

THE NATURE OF THE HIGH BOILER  
DEGRADATION PRODUCTS  
FROM IRRADIATED SANTOWAX OMP

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THE NATURE OF THE HIGH BOILER DEGRADATION  
PRODUCTS FROM IRRADIATED SANTOWAX OMP

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THE NATURE OF THE HIGH BOILER DEGRADATION  
PRODUCTS FROM IRRADIATED SANTOWAX OMP

ABSTRACT

Santowax OMP was irradiated in the M.I.T. research reactor under steady-state composition conditions at in-pile temperatures of 610°F and 750°F. The high boiler content was maintained constant at approximately 33 w/o by distillation and recycle.

HB samples removed from the loop from the beginning and end of the steady-state irradiations were fractionated by subliming the vapors evaporated from the HB in the liquid state. The fractions were compared in regard to number average molecular weights ( $MW_N$ ) and the compositions qualitatively compared by high temperature gas chromatography. The analyses indicated that equilibrium HB composition had been achieved. The equilibrium values of  $MW_N$  for the HB from the 610°F and 750°F irradiations were  $700 \pm 35$  and  $580 \pm 25$  respectively. The sublimation yields for the 750°F HB indicated that "thermal cracking" and/or pyrolysis is an important process in the radiolysis of Santowax OMP.

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1.0 Summary

Santowax OMP, an isomeric mixture of terphenyls whose composition is approximately:

ortho-terphenyl	10 w/o
meta-terphenyl	60 w/o
para-terphenyl	30 w/o,

was irradiated in the M.I.T. research reactor (1) under steady-state composition conditions at in-pile temperatures of 610°F and 750°F. The steady-state condition was maintained by distillation and recycle. The composition of the irradiated coolant during steady-state operation was in wt. percent (w/o):

<u>Constituent</u>	<u>Capsule Temperature</u>	
	610°F	750°F
biphenyl	1	1-2
ortho-terphenyl	6.0	6.1
meta-terphenyl	37.6	35.3
para-terphenyl	18.3	18.6
High Boilers (HB)	32.3	32.4
Low and Intermediate Boilers (LIB)	5.8	7.1

During the duration of the 610°F steady-state operations, approximately 2 loop volumes of coolant were processed and during the 750°F steady-state operations 1.2 loop volumes were processed. The average dose to the coolant during the 610°F and the 750°F irradiations was 25 watt-hrs/gm and 16 watt-hrs/gm respectively. Consequently, the HB generated should represent the HB to be expected in an Organic Cooled Reactor at steady-state at times long after

startup.

HB samples removed from the loop at the beginning and end of the steady-state irradiations were fractionated by sublimation<sup>(1)</sup> and the fractions were compared in regard to number average molecular weights ( $MW_N$ ) and their compositions qualitatively determined by high temperature gas chromatography. The sublimation yields, the molecular weights and the gas chromatograms indicated that equilibrium HB composition had been reached. The equilibrium values of  $MW_N$  for the HB from the 610°F and 750°F irradiations were:

$$MW_N = 700 \pm 35 \quad \text{for } 610^\circ\text{F HB}$$

$$MW_N = 580 \pm 25 \quad \text{for } 750^\circ\text{F HB}$$

The HB produced from Santowax OMP irradiated at 750°F exhibited larger proportions of low molecular weight species with corresponding higher volatility than did the 610°F HB. Also, the high molecular weight species formed in the 750°F irradiations were more volatile. These results infer that "thermal cracking" and/or pyrolysis is an important process in the formation of HB in the radiolysis of Santowax OMP.

The value of  $MW_N = 700 \pm 35$  for the HB produced at 610°F is in good agreement with the estimated value of  $650 \pm 25$  by Atomics International (2) for OMRE coolant which was irradiated at temperatures of approximately 600°F.

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(1) The term sublimation is used by convention, however evaporation may be more descriptive since the heated HB samples were liquid at the temperatures at which volatiles were evolved. The volatile materials were sublimed on a cold surface.

## 2.0 Introduction

Since the early 1950's, polyphenyl materials, principally terphenyls, have been considered (3, 4, 5, 6, 7, 8) and have been used (9, 10) as moderators and/or coolants for nuclear reactors.

The term terphenyls, is used in the general sense, since several commercially produced isomeric mixtures of the ortho-, meta-, and para-terphenyls have been used, the major difference in the mixtures being their para-terphenyl content. Para-terphenyl has the undesirable effect of raising the coolant melting point. Terphenyl mixtures whose para-terphenyl content is above 25 to 30 w/o generally exhibit a final liquidus point of approximately 300°F. One isomeric mixture, Santowax OMP, manufactured by the Monsanto Chemical Company, has a nominal composition of:

less than 2 w/o biphenyl plus degradation products DP<sup>(1)</sup>  
10 w/o ortho-terphenyl  
60 w/o meta-terphenyl  
30 w/o terphenyl

Santowax OMP is the coolant being used in the Piqua Reactor (10) and is the coolant whose HB formed from reactor irradiation is studied in this work.

Other isomeric mixtures which have been used or are being considered as reactor coolants are Santowax OM or Santowax WR both of which are characterized by melting points

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(1) Throughout this work the following definitions will be used: w/o Degradation Products (DP) = 100-w/o total terphenyls and w/o DP = w/o LIB + w/o HB

below 200°F and contain less than 5 w/o para-terphenyl.

Although the Organic Moderated Reactor Experiment (OMRE) (9) and four early in-pile loop experiments (3, 5, 6, 7) did much to prove the overall suitability of polyphenyl materials, as organic reactor coolants, the effect of long term reactor irradiation on the terphenyls was not known. The experimental programs of the OMRE and the earlier experiments did not permit operation long enough under any one set of conditions to allow the irradiated coolant to reach complete equilibrium especially with respect to the number average molecular weight of the coolant (2, 11).

That the molecular weight of the coolant is an important parameter in the evaluation of the radiolysis of terphenyl coolant can be shown when the types of radiolysis products or degradation products (DP), are considered. The DP of terphenyl organic reactor coolants produced when the terphenyls are exposed to mixed in-pile radiation can be qualitatively grouped into four classes according to their volatilities as listed in Table 2.1 from Keen (2). Also listed, are compound types in each volatility class. The data is derived primarily from references (6, 11, and 12) and supported by recent results in references (1, and 13).

The composition and yield of each class of the DP appear to be dependent upon the coolant temperatures during reactor exposure, DP content, and processing conditions (1, 6, 11, 13). In general, however, the yields and component types listed in Table 2.1 are typical.

The gases are composed mainly of hydrogen, methane,

Table 2.1

Classification of Degradation Products of Polyphenyls (2)

<u>Products</u>	<u>Boiling (1) Range (°C)</u>	<u>Approximate Yield (w/o)</u>	<u>Main Compound Types Present</u>
Gases	-259 to +80	1	Hydrogen, paraffins and olefins to C <sub>6</sub> and acetylenes
Low Boilers (LB)	20 to 254	1-2	Alkylated aromatics
Intermediate Boilers (IB)	254 to 383	5-10	Alkylated aromatics and polyphenyls
High Boilers (HB)	> 383	85-90	Fused ring aromatics polyphenyls, alkylpolyphenyl phenanthrenes, triphenylenes, and aromatic olefins

(1) The atmospheric boiling points of biphenyl, ortho-terphenyl, meta-terphenyl, and para-terphenyl are; 255°C, 332°C, 364°C, and 383°C respectively.

1  
5  
1

ethane, and propane with traces of unsaturated aliphatic hydrocarbons containing 4 or 5 carbon atoms and saturated and unsaturated hydrocarbons containing up to 6 carbon atoms (1).

The second and third classes of the degradation products can be grouped into one class referred to as low and intermediate boilers (LIB), because their volatilities lie in the range between the gases produced from radiolysis and the molecular species having volatilities less than the terphenyl material being irradiated. The species having volatilities less than para-terphenyl are defined as high boilers (HB) and will be discussed subsequently.

The low boilers (LB), which are the most volatile portion of the LIB, are comprised of the condensable gases (1, 6) and materials whose volatility decreases to that of the terphenyls. The LB is made up, in part, of benzene, toluene, substituted benzene ring compounds, and partially substituted or partially hydrogenated compounds of up to three benzene rings. The low volatility constituents of the LIB have been identified as quaterphenyls (11, 14), some alkyl substituted or partially hydrogenated, and perhaps higher molecular weight polyphenyls containing five benzene rings (quinquephenyls), which are alkyl substituted or partially hydrogenated to lower their volatility.

By far, the largest portion of the degradation products formed from the irradiation of terphenyls is comprised of compounds whose volatilities are less than para-terphenyl. These fractions are identified as HB. At low conversions the HB seems to be primarily formed as dimers of the ter-

phenyls (2, 15) but other higher molecular weight species may also form with continued irradiation of the HB and the irradiated coolant as shown in in-pile loop and the electron irradiations (and the OMRE) (2, 11, 16).

The presence of the higher molecular weight HB causes large changes in the physical, chemical, and thermodynamic properties of the coolant and causes substantial reduction in the heat transfer characteristics of the irradiated coolant (1, 6, 13). The greatest effect of the HB in the irradiated coolant is to cause a large increase in the viscosity, approximately a factor of two for 30 w/o HB (17). Also, it has been postulated that very high molecular weight DP may play a part in causing surface fouling of the fuel element heat transfer surfaces by combining with inorganic impurities which may be present in the irradiated coolant (18).

Therefore, in organic cooled reactors, a knowledge of the composition and properties of the irradiated coolant containing equilibrium concentrations of HB and LIB is an important prerequisite to reactor design.

A program utilizing an in-pile loop has investigated the effects of long term reactor irradiation on Santowax OMP at the Massachusetts Institute of Technology (1, 13). As part of this program, the coolant composition was maintained at a constant HB content (33 w/o) by coolant distillation and recycle for periods of several months. These periods of irradiation were called steady-state-HB operations and were carried out at in-pile irradiation temperatures of 610<sup>o</sup>F and

750°F. The results presented in reference (1) indicated that the irradiated coolant had reached equilibrium in terms of constant values of the physical properties, degradation rates, HB content, DP content, heat transfer, and the number average molecular weights of the irradiated coolant.

In view of the complex mixture of hydrocarbons formed upon continuous irradiation, and its importance on the heat transfer properties, and on coolant processing and reprocessing techniques (19, 20, 21, 22), further analysis of the HB formed in the M.I.T. irradiation was required to determine if complete equilibrium, especially in regards to molecular weight distributions, had been reached.



### 3.0 Experimental Procedures and Equipment

Prior to selecting a method of HB analysis a survey of the existing techniques of determining the HB composition and molecular weight distribution was made. Based on this survey of analytical methods available, molecular weight measurements, combined with sublimation (see footnote, page 2) and gas-solid chromatography were selected as the best methods to use for this investigation.

The following sections will discuss the methods surveyed as well as the final technique developed and adopted.

#### 3.1 Molecular Weight Measurements

One analytical technique commonly used to characterize the amount of radiation damage to the coolant, and particularly the character of the HB, is to measure the number average molecular weight of either the whole coolant or the HB fraction (See Section 4.4).

Methods for determination of the molecular weight depend, with the exception of mass spectroscopy, upon lowering the freezing point (cryoscopic methods), raising the boiling point (ebulliometric methods), or lowering the vapor pressure of a pure solvent (Signer Method of Isothermal Distillation (12) and Vapor Pressure Methods) and are in general, quite inaccurate. Furthermore, the foregoing methods also depend upon the complete solubility of the solute whose molecular weight is to be determined, in a suitable solvent.

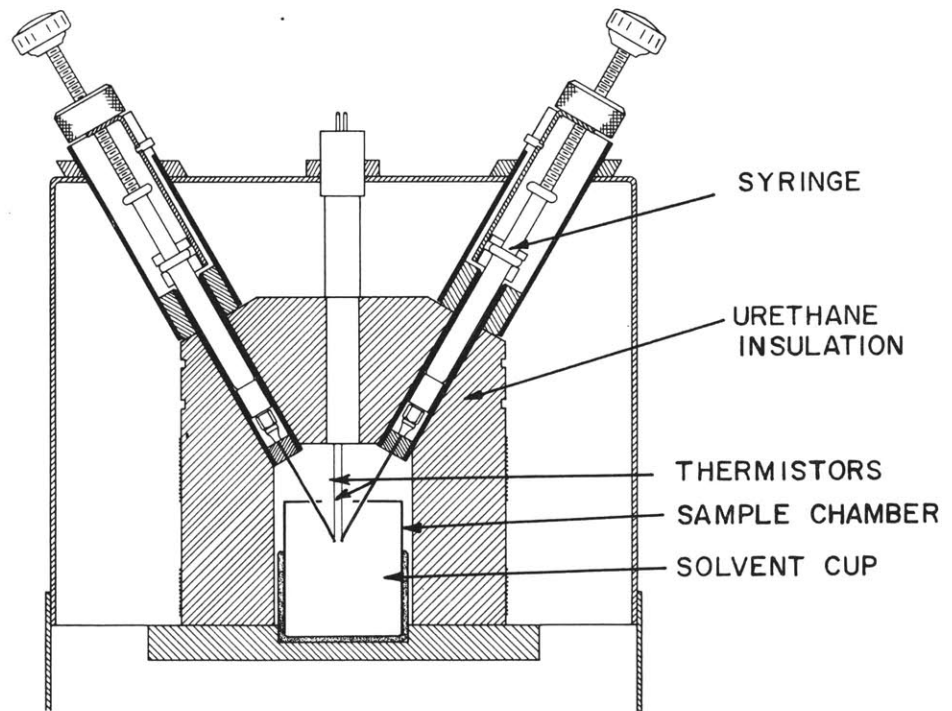
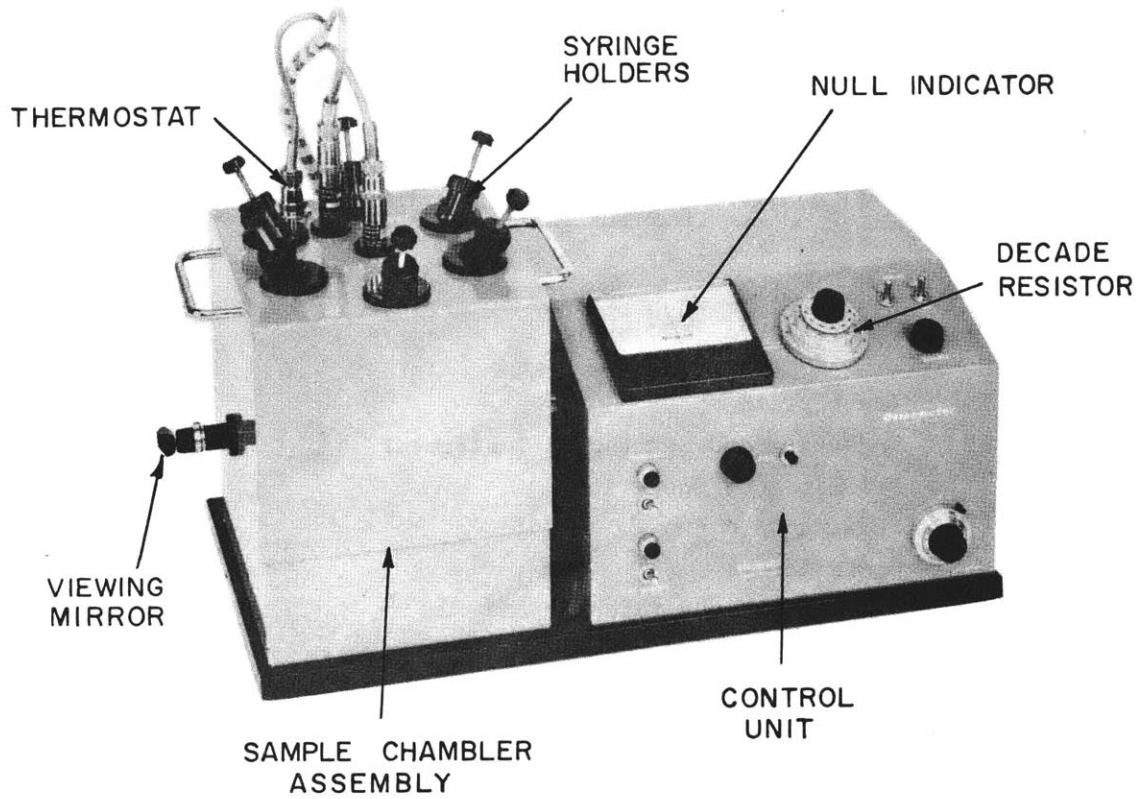
As a result of this strong dependence of solubility, an instrument was selected which allowed a wide selection of

solvents in its use and which depended upon measurement of temperature differences resulting from the lowering of the vapor pressure of a pure solvent. The instrument selected was a Mechrolab Model 301A osmometer,<sup>(1)</sup> a photograph and sketch of which is shown in Figure 3.1. The instrument consists of two principal units—the sample chamber assembly and the control unit. The sample chamber assembly is a urethane-insulated housing, thermostatically controlled at 37°C, consisting of a sample chamber, solvent cup, two thermistors, and six syringe guideholes and holders. The control unit is composed of a null indicator, a wheatstone bridge and a heater input control circuit. Two syringes in the sample chamber contain solvent, while the other four syringes contain solvent containing solute, either standards or "unknown" samples, whose mole concentration is to be determined.

The Model 301A is a "thermoelectric" type osmometer and for the detailed theory of its operation the reference by Brady et. al. (23) should be consulted. Simply stated, the operation of the instrument depends upon lowering the vapor pressure and therefore the evaporation rate of the solvent containing the solute of the unknown material. In the Model 301A Osmometer (Figure 3.1), a drop of solution and a drop of the reference solvent are suspended side by side on the two thermistors in the sample chamber which is saturated with

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(1) Mechrolab Incorporated, Mountain View, California



CROSS SECTION OF SAMPLE CHAMBER ASSEMBLY

FIGURE 3.1 MECHROLAB MODEL 301A OSMOMETER

pure solvent vapors from the sample cup. As a result of the unequal vaporization rates, a temperature difference exists between the two thermistors as predicted, for the ideal case, by the Clausius - Clapeyron equation:

$$\Delta T = \frac{RT^2}{\lambda} \cdot \frac{C}{1000} \quad (1)$$

where  $\Delta T$  is the temperature rise or temperature difference

$R$  is the gas constant

$\lambda$  is the heat of vaporization per gram of solvent

and  $C$  is the molarity or molality of the solution.

In the real case, the temperature rise will be somewhat smaller, due to heat losses, but the  $\Delta T$  and  $C$  are still related in a linear manner (24). Since the temperature shift is a colligative effect, dependent solely upon the number of dissolved molecules and independent of their chemical characteristics, the instrument may be calibrated with solutions of differing molalities using solutes whose molecular weights are known. Molal concentrations of unknowns in the same solvent may then be determined by reading the values directly from a calibration curve. See Appendix A-2 for a discussion of calibration and use of the instrument.

The scale of the instrument actually measures the difference in temperature by determining the resistance difference in the two thermistors by means of a bridge network. Concentrations between 0.005 and 0.1 molal are optimal, since at higher concentrations, a larger  $\Delta T$  will exist and condensation from the saturated atmosphere in the sample chamber may cause concentration shifts and at lower concentrations,

reproducibility is reduced. In this investigation, 0.02 to 0.05 molal solutions of HB in tetrahydrofuran were found to give the best results. Molal solutions were used in all cases since it made the concentrations independent of solvent density.

Sensitivity will vary somewhat with the solvent, being dependent primarily upon the heat of vaporization. Since the operation depends upon the solution drop retaining a constant concentration, or a slowly varying concentration while the measurement is being made, the instrument is limited to solutes of low vapor pressure. In this work the HB has a negligible vapor pressure. In general, the ratio of vapor pressure of solvent to that of the solute should be comparable to the per cent accuracy desired (25).

The instrument calibration, solvent selection and the effects of non-solution of the solute are presented in Appendix A1, Sections 4.1 and 4.42.

### 3.2 Sublimation<sup>(1)</sup> of HB Samples

Previous investigators have reported (1, 2, 6, 11, 26) the number average molecular weights of the total irradiated coolant or of the HB fractions to measure the effects of the irradiation on the coolant. In order to refine the analysis of the HB portion of the Irradiated coolant, a method of fractionating the HB into many portions was required. Each fraction could then be compared with other fractions by means of yields, number average molecular weights, ( $MW_N$ ), and composition. See Section 4.4 for a discussion of averaged molecular weights.

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<sup>(1)</sup> See footnote, page 2.

Three methods of HB separation were considered: rectification, solvent extraction, and high vacuum evaporation with sublimation.

Rectification was rejected because the low volatilities of the HB fractions would require high temperatures and would probably result in pyrolysis of the material. A solvent extraction method partially developed at Atomics International (2) presented too many development problems and questionable yields due to the insoluble nature of the HB. The method also required large amounts of HB for each separation, and an estimated 2 man-months per sample to effect separation (27).

Based on the foregoing considerations, a high vacuum, evaporation technique was developed which permitted separation of the HB into seven sublimed fractions plus a residue.

Sublimation time and temperatures were selected to give yields of approximately 5 to 10 w/o of the initial HB sample charge per sublimation from the 610<sup>o</sup>F irradiation.

The sublimations were performed in a glass microsublimation apparatus as shown in Figure 3.2. The bottom of the outer glass envelope was slightly flattened to assure an even distribution of sample on the bottom of the outer glass envelope and to minimize bumping of the material onto the cold finger in the center. The cold finger was water cooled to provide the necessary cold surface for sublimation.

A eutectic mixture of NaNO<sub>3</sub>, NaNO<sub>2</sub> and KNO<sub>3</sub> was used as a heating medium for the sublimation. Bath temperature was maintained by means of a Simplytrol Temperature Controller and a stirrer. A mechanical vacuum pump combined with an

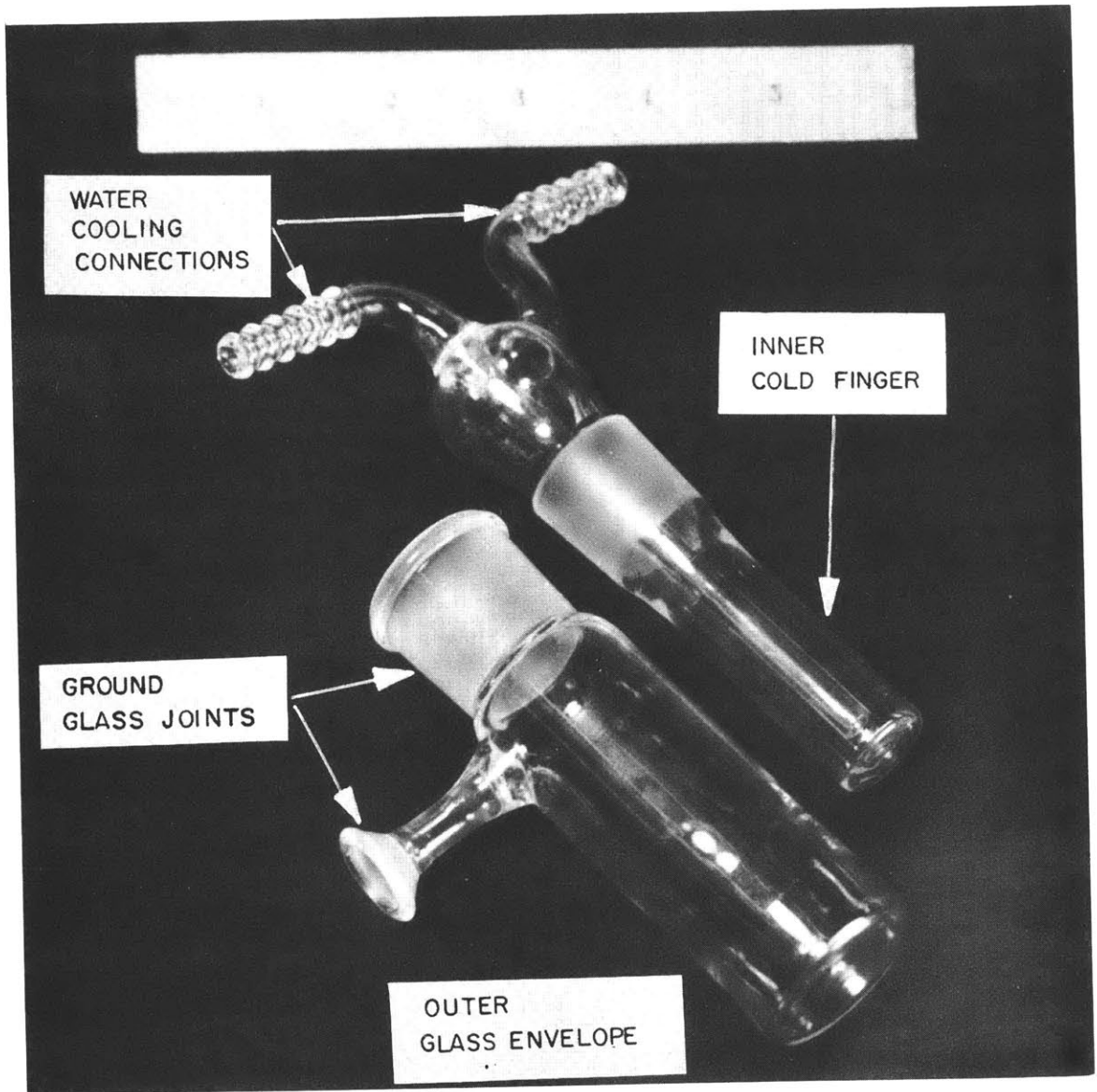


FIGURE 3.2 PHOTOGRAPH OF MICRO SUBLIMATION APPARATUS

oil diffusion pump was provided to maintain a high vacuum in the system. A McLeod mercury vacuum gage was used to measure the sublimation pressure. Table A2.5 in Appendix A2 presents an equipment list.

It was found necessary to immerse the sublimation apparatus gradually at each new sublimation temperature (see Section 3.22 and Appendix A2.2) in order to prevent "bumping" of the residue from the preceding sublimation. Therefore, the salt bath was supported by an adjustable platform which permitted slow immersion of the sublimation apparatus and quick cooling of the residue upon the completion of each sublimation. Figure 3.3 is a photograph of the assembled sublimation equipment.

### 3.21 Sublimation Conditions

The selection of starting sample size for the stepwise sublimation procedure (Section 3.2 and Appendix A2.2) and the temperatures of sublimation were developed during preliminary sublimations performed in duplicate on two 1 gm HB samples from the 610<sup>o</sup>F steady state (1) irradiation. Sample selection is discussed in Section 4.2. These initial sublimations of the 1 gm samples were carried out using the air cooled, oil diffusion pump and the vacuum pump with an absolute pressure of approximately 0.1 mm Hg and temperature of 200<sup>o</sup>C, 250<sup>o</sup>C, 290<sup>o</sup>C, 310<sup>o</sup>C, 350<sup>o</sup>C and 370<sup>o</sup>C. The temperature of 370<sup>o</sup>C was selected as a maximum so that pyrolysis of the residue could be assumed to be negligible during the last portion of the sublimations.

From the results obtained, (Section 4.3 and Appendix A2.1)



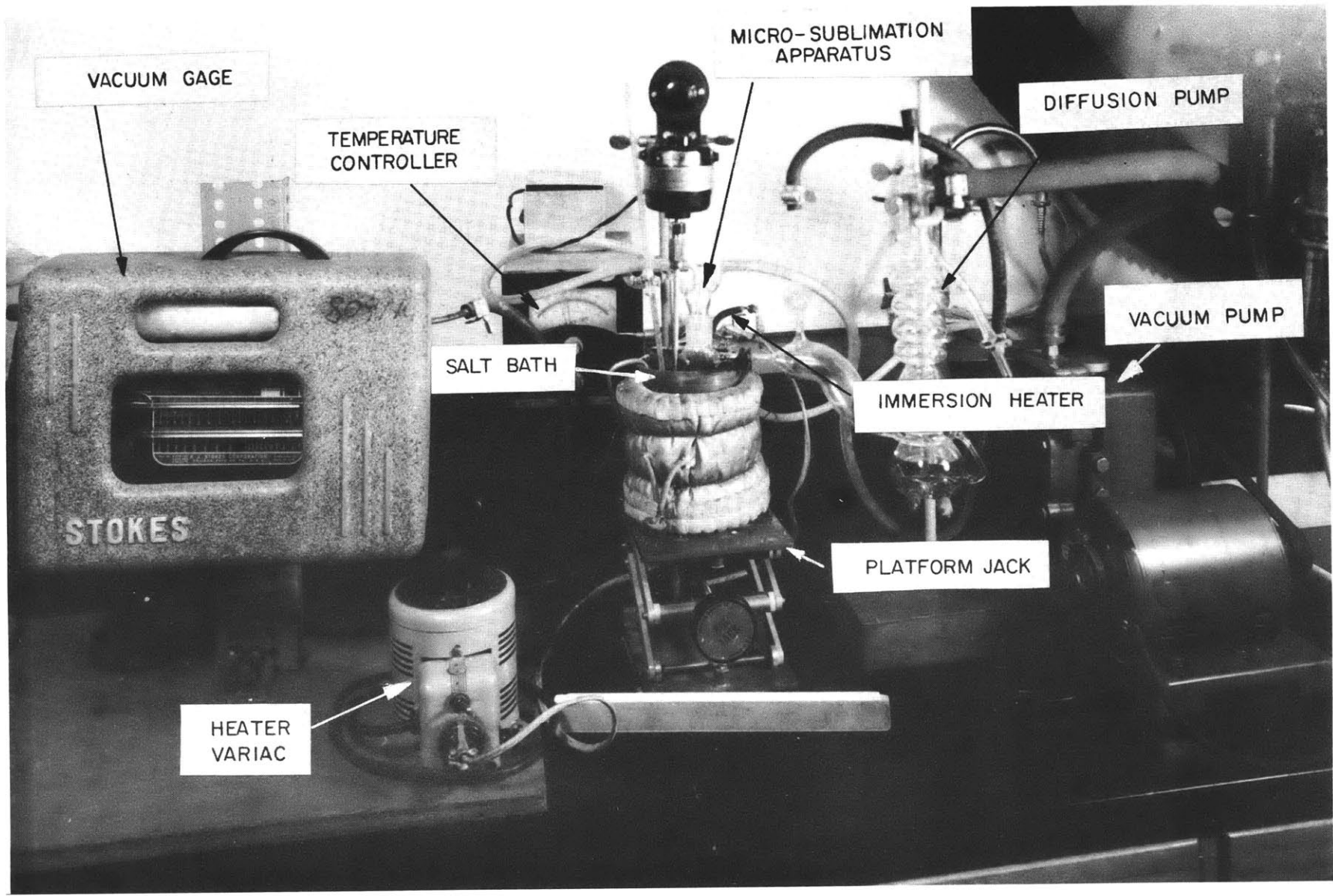


FIGURE 3.3 PHOTOGRAPH OF SUBLIMATION EQUIPMENT

it was apparent that the sublimation yields for each fraction from 1 gm samples were too small to make sufficiently concentrated solutions for the molecular weight measurements (see Section 3.1 and Appendix A1). Therefore, 2 gms of HB was selected as a suitable amount of HB for the sublimations which would require subsequent molecular weight measurements.

For the 2 gm samples an additional evaporation temperature of 270°C was used in order to achieve 5 - 10 w/o yields per sublimation for the 610°F HB samples. In addition, the use of the diffusion pump was discontinued for the 2 gm samples since it was found that the sublimation pressures could be lowered from 0.1 mm Hg absolute to approximately 0.02 - 0.03 mm Hg absolute by using the vacuum pump alone. The decrease in the sublimation pressure did not appear to have any appreciable effect on the sublimation yields (see Section 4.3).

### 3.22 Sublimation Procedure

Briefly stated, the fractionation of each HB sample was carried out in a stepwise fashion at each of the evaporation temperatures specified in the preceding section for a period of 3 hours. The sublimate at each temperature was removed from the "cold finger" of the Micro-Vacuum Sublimation Apparatus (Fig. 3.2) by dissolution with THF and prepared as a THF solution for subsequent molecular weight measurements. The remaining residue was then evaporated at the next higher sublimation temperature for 3 hours. The residue was liquid at each evaporation temperature. Appendices A2.1 and A2.2 present the experimental results and detailed procedures used.

### 3.3 Gas Chromatography

To further evaluate the similarities or dissimilarities of different HB samples, a qualitative analytical method to determine the composition of several of the sublimation fractions dissolved in tetrahydrofuran was developed utilizing high temperature vapor phase chromatography.

In addition to the gas chromatographic method of HB analysis adopted for this investigation, three other methods in wide use in organic analysis and the petroleum industry were considered. These were:

- (a) Ultra violet (UV) transmission analysis
- (b) Infrared (IR) transmission analysis, and
- (c) Low voltage mass spectroscopy.

Samples of M.I.T. loop samples were analyzed by all the techniques mentioned above and are reported in reference (1) section 5.11. However, due to the molecular complexity of the irradiated mixture, specific information concerning the composition of the mixture could not be resolved from methods (a) and (b).

Low voltage mass spectroscopy results in a considerable fragmentation (28) of the organic species in the samples resulting in a complex mass spectrum which is very difficult, if not impossible, to evaluate. Some results have been reported using method (c) by the workers at Atomics International (11, 12) for in-pile loop samples from MTR irradiations (6). However, in view of the difficulties encountered with M.I.T. samples (28) low voltage mass spectroscopy was not considered as a suitable analytical method for this work.

### 3.31 Gas Chromatographic Equipment

High temperature gas-solid chromatography has been used for several years at M.I.T. as the major analytical method for analysis of the terphenyls (11, 13). However, due to the higher column elution temperatures required for HB analysis (up to 500°C) some modifications and development of existing equipment was required.

The equipment selected for use and modification was an F + M<sup>(1)</sup> Model 1609 Flame Ionization Detector attachment with electrometer and an F + M Model 240 Silicon Controlled Linear Temperature Programmer. As received, the equipment was not capable of sustained operation, nor satisfactory temperature programming, in excess of 400° and modifications were required on the column and detector chassis shown in Figure 3.4. The modifications are described in Appendix A3.

### 3.32 Gas Chromatography Procedures

Once the necessary equipment modifications were completed, the selection of a suitable column packing material to give a qualitative comparison between HB fractions was made. Based on preliminary information, which has recently been reported in detail (29), a 10 w/o LiCl on a firebrick support (Chromasorb P) fired at 700°C for one hour was used to analyze the molecular weight solutions prepared from the sublimations (See Sections 3.1, 3.2, and Appendix A2).

Samples were injected into the helium carrier gas

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<sup>(1)</sup> F + M Scientific Corporation, Starr Road and Route 41, Avondale, Pennsylvania.

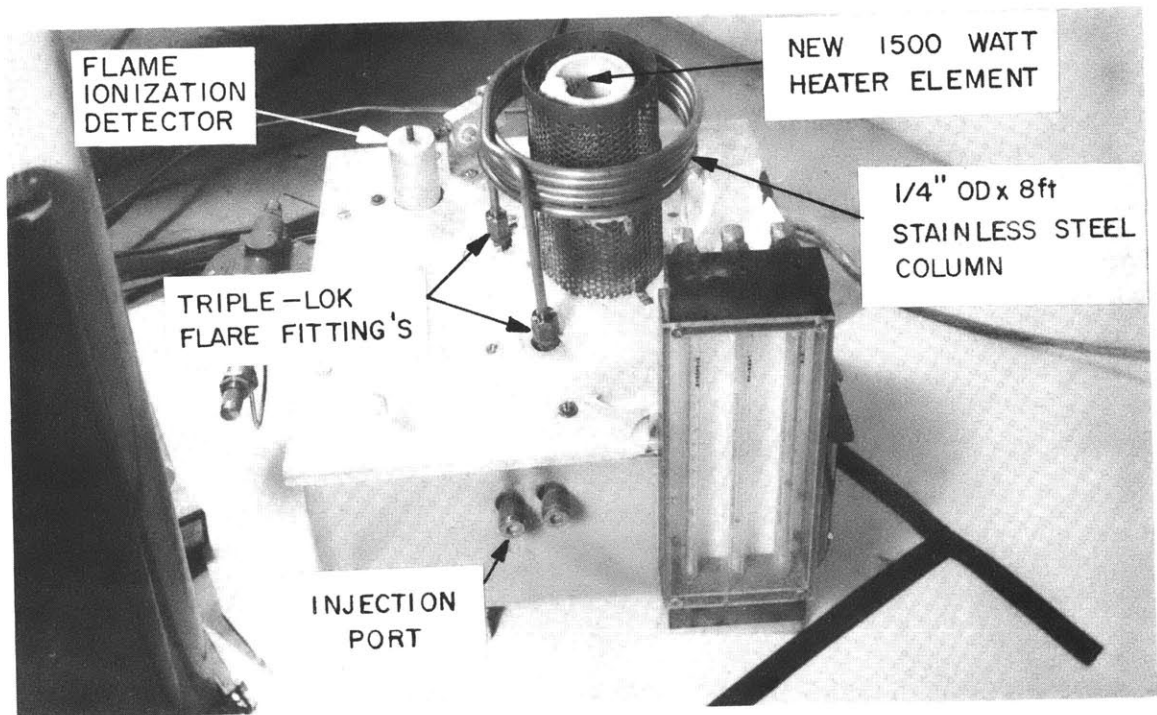
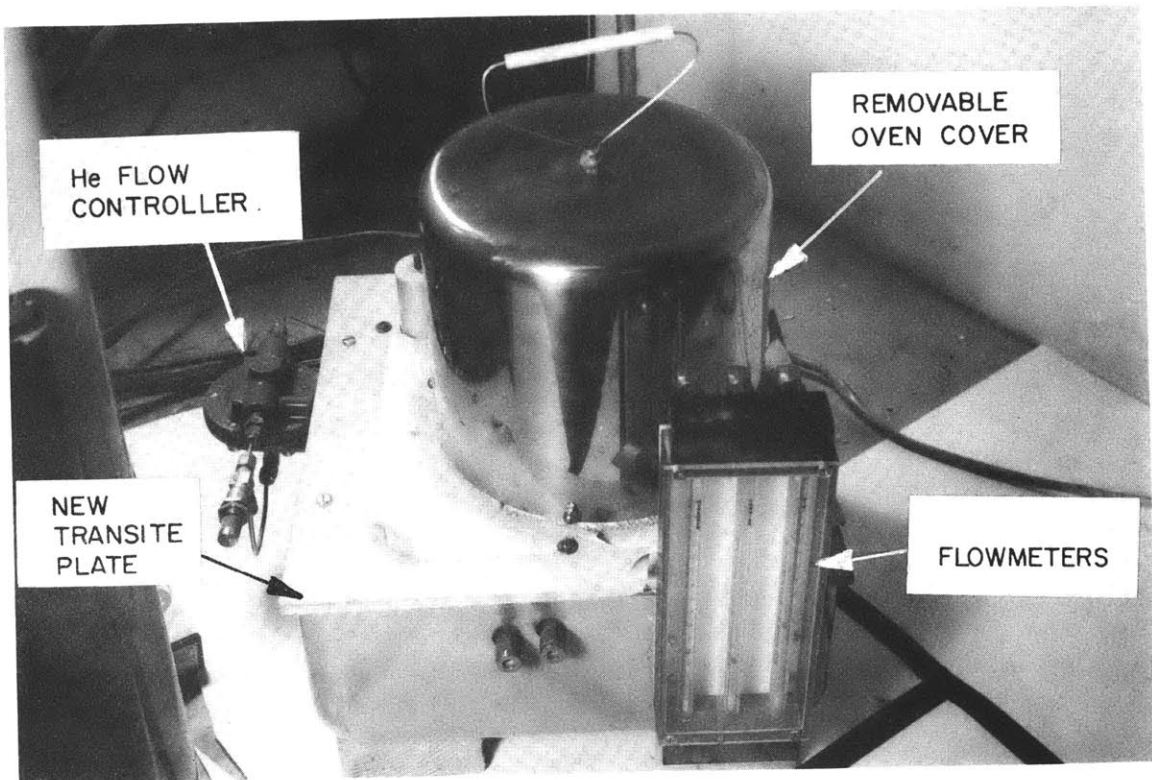


FIGURE 3.4 PHOTOGRAPH OF GAS CHROMATOGRAPH

stream by means of a 10 micro-liter syringe through a silicon rubber septum on the heated (380°C to 400°C) injection port at a column temperature of 120°C. After one minute, the temperature program was started at 5°C per minute and continued to 200°C, at which time the programming rate was changed to 7.5°C per minute. The 7.5°C per minute rate was continued to 420°C at which time the analysis was considered complete.

Time did not permit a complete gas chromatographic analysis of more than the first three sublimation fractions. However, the results achieved, (See Section 4.5) show the applicability of the method developed.

#### 4.0 Results and Discussion

Utilizing the procedures and equipment developed as described in Section 3.0, and Appendices A1 and A2, two HB samples numbered 1L251 and 1L265 (See Section 4.2 for sample descriptions) from the 610<sup>o</sup>F steady-state irradiation (1) of Santowax OMP were analyzed using the sublimation and molecular weight measurement procedures. Two samples, numbered 2L22 and 2L40 from the 750<sup>o</sup>F steady-state irradiation of Santowax OMP, were sublimed under identical conditions as the 2 gm samples from the 610<sup>o</sup>F irradiations to enable a comparison of molecular weight distributions of the HB from Santowax OMP irradiated at 610<sup>o</sup>F and 750<sup>o</sup>F.

As a final comparison of different sublimate fractions, high temperature vapor phase chromatography was used on several sublimate fractions to make qualitative comparisons of their composition. It was not possible to identify the peaks in the chromatograms, but the utility of the technique is amply demonstrated.

The following sections present the results of the sublimations and molecular weights obtained for the four samples analyzed plus several chromatograms which serve to substantiate the results obtained from the sublimation and molecular weight measurements.

#### 4.1 Solvent Selection

In view of the dependence of the molecular weight measurements upon complete solubility of the solute whose molecular weight was to be determined, (See Section 3.1) an evaluation was made between the use of benzene or tetra-

hydrofuran (THF) as a suitable solvent. Only these two solvents were considered since they are in wide use as solvents for gas chromatography by other investigators in the field of organic coolant development (30).

To evaluate the relative merits of the two solvents, approximately 4 w/o solutions of irradiated Santowax OMP containing approximately 50 w/o DP from the 610<sup>0</sup> F transient irradiations were filtered through 100 milli-micron pore size Millipore Filters.<sup>(1)</sup> Approximately 2 or 3 w/o benzene insolubles were collected on the filter. No insolubles could be collected on this pore size filter from the tetrahydrofuran (THF) solution. However, it was still possible to produce a Tyndall beam in the THF solutions indicating the presence of some insoluble particulates. Attempts to use smaller pore size Millipore Filters were unsuccessful due to the fact that the smaller pore size filters were manufactured from a material incompatible with THF.

Based on the above experiments, THF was selected as a suitable solvent for the use in the Osmometer (See Section 3.1).

Subsequent observation of a Tyndall beam and colloidal suspensions in some of the solutions required an estimate on the effect partial insolubility has on the molecular measurements. The effect on the measured molal concentration is discussed in Section 4.42. Based on visual observation of the samples it is estimated that the total insoluble content probably did not exceed 2 w/o.

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(1) Manufactured by Millipore Filter Corporation, Bedford, Massachusetts



As an additional evaluation of the suitability of THF as a solvent, and the degree of insolubility of the solute, several samples of HB from the 610<sup>o</sup>F irradiation were prepared in two concentrations of 2 and 4 w/o, and preliminary measurements of their molecular weights made with the osmometer. Table 4.1 presents the results. The agreement of the number average molecular weights for the two concentrations, indicates that the concentration of insolubles is essentially unchanged over the range of THF concentrations which was used in this work.

#### 4.2 Sample Selection

Samples for determination of equilibrium conditions during the steady-state HB irradiations were selected from the beginning and end of the steady-state HB irradiations when the physical properties, the heat transfer properties, the decomposition rates, and the ortho, meta, and para concentrations and molecular weight measurements on the total coolant had reached constant values as a function of time (i.e. of radiation dose) (See Reference (1)). Under these conditions if further fractionation and analysis of the HB fractions indicated that equilibrium had been reached; the properties presented in reference (1) could be regarded as equilibrium properties, and could be used for the long term design of an organic cooled reactor utilizing a procedure for reprocessing the reactor coolant similar to that described in references (31) and (32).

Table 4.2 presents the date each sample was withdrawn as well as the reactor exposure time in megawatt-hours,

Table 4.1  
Dilution Effects of THF on  
Number Average Molecular Weight Measurements

Solution Concentration →	<u>Molecular Weight</u>	
	4w/o	2w/o
Sample No.		
1L251	656	658
1L255	651	693
1L259	653	615
1L264	675	673

Table 4.2  
Source of Samples<sup>(1)</sup> for

Sample No.	Date Removed from In-Pile Loop	<u>HB Analysis</u>		DP <sup>(4)</sup> Content (w/o)	Irradiation Temp. (°F)
		Reactor <sup>(2)</sup> Exposure Time (MWH)	HB <sup>(3)</sup> Content (w/o)		
1L251	5/24/62	7880	33	40	610
1L265	8/14/62	9979	33	40	610
2L22	2/26/63	2278	33	41	750
2L40	4/18/63	3733	33	41	750

- 
- (1) The HB was obtained from each sample by distillation as part of the recycle operations described in references (31 and 32).
- (2) See text for explanation of MWH as a measure of exposure time.
- (3) Material less volatile than paraterphenyl.
- (4) Defined as (100 - w/o total terphenyls).

(MWH). Here, the term MWH is an index of exposure which represents the energy generated by the MITR during the period in which the organic was exposed. Generally, the reactor operated at a maximum power of 1.95 Megawatts, so that if the MWH in Table 4.2 is divided by 1.95 the exposure time (in hours) at full reactor power is obtained. It is a convenient time scale, and since the radiation dose is expressed in terms of the accumulated reactor energy, it allows computation of the dose at any reactor power level.

Prior to the initiation of the steady-state operations, the irradiations at 610<sup>o</sup>F and 750<sup>o</sup>F were conducted as transient semi-batch irradiations with samples removed for terphenyl analysis (See reference (1) for details). The DP concentration at the end of the 610<sup>o</sup>F transient irradiations was 60 w/o and the accumulated specific dose to the coolant was approximately 48 watt-hr/gm for 60 w/o conversion. For the 750<sup>o</sup>F transient irradiation the maximum conversion was 59 w/o and the accumulated specific dose to the coolant was approximately 24 watt-hr/gm.

During steady-state recycle operations in each irradiation the HB concentration was maintained at 33 w/o by removing 300 gm samples, distilling the irradiated sample to remove all material less volatile than para-terphenyl, adding makeup to the distillate, and returning the distillate with makeup to the loop. The HB analyzed in this work was the still bottoms obtained from the distillation of the 300 gm samples. References (31) and (32) should be consulted for a detailed description of the technique and apparatus

employed.

Since the system entire loop contents of approximately 5400  $\pm$  300 gms (Appendix A2.5 Ref. (1)) in both the 610<sup>o</sup>F and 750<sup>o</sup>F irradiations was maintained at a constant HB content, it is possible to compute the average specific dose to the coolant removed during the recycle operations.

Under steady-state operating conditions, the rate of coolant removal and makeup are adjusted so that the incremental amount of degradation products formed between any two sampling times, A and B, are removed in the sample taken at time B. Hence the dose which was effective in producing that amount of incremental degradation is the dose absorbed by all the coolant during the period from A to B. Consequently the specific dose, which influenced the degradation, is obtained by dividing the total dose absorbed over the sampling period by the mass of the sample taken; effectively this is a division of the total rate of energy absorption in the loop by the rate of coolant processing required to maintain constant concentrations in a steady irradiation, resulting in a specific dose expressed as watt-hr/gram coolant.

From reference (1) the dose rate is expressed as

$$\frac{\Delta \text{Dose}}{\Delta(\text{MWH})} = \bar{\rho} F_T \frac{\text{watt-hr}}{\text{MWH}} \quad (2)$$

where  $\bar{\rho}$  is the average density of the irradiated coolant during the period for which the dose is to be computed.  $\bar{\rho} = 0.913 \frac{\text{gm}}{\text{cc}}$  for the 610<sup>o</sup>F coolant during steady-state irradiation.  $\bar{\rho} = 0.842 \frac{\text{gm}}{\text{cc}}$  for the 750<sup>o</sup>F coolant during steady-state irradiation.

and  $F_T$  is an in-pile dose rate factor determined by calorimetry and corrected for fuel depletion in the MITR.

$$F_T = 58.3 \frac{(\text{watt-hr})(\text{cc})}{(\text{MWH})(\text{gm})}$$

$$F_T = 56.4 \frac{(\text{watt-hr})(\text{cc})}{(\text{MWH})(\text{gm})}$$

for the 610°F and 750°F steady-state irradiations respectively.

To compute the average dose/gm to the coolant material removed for recycle operations, multiply Equation (2) by the cycle (sampling) time and divide by the amount of coolant removed. For example from reference (1), the cycle time and the sample size during the 610°F steady-state irradiations were approximately 150 MWH and 320 gms respectively; during the 750°F steady-state irradiations the corresponding approximate values were 100 MWH and 300 gms. Using this method, the average specific dose to the coolant removed during the 610° and 750°F steady-state irradiations were 25 watt-hours/gm and 16 watt-hours/gm respectively. The lower value of the specific radiation dose for the degradation caused at 750°F is attributed to a higher pyrolysis contribution to the total rate of degradation (38) pyrolysis.

From the recycle and processing rate it is also possible to compute the total amount of coolant processed. In the 610°F irradiation, 15 samples of approximately 320 gms each were distilled and recycled during the period between 7880 and 9979 reactor MWH. This represents 4800 gms of coolant processed and should be compared to the

total contents of the loop which was  $5400 \pm 300$  gms during the period. Also, in the quasi-steady state period immediately preceding sample 1L251 (7800 MWH), there had been approximately 2000 MWH of reactor exposure time in which sampling and recycle of the coolant took place at approximately the same conditions as described between 1L251 and 1L265. Based on this additional sampling prior to sample 1L251 and ending at sample 1L265, approximately 9600 gms of irradiated Santowax OMP was processed at essentially steady-state HB conditions. Similarly, about 5900 gms of irradiated Santowax OMP was processed during the  $750^{\circ}\text{F}$  irradiation with the total loop content of  $5300 \pm 200$ .

Hence, it is believed that the samples in Table 4.2 represented those whose characteristics would approach the characteristics of irradiated Santowax OMP under long-term reactor exposure and use.

#### 4.3 Sublimation Yields and Molecular Weights

Sublimation and molecular weight measurements were performed on four HB samples as described in Sections 3.1 and 3.2, and Appendices A1 and A2. The results are summarized in Table 4.3 which compares the sublimation yields and molecular weights of each sublimate fraction for the 610°F and 750°F HB samples. Column 1 in Table 4.3 lists the evaporation temperatures at which sublimates were obtained. In columns 2, 3, 4, 6, 7, 8, 10, and 12 the sublimation yield for each HB sample listed in the heading is given in w/o followed by the cumulative yield in w/o through the sublimation at that temperature. Detailed results giving the sublimation conditions, yields, molecular weight solution concentrations, and notebook references are presented in Tables A2.1 through A2.4 in Appendix A2.

From comparison of columns 2, 3, 4, and 5 with columns 6, 7, 8 and 9 in Table 4.3 it is possible to deduce that the sublimate yields and molecular weights for the two 610°F HB samples 1L251 and 1L265 are similar to within a few per cent. Comparing columns 10 and 11 with 12 and 13 for the 750°F HB samples also shows close agreement. Figure 4.1 presents a graphical comparison of the cumulative yields in Table 4.3 from the 610°F samples and the 750°F samples. A comparison of the data in Table 4.3 and on Figure 4.1 shows a marked increase of the yields for each of the sublimate fractions for the 750°F HB samples. The higher yield for the 750°F HB fractions is also generally



**Table 4.3**

**Comparison of Sublimation Yields and Molecular Weights<sup>(4)</sup>  
for HB from Santowax OMP Irradiate at 610°F and 750°F**

1	2	3	4	5	6	7	8	9	10	11	12	13
Evaporation Temperature	Sample 1L251				Sample 1L265				Sample 2L22		Sample 2L40	
	Yields <sup>(1)</sup>			MW <sub>N</sub> <sup>(2)</sup>	Yields <sup>(1)</sup>			MW <sub>N</sub> <sup>(2)</sup>	Yields <sup>(1)</sup>	MW <sub>N</sub> <sup>(2)</sup>	Yields <sup>(1)</sup>	MW <sub>N</sub> <sup>(2)</sup>
	A	B	3		A	B	3					
200°C	4.12	3.51	3.20	325	4.96	6.27	3.10	328	8.16	318	8.33	316
250°C	12.51	10.95	12.34	403	13.60	15.16	17.29 <sup>(3)</sup>	413	24.59	388	24.42	385
Subtotal	16.63	14.46	15.54		18.56	21.43	20.39		32.75		32.75	
270°C	—	—	8.53	402	—	9.79	6.54	412	11.01	461	13.48	466
Subtotal	—	—	24.07		—	31.22	26.93		43.76		46.23	
290°C	15.52	15.96	7.83	454	15.45	6.38	7.72	494	7.78	521	7.28	539
Subtotal	31.85	30.42	31.90		34.01	37.69	34.65		51.54		53.51	
310°C	9.40	9.76	7.19	496	7.86	6.70	6.03	479	7.05	585	7.15	605
Subtotal	41.25	40.18	39.09		41.87	44.30	40.68		58.59		60.66	
350°C	9.27	8.38	11.94	601	9.71	8.54	11.83	584	8.58	711	7.03	734
Subtotal	50.52	48.56	51.03		51.58	52.84	52.51		67.18		67.69	
370°C	6.09	6.35	4.93	613	4.99	5.38	4.35	651	4.23	845	4.37	811
Subtotal	56.61	54.91	55.96		56.57	58.22	56.86		71.41		72.06	
Residue	43.71	43.95	44.42	1930	42.22	41.77	43.00	2005	28.48	1585	28.19	1695
Grand Total	100.32	98.96	100.38		98.79	99.99	99.86		99.88		98.35	

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See next page for footnotes.

Table 4.3 continued

Footnotes to Table 4.3 on page 33

- (1) Columns 2, 3, 4, 6, 7, 8, 10, and 12 present the yields for various portions of the same samples in w/o. See Tables A2.1, A2.2, A2.3, and A2.4 for detailed information: portions A and B are 1 gm samples. 1L251-3, 1L265-3, 2L22-1, and 2L40 are 2 gm samples.
- (2) Columns 5, 9, 11, and 13 present the  $MW_N$  values for the 2 gm samples whose fractional yields are presented in the column to the left of the  $MW_N$  column.
- (3) Sample bumped. See text in Appendix A2.
- (4) Error in  $MW_N$  is estimated to be  $\pm 5\%$ . See Section 4.42.
- (5) See footnote on page 2.

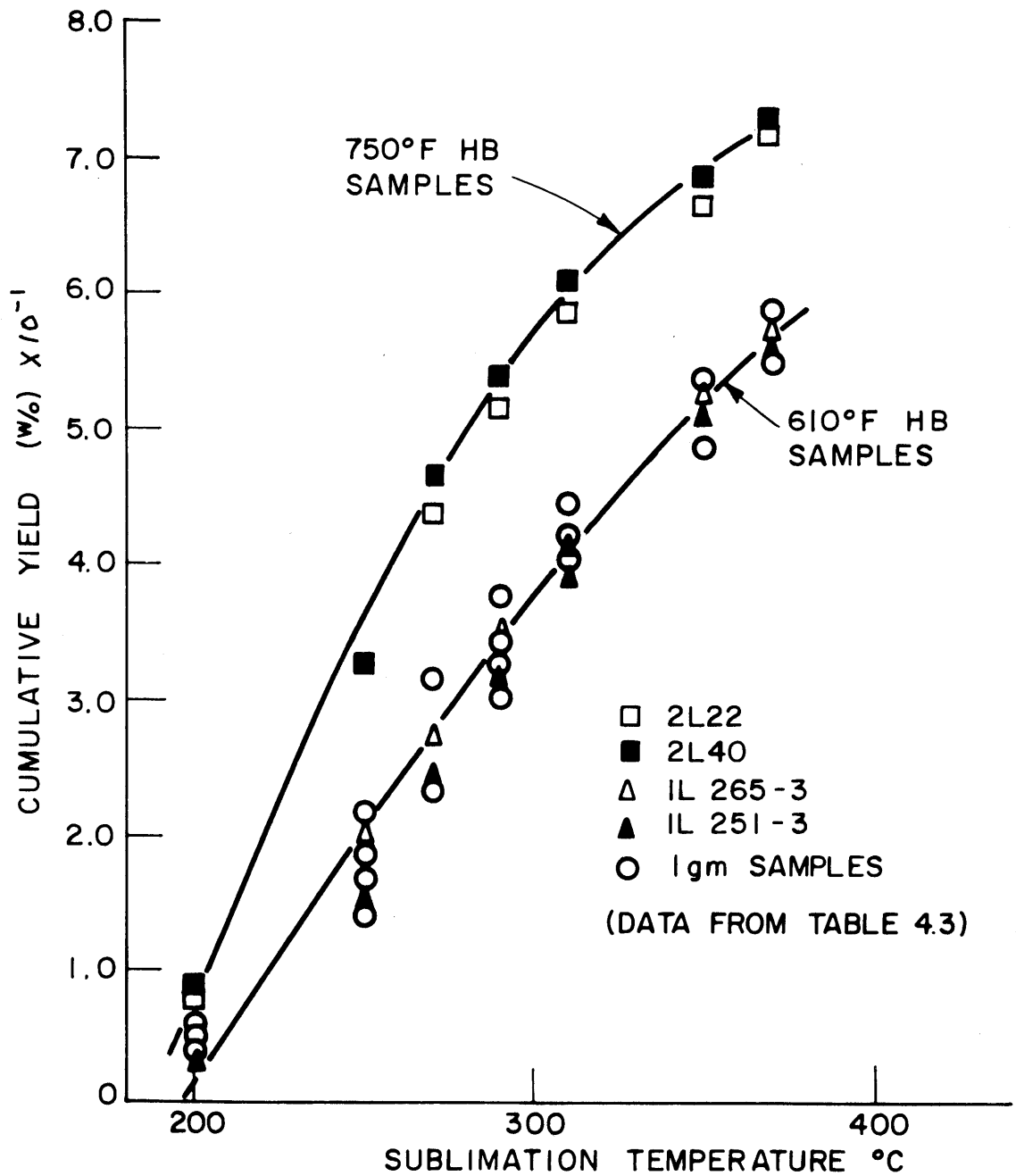


FIGURE 4.1 COMPARISON OF CUMULATIVE YIELDS FROM 610°F AND 750°F HB SAMPLES.

coupled with higher number average molecular weights for each fraction. This result is graphically presented in Figure 4.2 on which the  $MW_N$  values of columns 5, 9, 11 and 13 from Table 4.3 are presented. The results in Table 4.3, Figure 4.1, and Figure 4.2 indicate an overall increase in the volatility of the 750<sup>o</sup>F HB and a decrease in the amount of high molecular weight residue produced. This effect could be explained if we assume that degradation processes occurring under irradiation at higher temperatures produced molecular species of lower molecular weight and size due to the "pyrolytic cracking effect" accompanying irradiation at higher temperatures. Furthermore, Figure 4.2 shows an increase in the volatility above 300<sup>o</sup>C of the higher molecular weight materials produced in the 750<sup>o</sup>F irradiations. The increase in volatility may be an indication of ring rupture and/or alkylation which is discussed in the subsequent paragraphs.

The viscosity of the 750<sup>o</sup>F irradiated Santowax OMP is approximately 15% less than that of the 610<sup>o</sup>F irradiated material (See Section 5 of Reference (1)). This fact also supports the observed increase in the production of lower molecular weight species noted for the 750<sup>o</sup>F samples since solutions of high molecular weight species show high viscosities.

The sublimation yields and molecular weight results for each fraction presented in Table 4.3 do not permit fine resolution of the fractions as to molecular weights or

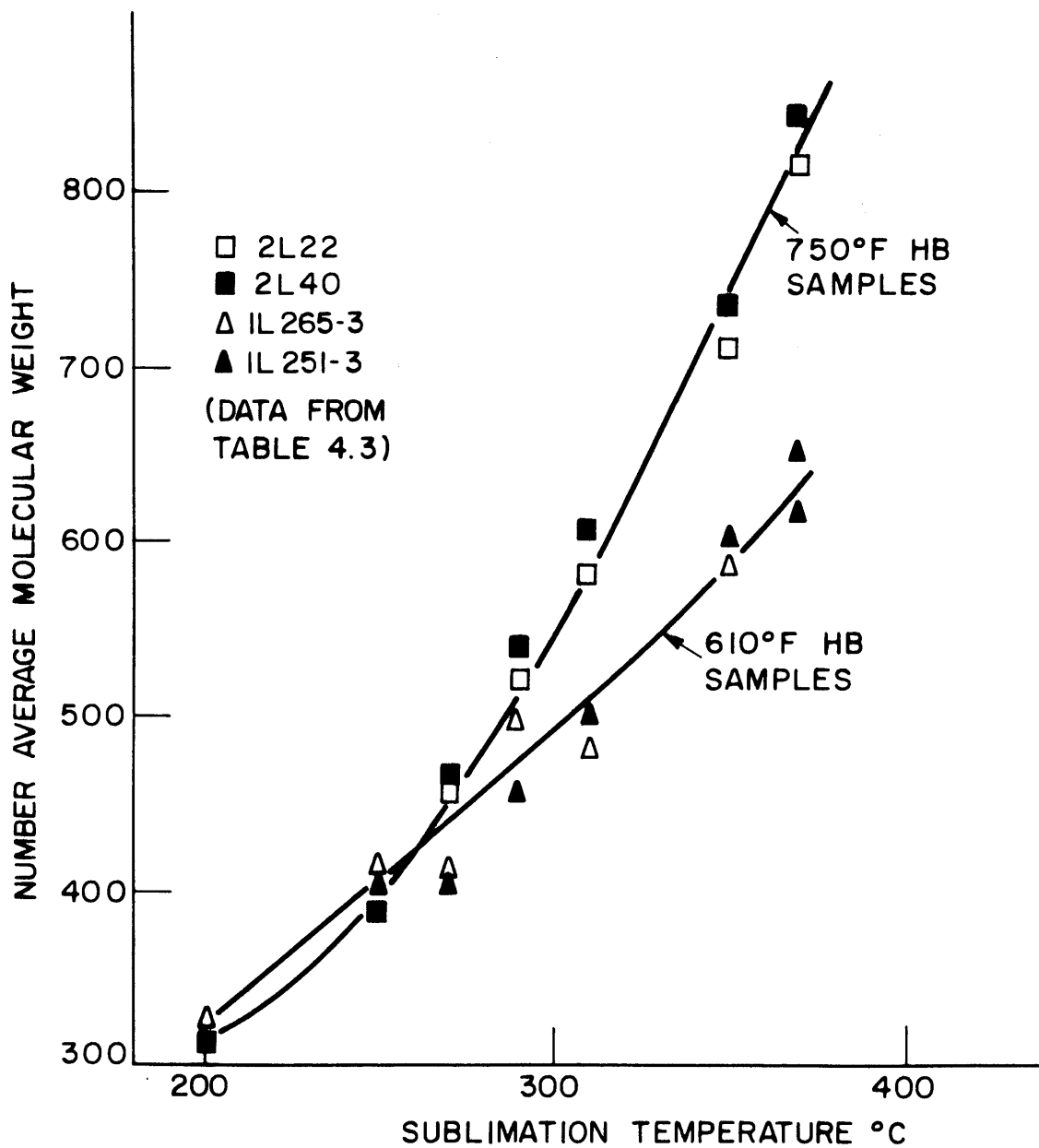


FIGURE 4.2 COMPARISON OF NUMBER AVERAGE MOLECULAR WEIGHTS VERSUS SUBLIMATION TEMPERATURE FOR 610°F AND 750°F HB SAMPLES

to permit a determination of the types of radiolytic reactions of the terphenyls which may occur. However, through the use of Reference (2) we may make some estimates of the probable composition of the HB. Keen (2) gives the following listing of types of radiolytically induced reactions which may occur:

(a) Polymerization-Depolymerization: The major products are the results of reactions of the type



where  $\phi$  represents a phenyl ring structure ( $C_6H_5$ ); no distinction is made between the phenyl group and the phenylene group ( $-C_6H_4-$ ) in the use of  $\phi_n$  or  $\phi_m$  to represent polyphenyls. The distribution of polyphenyls formed during an irradiation can be expected to depend on the relative amounts of  $\phi_m$  and  $\phi_n$  in the irradiated coolant, m and n are integers.

(b) Condensation of Ortho-Linked Phenyl Rings to Triphenylene: The presence of triphenylene in the irradiated coolant (approximately 3-5 w/o see Reference (1)) is indicative of ring closures and may be expected to compete strongly with Reaction (3) above.

(c) Hydrogenation and Dehydrogenation: The addition of hydrogen to polyphenyls producing partially and completely hydrogenated rings is indicated by such compounds as olefins and cycloalkyl polyphenyls. Volatile compounds of this type have been detected in the radiolytic gases from the MTR loops (6) and the MIT Loop (1, 13). Acetylenes in the gases (6)

are an indication of dehydrogenation.

(d) Ring Rupture: Minor high boiler constituents such as alkylpolyphenyls, alkyl triphenylenes, and phenylphenanthrenes result either from ring rupture or from reactions with fragments produced by ring rupture.

Using results obtained from mass spectrometer analysis of OMRE coolant and MTR in-pile loop coolant (11), the relative importance of the above radiolysis reactions was estimated by Keen et.al. (2); see Table 4.4.

Based on the estimates in Table 4.4 it is possible to consider the yields presented in Table 4.3 assuming the major reaction to be that of a polymerization reaction as shown in Equation (3). Table 4.5 presents the molecular weights of various  $\phi_n$  with  $3 < n < 10$ .

Since hydrogenation and dehydrogenation change the molecular weight of the  $\phi_n$ 's listed in Table 4.5 only slightly, the molecular weights of the  $\phi_n$ 's listed could also be coupled directly to the number of carbon atoms in a molecule. For reference; the number carbon atoms per mole is also listed in Table 4.5.

Another consideration of the molecular weights of the fractions sublimed in Table 4.3 is that the higher polyphenyls ( $n > 6$ ) exhibit very low volatilities. Therefore, it is unlikely that the 370°C fraction of the 750°F HB samples 2L22 and 2L40 whose molecular weights of 845 and 811 respectively would represent polyphenyls of approximately 11 phenyl groups. It is more plausible to assume

Table 4.4

Relative Importance of Decomposition Reactions (2)  
(Based on Polymerization = 100)

Polymerization	100
Condensation	5-20
Depolymerization (cleavage between rings)	2-5
Ring Rupture	2-5
Hydrogenation	2-5

---

(1) The values presented are based on experimental data from irradiated coolant from the OMRE and in-pile loop data. Irradiation temperatures were approximately 600°F.



Table 4.5

Molecular Weights of Various Polyphenyls ( $\phi_n$ )

<u>Generic Name</u>	<u>n</u>	<u>No. of Carbon Atoms</u>	<u>Molecular Weight</u>
Terphenyls	3	18	230
Quaterphenyls	4	24	306
Quinquephenyls	5	30	382
Hexaphenyls	6	36	458
Heptaphenyls	7	42	534
Octaphenyls	8	48	610
Nonaphenyls	9	54	686
Decaphenyls	10	60	762

that some ring rupture has occurred to give alkylpolyphenyls which are more volatile than the basic phenyl structure to which they are attached or from which they may be derived. An example of this effect would be isopropyl biphenyl (MW = 196) which is a substituted biphenyl ( $n = 2$ ) containing 3 additional carbon atoms and whose atmospheric boiling point at  $270^{\circ}\text{C}$  (39) is only  $15^{\circ}\text{C}$  higher than the boiling point of biphenyl, which has a MW = 154.

Based on the foregoing analysis we may therefore study the yields and molecular weights of the various sublimate fractions in Table 4.3 in terms of the most probable number of carbon atoms per molecule assuming that very little carbon is lost from ring rupture and that hydrogenation and dehydrogenation changes the molecular weight only slightly. In making this assumption it is assumed that each sublimate fraction represents a discrete molecular species, while in fact each fraction represents a mixture of species having a number average molecular weight (See Section 4.4). Using these assumptions, Table 4.6 presents probable values for the carbon atom content per molecule of each of the sublimed fractions. The values presented were obtained from the curves presented in Figures 4.1 and 4.2.

Note from Table 4.6 that the MITR samples did not exhibit any significant increase in the yield of fractions whose MW were multiples of terphenyl. Keen (2) reported such multiples from mass spectroscopy analyses on Core I OMRE coolant. However,

Table 4.6

Probable Carbon Atom Content for HB Fractions Sublimed  
from 610°F and 750°F HB Samples

Sublimation Temperature (°C)	Yields (1)		Molecular Weight (MW <sub>N</sub> )	Probable Carbon Content per mole. (3)	Nearest ϕ <sub>n</sub> (4)
	Fractional (w/o)	Cumulative			
<u>610°F HB Samples</u>					
200	2.0	2.0	324	25	ϕ <sub>4</sub>
250	19.2	21.2	406	31	ϕ <sub>5</sub>
270	7.2	28.0	436	33	ϕ <sub>5</sub> - ϕ <sub>6</sub>
290	6.5	34.5	472	36	ϕ <sub>6</sub>
310	7.5	41.0	508	39	ϕ <sub>7</sub>
350	9.0	52.0	584	45	ϕ <sub>8</sub>
370	4.5	56.5	628	48	ϕ <sub>8</sub>
Residue	43.5	100.0	1970	—	—
<u>750°F HB Samples</u>					
200	8.5	8.5	312	24	ϕ <sub>4</sub>
250	28.5	36.0	396	30	ϕ <sub>5</sub>
270	8.5	45.5	448	35	ϕ <sub>6</sub>
290	8.0	53.5	508	39	ϕ <sub>7</sub>
310	6.5	60.0	584	45	ϕ <sub>8</sub>
350	9.0	69.0	740	57	ϕ <sub>9</sub> - ϕ <sub>10</sub>
370	3.0	72.0	824	63	ϕ <sub>11</sub>
Residue	28.0	100.0	1630	—	—

(1) Data from Figure 4.1

(2) Data from Figure 4.2

(3) Assuming Carbon to be the major addition or subtraction from ϕ<sub>n</sub>

(4) Data from Table 4.5

during Core I operation, the HB concentration in the OMRE varied considerably, and in general the HB content was below 30 w/o. Extending the analysis presented in Section 4.2 to the continuous processing used at the OMRE, to a lower HB content, the specific dose to the OMRE coolant removed during processing would be lower than that achieved for the samples used in this work. A higher specific dose such as experienced in the MITR samples may result in the production of intermediate  $\phi_n$ 's which are not multiples of the original starting terphenyls.

The results on Table 4.6 also show the volatilization seen in Figure 4.2 of higher molecular weight species at sublimation temperatures of 270°C to 300°C and above. To graphically illustrate the differences between the molecular weight distribution of 610°F HB and 750°F HB samples, the cumulative yields and molecular weights from Table 4.3 were plotted and are shown in Figure 4.3. Slopes of the curves in Figure 4.3 at various values of the molecular weight then gave a measure of the differential yield in w/o per unit molecular weight. Slopes taken at approximately every 50 molecular weight units are plotted in Figure 4.4. Note that in Figure 4.3 (and in Figure 4.4) that the  $MW_N$  distribution starts at 230 which is the starting  $MW_N$  of the unirradiated coolant. It is a function of the method of processing. For example, if the distillation took a lighter cut (i.e. cut off at a lower temperature) IB and terphenyls would also be included. It is well to remember therefore that we are only looking at the

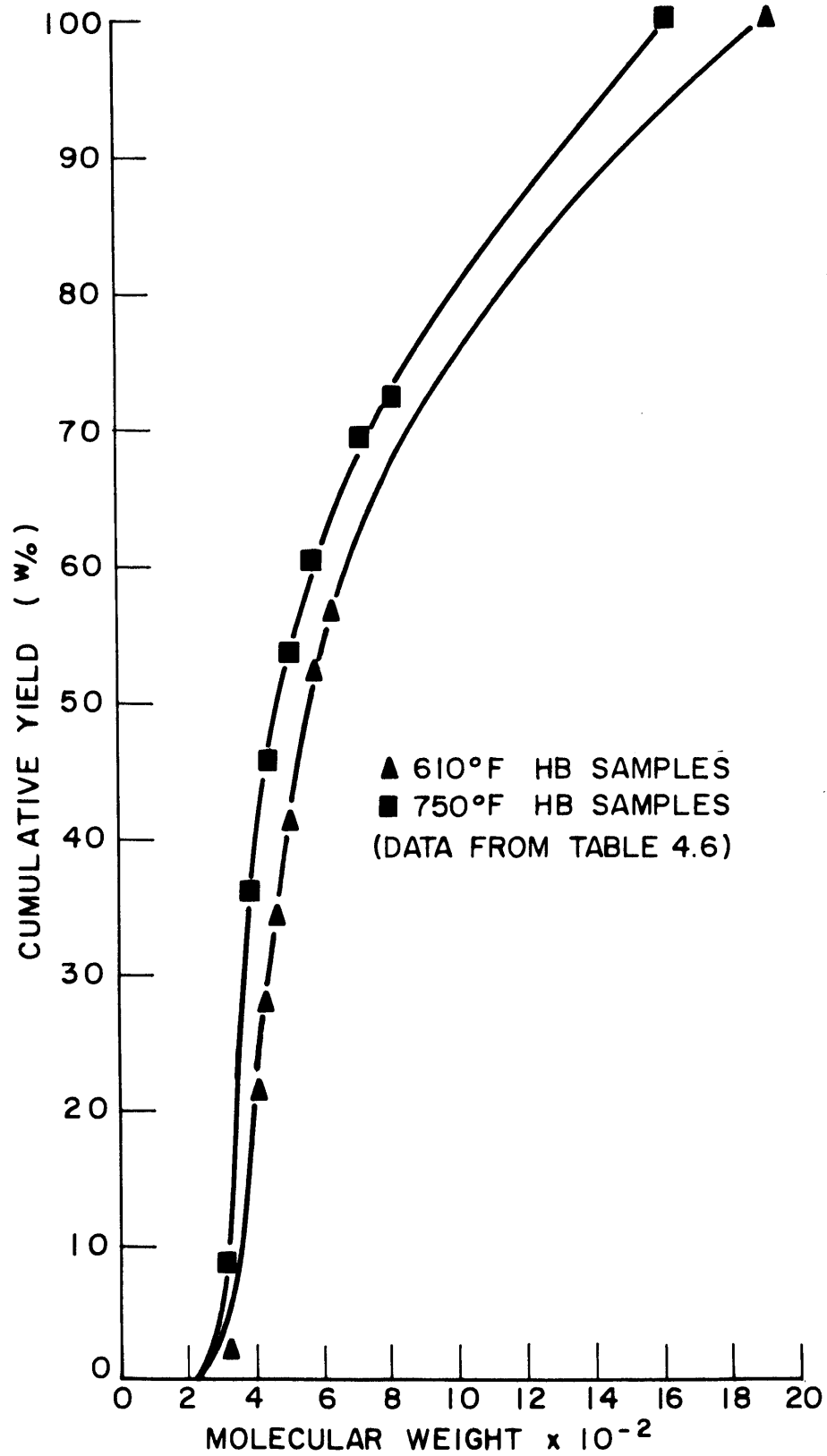


FIGURE 4.3 CUMULATIVE SUBLIMATE YIELD VERSUS MOLECULAR WEIGHT

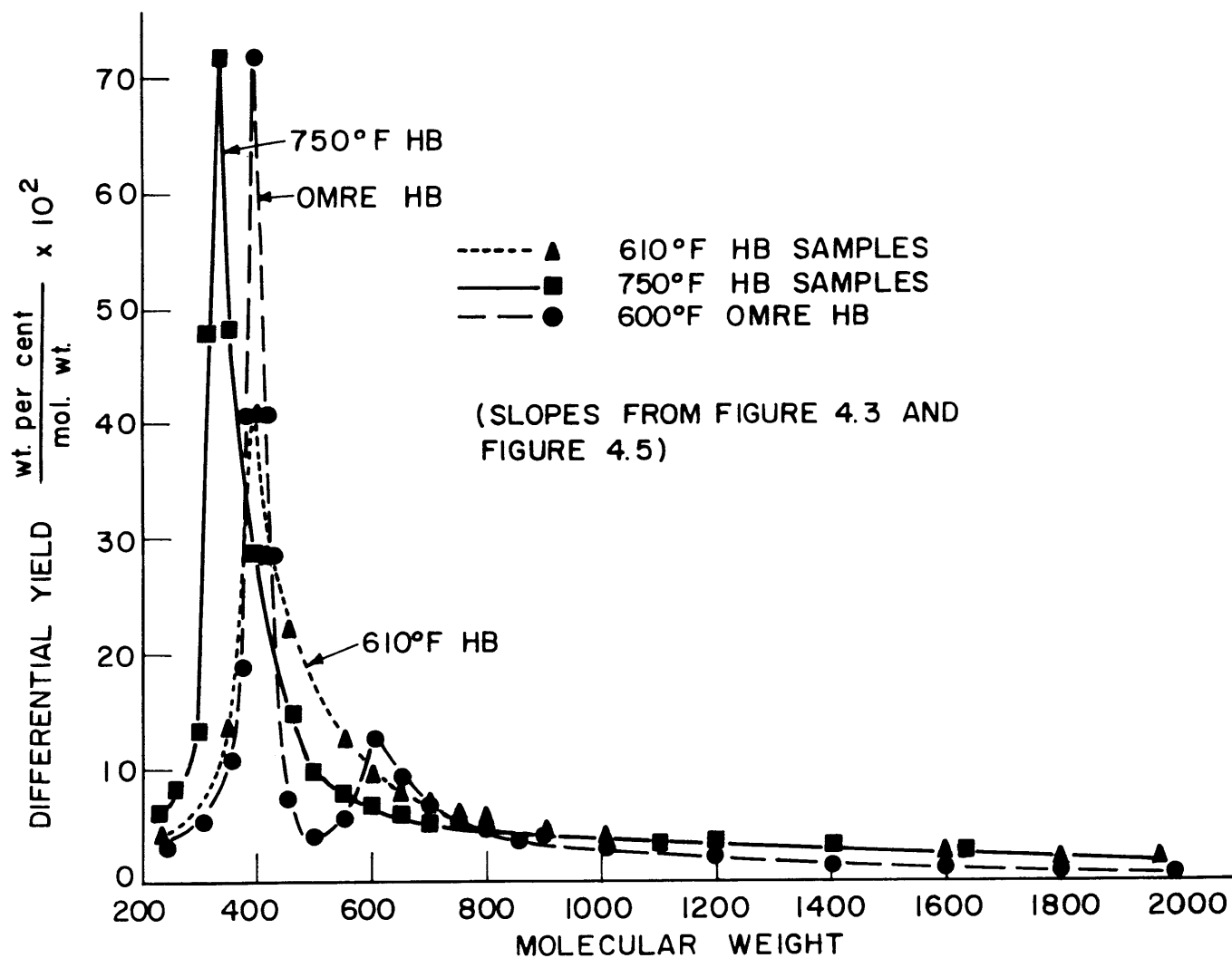


FIGURE 4.4 DIFFERENTIAL YIELDS W% PER UNIT MOLECULAR WEIGHT VERSUS MOLECULAR WEIGHT.

HB portion of the DP in this work, and the curves in this report do not include the LB and IB (See Table 2.1) which may total 10 - 15 w/o of the irradiated coolant containing 35 w/o HB (1). There is a peak at 400 molecular weight units for the 610<sup>o</sup>F HB samples and at 340 molecular weight units for the 750<sup>o</sup>F HB samples. The area under any section of the curves in Figure 4.4 gives the yield in weight per cent for any desired molecular weight interval which is in good agreement with the data presented in Table 4.3. Keen (2) has estimated a molecular weight distribution to be expected in OMRE coolant after extended irradiation based on mass spectroscopy results and probability of formation as presented in Table 4.4. Table 4.7 is a copy of the estimate presented in Reference (2). The differential yields for OMRE coolant can be obtained directly from Table 4.7. However, to make a comparison between the estimated OMRE molecular weight distribution and the samples obtained in this work from the 610<sup>o</sup>F irradiations utilizing the same method of analysis, the data from Table 4.7 was plotted in Figure 4.5 in a manner similar to that in Figure 4.3. The slopes from the smoothed data in Figure 4.5 are also plotted on Figure 4.4 to give a direct comparison of the estimated OMRE HB molecular weight distribution with 610<sup>o</sup>F HB samples from this work. The close correspondence between the estimated molecular weight distribution for the OMRE HB and the HB from 1L251 and 1L265 is quite good. The increased fine structure of the OMRE HB estimate gives peaks at  $\phi_6$  and  $\phi_9$  in Table 4.7

Table 4.7

Estimated Molecular Weight Distribution of High Boilers in  
OMRE Coolant After Extended Irradiation (2)  
(Based on Core I Sample 40-2 ML-1)

<u>Mass Interval</u>	<u>Mass Interval Range</u>	<u>Polyphenyl at Middle Mass of Range</u>	<u>Average MW of Range</u>	<u>w/o of HB in Interval</u>
1	226-268	3	230	4.5
2	269-344	4	306	3.4
3	345-420	5	382	14.1
4	421-496	6	458	27.3
5	497-572	7	534	3.0
6	573-800	9	686	17.47
7	801-1028	12	914	11.18
8	1029-1256	15	1142	7.16
9	1257-1484	18	1370	4.58
10	1485-1712	21	1598	2.93
11	1713-1940	24	1826	1.88
12	1941-2168	27	2054	1.20
13	2169-2396	30	2282	0.77
14	2397-2624	33	2510	0.49
15	2625-2852	36	2738	0.31
16	2853-3080	39	2966	0.20



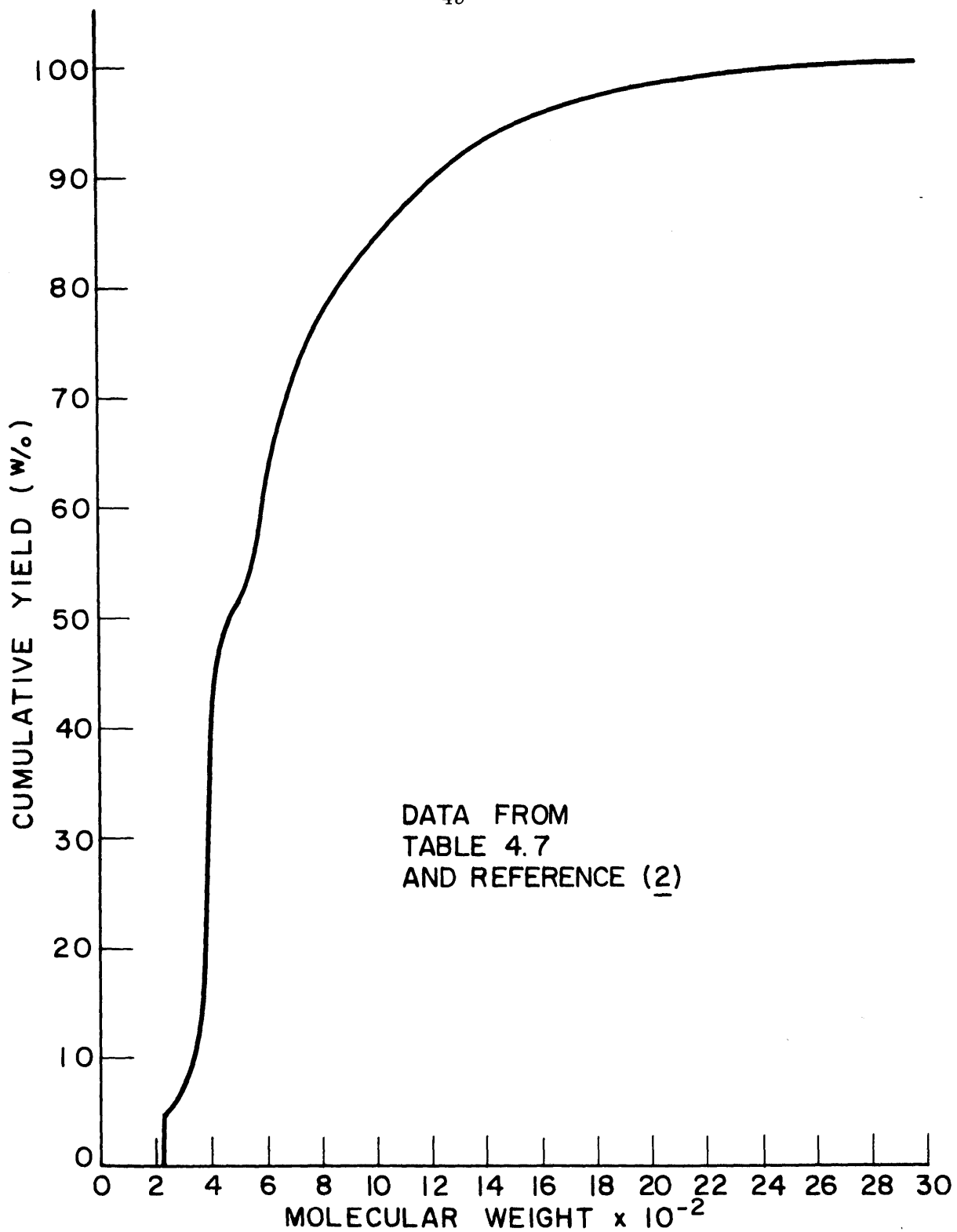


FIGURE 4.5 ESTIMATED CUMULATIVE YIELD FOR OMRE HB AFTER EXTENDED IRRADIATION VERSUS MOLECULAR WEIGHT

while Figure 4.4 gives peaks at 400 and 600. This lowering of the peak may be due to the treatment of the data in which integral curves are used to give differential results.

The estimated OMRE distribution in Table 4.7 yields a computed number average molecular weight ( $MW_N$ ) (See Section 4.4 for a discussion of average molecular weights) of 545.2 which is in good agreement with the measured value by Keen (2) of 535 for Core I Sample 40-2ML-1. Keen estimates that an equilibrium value for the  $MW_N$  of OMRE HB would be  $650 \pm 25$ . A value of  $MW_N = 650 \pm 25$  is in good agreement with the values obtained in this work for HB obtained from Santowax OMP irradiated at  $610^\circ\text{F}$  of approximately 700 (See Table 4.10 in Section 4.41).

Although OMRE Core I coolant, when compared to the Santowax OMP irradiated in this work, contained substantial amounts of biphenyl, about 3 times as much ortho terphenyl, less meta terphenyl and less para terphenyl (See Table 4.8), a comparison of the HB formed in each case is justified since the terphenyls are still the major constituents of the coolant. The technique as shown in Figure 4.4 gives good results with a minimum of data and can be expected to show trends (i.e. the difference between  $610^\circ\text{F}$  and  $750^\circ\text{F}$  HB samples) and overall distribution. The sublimation technique to give molecular weight distribution would be much improved if the number of fractions were increased.

Table 4.8

Comparison of OMRE (2) Core I and Core II Coolants  
with M.I.T. (1) Coolants

Source	OMRE Core I(3)	OMRE Core II(3)	MIT 610°F(4)	MIT 750°F(4)
<u>Constituent</u>	w/o	w/o	w/o	w/o
biphenyl	7-17	1-7	1	1-2
ortho-terphenyl	20-47	18-45	6.0	6.1
meta-terphenyl	17-33	21-36	37.6	35.3
para-terphenyl	2-8	2-13	18.3	18.6
HB	0-41 <sup>(1)</sup>	0-30 <sup>(1)</sup>	32.3	32.4
LIB	not given	not given	5.8 <sup>(2)</sup>	7.1 <sup>(2)</sup>

- 
- (1) During Core I operation the HB content varied considerably, whereas during Core II operation the HB content was allowed to rise to 30 w/o, and then held constant at 30 w/o.
- (2) Includes the small amount of biphenyl present.
- (3) For detailed analyses see references (33 and 34).
- (4) Steady-State Analyses.

#### 4.4 Calculated Number Average Molecular Weights, Weight Average Molecular Weights and an Estimate of Errors

The molecular weights of the individual sublimate fractions presented in Table 4.3 can be combined by number averaging or weight averaging to give the Number Average Molecular Weight ( $MW_N$ ) or the Weight Average Molecular Weight ( $MW_W$ ) for the whole HB fraction.

The number averaging and weight averaging of the separate fractions is presented in Section 4.41. The results obtained for  $MW_N$  are compared to experimental values of  $MW_N$  from reference (1). The  $MW_W$  are also presented for comparison. In addition, the formula for  $MW_N$  was used to compute the  $MW_N$  of the residue remaining after each sublimation to compare residue  $MW_N$ 's with results obtained by the Phillips Petroleum Company for Core II OMRE HB (26, 33).

Section 4.42 presents an estimate of the errors resulting from the insolubility of the HB fractions (see Section 4.1) in the tetrahydrofuran solvent.

#### 4.41 Computation of the $MW_N$ and $MW_W$ Values of the HB and the Individual Sublimate Residues

When molecular weight measurements are made on mixtures, the value of the molecular weight obtained represents an "average" molecular weight. The "average" value obtained depends on the measuring procedure employed. The procedures presented in Section 3.1, i.e., Cryoscopic, Ebulliometric, and Vapor Pressure Lowering Methods, give an "averaged" molecular weight defined as a "number average" molecular weight ( $MW_N$ ) (36). The term "number average" denotes a

method in which every molecule present, regardless of its size, gives rise to the same response in the characteristic being measured.

The  $MW_N$  of a mixture is the molecular weight computed by averaging the molecular weights of the individual fractions which are homogeneous with respect to the characteristic and is represented by the equation

$$MW_N = \frac{\sum W_i}{\sum W_i / M_i} \quad (4)$$

where  $MW_N$  is the number average molecular weight

$W_i$  is the mass of specie  $i$  in some consistent units (in this report w/o is used)

and  $M_i$  is the molecular weight of specie (or fraction)  $i$ .

Another mathematical representation of an averaging method, called a "weight average" molecular weight ( $MW_W$ ) is:

$$MW_W = \frac{\sum W_i M_i}{\sum W_i} \quad (5)$$

where  $MW_W$  is the weight average molecular weight and  $W_i$  and  $M_i$  are as defined for Equation (4).

Light scattering properties of solutions which are strongly dependent on molecular size result in "weight averages" of the molecular weight.

The distinction between number averaging and weight averaging becomes important when analyses of mixtures covering wide molecular weight ranges are considered. The number averaging process emphasizes the low molecular weight specie, while a weight average emphasizes the higher molecu-

lar specie (36). For a single species in solution,  $MW_N = MW_W$ , and also if the species in a fraction are concentrated at the median,  $MW_N$  approaches  $MW_W$  (2). It is seen, therefore, that comparison of results by number averaging and weight averaging procedures will furnish a measure of the molecular weight distribution.

Using the values of  $M_1$  and  $W_1$  presented in Table 4.9, the values of  $MW_N$  and  $MW_W$  for the 2 gm HB samples, 1L251-3, 1L265-3, 2L22 and 2L40 were calculated. The results are presented in Table 4.10 along with the experimentally determined  $MW_N$  results for the whole HB fraction from reference (1). The computed  $MW_N$  results agree very well with the experimental  $MW_N$  presented in Table 4.9 indicating the applicability of number averaging. Also, the agreement between Samples No. 1L251 and 1L265 and between Samples No. 2L22 and 2L40 is very good for both  $MW_N$  and  $MW_W$  indicating again that equilibrium in the molecular weight distribution for the HB had been reached during the extended irradiations at 610°F and 750°F. By comparing  $MW_N$  with  $MW_W$  for each sample the influence of the high molecular weight and the amount of residue remaining after the 370°C sublimation on the two averages is quite pronounced. The difference between  $MW_W$  and  $MW_N$  is reduced from approximately 400 to 250 molecular weight units when one compares the 610°F HB samples and the 750°F HB samples respectively. This result is due to the larger amount of residue of higher molecular weight remaining after the 370°C sublimation for the 610°F HB samples than in the case of the 750°F HB. The use of  $MW_W$

Table 4.9  
Values of  $M_i$  and  $W_i^{(1)}$  Used for  
Calculating  $MW_N$  and  $MW_W$  in Table 4.10

Sample No. 1L251	$M_i$	325	403	402	454	496	601	613	1930
	$W_i$	3.2	12.3	8.5	7.8	7.2	11.9	4.9	44.4
1L265	$M_i$	328	413	412	494	479	584	651	2005
	$W_i$	3.1	17.3	6.5	7.7	6.0	11.8	4.4	43.0
2L22	$M_i$	318	388	461	521	585	711	845	1585
	$W_i$	8.2	24.6	11.0	7.8	7.1	8.6	4.2	28.5
2L40	$M_i$	316	385	466	539	605	734	811	1695
	$W_i$	8.3	24.4	13.5	7.3	7.2	7.0	4.4	28.2

---

<sup>(1)</sup> Data for  $M_i$  and  $W_i$  taken from Tables A2.3, and A2.4 and also presented on Table 4.3 for the various  $i$  fractions.

Table 4.10  
Calculated  $MW_N$  and  $MW_W$  Values  
for HB Samples From 610°F and 750°F  
Steady-State HB Irradiations of Santowax OMP

Sample No.	<u>1L251</u>		<u>1L265</u>		<u>2L22</u>		<u>2L40</u>	
	This	Ref.	This	Ref. <sup>(1)</sup>	This	Ref.	This	Ref.
	Work	( <u>1</u> )	Work	( <u>1</u> )	Work	( <u>1</u> )	Work	( <u>1</u> )
$MW_N$	696	682	695	700	571	568	571	587 <sup>(2)</sup>
$MW_W$	1095	—	1137	—	803	—	829	—

<sup>(1)</sup> Estimated, because of spread in data in reference (1).

<sup>(2)</sup> Value for 2L40 not available. Value presented is for 2L26 which has essentially the same radiation exposure.



gives a good measure of the amount of high molecular weight specie in the whole sample.

The  $MW_N$  of each residue remaining after each sublimation was not measured. However, using Equation (4) for  $MW_N$ , in a step-wise fashion, it is possible to compute an  $MW_N$  for the remaining residue after the seventh sublimation at 370°C. The results will be useful for a comparison with results of other investigators.

Equation (4) can be rewritten as follows for each sublimation step:

$$MW_{N_{S+R}} = \frac{S+R}{\frac{S}{MW_{N_S}} + \frac{R}{MW_{N_R}}} \quad (6)$$

where  $MW_{N_{S+R}}$  is the  $MW_N$  for the sample prior to sublimation (for the first sublimation at 200°C  $MW_{N_{S+R}} = MW_N$  for the shale HB sample)

S is the  $W_i$  removed in the sublimation

R is the  $W_i$  remaining as residue after sublimation

$MW_{N_S}$  is the measured  $MW_N$  of the sublimate as presented in Table 4.9 as  $M_i$

$MW_{N_R}$  is the  $MW_N$  of the residue remaining after sublimation

Note that  $MW_{N_{S+R}}$  is the  $MW_{N_R}$  of the preceding sublimation step.

Equation (6) can be solved for  $MW_{N_R}$  to give:

$$MW_{N_R} = \frac{R}{\frac{S+R}{MW_{N_{S+R}}} - \frac{S}{MW_{N_S}}} \quad (7)$$

Equation (7) was computed in a step-wise fashion for

each value of  $i$  in Table 4.9 for samples 1L251, 1L265, 2L22 and 2L40. The results of  $MW_{N_R}$  for each sublimation are presented in Table 4.11 along with the values of  $i$ ,  $S$ ,  $R$ ,  $MW_{N_S}$  and the sublimation temperature. The last value of  $i = 7$  gives a value of  $MW_{N_R}$  which should correspond to the experimental value of  $M_1$  (parenthetically presented in Table 4.11) presented in Table 4.9 for the residue. The computed values and the experimental values appear to agree quite well except in the case of sample 2L40. A residue  $MW_N$  profile can be obtained from Table 4.11, and a comparison can be made with results obtained for OMRE Core II (26, 33) HB (see Table 4.8 for Core II coolant information). Figure 4.6 presents the results.<sup>(1)</sup> The OMRE operating temperatures were approximately 600°F and a comparison can be made between the 610°F HB and the OMRE Core II HB. We note here that the M.I.T. 610°F HB samples, 1L251 and 1L265 are in good agreement, and that the OMRE Core II HB molecular weight was not as high as the M.I.T. results indicating that equilibrium molecular weight was not reached during Core II operation. The 750°F HB residues show lower molecular weight distributions as previously noted in Section 4.3 for the sublimates.

#### 4.42 Estimate of Errors Due to Insolubles

Analysis of the osmometer operation and the sample preparation indicate two significant sources of error. These are the insolubility effects, already discussed in Sections 3.1, 3.2, and 4.1, and errors in the osmometer itself (See Appendix A1). To estimate the possible effect

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(1) The arrows on Sample 2L40 indicate correction required for agreement with 1L265.

Table 4.11

Computed Number Average Molecular Weights for Sublimate Residues

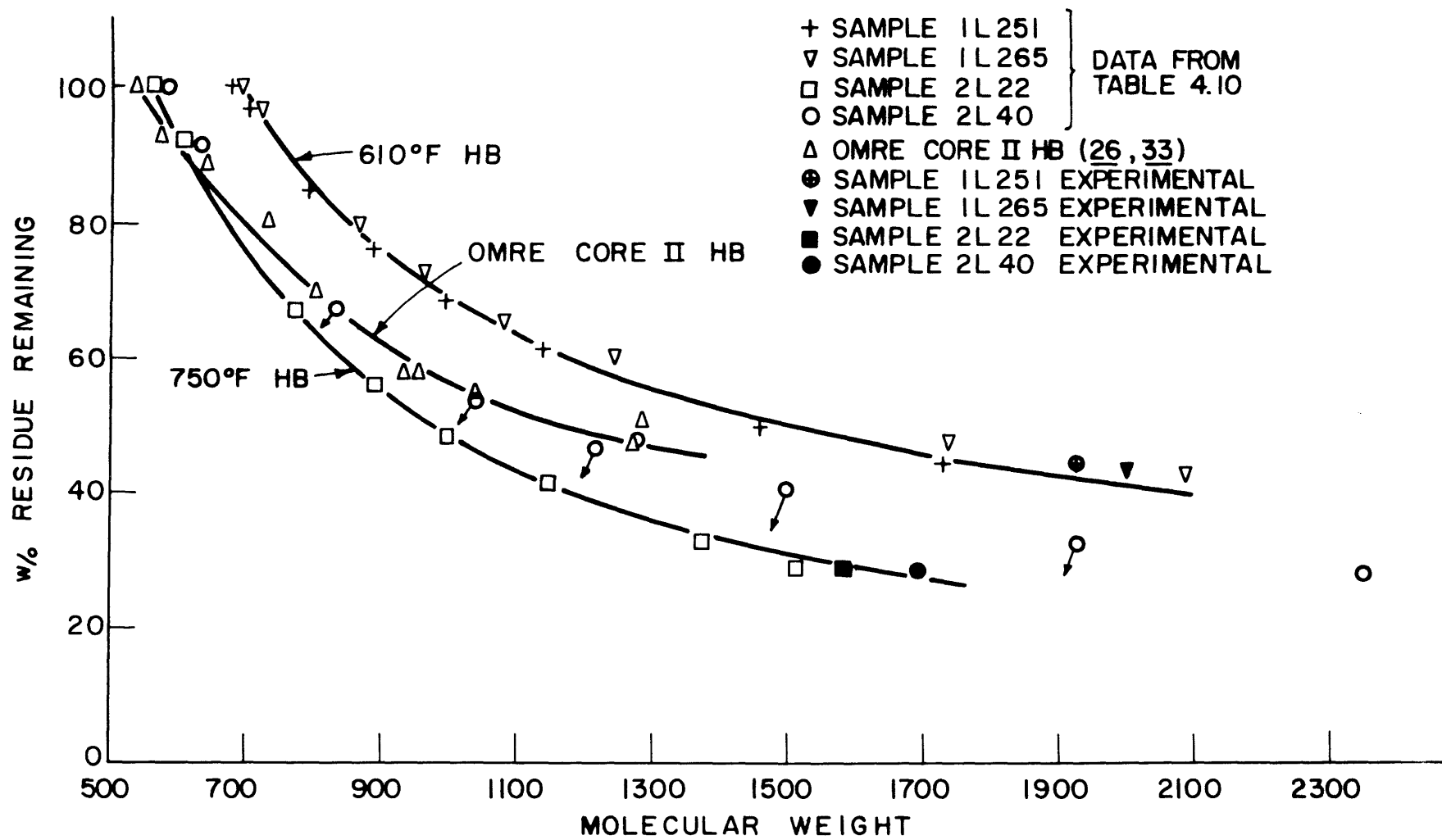
Temp. of Evaporation °C	MW <sub>NS</sub>	S w/o	S+R w/o	R w/o	MW <sub>NS+R</sub>	MW <sub>NR</sub>
<u>Sample No. 1L251-3</u>						
200	325	3.2	100.0	96.8	682	708
250	403	12.3	96.8	84.5	708	795
270	402	8.5	84.5	76.0	795	893
290	454	7.8	76.0	68.2	893	1004
310	496	7.2	68.2	61.0	1004	1142
350	601	11.9	61.0	49.1	1142	1460
370	613	4.9	49.1	44.2	1460	1725(1930)
<u>Sample No. 1L265-3</u>						
200	328	3.1	100.0	96.9	700	726
250	413	17.3	96.9	79.6	726	870
270	412	6.5	79.6	73.1	870	965
290	494	7.7	73.1	65.4	965	1087
310	479	6.0	65.4	59.4	1087	1247
350	584	11.8	59.4	47.6	1247	1736
370	651	4.4	47.6	43.2	1736	2090(2005)

(continued on next page)

Table 4.11 (continued)

Computed Number Average Molecular Weights for Sublimate Residues

Temp. of Evaporation °C	MW <sub>N<sub>S</sub></sub>	S w/o	S+R w/o	R w/o	MW <sub>N<sub>S+R</sub></sub>	MW <sub>N<sub>R</sub></sub>
<u>Sample No. 2L22</u>						
200	318	8.2	100.0	91.8	568	611
250	388	24.6	91.8	67.2	611	774
270	461	11.0	67.2	56.2	774	892
290	521	7.8	56.2	48.4	892	1007
310	585	7.1	48.4	41.3	1007	1150
350	711	8.6	41.3	32.7	1150	1373
370	845	4.2	32.7	28.5	1373	(1513(1585))
<u>Sample No. 2L40</u>						
200	316	8.3	100.0	91.7	587	636
250	385	24.4	91.7	67.3	636	834
270	466	13.5	67.3	53.8	834	1040
290	539	7.3	53.8	46.5	1040	1217
310	605	7.2	46.5	39.3	1217	1494
350	734	7.0	39.3	32.3	1494	1926
370	811	4.4	32.3	27.9	1926	2460(1695)



- + SAMPLE 1L 251
  - ▽ SAMPLE 1L 265
  - SAMPLE 2L 22
  - SAMPLE 2L 40
- DATA FROM TABLE 4.10
- △ OMRE CORE II HB (26, 33)
  - ⊕ SAMPLE 1L 251 EXPERIMENTAL
  - ▽ SAMPLE 1L 265 EXPERIMENTAL
  - SAMPLE 2L 22 EXPERIMENTAL
  - SAMPLE 2L 40 EXPERIMENTAL

FIGURE 4.6 MOLECULAR WEIGHT PROFILE OF HB

of the insoluble portion of the sample, Equation (4) for  $MW_N$  may be split into soluble and insoluble portions as follows:

$$MW_N = \frac{\sum_i W_i^{sol} + a}{\sum_i W_i^{sol} / M_i^{sol} + M_a} \quad (8)$$

where  $W_i$  and  $M_i$  have been defined for Equation (4) and "a" is the insoluble weight fraction whose molecular weight is  $M_a$ . The superscript "sol" describes the soluble portions.

It can be seen from Equation (8) that if the molecular weight,  $M_a$ , of the insoluble fraction is very large (about a factor of 100 higher) in comparison of the other  $M_i^{sol}$ , or if a is very small, the  $MW_N$  will be essentially correct. If the  $M_a$  is on the same order as the other  $M_i^{sol}$ , the error in  $MW_N$  will be on the order of the per cent insolubility. On the other hand, if the  $M_a$  is much smaller than the other  $M_i^{sol}$  a significant error will result in  $MW_N$ .

If one makes any assumptions regarding the types of molecular species which would result from irradiation (See Table 4.4 and References (2, 16, 35)) and their relative yields, the most reasonable assumption would be that  $M_a$  is approximately equal to; or perhaps two or three times greater than  $M_i^{sol}$ . This means that the error in  $MW_N$  would be on the order of the per cent insolubles which has been previously stated in Section 4.1 to be approximately equal to 2 w/o.

From analysis of the osmometer errors in calibration as presented in Appendix A-1 of  $\pm 1.5\%$ , an overall error of

+ 3% to - 2% is possible. However, due to the many assumptions required a more probable overall error would be on the order of  $\pm 5\%$ . Thus, the  $MW_N$  values in Table 4.3 could have a probable error of 25 to 30 molecular weight units.

#### 4.5 Gas Chromatography Results

A third analytical method in addition to sublimation and molecular weight measurements was used to qualitatively determine the existence of equilibrium in the steady-state HB irradiations of Santowax OMP at 610°F and 750°F. The third analytical method used was high temperature gas chromatography. The development of the equipment and method is presented in Section 3.3 and Appendix A3.

Micro-liter amounts of the THF solutions containing the dissolved sublimate (See Section 3.32 and Appendices A2.1 and A2.2) were injected by means of a syringe into the chromatograph under identical conditions of carrier gas flow and temperature programming so that the resultant chromatograms for similar fractions could be qualitatively compared for peak distribution. Table 4.12 presents the operating conditions for the analyses. The first three sublimates (at 200°C, 250°C, and 270°C) of the 2 gm. samples (1L251-3, 1L265-3, 2L22, and 2L40) were analyzed and a series of twelve chromatograms resulted. Four chromatograms resulting from the 270°C sublimate for the sublimates 1L251-53A, 1L265-53A, 2L22-S3A, and 2L40-S3A are presented in Figure 4.7. These four chromatograms serve to show the similarity of the fractions. In addition,

Table 4.12

Operating Conditions for Gas Chromatographic

Analysis of HB Samples

Injection Port Temp. °C	380°-400
Detector Block Temp. °C	380 -400

Temperature Program of Column

Inject at 120°C wait one minute

Program 120°C to 200°C 5°C/min.

200°C to 420°C 7.5°C/min.

Helium Carrier Gas

Pressure	30 psig.
Flowmeter Reading	7.4
Air Flowmeter Reading	6.9
Hydrogen Flowmeter Reading	4.5



NOTE: IN COMPARING UPPER AND LOWER SETS, LOWER SET IS SHIFTED TO THE RIGHT

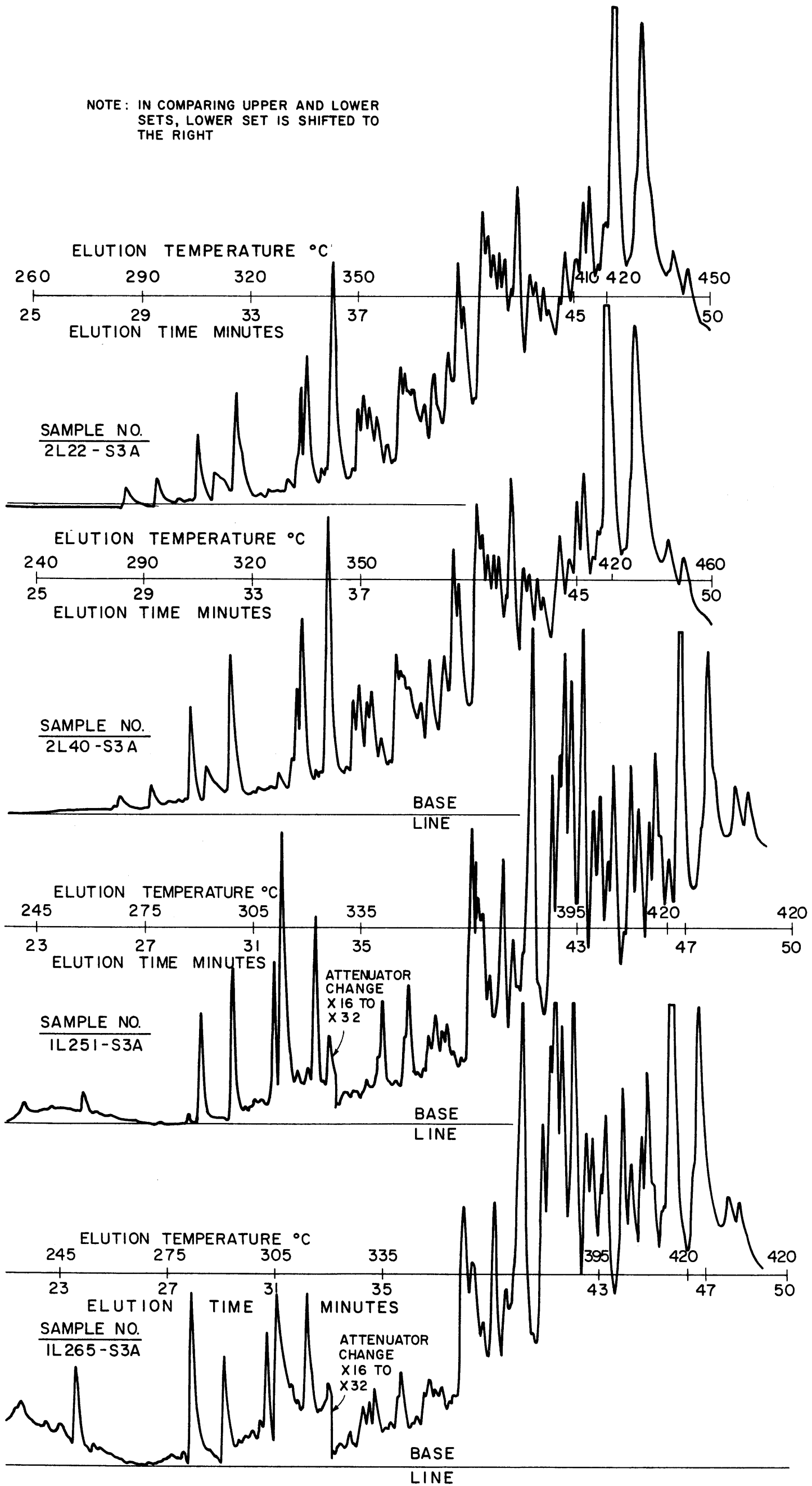


FIGURE 4.7 GAS CHROMATOGRAMS FOR THIRD SUBLIMATES FROM 610°F AND 750°F HB SAMPLES

there was considerable overlap on the chromatograms not presented here, that is, only peak sizes appeared to change, indicating that all the compounds shown in Figure 4.7 were present in some amount in all those sublimates.

The four curves presented in Figure 4.7 permit a qualitative comparison of the composition of the 610°F samples with each other and with the corresponding 750°F samples. The elution temperatures and elution times are marked on a linear scale for each chromatographic curve. The elution times and temperatures did not remain the same for each analyses due to slight changes in column characteristics. Therefore, the chromatograms have been shifted horizontally in Figure 4.7 to make the larger peaks eluting above 400°C appear to be one above the other.

Below a column temperature of 320°C, the chromatograms of the sublimed fractions at 200°C and 250°C gave the same peaks as shown in Figure 4.7. Above 350°C, the base line drift began, and it amounted to approximately 40 divisions when the temperature column reached 420°C. The base line drift was determined by using blank samples of THF with the same temperature program.

Some standard samples of quinquephenyls obtained from the Phillips Petroleum Company were run on the chromatograph to calibrate the range of the chromatograms in Figure 4.7. From the results obtained from the standards, the quinquephenyls elute between 275°C and 375°C for the column used. From the results of the extensive gas chromatography presented in reference (26), some hexaphenyls and some higher

polyphenyls and substituted polyphenyls would also be expected to elute prior to the maximum temperature of these chromatograms ( $420^{\circ}\text{C}$ ). Actual identification of the peaks would require addition of known standards to the unknown sample.

Comparison of the lower two chromatograms on Figure 4.7 for the  $270^{\circ}\text{C}$  sublimates from HB samples 1L251 and 1L265 shows the similarity of these two samples. The largest amount of material in the sample was eluted after the point where the scale attenuation was increased to 32 from 16. The change in attenuator setting infers that the amount of material eluted prior the attenuator change is approximately one-half the amount shown eluting after the attenuator change.

Comparison of the upper two chromatograms on Figure 4.7 also serves to show the similarity of the  $270^{\circ}\text{C}$  sublimates from the samples 2L22-S3A and 2L40-S3A. The important difference to note in the 2L22-S3A and 2L40-S3A chromatograms is the fact that the relation of the peaks prior to  $320^{\circ}\text{C}$  to those eluted after  $320^{\circ}\text{C}$  have a one to one ratio since no attenuation changes were required on these chromatograms.

By comparing either of the lower  $610^{\circ}\text{F}$  chromatograms with the upper  $750^{\circ}\text{F}$  chromatograms in Figure 4.7, it is possible to observe the difference in the production of the different organic species. Note the appearance of the two large peaks and two smaller peaks above  $400^{\circ}\text{C}$  on all the chromatograms. These peaks appear to represent major products in both the  $610^{\circ}\text{F}$  and  $750^{\circ}\text{F}$  irradiations. By relating other peaks on the chromatogram to these four

peaks, the other species eluting between 350°C and 400°C appear to be suppressed in the 750°C irradiations. It is difficult to estimate what molecular weight species these suppressed peaks represent since the  $MW_N$  for the 270°C fractions from the 610°F and 750°C irradiations have approximate values of 410 and 460 respectively. Also, the 270°C sublimates from the 750°F HB sample comprise material which sublimed between 33 and 46 w/o of the original sample. The 270°C sublimate fraction from the 610°F sample comprised the material which sublimed between 15 to 25 w/o of the original sample. Further comparison between the 750°F and 610°F samples would be very difficult without better separation or direct identification of the individual peaks in the chromatograms through the use of standards. Due to the similarity of the chromatograms of the samples from each irradiation, it is apparent that the HB had reached equilibrium composition.

## 5.0 Conclusions and Recommendations

From the results presented in Section 4.0, the following conclusions and recommendations may be stated:

1. The HB formed in the steady-state irradiations (1) of Santowax OMP at 610°F and 750°F at the MITR had reached equilibrium composition. Therefore the physical and thermo-physical properties measured and presented in Reference (1) should represent the properties to be expected in an Organic Cooled Reactor utilizing a similar coolant processing system of distillation and recycle.
2. The evaporation technique developed to obtain fractionation of the HB samples provided a sufficient number of fractions to determine a molecular weight distribution curve. The curves indicated that the molecular weight of the predominant specie produced from the 610°F irradiation was approximately 400. This result was in good agreement with OMRE samples from Core I HB and indicates that, at approximately 600°F, the dimer (MW = 460) of terphenyl (or hexaphenyl) is a major product from radiolysis. The  $MW_N$  of 610°F HB was  $700 \pm 35$  and is also in good agreement with a predicted value of  $650 \pm 25$  from OMRE results (2).

The HB formed at 750°F from Santowax OMP was appreciably lower in molecular weight than the material produced from Santowax OMP at 610°F. Also the molecular weight distribution indicated the production of more lower molecular weight species having higher volatility.

It would appear that "thermal cracking" or pyrolysis of the irradiated species in the HB is an important factor in its composition. The predominant specie produced in the 750° HB had a molecular weight of approximately 340. The  $MW_N$  of the whole HB fraction was  $570 \pm 30$ . It should be remembered that the values of  $MW_N$  obtained in this work only apply to systems utilizing a similar coolant processing technique to maintain equilibrium conditions.

By increasing the number of sublimates obtained by evaporation and by measuring the  $MW_N$  of each residue, resolution of molecular weight distribution of the HB would be much improved.

3. The methods of gas chromatography and the preliminary results presented herein give excellent resolution. Qualitative analyses of the chromatograms of the sublimate fractions indicated that equilibrium compositions had been obtained. The addition of known compounds to the unknown mixture is required for identification of the peaks observed.

APPENDIX A1

Operation and Calibration of the Osmometer

Sections 3.1 and 4.3 present the theory and results obtained for samples analyzed with the Osmometer. To develop the techniques employed, the instruction manual (reference (25)) supplied most of the information required except for the following comments related to the experience gained in the use of the instrument during this investigation.

The attainment of thermal equilibrium in the solvent cup is very important (refer to Figure 3.1) in obtaining accurate and reproducible measurements. It was found necessary to place the instrument in a draft-free location in the laboratory to prevent temperature changes during operation. In addition, 3 or 4 hours was required to attain thermal equilibrium in the sample cup whenever the Sample Chamber Assembly was opened to empty the solvent cup.

Immediately after placing the drop of the unknown solution on the thermistor, the drop changes temperature due to the effect of the unknown solute lowering the vapor pressure, and hence the evaporation rate, of the drop. Since the surface area of the drop effects the time the drop takes to reach thermal equilibrium, 3 minute readings were found to give more reproducible results and were unaffected by drop size as were the 2 minute readings recommended by the manufacturer.

The Osmometer was calibrated using known THF solutions of benzil,<sup>(1)</sup> o-terphenyl and biphenyl. Figure A1.1 presents

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<sup>(1)</sup> Diphenylglyoxal  $C_6H_5COCOC_6H_5$  MW = 210.22.

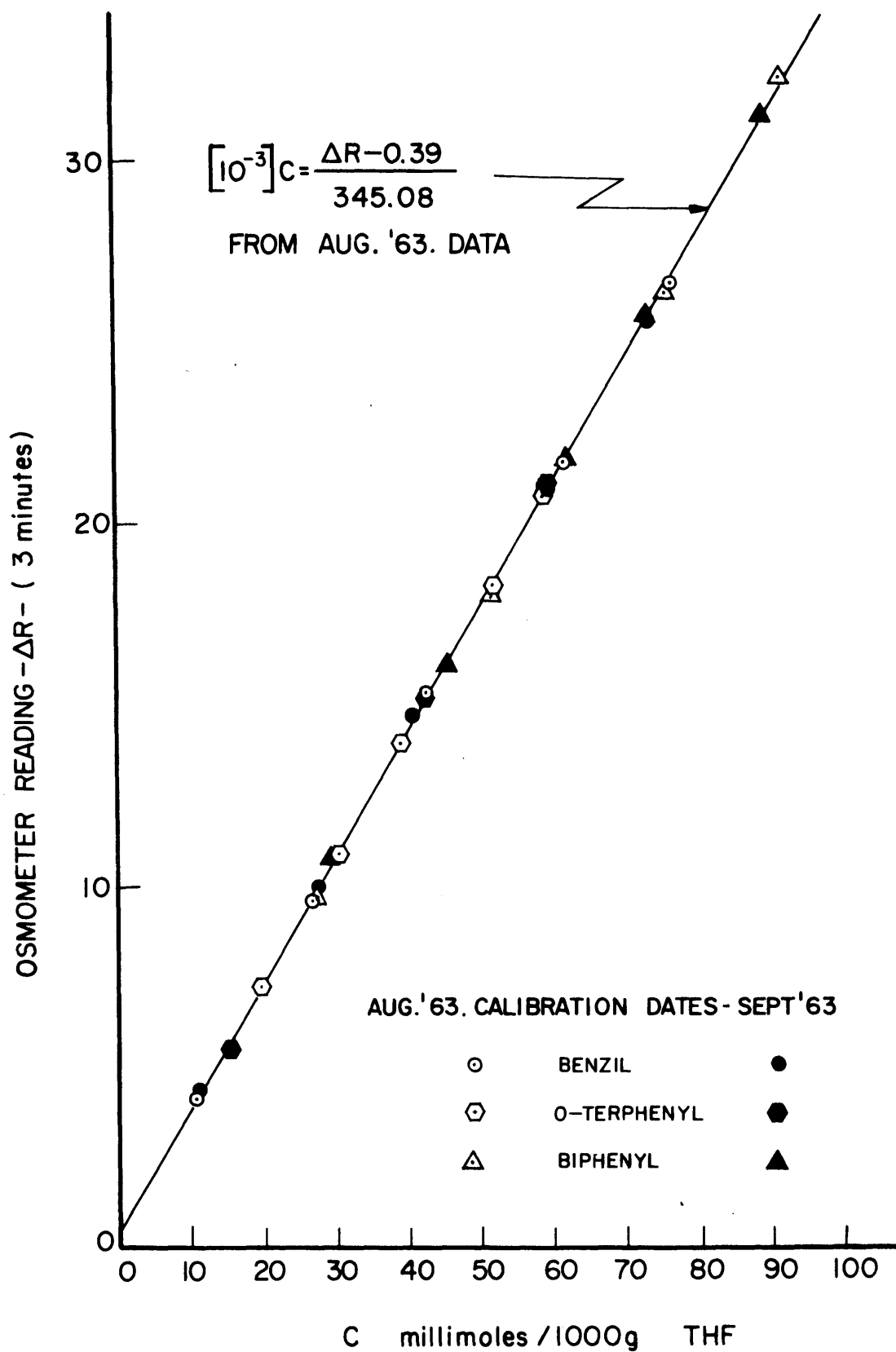


FIGURE A1.1 CALIBRATION CURVE MODEL 301A OSMOMETER FOR SOLUTES IN THF



the calibration curve used for all the measurements in this report. The calibrations were made about 2 months apart with a reproducibility of approximately 1% or 2%.

The equation of the curve presented on Figure A1.1 is the equation used to calculate molality on Tables A2.1, A2.2, A2.3 and A2.4.

Solvent selection and the effects of non-solution of the solute are discussed in Sections 4.1 and 4.42.

From an analysis of the osmometer calibration curves and reproducibility, the osmometer error is  $\pm 1.5\%$ , with an error of  $+ 3\%$  to  $- 2\%$  possible. However, due to the many assumptions required, including solubility, a more probable error would be on the order of  $\pm 5\%$ .

APPENDIX A2

Sublimation Results, Molecular Weights, Procedures and Equipment

A2.1 Sublimation Results and Molecular Weights

Using the methods and procedures described in Sections 3.1, 3.2 and Appendix A1, two 1 gram HB samples, numbered 1L 251 and 1L265, were sublimed in duplicate to check reproducibility and develop the sublimation method. Then 2 gram samples of HB, numbered 1L251, 1L265, 2L22 and 2L40, were sublimed, molecular weight solutions prepared, the molal concentrations measured, and the molecular weights of each fraction determined. Sections 4.1 and 4.2 discuss solvent selection and sample selection respectively.

Tables A2.1 and A2.2 present the results and the operating conditions for the duplicate sublimations of 1 gram HB samples, numbered 1L251 and 1L265, from the 610<sup>o</sup>F irradiation of Santowax OMP (1). Column 5 in Tables A2.1 and A2.2 present the laboratory notebook reference for the data in columns 1-4.

Tables A2.3 and A2.4 present the results and the operating conditions for the sublimations and molecular weight measurements of the 2 gram HB samples, numbered 1L251, 1L265, 2L22 and 2L40 respectively. Columns 5, 8 and 10 present the laboratory notebook references for the data presented in the tables in columns 1-4, column 7, and column 9 respectively.

Using the w/o yield per sublimation results presented in column 6 from Tables A2.1 and A2.2 and from column 11 in Tables A2.3 and A2.4, Table 4.3 in Section 4.3 was pre-

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(1) See footnote, page 2.

Table A2.1

Sublimation Yields for 1 gram HB Samples from  
610° F Steady-State HB Irradiation of Santowax OMP  
Sample No. 1L251 in Duplicate

1	2	3	4	5	6
Sample Fraction	Sublimate Yield (gms)	Absolute Pressure $\mu$ Hg	Temp. ( $^{\circ}$ C)	Laboratory Notebook(1) Book-Pg.	Yield (w/o)
Sample 1L251-A, Wt. 0.9966 gms.					
S1A1	0.0411	100	200	1-05	4.12
S2A1	0.1247	100	250	1-06	12.51
S3A1	0.1517	100	290	1-06	15.22
S4A1	0.0937	125	310	1-07	9.40
S5A1	0.0924	100	350	1-07	9.27
S6A1	0.0607	110	370	1-07	6.09
S7A1	0.4356	—	—	1-08	43.71
Sample 1L251-B, Wt. 1.007 gms.					
S1B1	0.0353	110	200	1-08	3.51
S2B1	0.1103	125	250	1-10	10.95
S3B1	0.1607	100	290	1-11	15.96
S4B1	0.0983	100	310	1-12	9.76
S5B1	0.0844	125	350	1-13	8.38
S6B1	0.0639	100	370	1-14	6.35
R7B1	0.4398	—	—	1-14	43.95

(1) Massachusetts Institute of Technology Laboratory  
 Notebook of William N. Bley

Table A2.2

Sublimation Yields for 1 gram HB Samples from  
610°F Steady-State HB Irradiations of Santowax OMP  
Sample No. 1L265 in Duplicate

1	2	3	4	5	6
Sample Fraction	Sublimate Yield (gms)	Absolute Pressure $\mu$ Hg	Temp. ( $^{\circ}$ C)	Laboratory Notebook (2) Book-Pg.	Yield (w/o)
Sample 1L265-A, Wt. 1.0086 gms.					
S1A1	0.0500	100	200	1-09	4.96
S2A1	0.1372	125	250	1-10	13.60
S3A1	0.1558	125	290	1-11	15.45
S4A1	0.0793	100	310	1-12	7.86
S5A1	0.0797	80	350	1-13	9.71
S6A1	0.0503	100	370	1-14	4.99
R7A1	0.4258	—	—	1-14	42.22
Sample 1L265-B, Wt. 1.0009 gms.					
S1B1	0.0628	125	200	1-09	6.27
S2B1	0.1517	125	250	1-15	15.16
S3B1 <sup>(1)</sup>	0.0980	100	270	1-15	9.79
S4B1	0.0639	110	290	1-16	6.38
S5B1	0.0671	140	310	1-16	6.70
S6B1	0.0855	150	350	1-17	8.54
S7B1	0.0538	100	370	1-17	5.38
R8B1	0.4181	—	—	1-18	41.77

(1) Note additional fraction at 270 $^{\circ}$ C. See text for explanation.

(2) Massachusetts Institute of Technology Laboratory Notebook of William N. Bley

Table A2.3

Sublimation Yields and Molecular Weights for  
2 Gram HB Samples of the 610°F Steady-State HB Irradiation  
of Santowax OMP

1	2	3	4	5	6
Sample Fraction	Sublimate Yield (gms)	Solution Conc. grams 1000g THF	Absolute Press. $\mu$ Hg	Temp. ( $^{\circ}$ C)	Laboratory Notebook <sup>(2)</sup> Book-Pg.
Sample Number 1L251-3, Sample Wt. 2.0041 gms.					
S1A	0.0642	12.87	35	200	1-18
S2A	0.2474	21.07	20	250	1-19
S3A	0.1709	17.33	55	270	1-20
S4A	0.1569	15.99	55	290	1-21
S5A	0.1440	14.82	33	310	1-22
S6A	0.2393	21.49	35	350	1-23
S7A	0.0989	10.91	70	370	1-24
R8	0.8903	42.34	—	—	1-24
Sample Number 1L265-3, Sample Wt. 2.0518 gms.					
S1A	0.0634	10.25	36	200	1-19
S2A <sup>(1)</sup>	0.3547	21.38	40	248	1-20
S3A	0.1342	15.79	29	270	1-21
S4A	0.1586	11.44	30	293	1-22
S5A	0.1238	10.61	29	310	1-23
S6A	0.2428	18.33	35	350	1-24
S7A	0.0893	7.69	34	370	1-25
R-8	0.8823	35.85	—	—	1-24

(1) Sample bumped - see text

(2) Massachusetts Institute of Technology Laboratory  
 Notebook of William N. Bley

Table A2.3 continued

Sublimation Yields and Molecular Weights for  
2 Gram HB Samples of the 610°F Steady HB Irradiation  
of Santowax OMP

7	8	9	10	11	12
Osmometer Reading $\Delta R$	Laboratory Notebook Book-Pg.	Molal <sup>(2)</sup> Conc. $\frac{\text{millimoles}}{1000\text{g THF}}$	Laboratory <sup>(4)</sup> Notebook Book-Pg.	Sublimate Yield (w/o)	Mol. <sup>(3)</sup> Wt. $\frac{\text{gms.}}{\text{mole}}$
Sample Number 1L251-3, Sample Wt. 2.0041 gms.					
14.34	3-67	39.6	2-09	3.20	325
18.75	3-70	52.3	2-09	12.34	403
15.56	3-71	43.1	2-09	8.53	402
12.43	3-71	34.2	2-09	7.83	454
10.86	3-72	29.8	2-09	7.19	496
13.01	3-16	35.8	2-09	11.94	601
6.69	4-02	17.8	2-09	4.93	613
8.10	4-02	21.9	2-09	44.42	1930
Sample Number 1L265-3, Sample Wt. 2.0518 gms.					
11.38	3-67	31.2	2-10	3.10	328
18.59	3-68	51.8	2-10	17.29	413
13.76	3-69	38.3	2-10	6.54	412
8.57	3-69	23.2	2-10	7.72	494
8.20	3-69	22.2	2-10	6.03	479
11.46	3-69	31.4	2-10	11.83	584
4.59	4-03	11.8	2-10	4.35	651
6.71	4-04	17.9	2-10	43.00	2005

(2) Calculated from  $10^{-3}C = \frac{\Delta R - 0.39}{345.08}$ , where C = col.9,

$\Delta R = \text{col.7}$  See Appendix A1 and Figure A1.1.

(3) (Col.3 divided by col.9) x  $10^3$ . Value given is  $MW_N$

(4) Massachusetts Institute of Technology Laboratory,  
Notebook of William N. Bley

Table A2.4

Sublimation Yields and Molecular Weights for  
2 Gram HB Samples of the 750° F Steady-State HB Irradiation  
of Santowax OMP

1	2	3	4	5	6
Sample Fraction	Sublimate Yield (gms.)	Solution Conc. <u>grams</u> 1000g THF	Absolute Press. $\mu$ Hg	Temp. ( $^{\circ}$ C)	Laboratory Notebook (1) Book-Pg.
Sample Number 2L22-Sample Wt. 2.5849 gms.					
S1A	0.2110	14.02	29	200	1-26
S2A	0.6357	29.96	19	251	1-28
S3A	0.2847	16.62	34	270	1-28
S4A	0.2010	10.84	33	290	1-29
S5A	0.1823	13.00	29	314	1-30
S6A	0.2221	11.67	27	350	1-31
S7A	0.1093	9.54	31	370	1-32
R-8	0.7362	39.37	—	—	1-33
Sample Number 2L40-Sample Wt. 2.3530 gms.					
S1A	0.1963	18.50	23	200	1-27
S2A	0.5749	29.13	19	250	1-27
S3A	0.3174	13.47	29	270	1-29
S4A	0.1714	9.05	31	290	1-30
S5A	0.1683	12.03	22	314	1-31
S6A	0.1654	12.75	21	351	1-32
S7A	0.1029	9.57	25	370	1-33
R-8	0.6635	32.58	—	—	1-34

(1) Massachusetts Institute of Technology Laboratory  
 Notebook of William N. Bley

Table A 2.4 continued

Sublimation Yields and Molecular Weights for  
2 Gram HB Samples of the 750° F Steady-State HB Irradiation  
of Santowax OMP

7	8	9	10	11	12
Osmometer Reading $\Delta R$	Laboratory Notebook Book-Pg.	Molal <sup>(1)</sup> Conc. <u>millimoles</u> 1000 g THF	Laboratory Notebook Book-Pg.	Sublimate Yield (w/o)	Mol. <sup>(2)</sup> Wt. <u>gms.</u> mole
Sample Number 2L22-Sample Wt. 2.5849 gms.					
15.89	4-05	44.1	2-10	8.16	318
27.56	4-06	77.3	2-10	24.59	388
13.10	4-08	36.1	2-10	11.01	461
7.73	4-65	20.8	2-10	7.78	521
7.88	4-67,72	22.2	2-10	7.05	585
6.20	4-66	16.4	2-10	8.58	711
4.40	4-73	11.3	2-10	4.23	845'
9.14	4-17	24.8	2-10	28.48	1585
Sample Number 2L40-Sample Wt. 2.3530 gms.					
20.96	4-04	58.5	2-11	8.33	316
26.96	4-06	75.6	2-11	24.42	385
10.57	4-08	28.9	2-11	13.48	466
6.32	4-71	16.8	2-11	7.28	539
7.43	4-71	19.9	2-11	7.15	605
6.52	4-72	17.4	2-11	7.03	734
4.59	4-16	11.8	2-11	4.37	811
7.18	4-17	19.2	2-11	28.19	1695

(1) Calculated from  $10^{-3}C = \frac{\Delta R - 0.39}{345.08}$ , where C = col.9,  $\Delta R$  = col.7. See Appendix A1 and Figure A1.1.

(2) (Col. 3 divided by col. 9) x  $10^3$

(3) Massachusetts Institute of Technology Laboratory Notebook of William N. Bley



pared for sample comparisons. The molecular weights from column 12 in Tables A2.3 and A2.4 are also presented in Table 4.3.

Note that an additional sublimate fraction at 270°C was added in Table A2.2 and the subsequent Tables A2.3 and A2.4. The additional fraction was used to reduce the approximately 15 w/o yields noted on the previous 1 gram sublimations for the sample series 1L251 SA1, 1L251 SB1 and 1L265 SA1. Note also the one unit increase in the sample number designations from this point on, making the residues the eighth fraction, (R8), for all sublimations in Tables A2.3 and A2.4.

In all cases except one, the sublimations proceeded smoothly without bumping (see Appendix A2.2 for detailed procedures). In this instance the residue being sublimed at 250°C bumped onto the cold finger. The apparatus was disassembled and the material on the finger washed into the material remaining unsublimed with THF. The resulting solution was carefully boiled and dried under a vacuum to drive off all the THF. The resulting residue was then resublimed at 250°C with the high yield shown. However, note that the subsequent yield at 270°C was correspondingly lower, and by the time sublimations were completed through 350°C on sample 1L265 the cumulative yield was about the same as the 1 gm sublimations presented in columns 6 and 7.

## A2.2 Detailed Sublimation Procedures

Sublimations were performed as follows:

(a) 1 or 2 gm sample of liquified and mixed HB residue from a recycle distillation (31, 32) was withdrawn with an eye dropper and placed in the outer envelope of the sublimation apparatus (see Figure 3.2). The amount of sample was weighed to the nearest 0.1 mg.

(b) The ground glass joints on the Micro-Vacuum Sublimation Apparatus (Figure 3.2) were carefully coated with vacuum grease so that sample contamination would not occur and the apparatus was assembled and installed at the vacuum connection to the diffusion pump. The salt bath was maintained in a lowered position (see Figure 3.3) during the assembly.

(c) With the salt bath lowered, a vacuum (0.02 to 0.12 mm Hg absolute) was drawn on the sample and maintained for at least 1/2 hour to degassify the sample. After this period the bath whose temperature was preset at the desired value was raised slowly to preheat, melt, and further degassify the sample and prevent bumping. In every case, it was necessary to immerse the sublimation apparatus for a short period of time and then to lower the bath several times while maintaining the residue in a liquid state, as air and entrapped volatiles were released to prevent "bumping". Generally, this procedure took another 1/2 hour. Finally, when the surface of the residue was calm and indicated no formation of bubbles, the sublimation apparatus was immersed so that the salt level reached a point about 1" below the

vacuum connection on the outer glass envelope.

(d) After completion of step (c) above each sublimation was conducted at the prescribed bath temperature, whose temperature was maintained to  $\pm 1^{\circ}\text{C}$ , for 3 hours. At the end of the period, the bath was lowered to terminate the sublimation. The residue was allowed to cool to approximately  $45^{\circ}\text{C}$  before admitting air to the system. This was done to minimize reactions between the hot residue and the oxygen in the air.

(e) The sublimation apparatus was disconnected from the inlet to the diffusion pump and the water lines disconnected. With the inner finger still inserted, the residual salt was washed from the outer envelope and acetone and air used to dry the water coolant passages in the finger. The finger was then carefully withdrawn to prevent touching the sublimate on the finger against the vacuum grease on the ground glass joint. After disassembly the vacuum grease was carefully removed from the tapered ground glass joint and the ground glass ball and socket joint using cleansing tissues and tetrahydrofuran as a solvent.

(f) The outer glass envelope and the finger were weighed to the nearest 0.1 mg and the loss in weight of the residue prior to the beginning of the sublimation compared to the gain in weight of the finger. For a satisfactory sublimation the weight loss and weight gain agreed to within 5 or 10 mg. If agreement of these two weights was not achieved, the ground glass joints, the water passages, and the portions of glassware previously cleaned were recleaned

until agreement of the weight loss and weight gain was achieved within the limits stated above.

(g) For those samples to be used in subsequent molecular weight determinations, the sublimate on the finger was rinsed into a clean beaker using tetrahydrofuran from a polyethylene wash bottle. The finger was reweighed to check the tare weight and to assure that all the sublimate was removed from the finger. The difference in the tare weight of the finger and the gross weight of the finger obtained in step (f) was the yield of the sublimation appearing in column 2 in Tables A2.1 through A2.4.

(h) The solution in the beaker from step (g) was rinsed into a previously cleaned, dried, and weighed sample bottle with a teflon or a polyethylene sealed screw cap. Teflon or polyethylene being selected since tetrahydrofuran was found to attack rubber based materials.

Additional solvent (tetrahydrofuran) was added to the sample bottle if required, otherwise a minimum amount of solvent was used in steps (g) and (h) so that the solution concentration would be approximately 1 to 4 w/o and yield 0.02 to 0.05 molal solutions for subsequent molecular weight determinations (see Section 3.1).

The solution concentration was determined on a weight basis from the gross weight of the sample bottle and cap plus the solution and the yield determined in step (g). After this weighing the sample was kept tightly capped, except for brief periods when samples were to be withdrawn, to maintain solution concentration for molecular weight

measurements. The solution concentrations from this step are in column 3 in Tables A2.1 through A2.4.

(i) The outer glass envelope and the inner cold finger were then reassembled as in step (b) and the process repeated through this step, at as many sublimation temperatures as desired.

Upon completion of the last sublimation, solvent was admitted into the outer glass envelope, the residue dissolved, and transferred by means of a pipette to a sample bottle as in step (h) for subsequent molecular weight measurements. Residue solution concentrations was computed by using the gross and tare weight of the outer glass envelope. This result appears in column 3 for all the R (for residue) samples in Tables A2.1 through A2.4.

(j) As a final check, the cumulative yield for the sublimate fractions and the residue obtained by summing column 2 in Tables A2.1 through A2.4 was compared to the initial sample weight of step (a). The cumulative and initial weights agreed to within 1% or 2% (See Section 4.3 and Table 4.3).

### A2.3 Sublimation Equipment

Table A2.5 lists the name and the source of the equipment shown in Figure 3.3.

Table A2.5

#### Sublimation Equipment List (Refer to Figure 3.3)

Vacuum Gage - Stokes McLeod Gage No. 276 AC	F. J. Stokes Corp. Philadelphia, Pa.
Temperature Controller-Simplytrol Pyrometer Controller, Model 200	Assembly Products, Inc. Chesterland, Ohio
Micro-Sublimation Apparatus Part No. JM 7395	Scientific Glass Apparatus Co., Bloomfield, N. J.
Diffusion Pump, Oil, 1-stage, Air-Cooled, Part No. JV 4570	Scientific Glass Apparatus Co., Bloomfield, N. J.
Vacuum Pump - Duo Seal Model 1400B	W. M. Welch Co. Chicago, Illinois
Immersion Heater - Formed from Straight Tubular Heater Calrod, 750 watts, 120 volts	General Electric Supply Co., Boston, Mass.
Salt Bath - Eutectic Mixture - 53% $\text{KNO}_3$ , 7% $\text{NaNO}_3$ , 40% $\text{NaNO}_2$ , m.p. $120^\circ\text{C}$ , useable to $450^\circ\text{C}$ . Container for salt bath is 1000 GM stainless steel beaker	
Platform Jack - "Big Jack"	Precision Scientific Co. Chicago, Illinois
Heater Variac - Variabte Trans- former, Type 116 Powerstat	Superior Electric Bristol, Connecticut

Appendix A3

Modifications to F + M Model 1609 Flame Ionization Detector

The equipment, as received, would operate satisfactorily at the conditions required for chromatographic analysis. The following comments which outline the major changes required refer to Figure 3.4

Above 400°C heat losses from the insulated oven cover were so excessive that the heater capacity of 400 watts originally provided was insufficient to permit satisfactory temperature programming above 2 or 3°C per minute. The heater mounts were modified and the heater was replaced with a 1500 watt (1) radiant heater element to permit programming to 500°C at rates as high as 20°C per minute.

Initially, the top mounting plate of the detector and column assembly was constructed of a 1/16" thick stainless steel plate. The injection port, the detector block, the column, the blower motor, and the heater were all mounted on this plate. However, above 350°C, the plate warped due to thermal expansion and affected the adjustment between the collector ring and the flame ionization jet resulting in changing sensitivity. To eliminate the warpage at elevated temperatures, a new mounting plate was constructed from a 1/4" thick commercially available asbestoes composition board called, "Transite". (2) Also to permit better cooling

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(1) General Electric Appliance Company, Boston, Massachusetts

(2) Manufactured by the Johns Mansville Asbestoes Company, Boston, Massachusetts

of the blower motor mounted beneath the plate, longer motor standoffs were installed requiring that the entire assembly be mounted on blocks to provide clearance for the blower motor.

Additional difficulties were experienced with the electrical connections to the flame igniter assembly due to severe oxidation at elevated temperatures. Welding the igniter standoffs to the detector block and silver soldering the electrical connections to the igniter wire alleviated these difficulties.

Finally, to assure gas tight connections to the columns, the Swagelok fittings <sup>(1)</sup> on injection and detector blocks were removed and Triple-Lok <sup>(2)</sup> flare fittings welded in their place.

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(1) Manufactured by Crawford Fitting Company, Cleveland, Ohio

(2) Manufactured by Parker-Hannifin Corporation, Cleveland, Ohio



Appendix A4

R E F E R E N C E S

- (1) C. D. Sawyer and E. A. Mason, "The Effects of Reactor Irradiation on Santowax OMP at 610°F and 750°F, MITNE-31, IDO-11, 007, Dept. of Nuclear Engineering, M.I.T., Cambridge, Mass., September 1963.
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- (4) E. L. Colichman and R. H. J. Gercke, "Radiation Stability of the Terphenyls and Other Polyphenyl Materials as Measured by Gas Evolution," NAA-SR-1288, June 15, 1955.
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- (6) W. N. Bley, "An In-Pile Loop Study of the Performance of Polyphenyl Reactor Coolants," NAA-SR-2470, September 15, 1958.
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