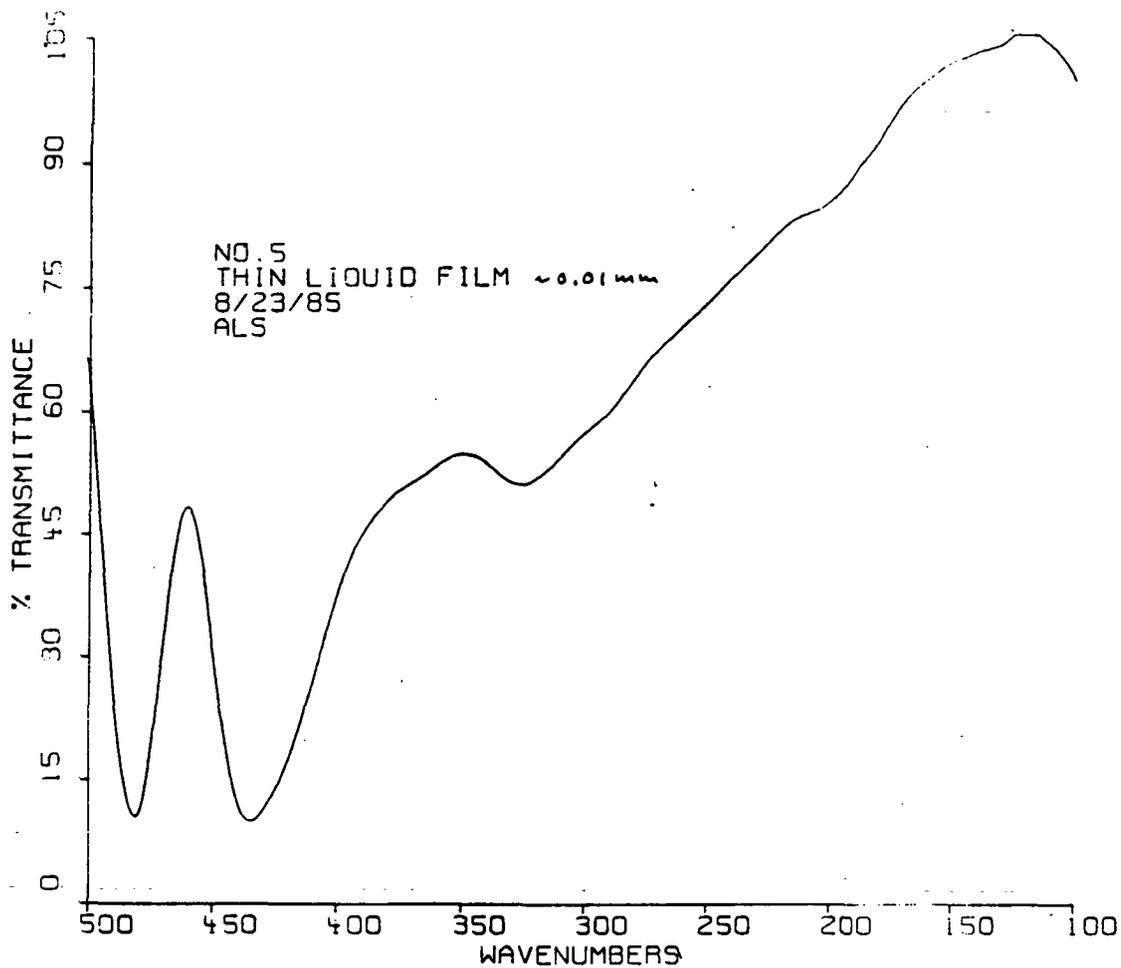
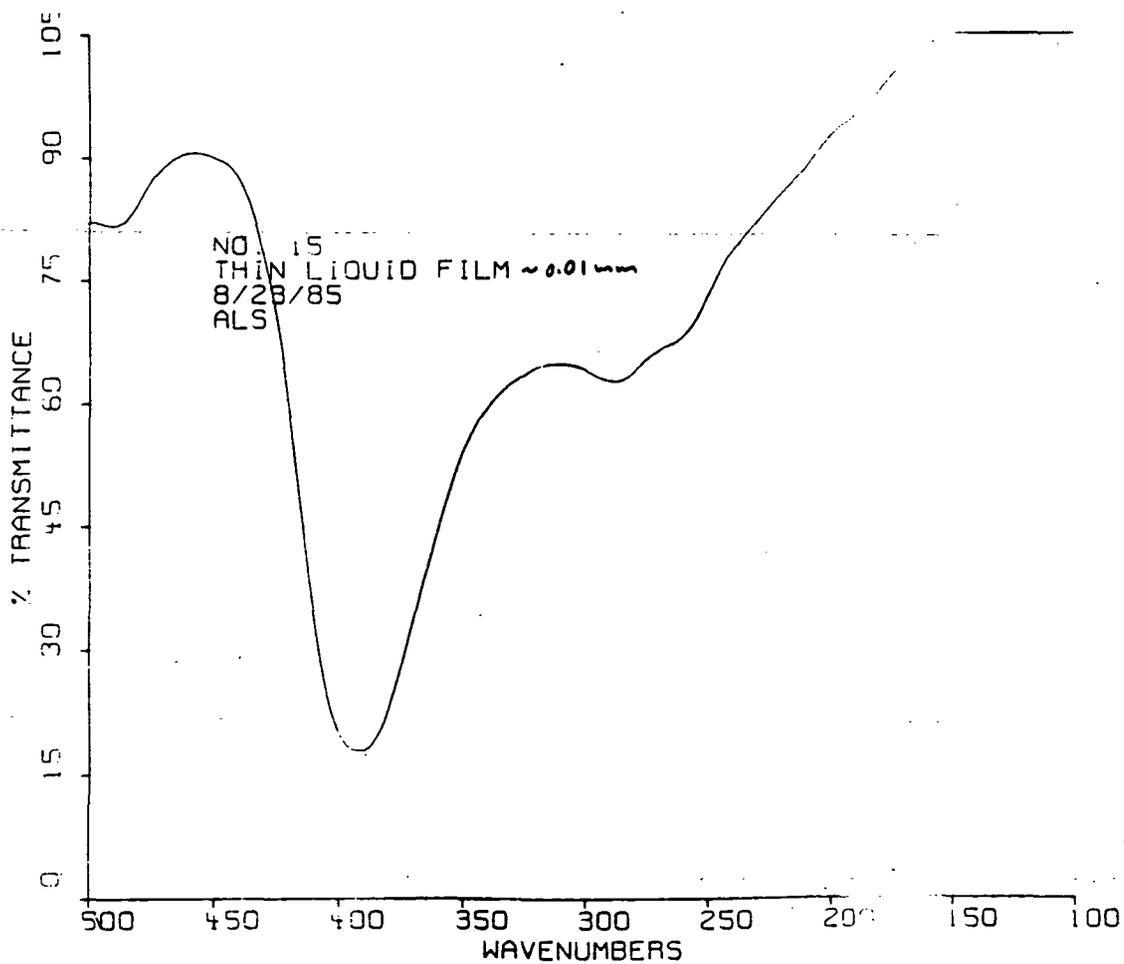


Fig. 10. Transmission spectra of a ca. 0.01 mm layer of fluids in the far IR region.



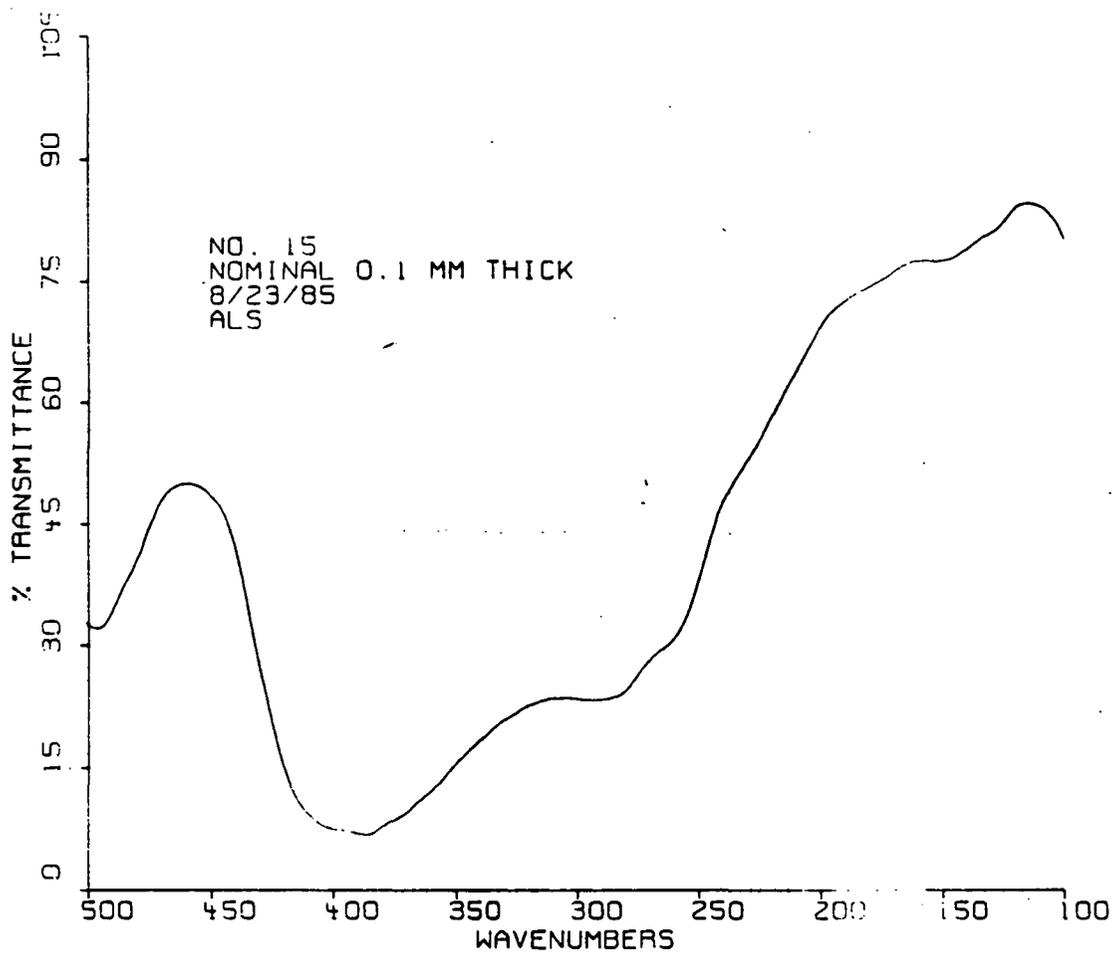
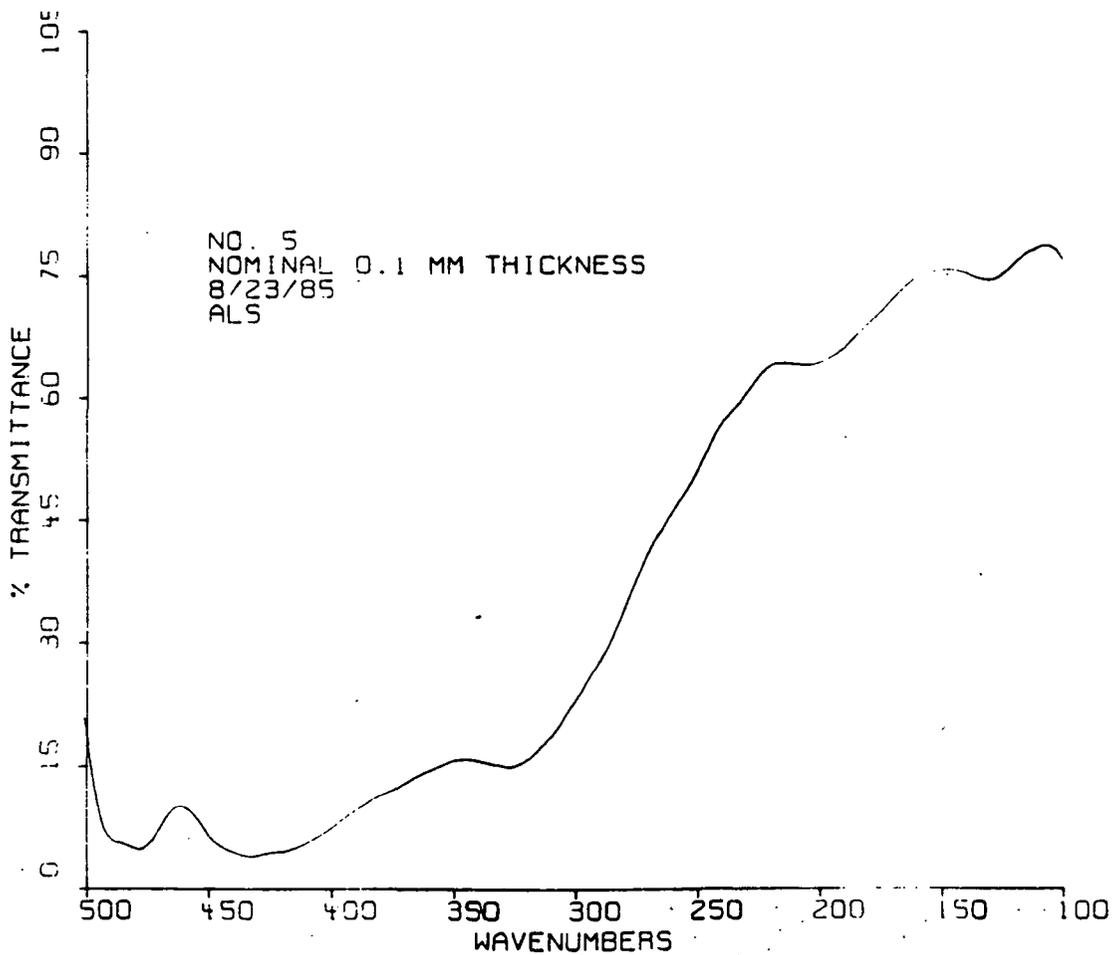


Fig. 11. Transmission spectra of a ca. 0.1 mm layer of fluids in the far IR region.



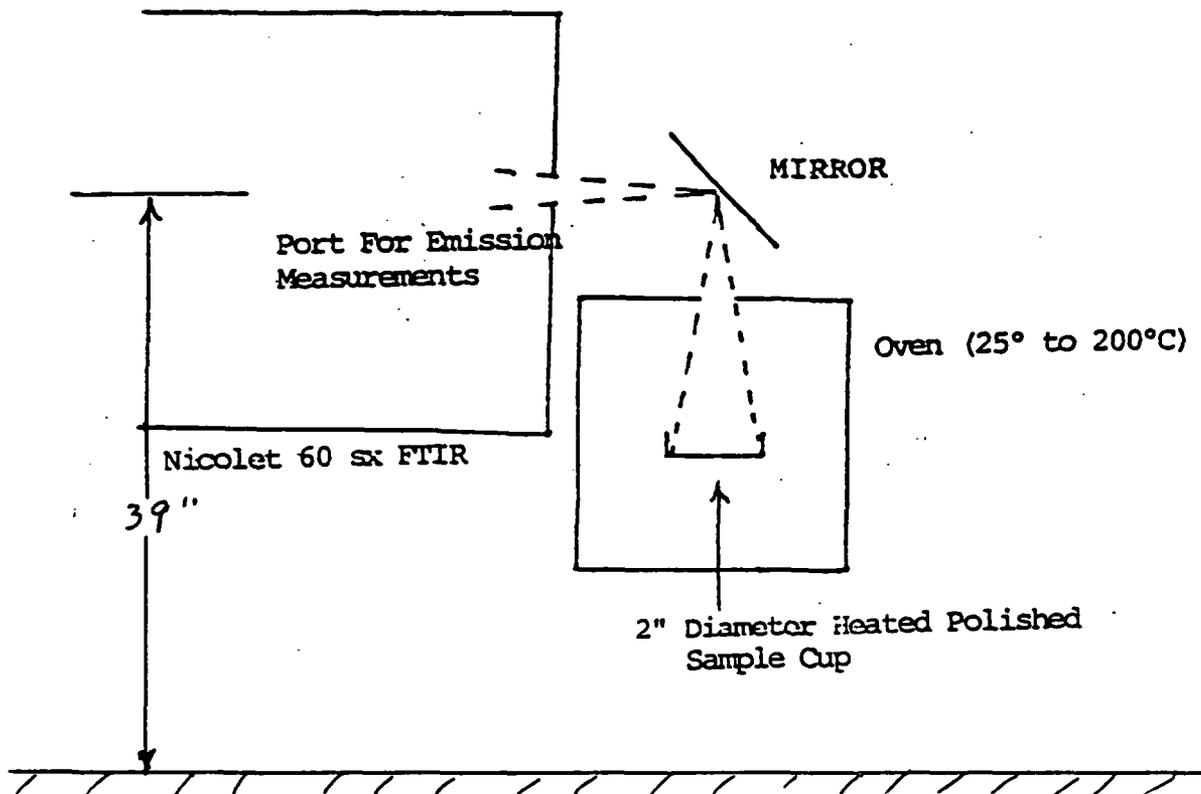


Fig. 12. Schematic drawing of oven and optical arrangement for collecting emission spectra.

APPENDIX IV

ACUTE TOXICOLOGICAL REPORT ON DOW CORNING® 710 FLUID

APPENDIX IV

DOW CORNING CORPORATION
Health & Environmental Sciences
Toxicology Department

ACUTE TOXICOLOGICAL REPORT ON DOW CORNING® 710 FLUID

A sample of DOW CORNING® 710 Fluid was submitted to the Toxicology Department for the determination of oral toxicity, primary eye and skin irritation potential and an assessment of industrial handling hazards associated with acute exposure.

DOW CORNING® 710 Fluid is practically non-toxic when ingested on an acute basis by laboratory rats (ALD₅₀ >15.0 g/kg body weight). It is unlikely that serious injury would result from ingestion of amounts normally encountered incidental to its industrial use.

Direct eye contact with this material may result in very slight transient conjunctival redness for a few hours or so. Precautions should be taken to avoid direct eye contact with this material. If eye contamination should occur, the eyes should be flushed with copious amounts of water as soon as practical.

Single, repeated or prolonged exposures of DOW CORNING® 710 Fluid to the skin of rabbits produces no observable effect and there are no indications that this fluid is absorbed through the skin in acutely toxic amounts. No special precautions appear necessary in order to handle this material safely for skin exposure.

CLG/kld
2-3-84

APPENDIX V
NOMENCLATURE

APPENDIX V

NOMENCLATURE

ASTM	American Society for Testing and Materials
CCS	Cold-Cranking Simulator
CTM	Dow Corning Corporate Test Method
D	Polydispersity, \bar{M}_w/\bar{M}_n
DSC	Differential Scanning Calorimeter
DTA	Differential Thermal Analysis
GPC	Gel Permeation Chromatography
Hex	Hexyl ligand, $n\text{-C}_6\text{H}_{13}\text{-}$
IR	Infrared Spectroscopy
LC	Liquid Chromatography
LDR	Liquid Droplet Radiator
\bar{M}_n	Number Average Molecular Weight (p. 7)
\bar{M}_w	Weight Average Molecular Weight (p. 7)
Me	Methyl ligand, $\text{CH}_3\text{-}$
NMR	Nuclear Magnetic Resonance Spectroscopy
O(3p)	Atomic oxygen, ground state
P	Pressure, Pascals unless stated otherwise
PDMS	Polydimethylsiloxane
Ph	Phenyl ligand, $\text{C}_6\text{H}_5\text{-}$
PMPS	Polymethylphenylsiloxane
SBT	Scanning Brookfield Viscometer Technique
T	Temperature, Kelvin unless stated otherwise
TBS	Tapered Bearing Simulator Viscometer
TGA	Thermogravimetric Analysis
USLCV	Ubbelohde Suspended Level Capillary Viscometer

I	Refers to Fluids isolated in Task I
II	Refers to Fluids isolated in Task II
1	Refers to Series 1 evaporation rate data (p. <u>11</u>)
2	Refers to Series 2 evaporation rate data (p. <u>11</u>)
704	Tetramethyltetraphenyltrisiloxane Dow Corning® 704 Fluid
705	Trimethylpentaphenyltrisiloxane Dow Corning® 705 Fluid
710	Trimethylendblocked methylphenylsiloxane Dow Corning® 710 Fluid
Cp	Specific heat
ΔH_v	Heat of vaporization
γ	Surface tension
λ	Thermal conductivity
ν	Kinematic viscosity
ρ	Density
σ	Electrical resistivity

1. Report No. NASA CR-175033		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Organosiloxane Working Fluids for the Liquid Droplet Radiator				5. Report Date December, 1985	
				6. Performing Organization Code	
7. Author(s) R. R. Buch, A. R. Huntress				8. Performing Organization Report No.	
				10. Work Unit No.	
9. Performing Organization Name and Address Dow Corning Corporation Midland, MI 48640				11. Contract or Grant No. NAS3-24400	
				13. Type of Report and Period Covered Contractor Report	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546				14. Sponsoring Agency Code 506-41-5A	
15. Supplementary Notes Final report. Project Manager: K. Alan White, Power Technology Division, NASA Lewis Research Center, Cleveland, Ohio 44135					
16. Abstract <p>Siloxane-based working fluids for advanced space radiators requiring direct fluid exposure to the space environment are evaluated. Isolation of five candidate fluids by vacuum distillation from existing siloxane polymers is discussed. The five fluids recovered include a polydimethylsiloxane, three phenyl-containing siloxanes, and a methylhexylsiloxane. Vapor pressures and viscosities for the five fluids are reported over the temperature range of 250 to 400 K. Use of thermal-gravimetric analysis to reliably estimate vapor pressures of 10^{-8} Pascals is described.</p> <p>Polydimethylsiloxane (PDMS) and polymethylphenylsiloxane (PMPS) were selected from the five candidate fluids based on favorable vapor pressure and viscosity, as well as perceived stability in low-earth orbit environments. Characterization of these fluids by infrared spectroscopy, Si^{29} NMR, gel-permeation chromatography, and liquid chromatography is presented. Both fluids consisted of narrow molecular weight distributions, with average molecular weights of about 2500 for PDMS and 1300 for PMPS.</p> <p>Vapor pressure, viscosity, rheological behavior, density, surface tension, specific heat, thermal conductivity, and electrical conductivity for PDMS and PMPS are presented for the temperature range 250 to 400 K. Pour point, flash point, and fire point for each fluid are also reported, as are heats of vaporization calculated from the Clausius-Clapeyron relation. Emission spectra for the two fluids at 430 K are presented for the infrared region. Transmission spectra in the infrared region are also reported for thin films of several thicknesses.</p> <p>Thermal, oxidative, and radiative stability, as well as flammability and toxicity, are discussed based on results of a search of relevant siloxane literature. Methods for adjusting viscosity and vapor pressure, and for improving stability in the low-earth environment, are suggested.</p>					
17. Key Words (Suggested by Author(s)) Organosiloxane; Low vapor pressure fluids; Liquid Droplet Radiator			18. Distribution Statement Unclassified - unlimited STAR Category 27		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of pages 166	22. Price* A08