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ISOTHERMAL DECOMPOSITION STUDIES OF AROMATIC AND AROMATIC-HETEROCYCLIC POLYMERS IN AIR

POLYMER BRANCH
NONMETALLIC MATERIALS DIVISION

JUNE 1976

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AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
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Project Monitor

FOR THE COMMANDER

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Ten aromatic and aromatic-heterocyclic polymers were subjected to aging in air at temperatures of 316°C (600°F) and 371°C (700°F) for up to 600 hours, and the volatile decomposition products were determined by gas chromatography. The predominant volatiles by far were carbon dioxide and carbon monoxide -- being 91 to 99.6% of the total volatiles. Small amounts of water, methane and traces of other aliphatic hydrocarbons were found. Nitrogen containing polymers produced small amounts of nitrogen oxides, cyanogen and hydrogen cyanide, all of which tend to form, and reach a maximum, later than the other volatiles.
The volatiles reach their peak concentration only after a certain aging time, roughly related to the thermal stability of the polymers, and ranging between 1/2 and 500 hours at 371°C.

FOREWORD

This report was prepared in the Polymer Branch (MBP) of the Nonmetallic Materials Division of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. The decomposition studies in air were performed at the University of Dayton Research Institute, while the vacuum data reported here were obtained during earlier studies in the Polymer Branch laboratories. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers," with Dr. Gerhard F. L. Ehlers as subtask scientist. Co-authors were Wayne A. Rubey and Don S. Duvall, University of Dayton Research Institute. Isothermal Weight-Loss data were provided by K. R. Fisch, AFML/MBP.

The report covers research conducted from March 1971 to April 1974. It was released by the authors for publication in February 1976.

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SECTION I

INTRODUCTION

This work is an extension of earlier studies of the breakdown mechanism of aromatic and aromatic-heterocyclic polymers (references 1-6). During the earlier approach, the polymer samples were heated stepwise at 3 to 4 different temperatures, between 200 and 650°C, in vacuum. Residues and sublimates were analyzed, whenever possible, and the composition of the volatiles determined by mass spectroscopy.

In this study, aromatic and aromatic-heterocyclic polymers were subjected to isothermal aging in air over periods up to 600 hours, and predominantly at temperatures of 316°C (600°F) and 371°C (700°F). At intervals, the volatile products were analyzed by gas chromatography. It was not the objective of this work to postulate breakdown mechanisms on the basis of these limited data. Rather, this study was done to obtain information about the nature and the relative amounts of the volatiles formed, and their change over the time period of the test.

SECTION II

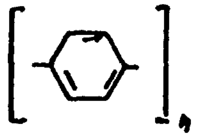
DISCUSSION

Ten aromatic and aromatic-heterocyclic polymers were subjected to isothermal aging in air, essentially at temperatures of 316°C (600°F) and 371°C (700°F), and the volatiles analyzed by gas chromatography. The ten polymers under investigation were:

Poly-1,4-phenylene
Poly-1,3-phenylene oxide
Poly-2,6-dimethyl-1,4-phenylene oxide (PPO)
Poly-2,6-diphenyl-1,4-phenylene oxide (P_3O)
Poly-(p-phenylene)iso-terephthalate
Poly-p-benzamide Fiber
Poly-2,2'-(1,3-phenylene)-5,5'-bibenzimidazole
Ladder-type polyquinoxaline
Polybenzimidazobenzophenanthroline (BBB)
Polybenzimidazoisoquinoline (BBL)

In the following discussion, results of the earlier decomposition studies in vacuum (at temperatures comparable to those of the present study) are listed for comparison with the isothermal aging data in air. The concentration/time plots of the volatiles from these isothermal aging studies are given in the figures, while peak times and peak concentrations derived from these figures are listed in tables throughout the text.

<u>Poly-1,4-phenylene</u>.



This polymer was prepared according to the method of Kovacic and coworkers (references 7-9) from 2 moles of benzene, 1 mole of ferric chloride and 1 mole of water. Elemental analysis indicated that the polymer contains chlorine, and suggests the structure of a crosslinked polyphenylene with one chlorine on every 7th ring. The polymer was subjected previously to decomposition in vacuum (reference 1). The volatiles formed in vacuum at 450°C, the temperature closest to the one used in this study, had the composition shown in Table 1.

TABLE 1

Volatile Decomposition products of Poly-1,4-phenylene at 450°C in Vacuum (mole %)

H_2	36.9
HCl	23.5
H_2O	16.6
CO_2	8.3
CH_4	6.5
CO	4.5
C_6H_6	3.7

The present investigation was performed in air (flow rate 1.6 cc/min) at 371°C (700°F) over a time period of 94 hours, during which the sample (21.9 mg) lost 80% of its weight. Figure 1 shows the concentration of the volatiles in air, in ppm (vol/vol).

Also shown in Figure 1 is the weight loss curve and the rate of volatilization of a separate run at 371°C in air. As the figure shows, the major volatile oxidation product is carbon dioxide, followed by carbon monoxide. Methane and water are present in much smaller amounts. Still smaller quantities of ethylene, acetylene, ethane and a C_3 hydrocarbon were also detected. This technique was not capable of detecting hydrogen chloride or chlorine. Peak times and concentrations of the major volatiles are as shown in Table 2.

TABLE 2

Peak Times and Peak Concentrations of the major Volatiles formed during Aging of Poly-1,4-phenylene at 371°C in Air.

Volatile	Peak Time (Hrs.)	Peak Concentrations (ppm)
CO_2	50	5600
CO	50	1700
CH_4	42	77
H_2O *	41	22

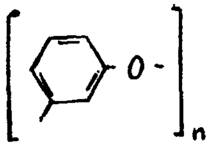
---

*as C_2H_2

In this and the subsequent determinations, water has been converted to, and determined as, acetylene by directing the volatile products through a heated calcium carbide tube.

Throughout the aging period, the quantities of the volatiles showed relatively little fluctuation, but they reached a maximum between 45 and 65 hours of aging time. Methane formation seemed to increase again after 72 hours, when only about 25% of the polymer was left. It can be seen that the volatilization rate curve reaches its peak before the major gases, carbon dioxide and carbon monoxide, reach <u>their</u> maximum. This suggests that condensable products are being formed during the early part of the run.

<u>Poly-1,3-phenylene oxide</u>.



This polymer was prepared by Wyandotte Chemicals Corporation under Air Force contract by a method described by Brown et al. (reference 10). The procedure involves the reaction of the potassium salt of m-chlorophenol with copper powder in mineral oil at 200°C. Decomposition of this polymer in vacuum at 450°C (reference 4) gave the following volatiles (Table 3):

TABLE 3

Volatile Decomposition Products of Poly-1,3-phenylene oxide at 450°C in Vacuum (Mole %)

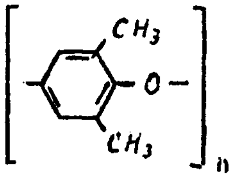
H_2O	32.8
H_2	26.0
CO	23.2
CO_2	9.6
CH_4	7.3
C_6H_6	1.1

The major decomposition product, however, was a sublimate consisting of polymer fragments.

The present, isothermal decomposition study was run in air (1.7 cc/min) at 371°C with a sample weight of 39.8 mg. Weight loss after 100 hours of aging was 84.6%. Carbon dioxide was the major volatile product. Suprisingly (especially when comparing the results with those of PPO below), only trace levels of carbon monoxide were found. Hydrocarbons and water were not determined. Figure 2 presents the weight loss and volatilization rate, as well as the concentration of carbon dioxide. The carbon dioxide concentration was very high at the beginning of the aging experiment, dropped to a low level after 4 hours and then reached a peak after about 50 hours. The peak concentration of carbon dioxide was 5750 ppm after about 47 hours.

The volatilization rate curve reached its maximum much earlier than the CO_2 concentration, which suggests that a major condensable decomposition product was formed in the early part of the run. A sublimate was observed during the earlier decomposition studies in vacuum.

Poly-2,6-dimethyl-1,4-phenylene oxide (PPO)



This polymer sample, obtained from the General Electric Company in 1965, was subjected previously to thermal decomposition in vacuum (reference 1). At 375°C, the following volatiles were obtained (Table 4):

TABLE 4

Volatile Decomposition Products of Poly-2,6-dimethyl-1,4-phenylene oxide at 375°C in Vacuum (Mole %)

CH_4	43.1
H_2	22.6
H_2O	19.0
CO	10.9
CO_2	3.5
$C_6H_5CH_3$	0.9
C_6H_6	traces

However, these volatiles constituted only a minor part of the overall weight loss. The major part of the decomposition products consisted of a sublimate containing chain fragments with one to four repeat units, and hydroxyl end groups.

The present study involved aging in air (and in two instances in helium for comparison) at 200, 250, 316 and 371°C for periods up to 200 hours. Sample sizes of 40 mg and air flow rates of 1.6 - 1.7 cc/min were used. Figure 3 shows the formation of carbon dioxide, the major volatile product, at different temperatures in air and in helium. It can be seen that the quantities of carbon dioxide formed in helium are about two orders of magnitude lower than the corresponsing values in air. Table 5 lists peak times and amounts of carbon dioxide at the different temperatures.

TABLE 5

Peak Times and Peak Concentrations of Carbon Dioxide formed during Aging of Poly-2,6-dimethyl-1,4-phenylene oxide at several temperatures in Air.

Aging Temp(°C)	Peak Time (hrs.)	Peak Concentration (ppm)
200	74	940
250	7.5	4340
316	0.5	29750
371	0.5	52830

The table shows that the elapsed time needed to reach the peak in carbon dioxide formation decreases with increasing temperature, and that the quantities formed at 200 and 250°C are much smaller than at the higher temperatures. The weight changes of the polymer at the lower temperatures are also small. After 100 hours at 200°C, the polymer shows a weight gain of 3.5%; apparently, oxygen absorption and formation of non-volatile oxidation products exceeded the formation of volatiles. After 100 hours at 250°C, a slight weight loss of 2.7% can be observed.

At 316°C, a more detailed study was undertaken. Figure 4 shows the weight loss curve and the volatilization rate of the polymer at 316°C in air; the concentration of the volatiles can be seen in Figure 5.

Figure 4 indicates a rate increase after 120 hours, which is not visible in the concentration curves of Figure 5, and which is probably caused by increased formation of larger fragments after 120 hours. The major product is again carbon dioxide, followed by carbon monoxide, which fell below the detection limit after 20 hours. Water has not been determined in this run. Some methane and very little ethane and ethylene were detected. The hydrocarbons appeared to have a peak formation at about 10 hours, but as the result of the high concentration at the beginning of the run, the peaks appeared as shoulders. Table 6 gives the approximate peak times and concentrations.

TABLE 6

Peak Times and Peak Concentrations of the major Volatiles formed during the Aging of Poly-2,6-dimethyl-1,4-phenylene oxide at 316°C in Air.

Volatile	Peak Time (hrs.)	Peak Concentration (ppm)
CO_2	0.5	25800
CO	0	7300
H_2O	Not determined	
CH_4	~ 10	~ 40
C_2H_6	~ 10	~ 34
C_2H_4	0	30

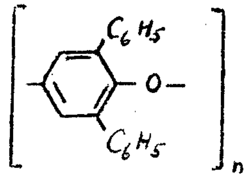
During the aging at 371°C, the polymer had a high initial weight loss (Figure 6). The concentrations of the volatiles (Figure 7) were also high in the beginning but had an additional peak or a shoulder between 0.5 and 3.5 hours. The initially high methane concentration and the large variety of hydrocarbons is indicative of the early decomposition of the pendant methyl groups. The polymer residue was hygroscopic and may contain hydroxyl end groups originating from the ether linkage. Elapsed times and volatile concentrations for the peak (shoulder) of volatile formation are listed in Table 7.

TABLE 7

Peak Times and Peak Concentrations of the Major Volatiles Formed during the Aging of Poly-2,6-dimethyl-1,4-phenylene oxide at 371°C in Air

Volatile	Peak Times (hrs.)	Peak Concentration (ppm)
CO_2	0.5	52830
CO	0.5	34320
H_2O *	3	2250
CH_4	3	380
C_2H_4	3.5	23
C_2H_6	3.5	7
C_3H_6	3.5	3
C_3H_8	3.5	2

Poly-2,6-diphenyl-1,4-phenylene oxide (P_3O)



The polymer was obtained from the General Electric Company in 1969. Isothermal aging at 316 and 371°C in air was conducted with this polymer. At 316°C, with a sample size of 41 mg, and air flow rate of 1.7 cc/min and a test duration of 360 hours, carbon dioxide was found to be the major product. As Figure 8 shows, the initially fairly high concentration (1130 ppm) dropped to 120 ppm after 20 hours and then increased steadily over the test period. It reached 1140 ppm after 357 hours and apparently had not yet reached a peak. Carbon monoxide was present only in very small concentrations. The same is true for hydrocarbons, with methane (always < 5 ppm) being the most prominent, and ethylene about 0.5 ppm. Liquid and solid deposits downstream from the sample contained numerous compounds, possibly paraffinic, in the 250 molecular weight range and higher. Other organic compounds were trapped in a charcoal collection tube and extracted with carbon disulfide. They consisted of benzene, toluene, trace levels of C_4 and C_5 hydrocarbons, and 2 compounds which had a chromatographic behavior similar to that of methylcyclohexane and xylene.

At 371°C, carbon dioxide and carbon monoxide were the major products followed by water and very small amounts of methane. As can be seen in Figure 9, the concentrations involved were much lower than those observed for PPO (Figure 7); this is also true for the overall weight loss. Overall volatilization rate and concentration of volatiles for this polymer at 316°C do not agree very well, which is an indication that other major decomposition products were formed, especially at the beginning and the end of the run. Liquid and solid deposits were, in fact, observed in the apparatus.

The following peak times and concentrations were found (Table 8):

TABLE 8

Peak Times and Peak Concentrations of the major Volatiles formed during the Aging of Poly-2,6-diphenyl-1,4-phenylene oxide at 371°C in Air.

Volatile	Peak Times (hrs.)	Peak Concentration (ppm)
CO_2	36	~ 22000
CO	38	~ 14000
H_2O *	~ 37	763
CH_4	23	15

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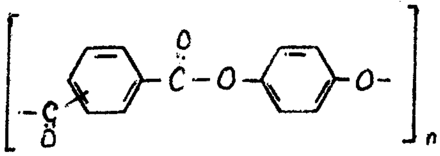
* as C_2H_2

Poly(p-phenylene)iso-terephthalate.



The polymer, received from the General Electric Company in 1962, was prepared from hydroquinone with approximately 85% isophthaloylchloride and 15% terephthaloylchloride in chlorinated diphenylether at 300°C. A decomposition study (reference 3) conducted earlier in vacuum at 450°C yielded volatiles as shown in Table 9, and a sublimate which consisted mainly of hydroquinone. The weight loss which can be attributed to the volatiles was 29%, while the sublimate accounted for 23%. In vacuum, the amount of carbon monoxide was much higher than that of carbon dioxide, while the opposite was the case during aging in air. The same observation has been made during the decomposition studies of poly-1,3-phenylene oxide and PPO.

TABLE 9

Volatile Decomposition Products of Poly(p-phenylene)-iso-terephthalate at 450°C in Vacuum (mole %)

CO	61.7
CO_2	34.8
H_2	2.0
C_6H_6	0.7
H_2O	0.4
CH_4	0.4

At 316°C in air, carbon dioxide was the only significant product evolving from the sample and even its amount was small (See Figure 10, dashed line). The concentration plot shows a peak after 47 hours and seems to develop a second maximum after 200 hours. The overall weight loss of the polymer after 200 hours at 316°C was only 3.4%. The sample size of this run was 37 mg, the air flow rate 1.7 cc/min.

At 371°C, concentration plots of the volatiles clearly show two maxima (Figure 10): a smaller after 50 hours for all of the products, a larger after about 125 hrs for carbon dioxide, carbon monoxide and water, and after 105 hrs for methane. The fact that the weight losses associated with the 2 maxima are about the same, suggests that a major amount of condensables forms during the first reaction step, and predominantly non-condensable volatiles in the second. Oxidative effects of the air present do not seem to be a significant factor of the two-part decomposition pattern, since the TGA curves of this polymer in inert atmosphere and in air are almost identical up to 550°C. One can postulate that the first peak consists mainly of the fracture of the polymer chain with formation of hydroquinone (as observed in vacuum), while decarbonylation and decarboxylation of the residual polymer occurs after the longer aging time. With the disappearance of the hydroquinone moieties, less carbon dioxide is likely to form, and the amount of carbon monoxide relative to carbon dioxide increases (Figure 5).

The observed peak times and concentrations are listed in Table 10.

TABLE 10

Peak Times and Peak Concentrations of the major Volatiles formed during the Aging of Poly(p-phenylene) iso-terephthalate at 371°C in Air.

Volatile	Peak Time (hrs.)	Peak Concentration (ppm)
CO_2	125	2780
CO	125	1440
H_2O *	125	24
CH_4	105	5

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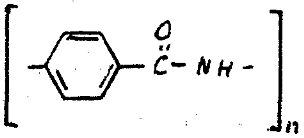
*as C_2H_2

Poly-p-benzamide Fiber

A polymer closely related to the one investigated here (below) in air



has been studied earlier in vacuum (reference 4). The volatile products obtained during that study at 375°C in vacuum are listed in Table 11.

TABLE 11

Volatile Decomposition Products of an aromatic Polyamide at 375°C in Vacuum (Mole %)

CO_2	86.6
CO	11.5
H_2O	0.6
H_2	0.5
HCN	0.4
C_6H_6	0.3
CH_4	0.1

Aging in air was performed with a 22 mg sample at 371°C and an air flow rate of 1.6 cc/min. Major volatiles found were carbon dioxide and carbon monoxide, along with some methane, water, nitrogen oxides, ethylene and propylene. Hydrogen cyanide, which had been detected in an exploratory test tube trial (without temperature control) was not found in this test. The nitrogen oxides seem to reach the peak area later than the other gases. This is in line with observations made for other nitrogen containing polymers discussed below. In those cases, the formation of nitrogen containing volatiles also occurs later than that of carbon dioxide and carbon monoxide. This suggests that the formation of these gases results from secondary processes. A comparable situation is the formation of nitrogen containing products during the stepwise decomposition in vacuum; under these conditions, hydrogen cyanide, ammonia, hydrogen and sometimes methane reach their maximum formation at higher temperatures than carbon monoxide, carbon dioxide, water and other volatiles.

Peak concentration of volatiles are listed in Table 12.

TABLE 12

Peak Concentrations of the Major Volatiles formed during Aging of Poly-p-benzamide Fiber at 371°C in Air

Volatile	Peak Concentration (ppm)
CO_2	4000
CO	1130
CH_4	36
H_2O *) **)	35
NO_x ***)	15
C_2H_6 **)	7
C_3H_6 **)	4,5

---

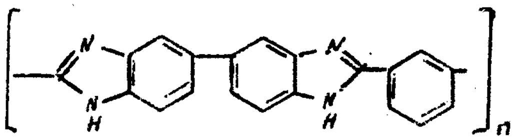
*) as C_2H_2

**) after 50 hours

***) after 60 hours

In a repeat run the fibers were cut into very small pieces and packed tightly into the boat to accommodate more material; the concentration of the volatiles, however, was lower, probably as a result of reduced access of air to the sample.

Poly-2,2'-(1,3-phenylene)-5,5'-bibenzimidazole



This polymer was synthesized by the Celanese Research Company under Air Force Contract. A polymer of the same structure, but synthesized in our Polymer Branch Laboratories, was subjected previously to decomposition in vacuum (reference 5). The volatiles found during this study, at a temperature of 450°C, are listed in Table 13. The results show that the major product was water. The corresponding weight loss after one hour at this temperature was 5%.

TABLE 13

Volatile Decomposition Products of Poly-2,2'-(1,3-phenylene)-5,5'-bibenzimidazole at 450°C in Vacuum (Mole. %)

H_2O	45.7
CO_2	27.0
H_2	10.5
CO	9.5
CH_4	2.8
HCN	0.9
CH_3CN	0.2
NH_3	0.2
C_6H_6	0.2

In the present study, a 40 mg sample of the polymer was aged at 316°C in air (air flow rate 1.7 cc/min) over a period of 200 hours. The volatile were only analyzed for carbon monoxide and carbon dioxide. Very small levels of carbon monoxide were detected. The initial, relatively high carbon dioxide concentration dropped to a low level during the first 8 hours and then increased again without reaching a maximum during the test period (Figure 13). The profile of the CO_2- concentration curve resembles the overall volatilization rate plot. The residue after aging is hygroscopic; the same observation was made during the earlier decomposition study in vacuum.

At 371°C in air (81 mg, air flow rate 1.6 cc/min), a large variety of products was formed, as shown in Figures 15 and 16. The most prominent volatiles were again carbon dioxide and carbon monoxide, followed by water, hydrogen cyanide, methane, ethylene, ethane, nitrogen oxides, propylene, propane and cyanogen. There was a discrepancy between the peak formation time of the individual volatiles, which occurred between 5 and 22 hours, and the peak of the overall volatilization rate curve, which appeared after 60 hours (Figure 14). Since no appreciable formation of condensables was observed, either during isothermal aging or during the aforementioned decomposition in vacuum, this discrepancy cannot readily be explained.

The nitrogen containing volatiles either reach the peak of formation later than the other volatiles, or decrease less, or later, in concentration than the nitrogen-free gases. This suggests, as pointed out before, that the processes leading to the formation of HCN, NO_x and $(CN)_2$ are secondary reactions.

Peak concentrations of the volatiles from Figures 15 and 16 are shown in Table 14.

Table 14

Peak Times and Peak Concentrations of the major Volatiles formed during Aging of Poly-2,2'-(1,3-phenylene)-5,5'-bibenzimidazole at 371°C in Air.

Volatile	Peak Time (hrs)	Peak Concentration (ppm)
CO_2	7	5700
CO	8	2200
H_2O *)	7	540
HCN	22	82
CH_4	36	59
C_2H_4	5	33
C_2H_6	4	9.8
NO_x	-	~7 **)
C_3H_6	7	6
$(CN)_2$	-	1 **)
C_3H_8	7	1

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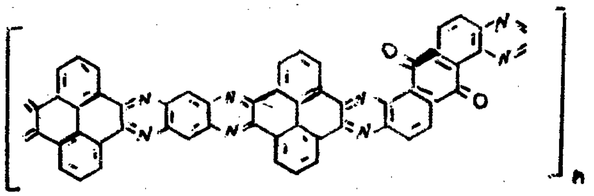
*) as C_2H_2

**) after 20 hours

Ladder Type Polyquinoxaline.



This polymer was synthesized by J. K. Stille and coworkers (reference 11) under Air Force contract. It was subjected to aging at 371°C in air, with a sample weight of 40 mg and an air flow rate of 1.5 cc/min.

Carbon dioxide was again the most prominent volatile, followed by carbon monoxide. Much smaller amounts of water, methane, ethylene and hydrogen cyanide were formed. All of the volatiles, with the exception of hydrogen cyanide, had a concentration minimum in the 3 to 6 hour range, after an initial high concentration, and reached a maximum, or a shoulder, in the 20 to 25 hour range (Figure 18). The overall volatilization rate curve (Figure 17) also shows a moderate maximum after 24 hours. Methane, ethylene and an unknown compound, apparently an aliphatic structure with 4 carbon atoms had a small peak after 5 hours before they approached a shoulder in the 20 hour range. Hydrogen cyanide, on the other hand, was not detected before 18 hours had passed, and reached its maximum later (after 31 hours) than the other volatiles. All in all, it seems that the breakdown mechanism is relatively complex and distinctly different at different time periods of the test.

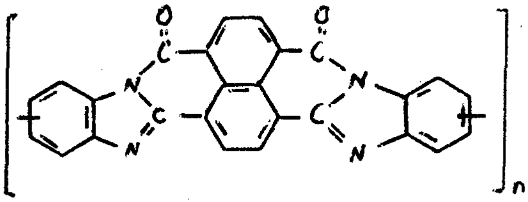
The following peak times and temperatures (not considering the initial high level of concentration) can be derived from Figure 18 (Table 15):

Table 15

Peak Times and Peak Concentrations of the major Volatiles formed during Aging of a Ladder Polyquinoxaline at 371°C in Air.

Volatile	Peak Time (hrs)	Peak Concentration (ppm)
CO_2	24	13000
CO	21	4700
H_2O	18	43
HCN	31	32
CH_4	4	18
C_2H_4	5	6
unknown C_4 comp.	5	11

Polybenzimidazobenzophenanthroline (BBB).



This polymer was synthesized by Monsanto Research Corporation under Air Force contract (reference 12). During an isothermal weight loss study at 371°C in air, the polymer showed a 1% weight gain after 200 hours. A sample from a different batch began losing weight after about 150 hours, and had a weight loss of 28% after 600 hours.

Three experiments were conducted in the pyrolysis effluent gas analysis equipment at 371°C in air. The first trial, with a sample weight of 81 mg and an air flow rate of 1.3 cc/min, was run for 308 hours. After this time, the sample had lost 36% of its weight, and the evolved gases had not reached their maximum concentration. Particularly, the hydrocarbons increased in amounts, and also in variety, towards the end of the run.

A second run, with a test duration of 600 hours was performed with a sample weight of 80 mg and an air volume flow of 1.5 cc/min. The sample lost 81% of its weight after 600 hours. Major products were carbon dioxide and carbon monoxide, followed by nitrogen oxides, water, methane and small amounts of hydrocarbons (Figures 19 and 20). No hydrogen cyanide was observed during this run, but was found in an exploratory test tube trial, during which the temperature was not controlled and apparently higher than 371°C. Considering the large amount of sample, the concentrations of the volatiles are relatively low. Most volatiles, after an initially higher concentration, reached a minimum after 100 to 200 hours and a maximum after 350 to 500 hours. Carbon dioxide, carbon monoxide and water reached their maximum concentration earlier than methane, ethylene and nitrogen oxides. Although the initial concentrations of all volatiles were relatively high, possible as a result of weak links (incomplete cyclization?), the major portion of the polymer seemed to undergo decomposition only after a long initiation period. The mechanisms of decomposition seemed to be different at different time periods, as the concentration curves of the volatiles in Figures 19 and 20 suggest.

A third run, also performed at 371°C in air for 600 hours with an 80 mg sample, had a slightly higher air flow rate (1.7 cc/min instead of 1.5 cc/min). This higher air flow rate noticeably accelerated the decomposition. The total weight loss was 90% (before 81%), and the maximum concentration of the volatiles also was higher (peak concentration of carbon dioxide 3900 ppm vs. 3300 before).

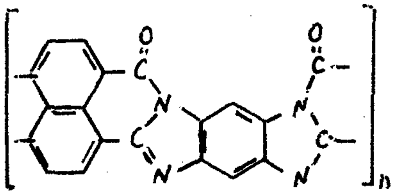
The peak times and concentrations from Figures 19 and 20 are listed in Table 16.

Table 16

Peak Times and Peak Concentrations of the major Volatiles formed during Aging of Polybenzimidazobenzophenanthroline at 371°C in Air.

Volatile	Peak Time (hrs)	Peak Concentration (ppm)
CO_2	420	3400
CO	380	810
NO_x	510	10
H_2O	380	6
CH_4	480	4
C_2H_4	330	0.3
C_3H_6	510	0.2

Polybenzimidazoisoquinoline (BBL).



This polymer was synthesized by Midwest Research Institute under Air Force Contract (reference 13). An isothermal weight loss study at 371°C in air showed a weight loss of 11% after 150 hours. The effluent gas analysis study at the same temperature in air (sample weight 77 mg, air flow rate 1.8 cc/min) had a weight loss of 53% after 504 hours of aging. During this run, essentially the only volatile product was carbon dioxide, which was present in high concentrations initially, dropped to a minimum after about 50-70 hours and reached a maximum at about 475 hours (Figure 21). Only traces of methane, ethylene and ethane, other light hydrocarbons and benzene were found, but no naphthalene. All these compounds were hardly detectable. A white, waxy deposit, which was not soluble in benzene or acetone, was formed in the cooler regions of the tube.

SECTION III
EXPERIMENTAL

The apparatus described in this section has resulted from several modifications to a bench mounted assembly of components which has been utilized in conducting many isothermal aging (ITA) examinations. Downstream of the ITA apparatus is an in-line gas chromatograph for measuring the evolved light gases. Methods for chromatographically analyzing the other evolved products are discussed later in this section.

The ITA apparatus is depicted in the schematic diagram shown in Figure 22. With this ITA apparatus, a specimen can be maintained at a constant elevated temperature (from 100° to 450°C) for extended periods of time. The thermal control system maintained the sensed temperature to within ± 0.5°C once thermal equilibrium had been attained. The circuitry of this thermal measurement and control system is shown in diagram form in Figure 23.

The inlet and outlet gas lines for the ITA apparatus consisted of copper tubing and stainless steel tubing, respectively. Also Swagelok metal fittings were used for the tubing connections, with the exception of the ground glass joint on the fabricated Pyrex tube which was sealed with Apiezon "N" grease. Flexible plastic tubing was found to be unsatisfactory in this system. Either small leaks at the connections, or the permeation of gases through the tubing wall prevented the detection of the trace levels of evolved products. The gas flow control for this apparatus provided an observed variation of ± 0.05 cm^3 per min throughout a typical ITA test.

Special attention was given to the design of the sample holder and the surrounding components. The sketch shown in Figure 24 depicts the sample holding components and their placement within the cylindrical Pyrex tube. Dual thermocouples are used for temperature measurement and control. Also, to provide a one-way purging of the sample region, a thick-walled Pyrex spacer was placed upstream of the sample location. With small clearances between these cylindrical components, the purging environment flowing through these narrow passages would be of higher velocity, thereby hindering the back-diffusion of the sample decomposition products.

Evolved Gas Analysis

The approximate volume flow rate of purging air that was eventually selected for this apparatus was 1.7 cc/min. At this flow rate, the in-line Barber-Colman Model 61-C gas chromatograph, which was equipped with a sensitive Carle #1150 Micro-detector, showed only oxygen and nitrogen to be present in the purging air. (Argon was not separated from the oxygen peak, and the trace levels of neon and helium found in atmospheric air would not be detected with this instrument).

The gas chromatographic analysis of a system's exit stream is usually accomplished in one of two modes. If the composition of the effluent is relatively simple and the molecular weight range of the components is small, then isothermal gas chromatography (ITGC) is generally employed. If however, the effluent composition is not simple and contains material of widely differing volatility, then programmed temperature gas chromatography (PTGC) is usually invoked. For the analysis of the effluents from the ITA apparatus, it was decided to employ both ITGC and PTGC.

The in-line isothermal gas chromatograph, Figure 25, was used exclusively for determining evolving CO and CO_2 concentrations. The volatile hydrocarbons, hydrogen cyanide, cyanogen and the water (as acetylene) quantitations were performed using a Varian Aerograph 2440 Series instrument. The gas phase sample taken from the sampling vessels was analyzed with the Varian chromatograph as were the contents from the in-line collection tube O. The 2440 Series gas chromatograph utilized a hydrogen flame ionization detector and a scandium-tritium electron capture detector. All of the analytical determinations of the evolved gases were established relative to chromatographic peak height calibrations. Nitrogen oxides were analyzed separately, using a modified Saltzman technique (reference 14).

Testing Procedure

A weighed amount of polymer is evenly distributed in the aluminum boat, which is also of known weight. The boat and its contents are then carefully placed in the thin wall Pyrex container, and this assembly is gently inserted into the cylindrical Pyrex tube. Next, the thick wall Pyrex spacer is fitted over the thermocouple sheath which is also fitted into the transparent tube. The thermocouples are then carefully positioned in the center of the aluminum boat, and the cylindrical Pyrex tube assembly is sealed with the use of Apiezon "N" grease applied to the glass joint (this seal remains essentially at room temperature). With the sample and the thermocouples in proper position, the remaining components of the ITA apparatus are then connected.

If during the extended ITA test evolved water is to be converted to acetylene, then a packed calcium carbide tube K is attached to the exit of the fabricated Pyrex tube. As new calcium carbide is used for each ITA test, it is desirable to condition this packed tube just prior to starting the test. Therefore, this packed tube member is heated to approximately 200°C, and purged for a minimum of two hours before starting the ITA test.

Before initiating the specimen heating, it is necessary to verify that the effluent from the ITA apparatus is of the same composition as the gas leaving the supply cylinder. Therefore, effluent samples are subject to GC analysis just prior to starting the ITA test.

Immediately before applying power to the heating circuit, the sample is visually inspected while in the apparatus. The sample furnace is then carefully positioned over the sample and the gas volume flow rate is again measured with the soap bubble flow meter U. The ITA test is then started and the specimen temperature is monitored with a Leeds and Northrup #8662 laboratory potentiometer.

Once a specimen has reached thermal equilibrium at the ITA temperature the effluent is subjected to evolved gas analysis (EGA). The actual start of the ITA exposure is timed from the point when the specimen reaches the ITA temperature. The volume flow rate of the purging gas is again measured after the sample reaches temperature, and periodically throughout the ITA.

The middle fraction collection tube O is likewise changed on a daily basis. During the changing of the collection tube, the sample is visually inspected by momentarily sliding the sample furnace out of position. The contents of the extracted collection tube are then subjected to GC analysis.

The weight loss plots and overall volatilization rates were obtained on separate samples in an automatic isothermal aging apparatus described by K. R. Fisch (reference 15).

SECTION IV

CONCLUSIONS

The most prominent feature of the isothermal decomposition studies in air is the fact that carbon dioxide and carbon monoxide are by far the major volatile decomposition products, comprising between 91 and 99.6% of the identifiable volatiles. Carbon dioxide is always the major product, with 59 to 78% of the total volatiles at the peak of gas formation, while carbon monoxide is present at 18 to 38%.

After carbon dioxide and carbon monoxide, water is the most prominent volatile with less than 1%. All of the other volatiles, such as hydrocarbons and nitrogen containing volatiles, are present in even smaller amounts.

During the test period, the concentration of the individual volatiles generally first increases, reaches a maximum and then decreases. The nitrogen containing volatiles normally reach their maximum later than the other gases. As can be expected, the elapsed time to reach maximum concentration decreases with increasing temperature. A plot of the overall volatilization rate (from weight loss studies) normally resembles the concentration curves of the volatiles. If deviations occur, they seem to be caused by the formation of major amounts of condensable decomposition products.

In a few instances (poly-1-3-phenyleneoxide; polyquinoxaline, BBB and BBL) a very high initial concentration of volatiles was observed, which dropped to a minimum before approaching the peak area. This initially high volatile concentration, which has no noticeable effect on the overall weight loss, may be the result of the presence of impurities, weak links, incomplete cyclization, etc.

Only in two cases (of the polyester and of the polyamide) the composition of the volatiles obtained during aging in air resembles the one obtained on vacuum. The TGA curves of these polymers, in air and nitrogen are almost identical up to, and including, the major breakdown step. It can be assumed that the initial breakdown mechanism of the two polymers in air and inert atmosphere is essentially the same, namely a thermal, and not oxidative, breakdown. The other polymers show a composition of volatiles in air which is completely different from the one in inert atmosphere. The time to reach peak carbon dioxide concentration should be some indication of the oxidative stability of the polymer:

Table 17

Peak Time (hrs) of Carbon Dioxide Formation of Several Polymers During Aging at 371°C in Air.

PPO	0.5	PRD-49	50*)
PBI	7	Poly(p-phenylene) iso-terephthalate	125*)
Polyquinoxaline	24	BBB	420
P_3O	36	BBL	475
Poly-1,4-phenylene	50		
Poly-1,3-phenylene oxide	50		

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*) Thermal (not oxidative) breakdown

One observation made during this study was the fact that higher air flow rate accelerated decomposition and produced larger amounts of volatiles, while the opposite occurred when a sample was packed more tightly, with less access of air.

Some observations concerning specific polymers may be of interest:

Poly-1,3-phenylene oxide: The volatilization rate curve (Figure 2) reaches its peak before the major gases, carbon dioxide and carbon monoxide, have their maximum concentration. This suggests that condensable products are being formed during the early part of the run.

Poly-2,6-dimethyl-1,4-phenylene oxide. At 316°C, the overall rate of volatilization increases again after 120 hours, while the concentration of the individual volatiles decreases (Figure 4 and 5). Indications are that larger fragments, not detected by gas chromatography, are being formed in the later part of the run. The initially high concentration of methane and other hydrocarbons at 371°C (Figure 7) is indicative of the early breakdown of the pendant methyl groups.

The formation of carbon dioxide in air (at 200 and 250°C) is about two orders of magnitude higher than in helium (Figure 3).

Poly-2,6-diphenyl-1,4-phenylene oxide. Differences between the volatilization rate curve and the concentration curves of the individual volatiles (Figure 9) are an indication that condensables must have formed at the beginning and the end of the run. Liquid and solid condensation products were observed in the reaction tube.

Poly(p-phenylene)iso-terephthalate. A two-step breakdown was observed during the isothermal decomposition at 371°C in air. From comparison of the overall volatilization rate curve with the individual concentration curves of the effluents, it can be concluded that the first step consists mainly of the fracture of the polymer chain with formation of hydroquinone, while decarbonylation and decarboxylation of the residual polymer occurs during the second step.

PRD-49-I Fiber Polybenzimidazole Polyquinoxaline (BBB). All of these polymers form nitrogen containing volatiles, with their peak of formation occurring at a later time than that of carbon dioxide and carbon monoxide. This suggests that the formation of these gases results from secondary processes, and may be comparable to observations made during the stepwise decomposition of polyamides and polybenzimidazoles in vacuum (references 4 and 5). In those cases, nitrogen containing volatiles had their peak formation at the higher temperature steps. The complex concentration pattern of the volatiles from the polyquinoxaline and BBB is an indication that the decomposition mechanisms for these polymers are quite different at different time periods of the runs.

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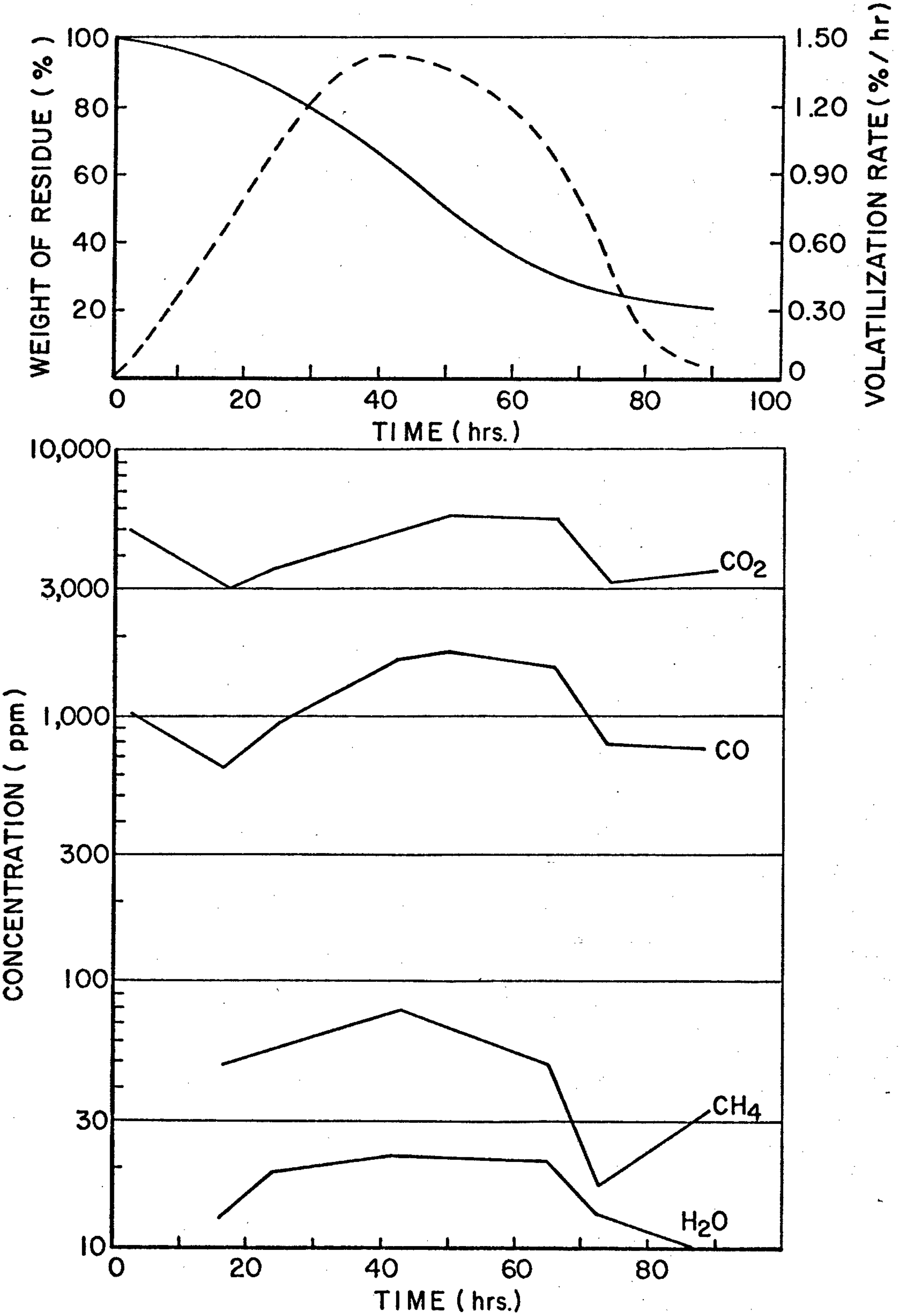
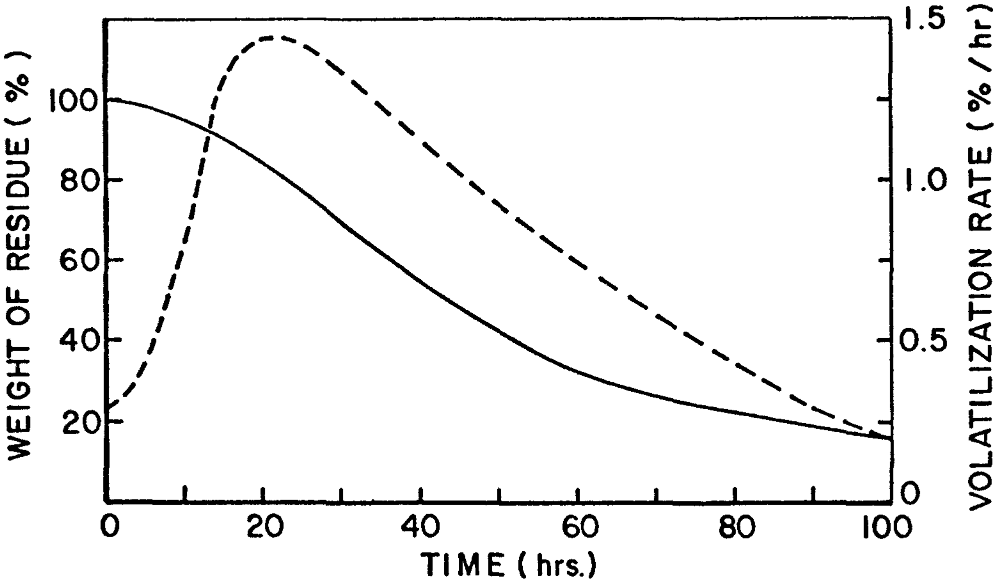


Figure 1. Weight loss and volatilization rate of, and concentration of volatiles from poly-1,4-phenylene during isothermal aging at 371°C in air



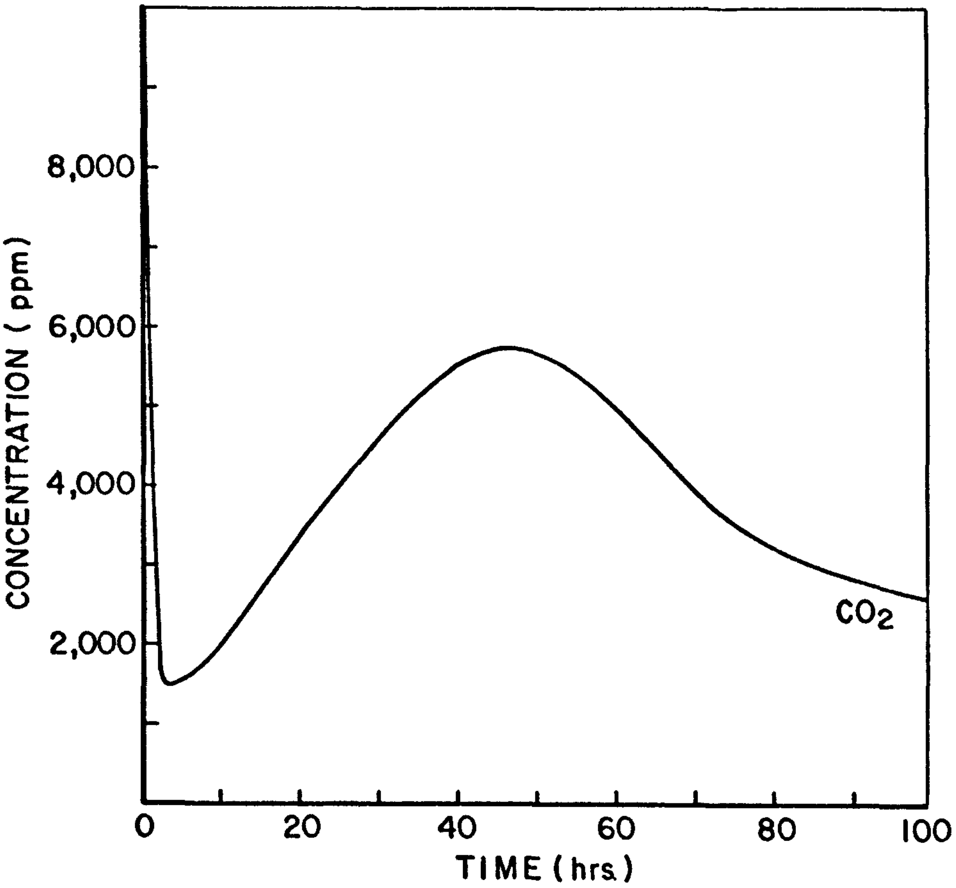


Figure 2. Weight loss and volatilization rate of, and carbon dioxide concentration from, poly-1,3-phenylene oxide during isothermal aging at 371°C in air

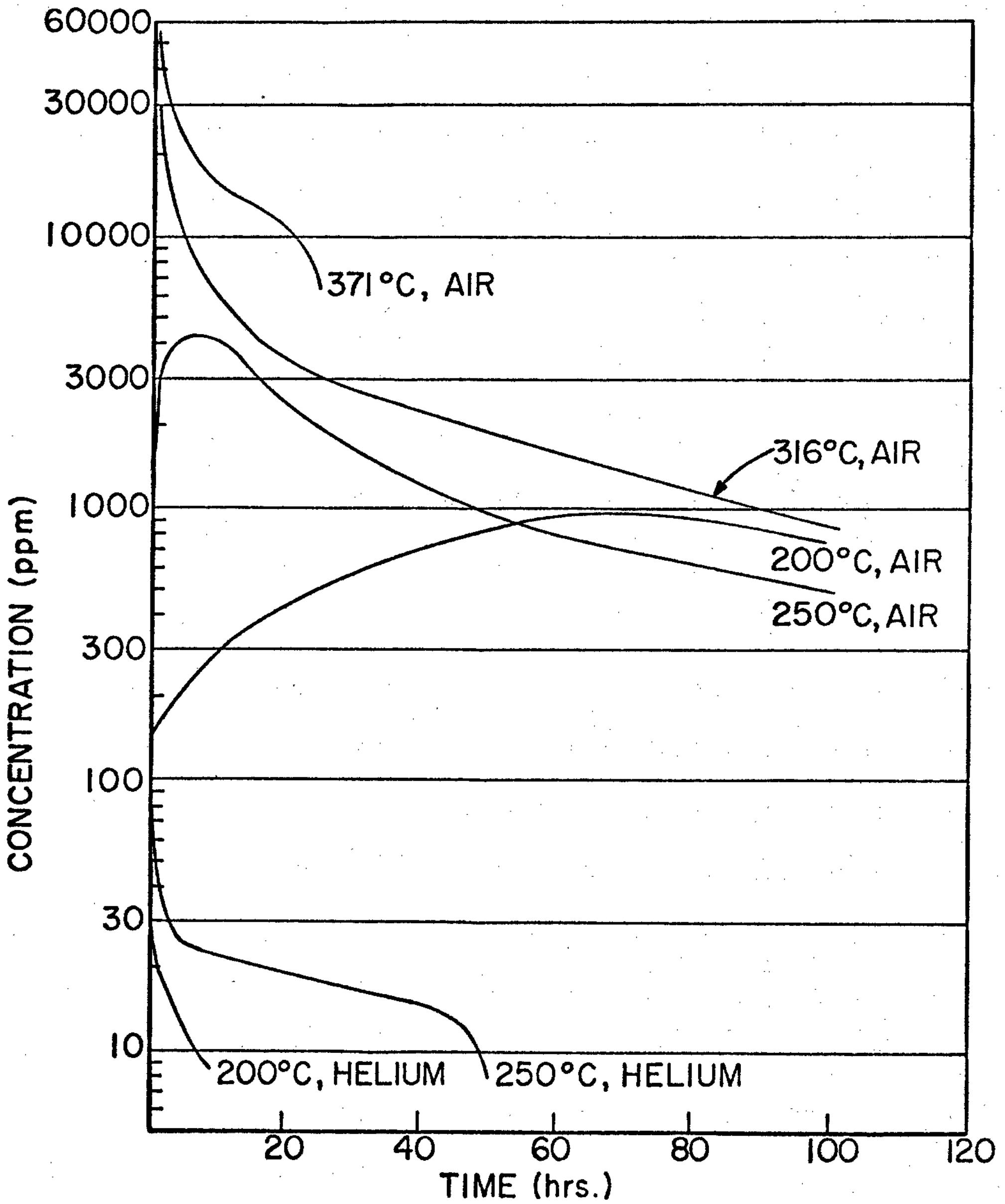


Figure 3. Concentrations of carbon dioxide from poly-2,6-dimethyl-1, 4-phenylene oxide (PPO) during isothermal aging at 200, 250,316, and 371°C in helium and in air

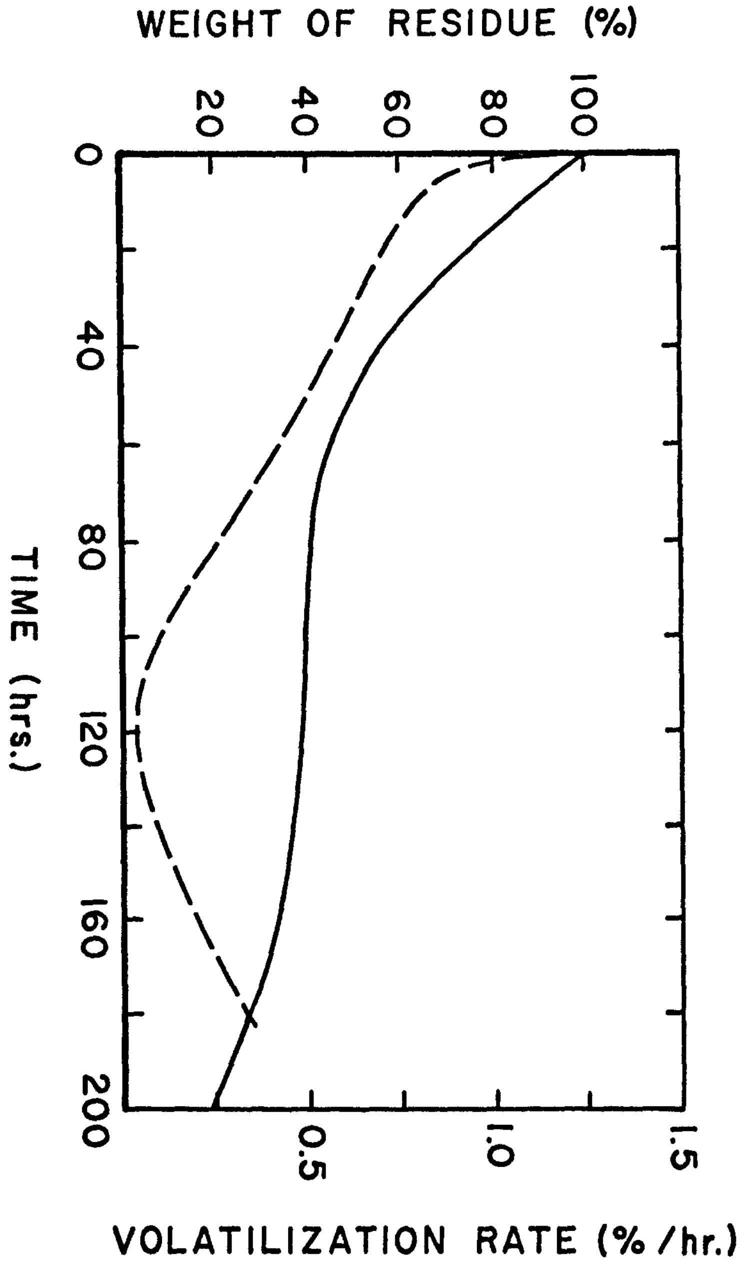


Figure 4. Weight loss and volatilization rate of poly-2,6-dimethyl-1, 4-phenylene oxide (PPO) during isothermal aging at 316°C in air

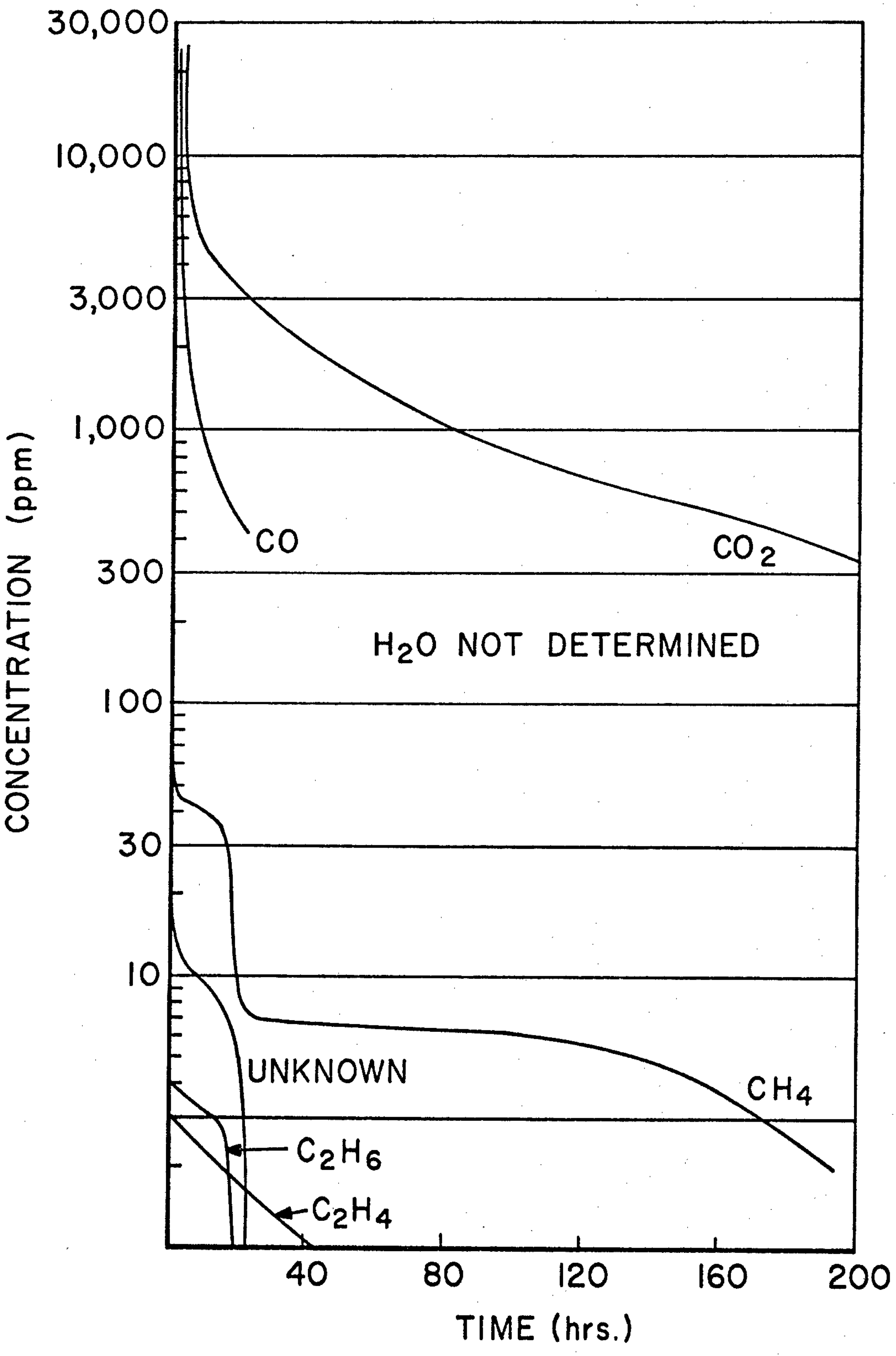


Figure 5. Concentration of volatiles from poly-2,6-dimethyl-1,4-phenylene oxide (PPO) during isothermal aging at 316°C in air

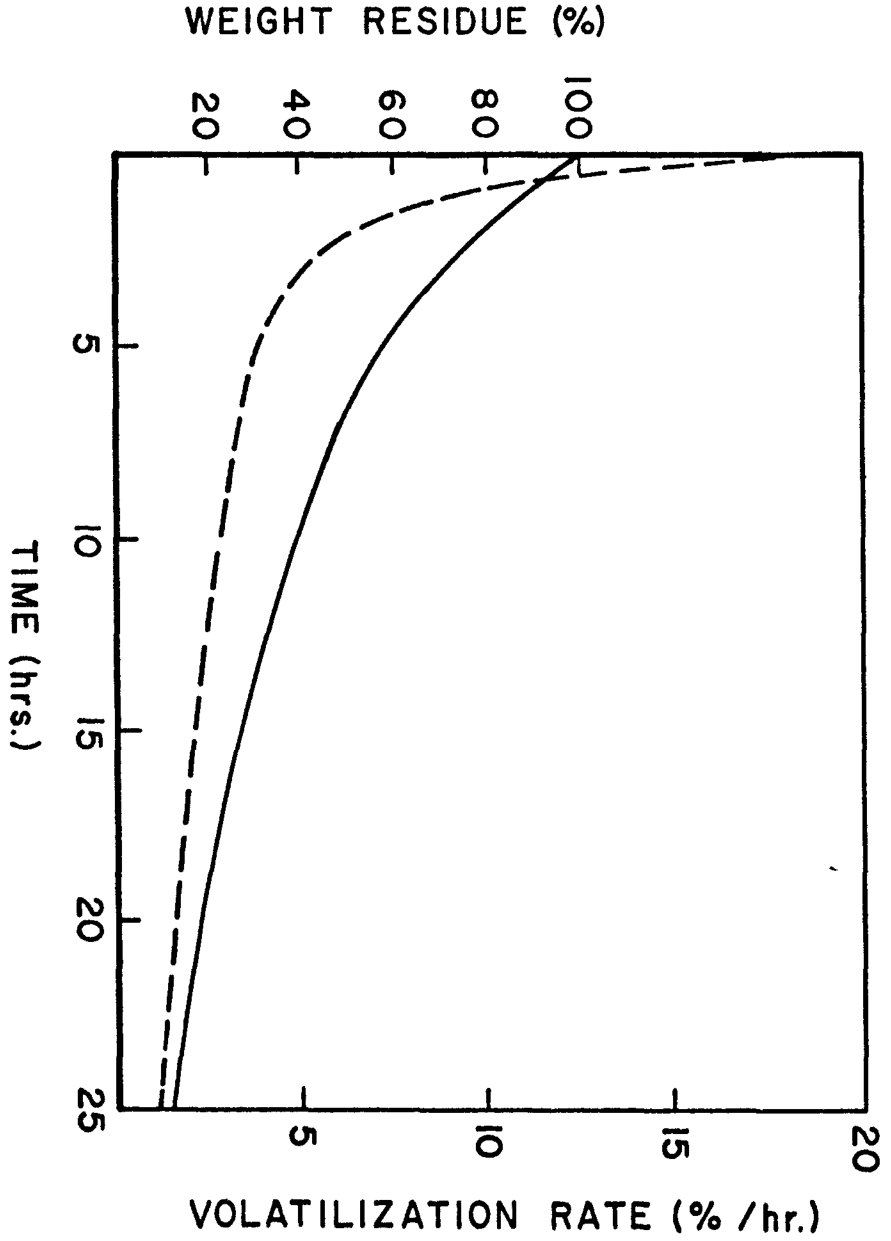


Figure 6. Weight loss and volatilization rate of poly-2,6-dimethyl-1, 4-phenylene oxide (PPO) during isothermal aging at 371°C in air

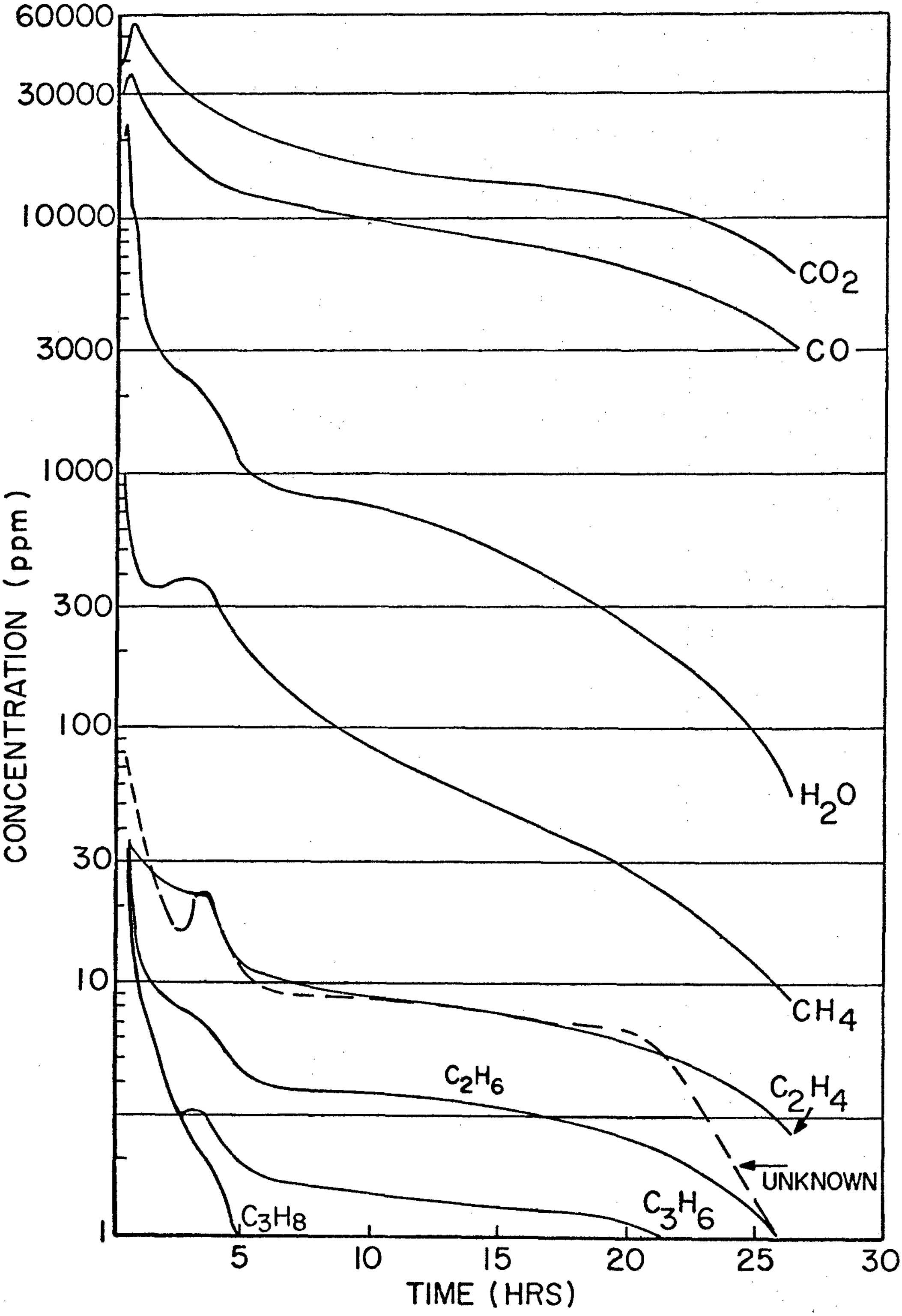


Figure 7. Concentration of volatiles from poly-2,6-dimethyl-1,4-phenylene oxide during isothermal aging at 371°C in air

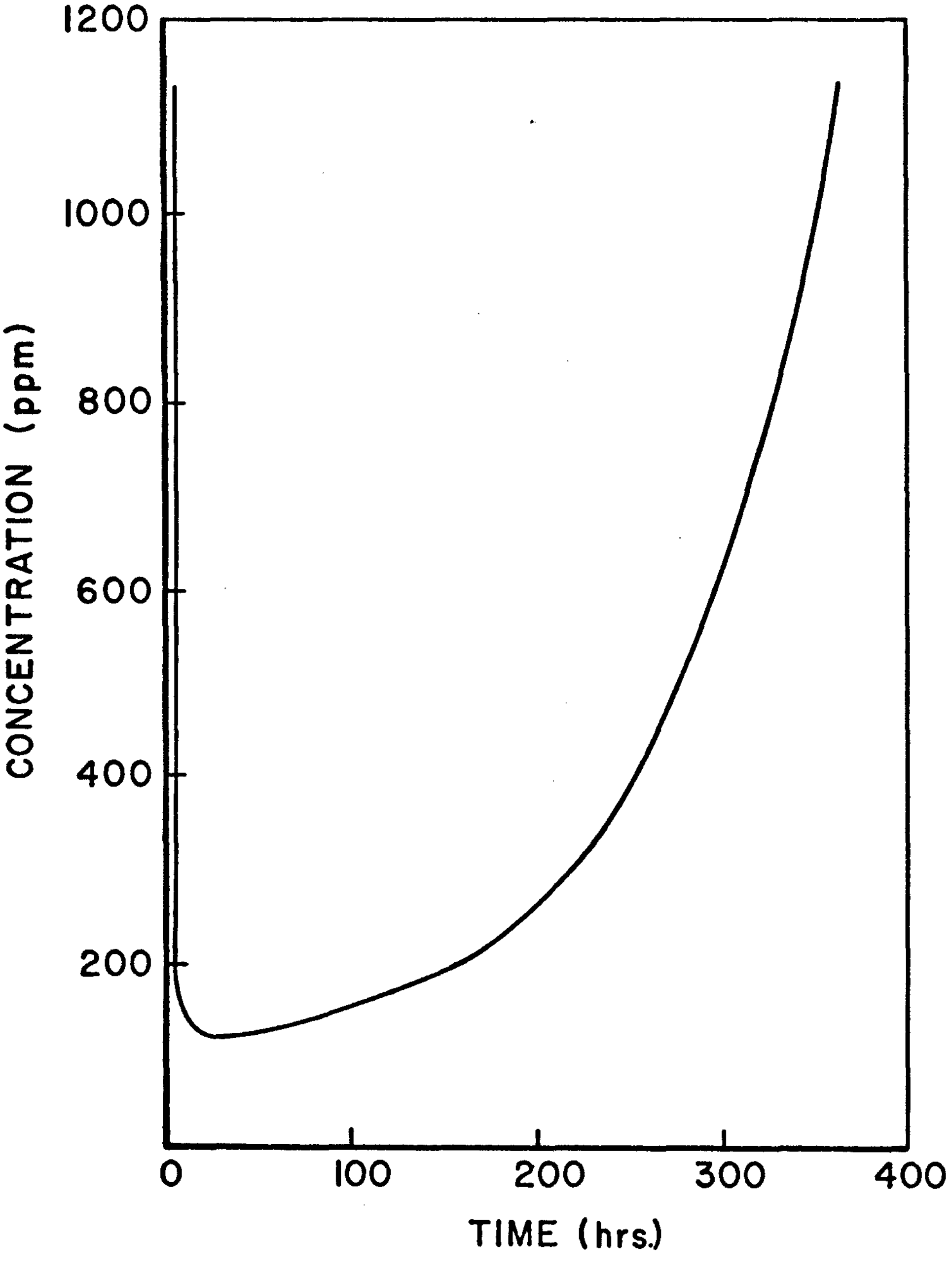


Figure 8. Concentration of carbon dioxide from poly-2,6-diphenyl-1, 4-phenylene oxide (P_3O) during isothermal aging at 316°C in air

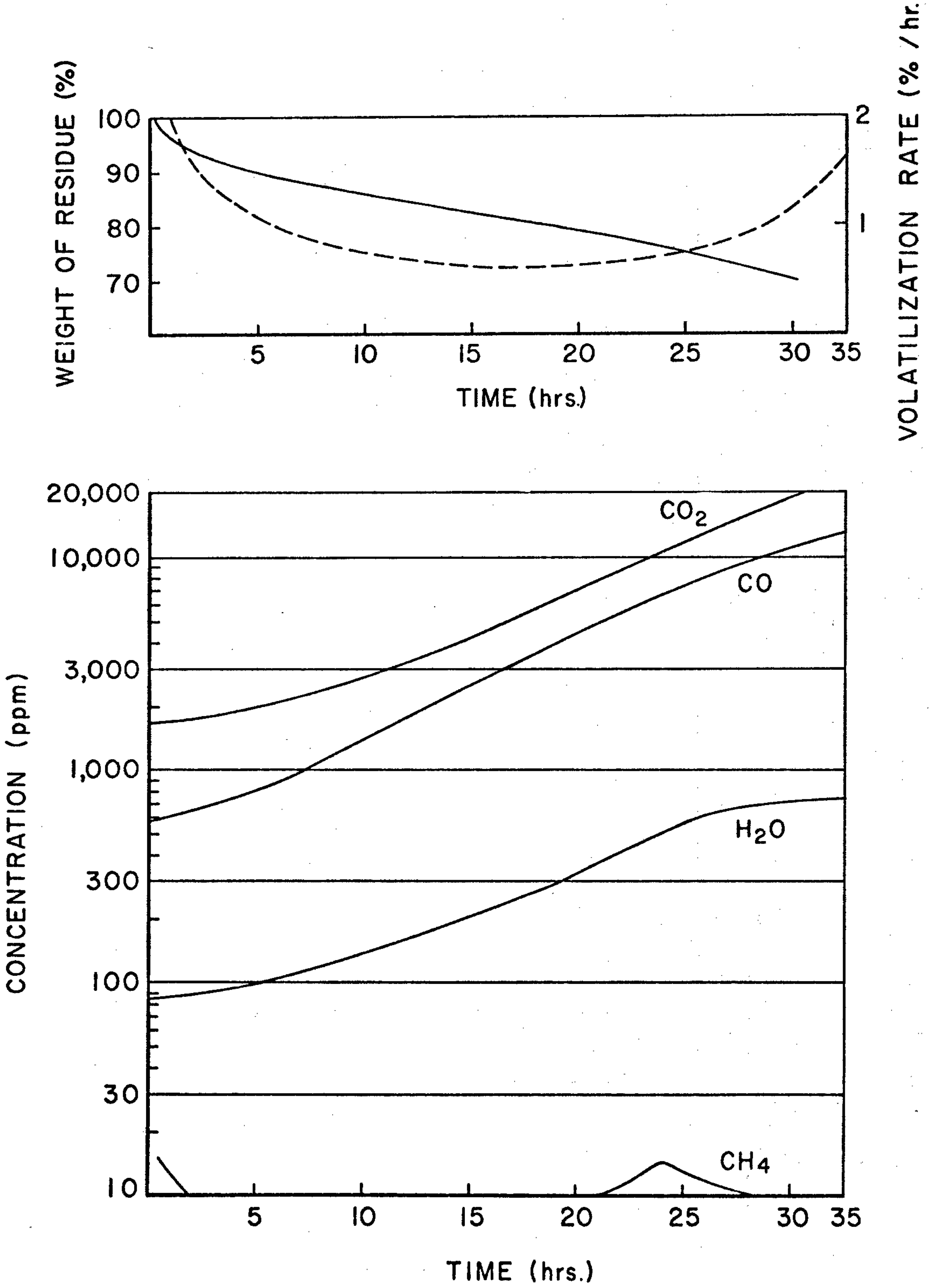


Figure 9. Weight loss and volatilization rate of, and concentration of volatiles from, poly-2,6-diphenyl-1,4-phenylene oxide (P_3O) during isothermal aging at 371°C in air

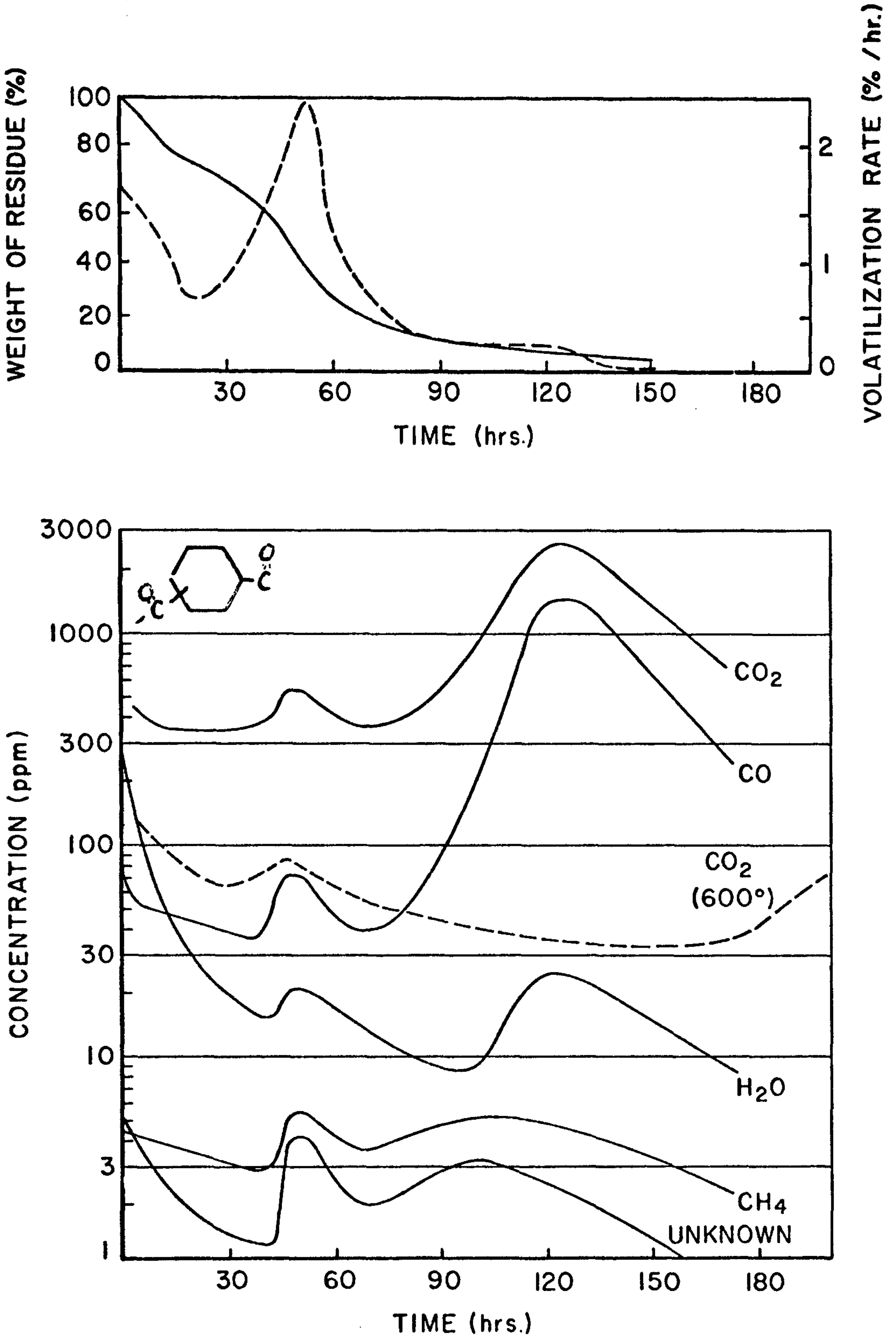


Figure 10. Weight loss and volatilization rate of, and concentration of volatiles from poly(p-phenylene) iso-terephthalate at 371°C, and of carbon dioxide at 600°F, in air

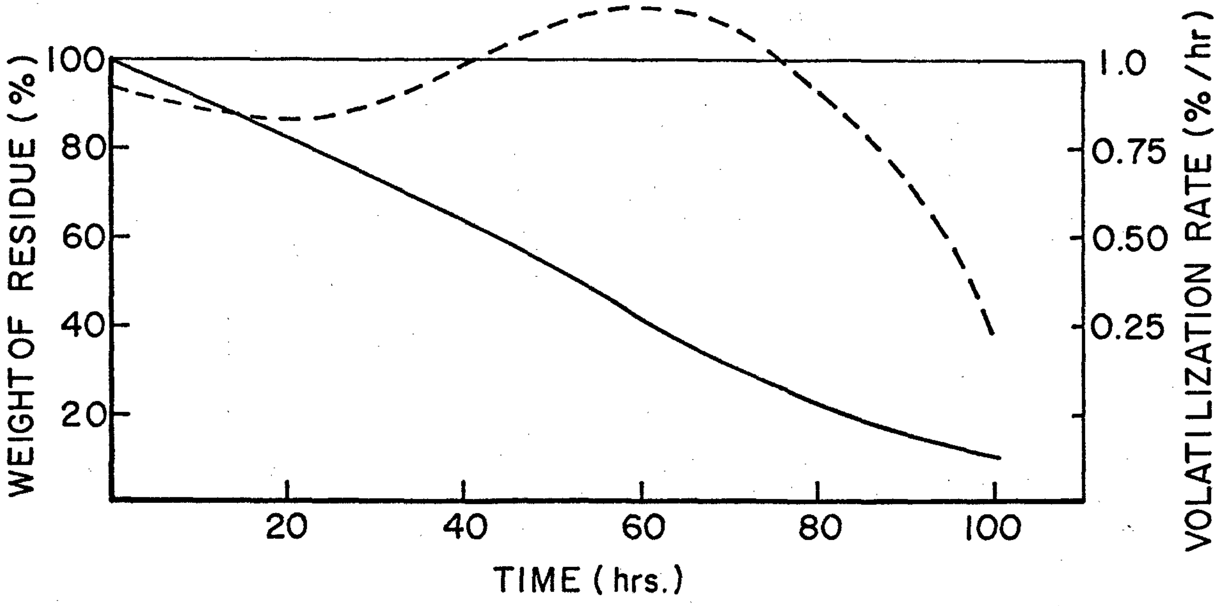


Figure 11. Weight loss and volatilization rate of poly-p-benzamide fiber during isothermal aging at 371°C in air

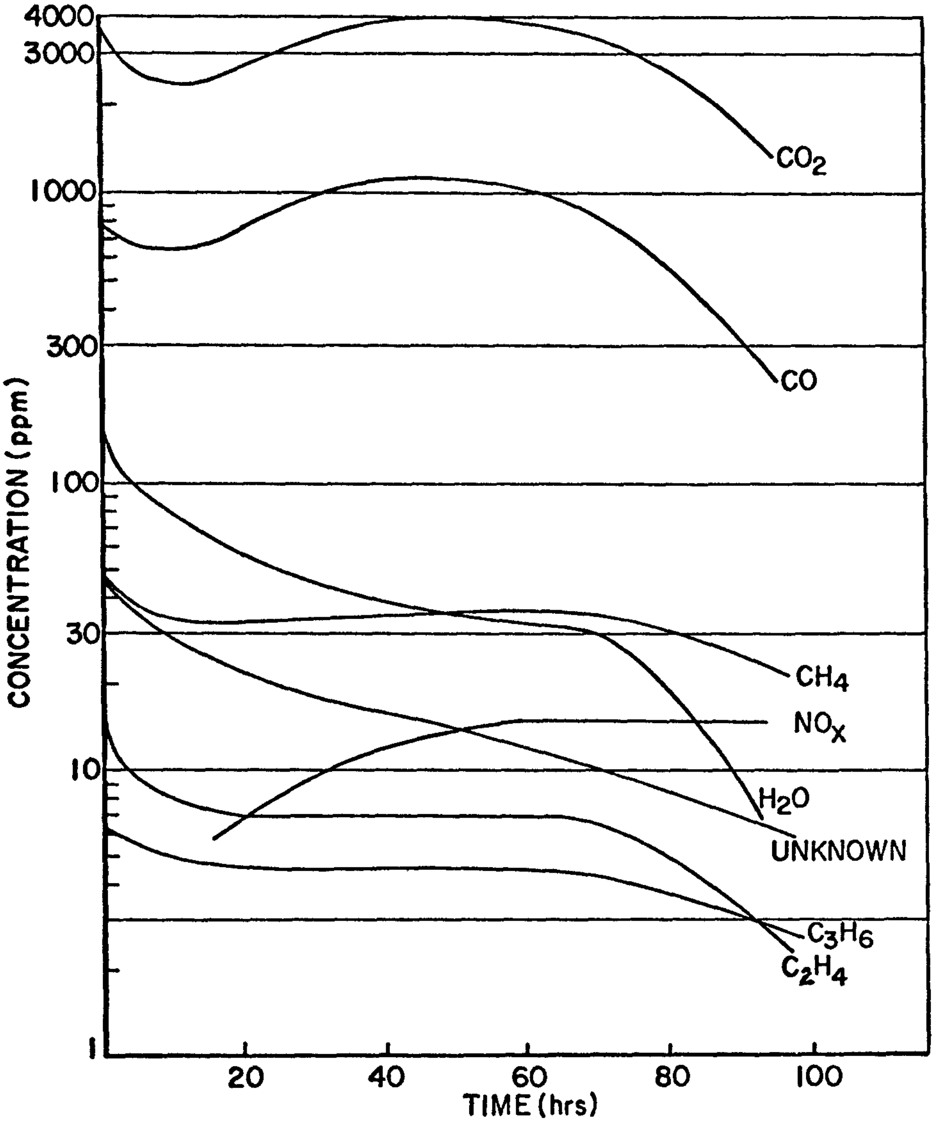
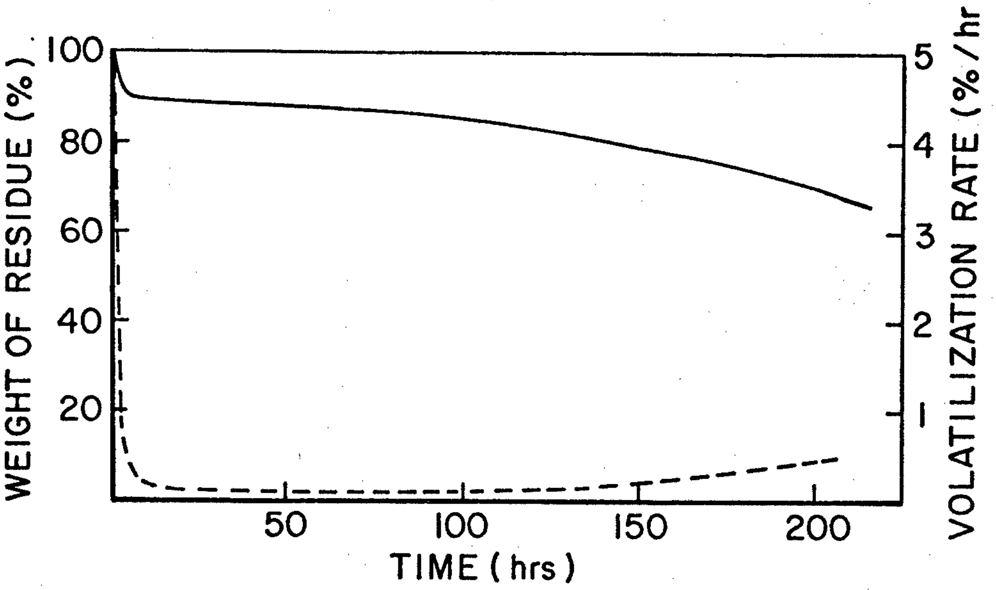


Figure 12. Concentration of volatiles from poly-p-benzamide fiber during isothermal aging at 371°C in air



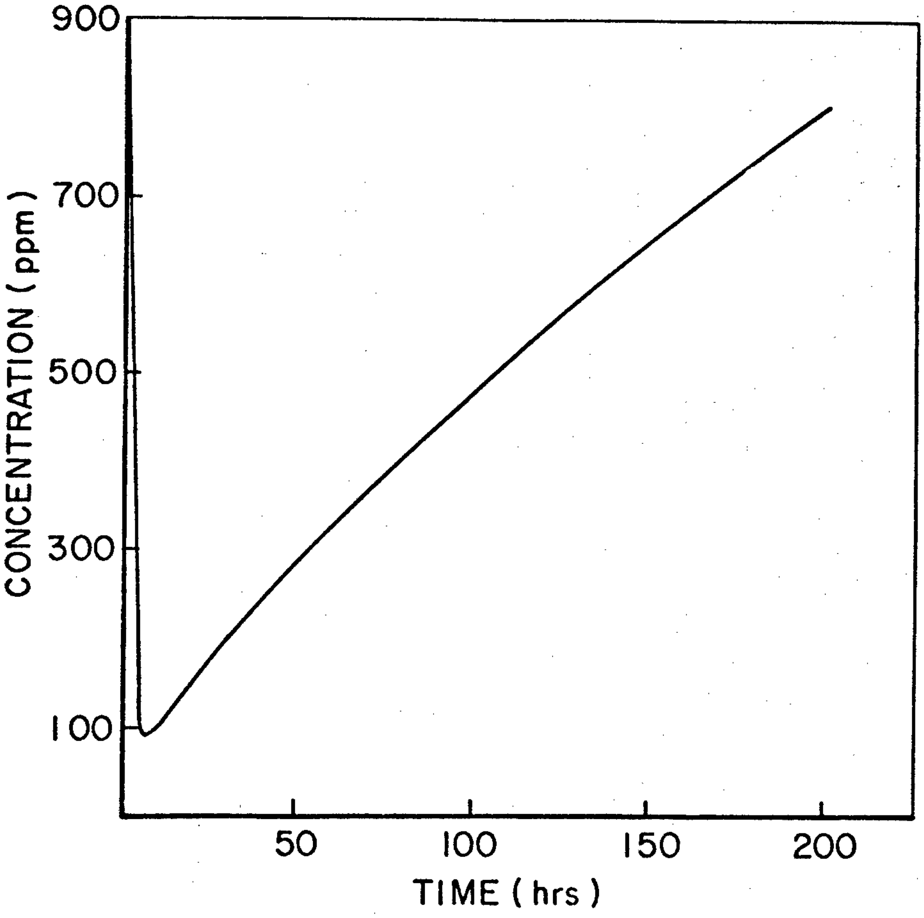


Figure 13. Weight loss and volatilization rate of, and concentration of carbon dioxide from, poly-2,2'-(1,3-phenylene)-5,5'-bibenzimidazole during isothermal aging at 316°C in air

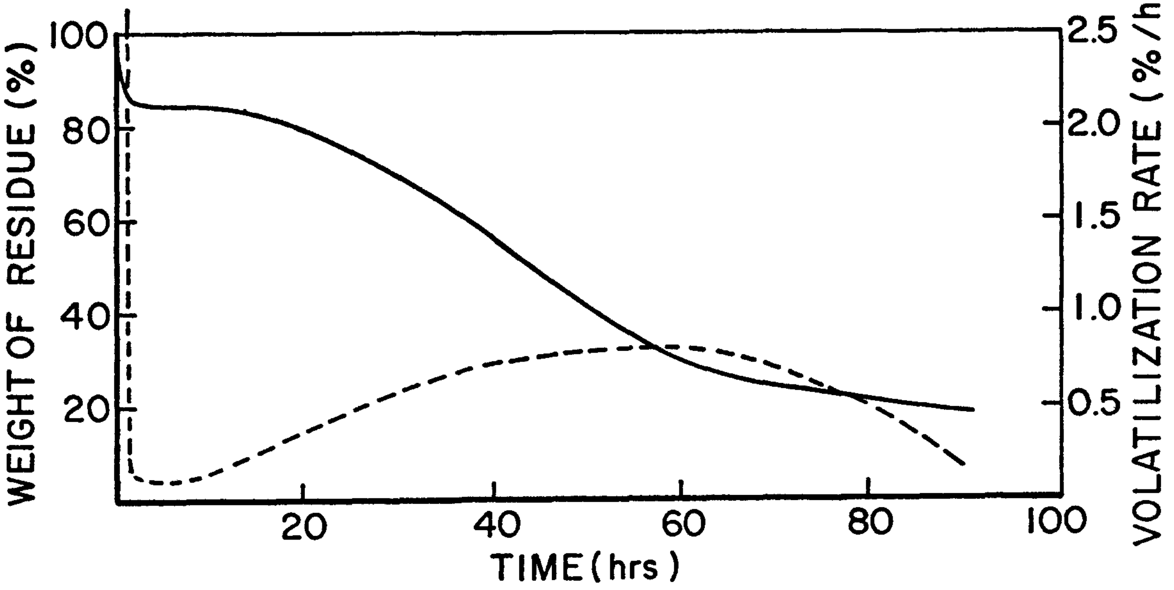


Figure 14. Weight loss and volatilization rate of poly-2,2'-(1,3-phenylene)-5,5'-bibenzimidazole during isothermal aging at 371°C in air

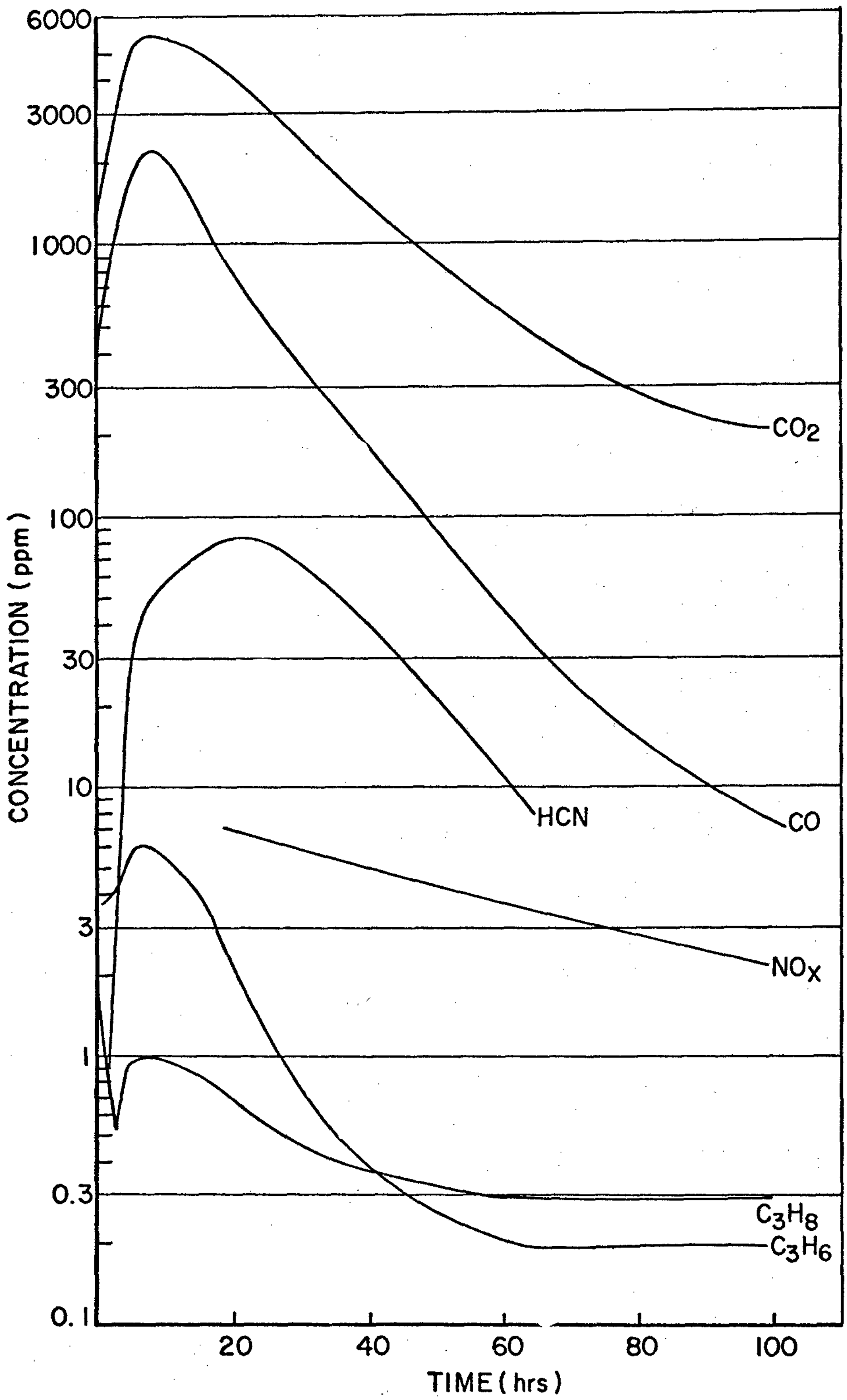


Figure 15. Concentration of volatiles (I) from poly-2,2'-(1,3-phenylene)-5,5'-bibenzimidazole during isothermal aging at 371°C in air

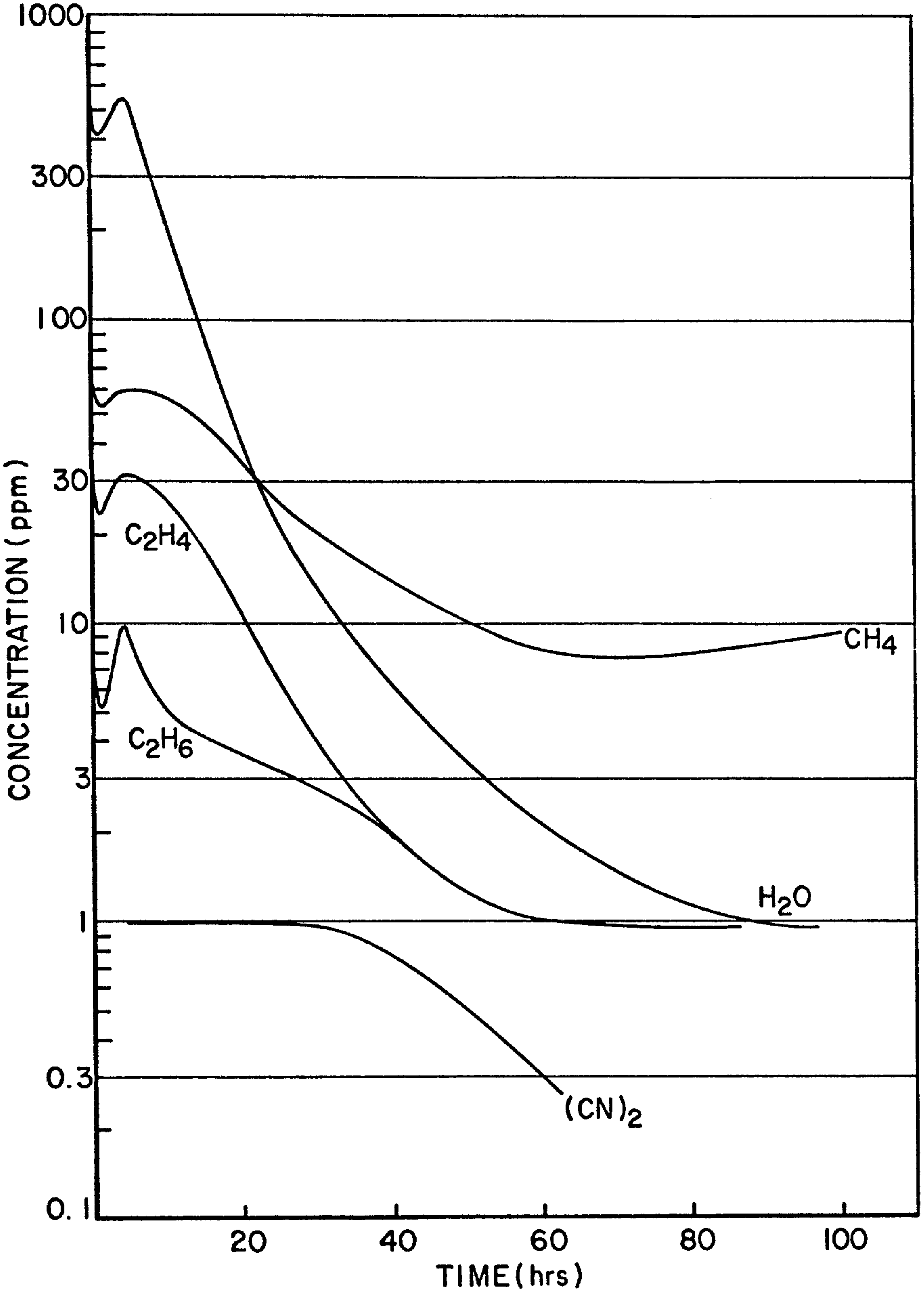


Figure 16. Concentration of volatiles (II) from poly-2,2'-(1,3-phenylene)-5,5'-bibenzimidazole during isothermal aging at 371°C in air

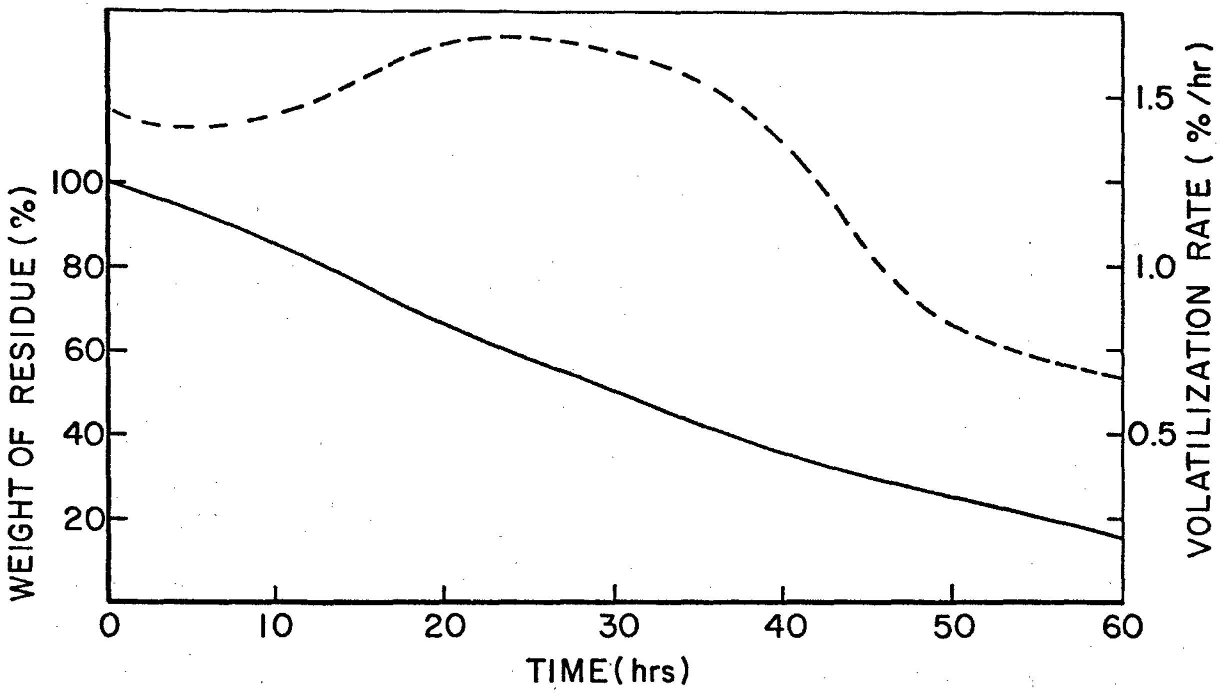


Figure 17. Weight loss and volatilization rate of a ladder polyquinoxaline during isothermal aging at 371°C in air

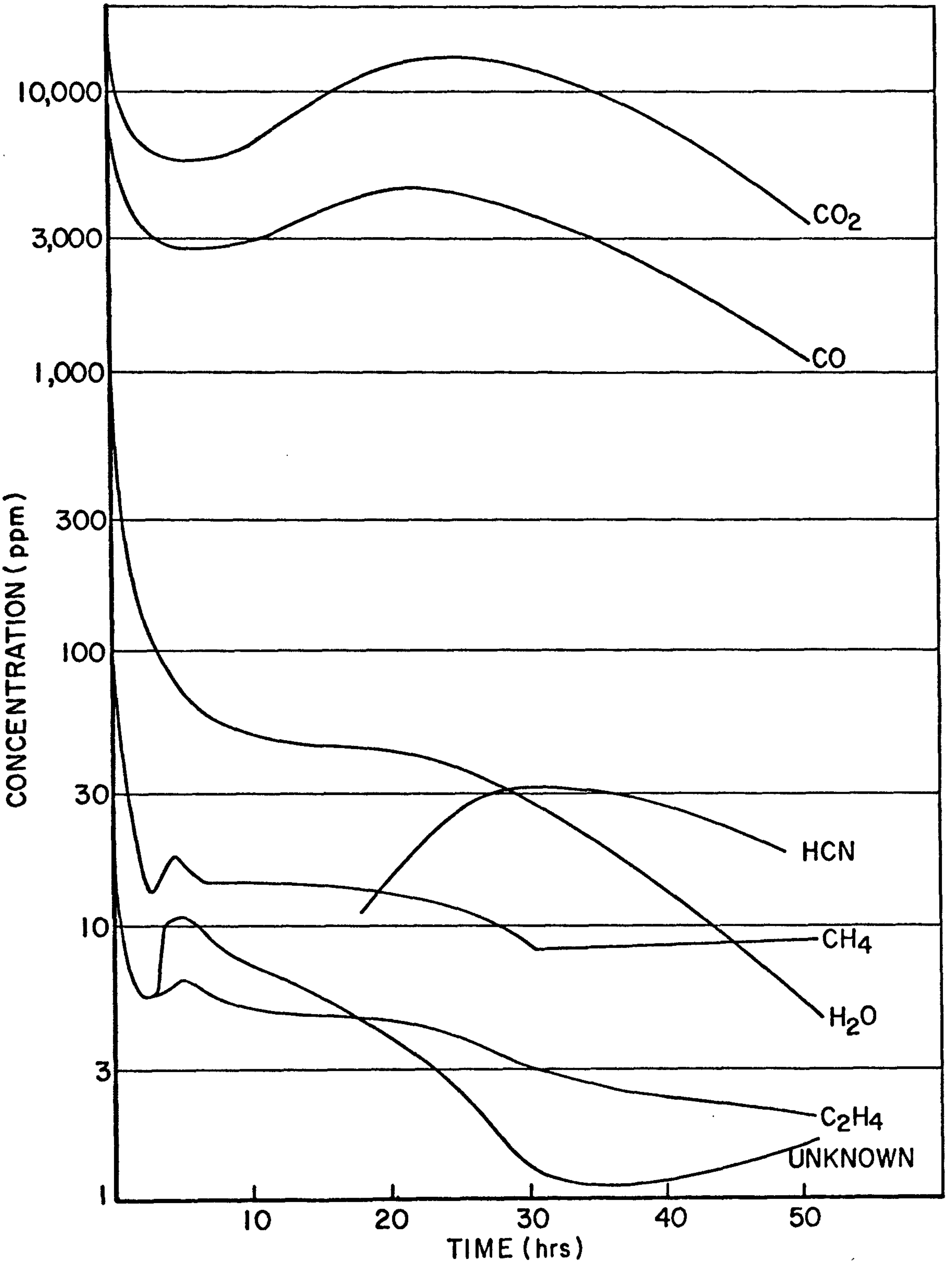


Figure 18. Concentration of volatiles from a ladder polyquinoxaline during isothermal aging at 371°C in air

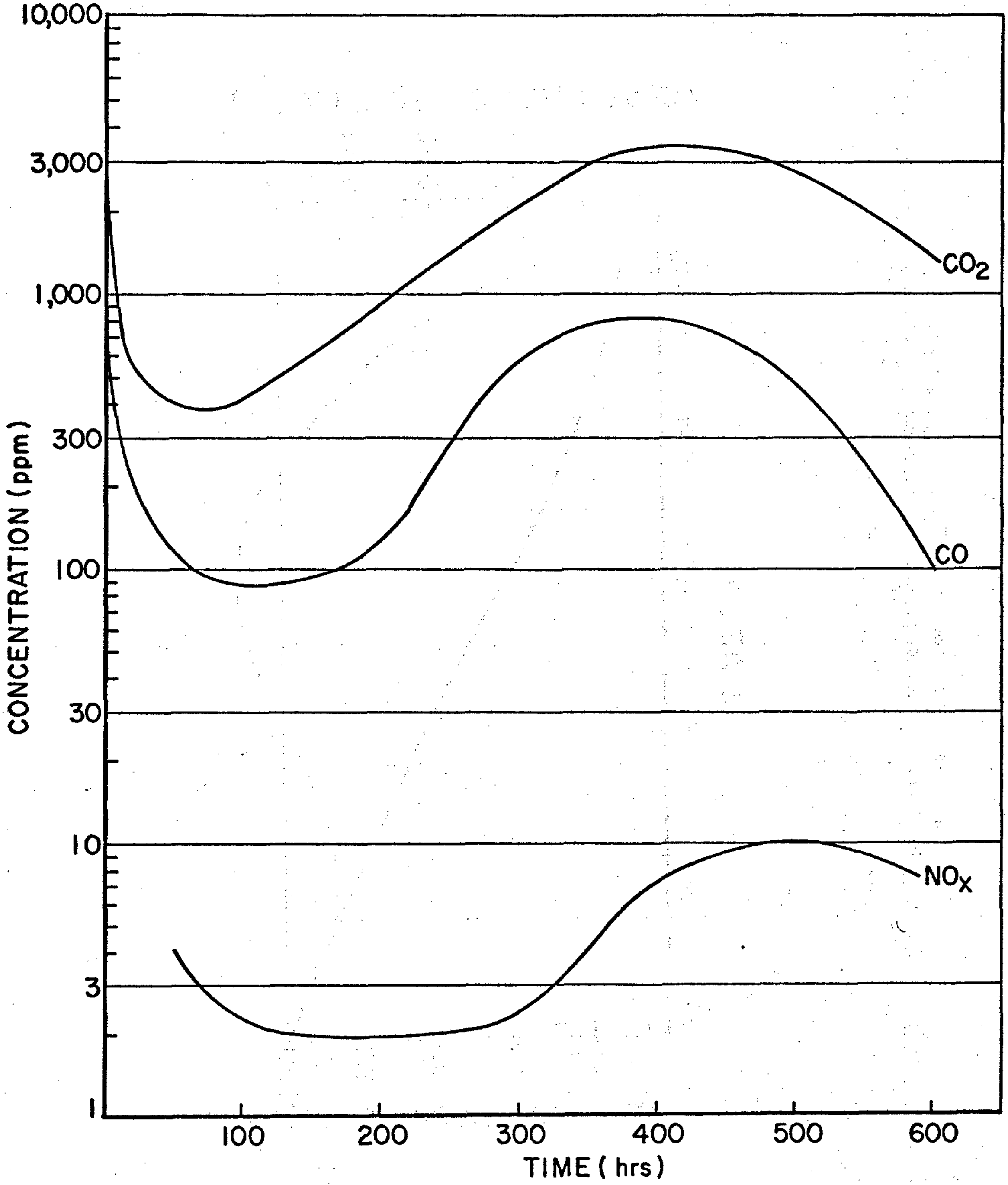


Figure 19. Concentration of volatiles (I) from polybenzimidazobenzophenanthroline (BBB) during isothermal aging at 371°C in air

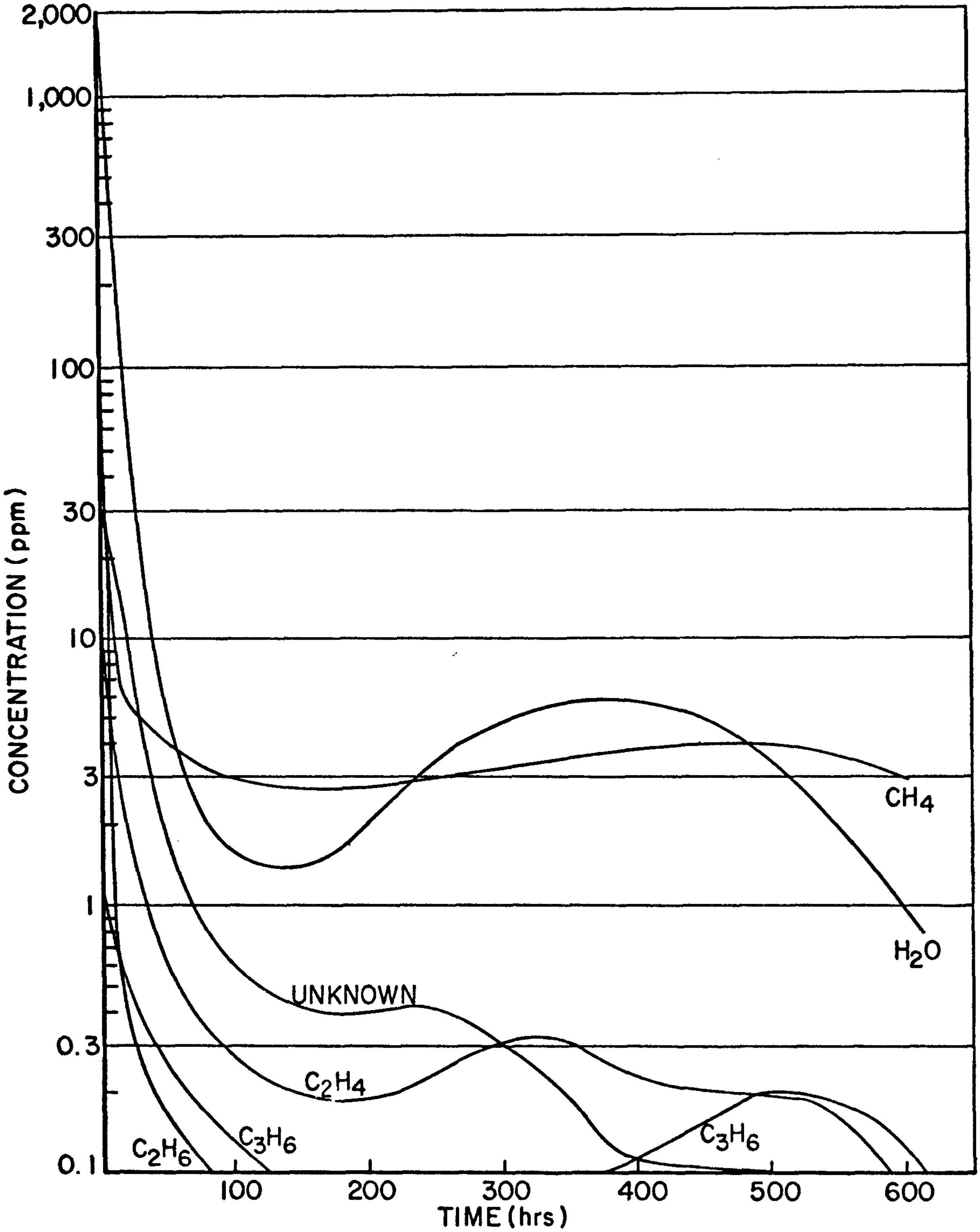


Figure 20. Concentration of volatiles (II) from polybenzimidazobenzophenanthroline (BBB) during isothermal aging at 371°C in air

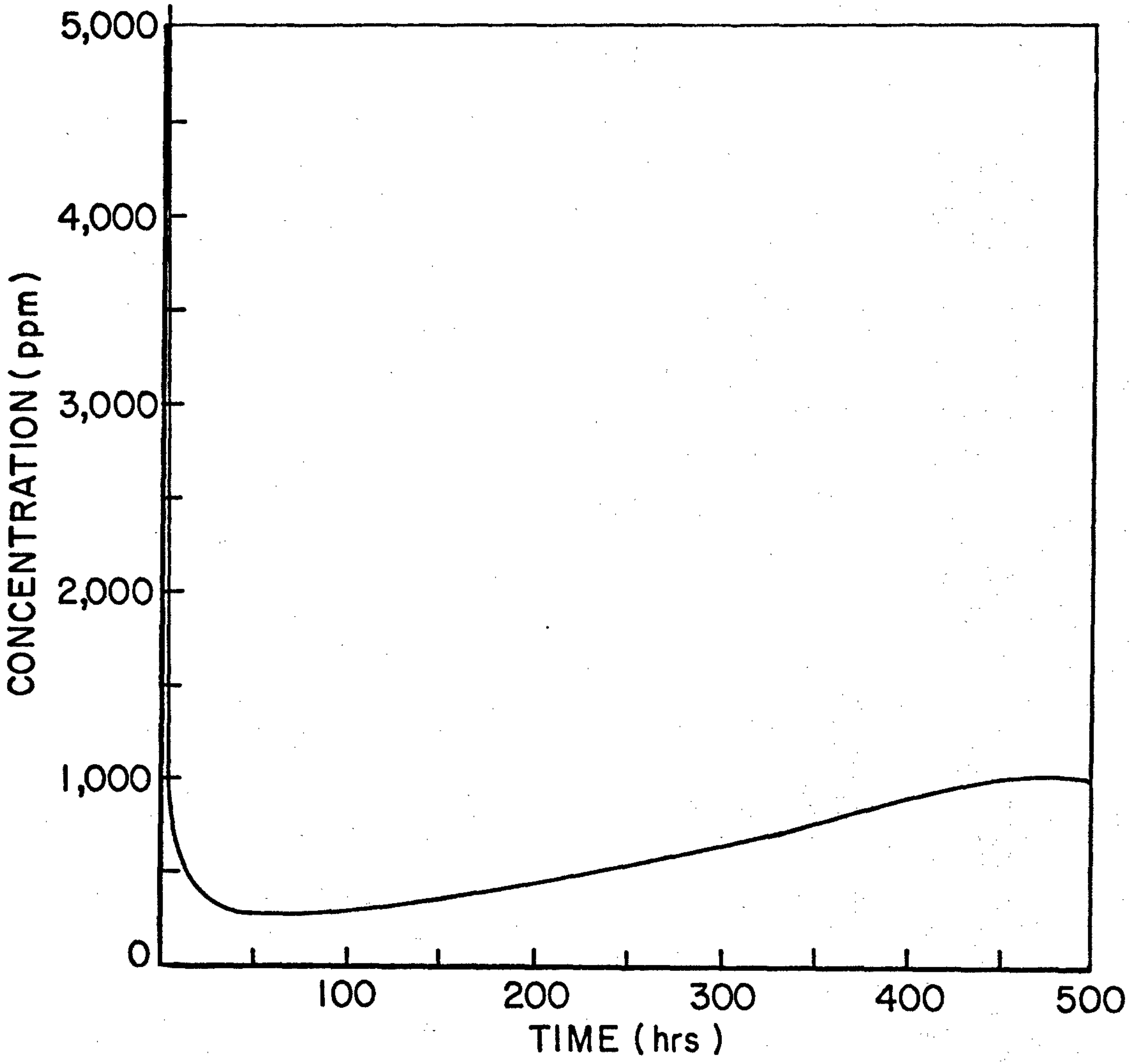
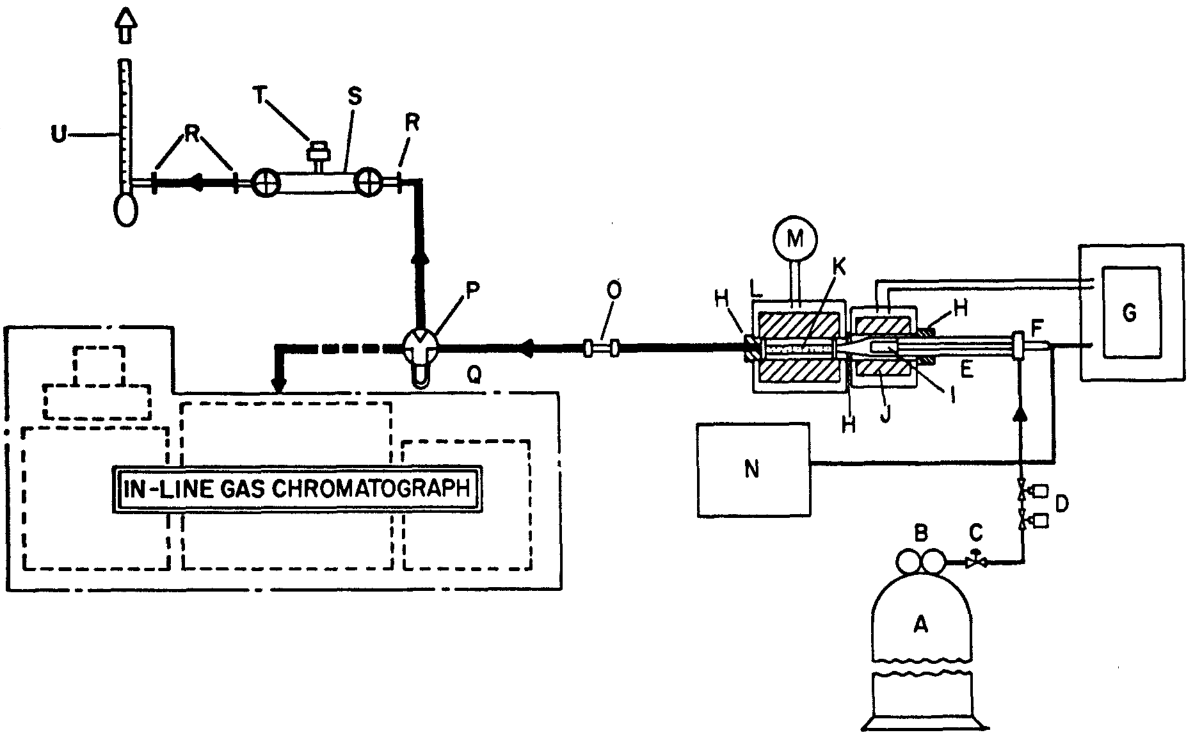


Figure 21. Concentration of carbon dioxide from polybenzimidazoisoquinoline (BBL) during isothermal aging at 371°C in air



A. SUPPLY GAS MIXTURE
B. PRESSURE REGULATOR
C. ON-OFF VALVE
D. MICROMETER NEEDLE VALVES
E. FABRICATED PYREX TUBE
F. INSULATED THERMOCOUPLES
G. TEMPERATURE MEASUREMENT AND CONTROL
H. GLASS WOOL INSULATION
I. SPECIMEN
J. SPECIMEN TUBE FURNACE

K. CALCIUM CARBIDE PACKED TUBE
L. REACTOR TUBE FURNACE
M. VARIAC
N. AUXILIARY POTENTIOMETER
O. COLLECTION TUBE (CHARCOAL OR TENAX GC)
P. GAS SAMPLING VALVE
Q. SAMPLE LOOP (FOR IN-LINE GC)
R. HYPODERMIC NEEDLE APERTURES
S. SAMPLING VESSEL (PYREX)
T. SAMPLING SEPTUM
U. SOAP BUBBLE FLOW METER

Figure 22. Schematic Diagram of Isothermal Aging - Effluent Gas Analysis Equipment

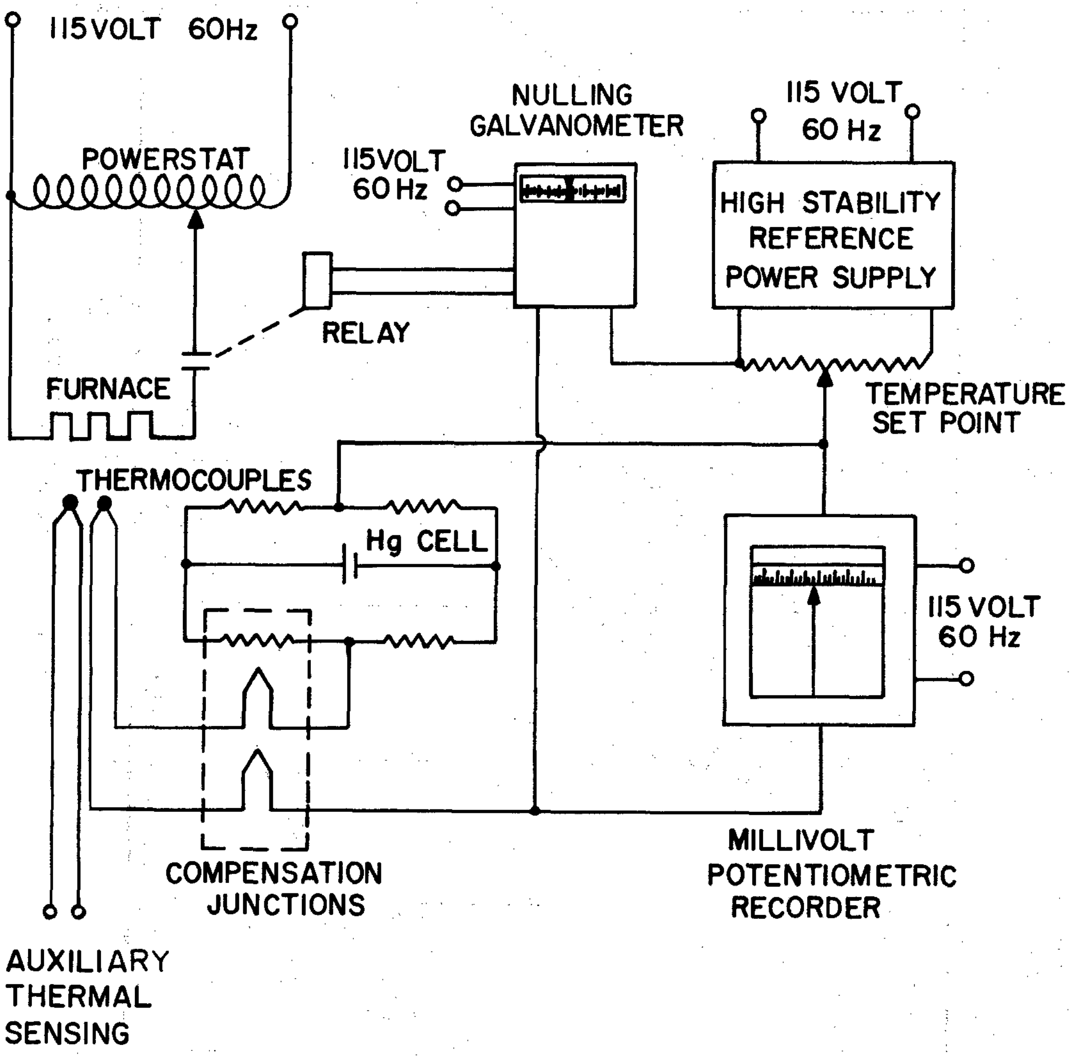


Figure 23. Circuit Diagram of the Thermal Measurement and Control System

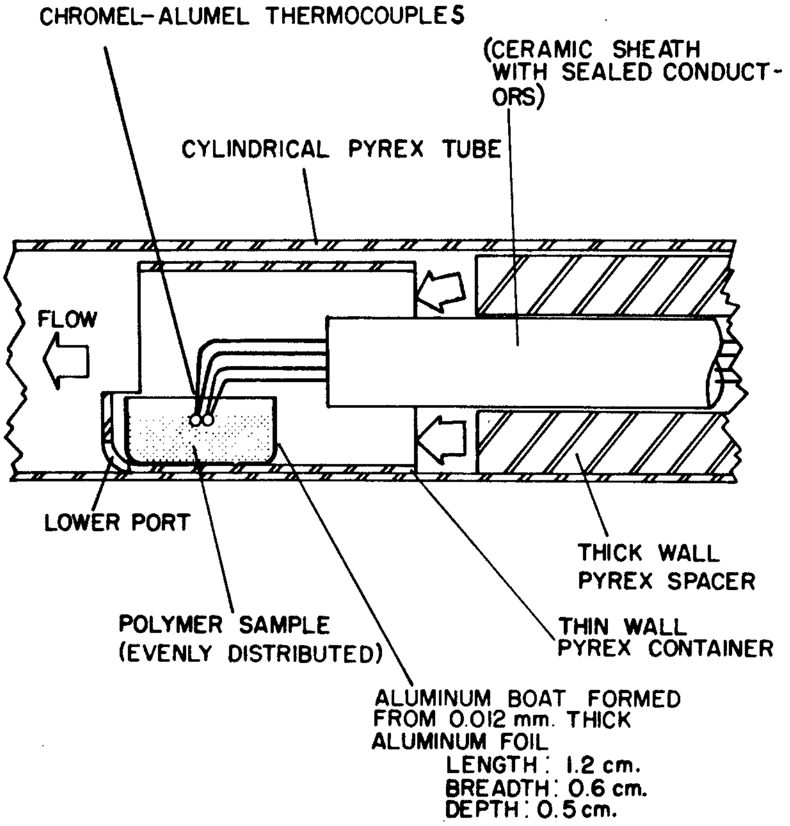
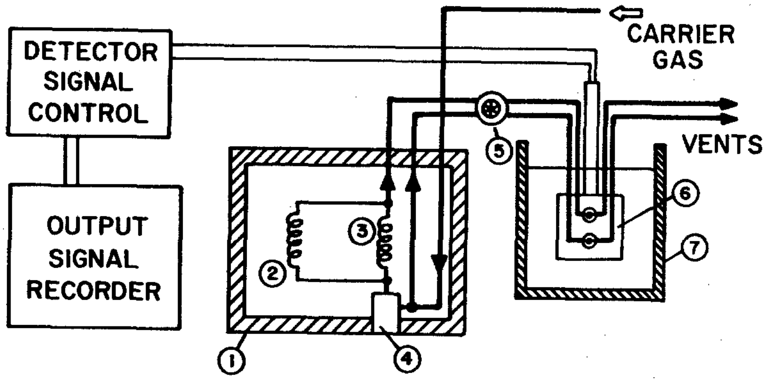


Figure 24. Sampleholder of the Isothermal Aging - Effluent Gas Analysis Equipment



1	GAS CHROMATOGRAPH
2	COLUMN "A"
3	COLUMN "B"
4	SAMPLE INLET
5	SWITCHING VALVE
6	CARLE DETECTOR
7	WATER BATH

Figure 25. In-Line Gas Chromatograph

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