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Investigation of the Properties of the Combustion Products Generated by Building Fires

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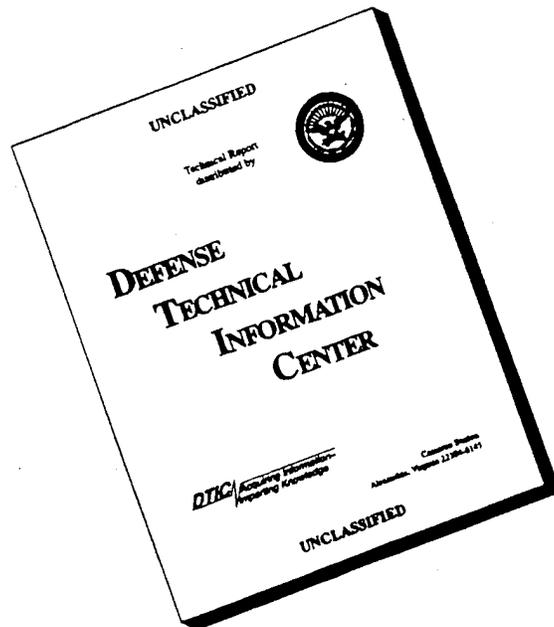
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INVESTIGATION OF THE PROPERTIES OF THE COMBUSTION
PRODUCTS GENERATED BY BUILDING FIRES

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NATIONAL BUREAU OF STANDARDS
WASHINGTON, DC 20234

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This report describes the research conducted under a National Bureau of Standards grant entitled "Investigation of the Properties of the Combustion Products Generated by Building Fires." Eleven polyvinyl chloride and seven polypropylene samples of different compositions have been burned under non-flaming conditions and measurements made of smoke particle size distributions, total smoke particulate mass generated, smoke mean particle diameter, smoke optical density and sample weight loss. Measurements have also been taken for the polypropylene samples burned in a heated ventilation gas. Results show that the characteristics of the smoke particulates and sample weight loss behavior are affected by the presence or absence of different chemical additives for both PVC and polypropylene. Also, the burning and smoke characteristics of the polypropylene samples are influenced by the ventilation gas temperature.

In addition to the physical properties measurements, the chemical analysis of smoke particulates has also been carried out. Specifically, a general scheme for the analysis of particulates collected from burning PVC samples under non-flaming conditions has been developed, which has provided good separation of the complex mixture and has enabled many compounds to be identified by high pressure liquid chromatography and gas chromatography/mass spectrometry techniques. Many compounds which were only partly resolved previously have now been more fully resolved.

Modifications to the in situ smoke optical analysis system which will allow the accurate measurement of the smoke volume concentration and the complex index of refraction are also reported. Furthermore, a review of progress toward the cataloging in a separate volume of previously obtained smoke physical properties data is included in this report.

Finally, a description is provided of a theoretical model which describes the smoldering decomposition of a charring polymeric material subjected to an incident radiant heat flux. The model has been developed for the purposes of predicting smoke particulate formation by inclusion of candidate smoke formation mechanisms.

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The authors would like to thank the Bell Laboratories, Murray Hill, NJ for the supply of PVC compositions which were tested in this research program.

Also, we would like to express our gratitude to the Diamond Shamrock Corporation, Painesville, OH, for providing polypropylene samples also for testing in this program.

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I. INTRODUCTION

This report describes the efforts conducted under National Bureau of Standards Grant No. G7-9001 during the period October 1, 1976 to September 30, 1977. The subject grant is entitled "Investigation of the Properties of the Combustion Products Generated by Building Fires." The objectives of this program have been: (1) continued development and utilization of facilities and experimental techniques required for the determination of particle size distributions and particulate mass concentrations, the chemical properties of smoke particulate products, and the optical properties of smoke produced by burning various building materials; (2) determination of the dependence of the properties of smoke generated by the combustion of various materials on the temperature and composition of the chamber atmosphere, the type of burning, the radiant heat flux to the sample in non-flaming combustion, the orientation of the sample, and the amount of ventilation; (3) determination of the dependence of smoke and gaseous products generated by burning synthetic polymers on the type and amount of chemical additives found in those polymers; and (4) utilization of small-scale test data with related theoretical models to predict the smoking properties of various materials.

To pursue the objectives outlined above, the efforts of this research project have been divided into four major categories or tasks. Task 1 is concerned with the continued improvement of and modifications to the experimental capabilities of the fire research facility; Task 2 deals with the actual determination of the detailed characteristics of the products generated during the combustion of materials in a ventilated, small-scale Combustion Products

Test Chamber under carefully controlled conditions; Task 3 is concerned with the theoretical modeling of smoke production from burning materials; and Task 4 deals with cataloging the measured physical properties data in a form that will make it useful for smoke detector designers and toxicologists. This program has been directed by Drs. Ben T. Zinn and Robert A. Cassanova in the School of Aerospace Engineering of the Georgia Institute of Technology. Other contributing professional personnel include Drs. C. P. Bankston, R. F. Browner, E. A. Powell and J. U. Rhee. Also assisting was Mr. K. Kailasanath, Graduate Research Assistant.

II. EXPERIMENTAL FACILITIES

A. Previously Developed Experimental Facilities

The smoke research program described herein has been conducted utilizing the following facilities which have been developed at the School of Aerospace Engineering, Georgia Institute of Technology: (1) A Combustion Products Test Chamber, (2) A Combustion Products Sampling System; (3) An In Situ Optical Aerosol Measurement System; and (4) A Chemical Analysis Laboratory.

The ventilated Combustion Products Test Chamber (CPTC) is capable of simulating a wide variety of environmental conditions that may be encountered in actual fire situations. Specifically, the design of the CPTC permits easy control and measurement of the following variables during the combustion of small samples of materials: (1) The mode of combustion (i.e., flaming vs. smoldering combustion); (2) The sample radiant heating rate (up to 10 watts/cm²); (3) The sample weight loss during the test; (4) The composition of the ventilating gas surrounding the sample; (5) The temperature of the ventilation gas (up to 650°C) and; (6) An option to test the sample under either vertical or horizontal mounting. A complete description of the CPTC including operating procedures, can be found in References 1 and 2.

During testing, a Combustion Products Sampling System is used to analyze smoke samples that are continuously withdrawn from the gases flowing from the CPTC. Information obtained by the Aerosol Sampling System includes particle size distributions and total particulate mass generated. Some of the collected smoke samples are also retained for chemical analysis. A description of the sampling system can also be found in References 1 and 2.

In addition to the data obtained by sampling techniques, an In Situ Optical Aerosol Measurement System is utilized to make simultaneous mean particle size and concentration measurements. With this optical smoke analysis system measure-

ments of scattered blue light at forward angles of 5° and 15° and measurements of transmitted red and blue laser lights provide time resolved data describing the average size, volume concentration of the smoke particles, their index of refraction, and their optical density. Details of the optical system are available in References 2 and 3.

An on-line data acquisition system utilizing a Hewlett-Packard 2100 mini-computer is being used for acquiring, reducing and plotting all of the optical and sampling data with the exception of Anderson Sampler (cascade impactor) data which calls for the weighing of the samples collected on the various impaction plates.

Finally, a chemical laboratory containing analytical equipment for the determination of the chemical composition of smoke particulates sampled during tests in the CPTC has been developed. The available equipment includes a high pressure liquid chromatograph, an infrared spectrophotometer, a gas chromatograph equipped with a thermal conductivity detector and a gas chromatograph which is equipped with dual flame ionization detectors and is interfaced to a mass spectrometer. The gas chromatograph/mass spectrometer system is also equipped with a computerized data acquisition and analysis system that records the total-ion chromatograms and the mass spectra.

B. Further Development of the Optical System

The in situ optical system has been modified in order to obtain reliable refractive index and volume concentration measurements. These modifications are necessary because the smoke particles appear to absorb as well as scatter light, especially during flaming combustion when sooty particulates are obtained. In order to determine the imaginary part of the complex refractive index (i.e., the absorption index), additional scattered light measurements are made at an angle of 90° to the polarized incident light beam (He-Ne

laser, $\lambda = .633 \mu\text{m}$). Thus, two additional detectors have been incorporated into the present system (see Figure 1). These detectors measure the 90° - scattering intensities parallel to (I_{\parallel}) and perpendicular to (I_{\perp}) the plane of polarization of the incident light beam. The ratio of I_{\parallel}/I_{\perp} will be used along with the mean particle size D_{32} (from the forward scattering measurements) and the ratio of optical densities at the two laser wavelengths ($\lambda_1 = .458 \mu\text{m}$ and $\lambda_2 = .633 \mu\text{m}$) to obtain the complex refractive index, m , of the smoke particles.

Work on the optical system modifications has been divided into the following two tasks: (1) design, acquisition of materials, fabrication and installation of the 90° -scattering system, and (2) development of data reduction procedures for determining the complex refractive index from the measured 90° - scattering intensities and optical densities.

In the first task, design of the 90° -scattering detectors and acquisition of the needed optical components (lenses, filters, etc.) and photodiodes has been accomplished. The detector design is shown on Figure 2 and it consists of an achromatic focusing lens, a $600 \mu\text{m}$ pinhole aperture, a collimating lens, a laser-line interference filter centered at $.633 \mu\text{m}$ wavelength, and a photodiode detector (United Detector PIN 6DP). Because of lack of space within the sampling section and the high temperature of the heated ventilation gases, the 90° -scattering detectors are mounted outside the sampling section. The 90° - scattered light is viewed through two optical windows located on the sides of the sampling section; the optical axes of these windows and the detectors are at 45° angles to the axis of the sampling section (and smoke plume) and they intersect the incident light beam at the center of the smoke plume (see Figure 3). The He-Ne laser is provided with a half-wave plate to rotate the initially vertical polarization plane to the required 45° angle. With this system, 90° -scattered

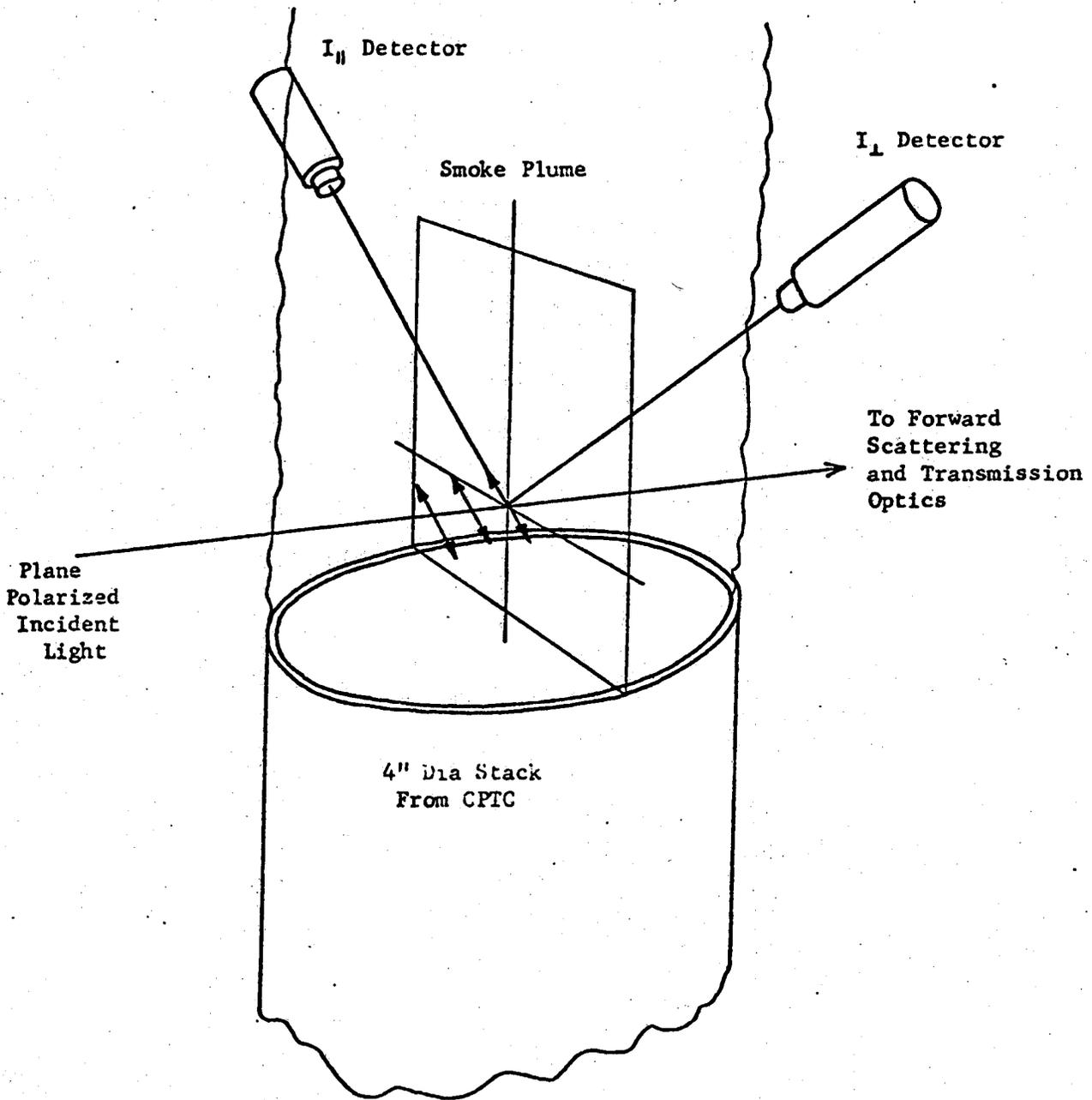


Figure 1. Optical System for 90°-Scattering Measurements.

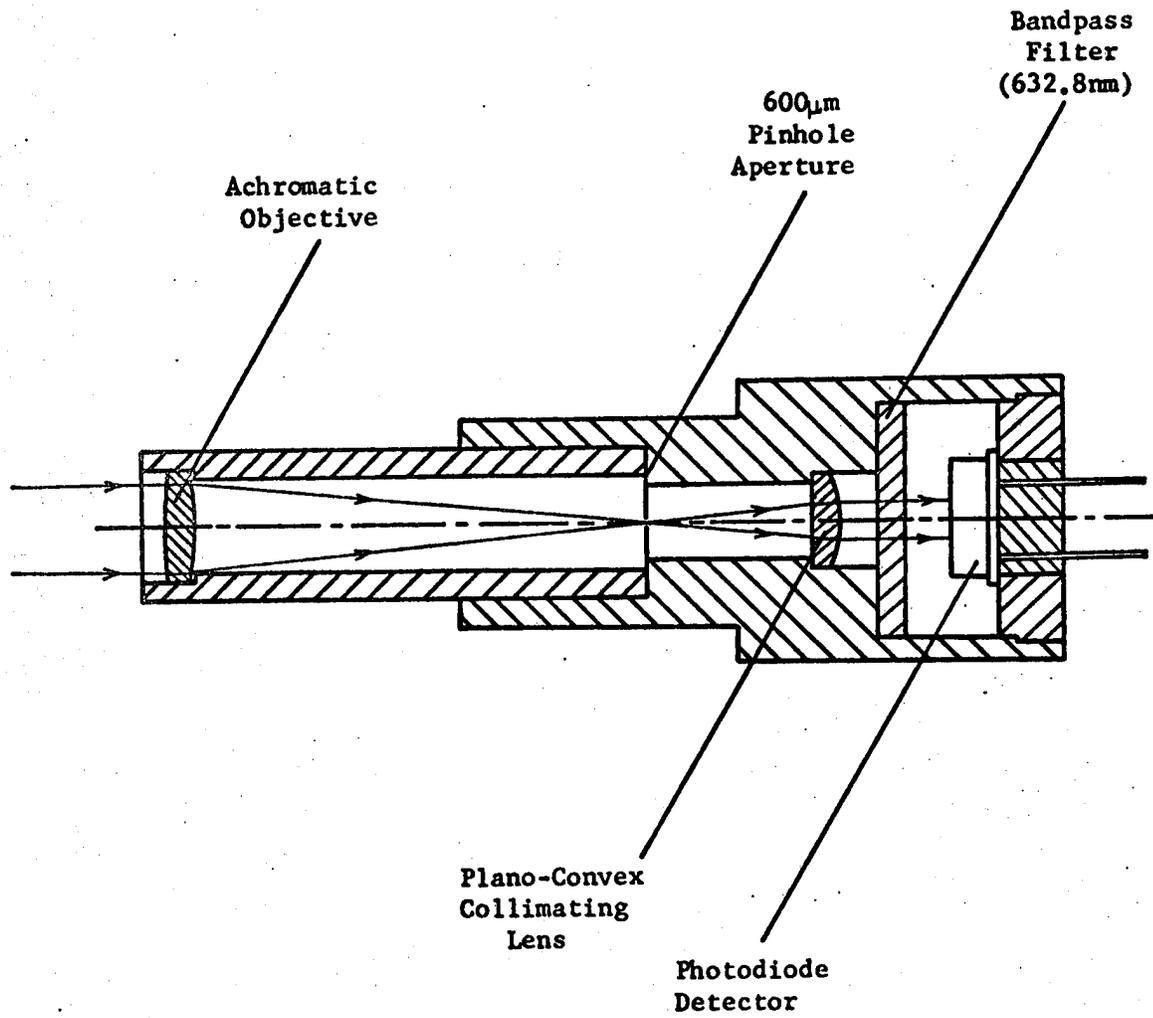


Figure 2. 90°-Scattering Detector Design.

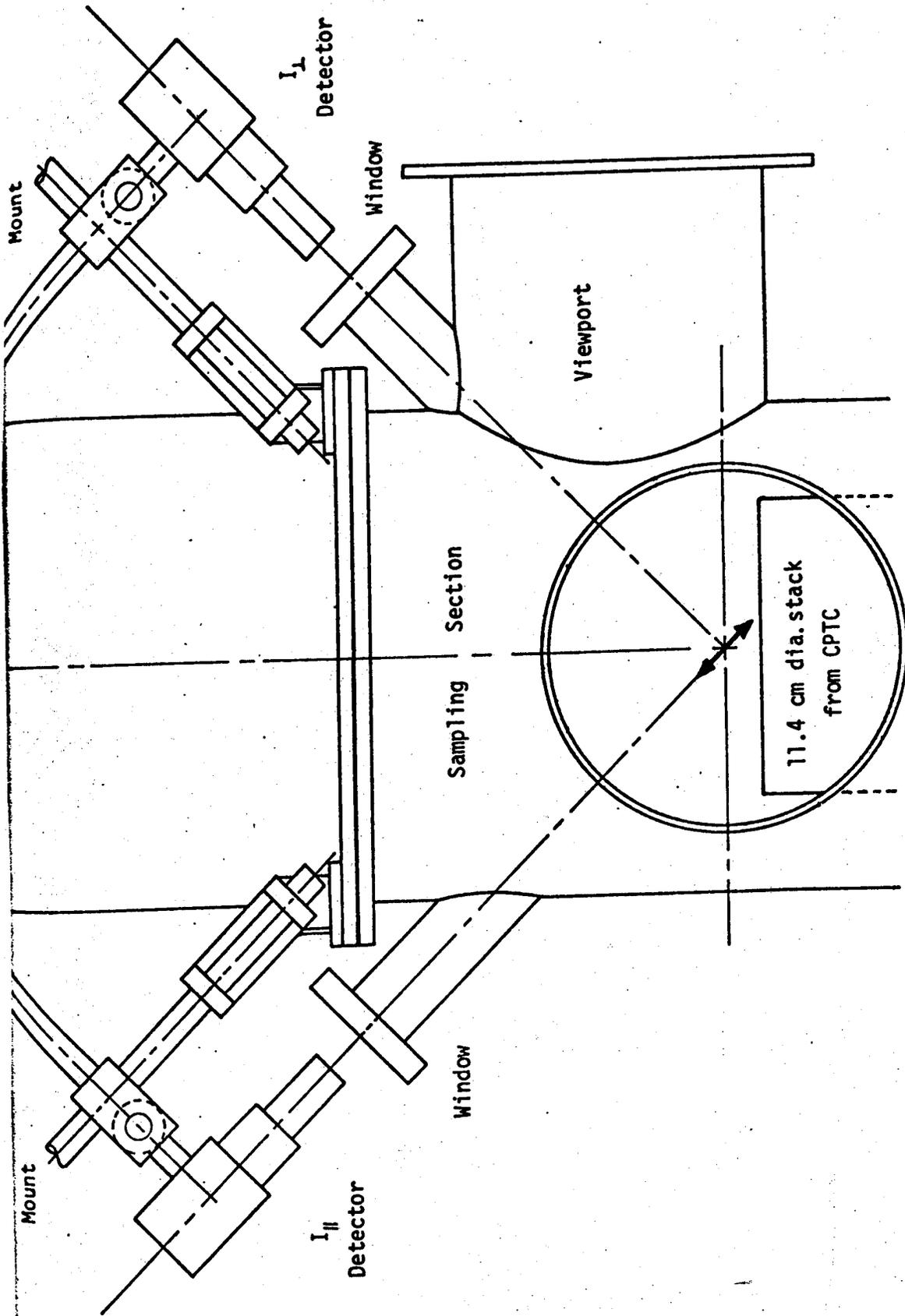


Figure 3. 90° - Scattering Detector Mounting Configuration.

light is detected over a cylindrical scattering volume about 1 mm in diameter and about 1 cm in length. Fabrication and assembly of the detectors, modification of the sampling section (to provide the necessary optical windows), and installation of the complete 90°-scattering system has also been completed.

In the second task, the dependence of the ratio $I_{\parallel} / I_{\perp}$ upon the smoke particle characteristics was investigated. The Mie scattering intensities for single particles were integrated over an assumed Upper Limit Distribution Function (ULDF) to obtain calculated values of I_{\parallel} and I_{\perp} . As in the case of the forward scattering intensities and the ratio of optical densities at two wavelengths, moderate variations in the ULDF parameters a and δ had little effect on the calculated ratios $I_{\parallel} / I_{\perp}$. Thus the remaining calculations were performed for the "standard" distribution function given by $a = 1.13$ and $\delta = 1.26$. The dependence of $I_{\parallel} / I_{\perp}$ upon absorption index, k , for $m = 1.5 - ik$ is shown in Figure 4 for mean particle diameters (D_{32}) typical of smoke. Similar curves were also obtained for $m = 1.4 - ik$ and $m = 1.6 - ik$ (see Figure 5). These results show that measurements of $I_{\parallel} / I_{\perp}$ can be used to determine the absorption index, k , of typical smokes for absorption indices up to about 0.4.

To use the above technique to determine k , the real part (n) of the refractive index must also be known. This was previously determined from the ratio of optical densities at two wavelengths by assuming that the smoke particles are nonabsorbing ($k = 0$). Mie theory calculations of extinction efficiencies for absorbing particles indicate that the ratio of optical densities at two wavelengths depends upon k as well as n (see Figure 6). Thus both 90°-scattering data ($I_{\parallel} / I_{\perp}$) and optical density data must be considered together with the previously measured value of D_{32} (the forward scattering technique is insensitive to refractive index) in order to determine the complex refractive index, $m = n - ik$. The present computer program has been modified to perform these additional calculations.

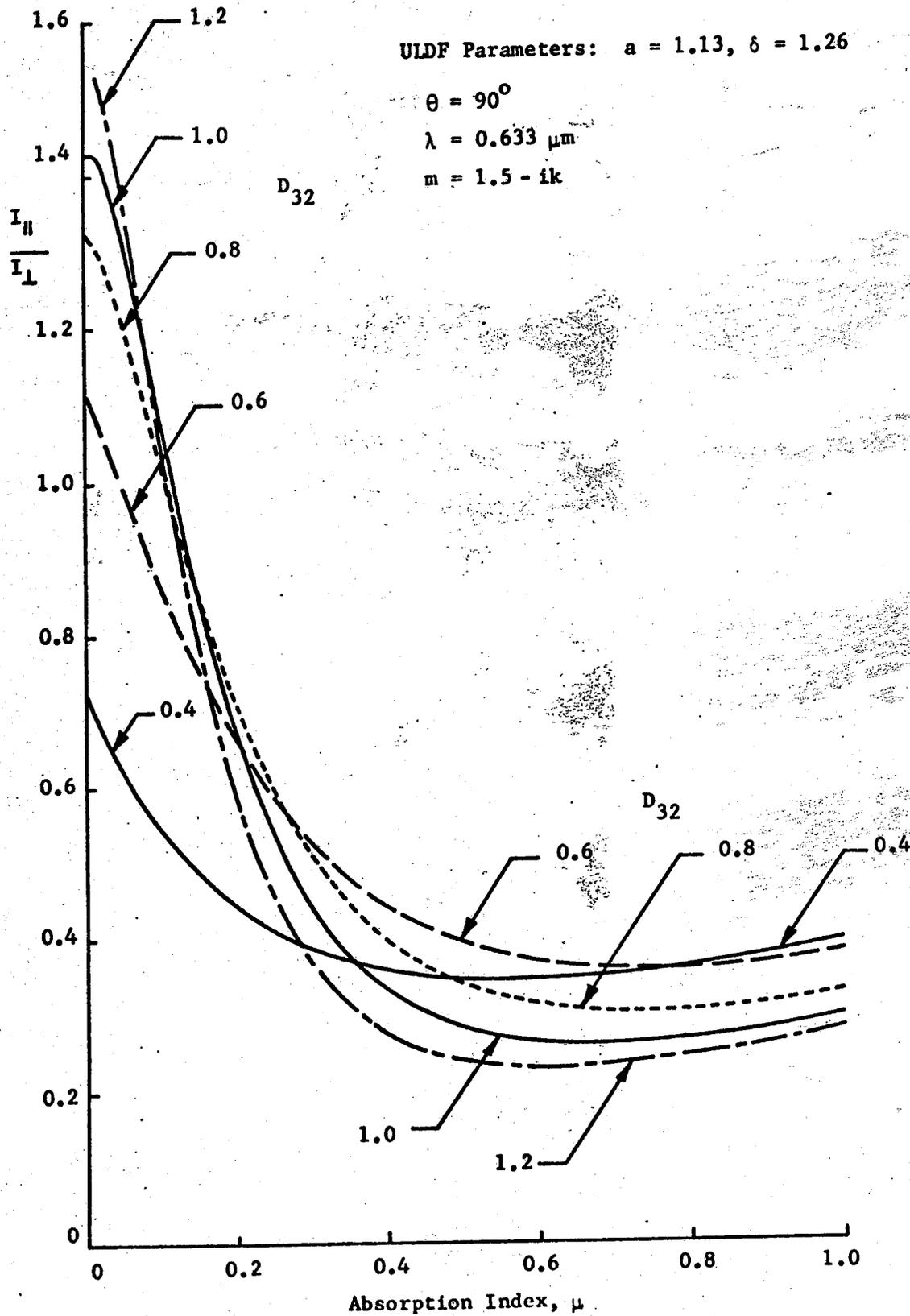


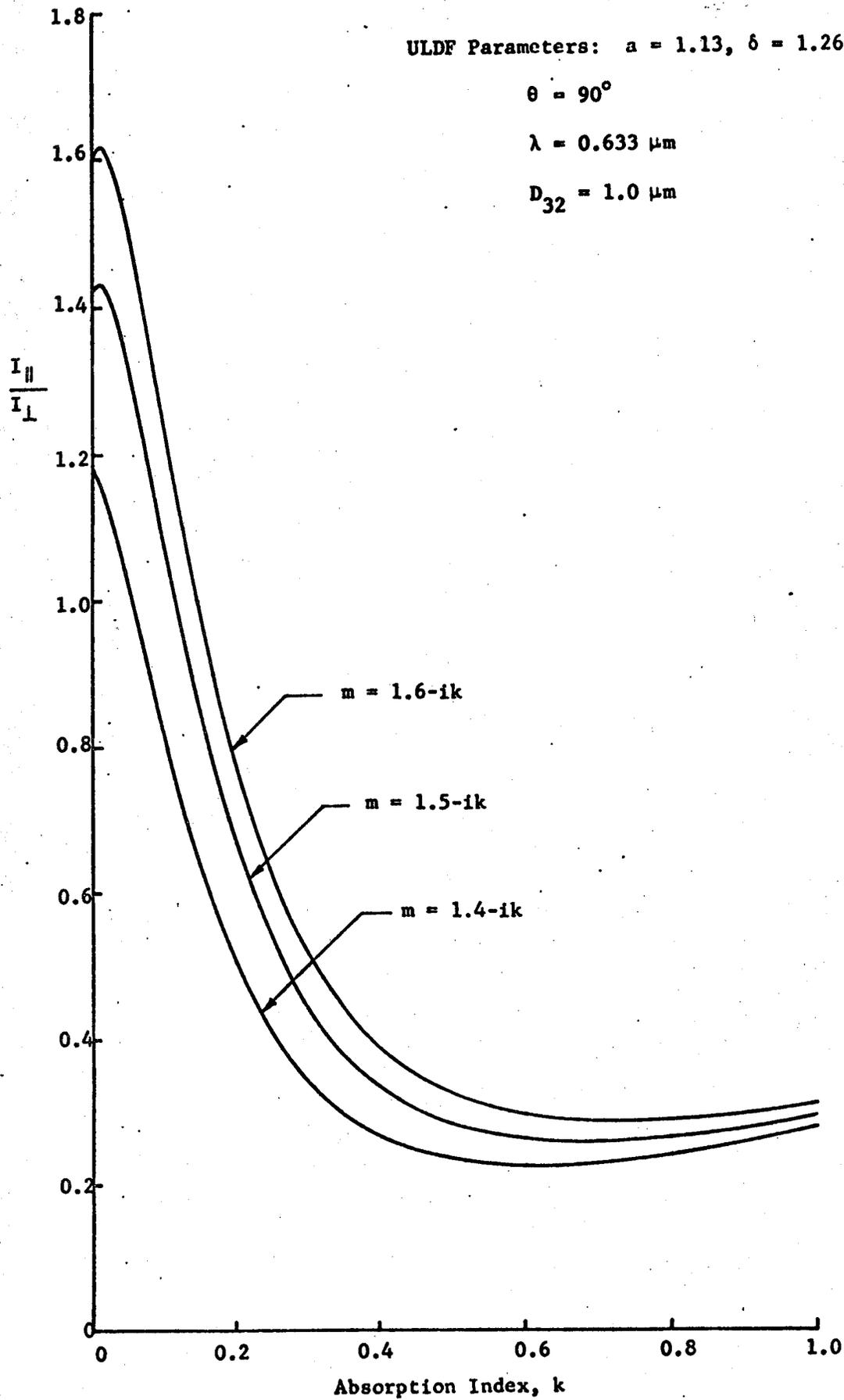
Figure 4. Dependence of I_{\parallel}/I_{\perp} Upon Absorption Index.

ULDF Parameters: $a = 1.13$, $\delta = 1.26$

$$\theta = 90^\circ$$

$$\lambda = 0.633 \mu\text{m}$$

$$D_{32} = 1.0 \mu\text{m}$$

Figure 5: Effect of Refractive Index Upon $I_{\parallel} / I_{\perp}$.

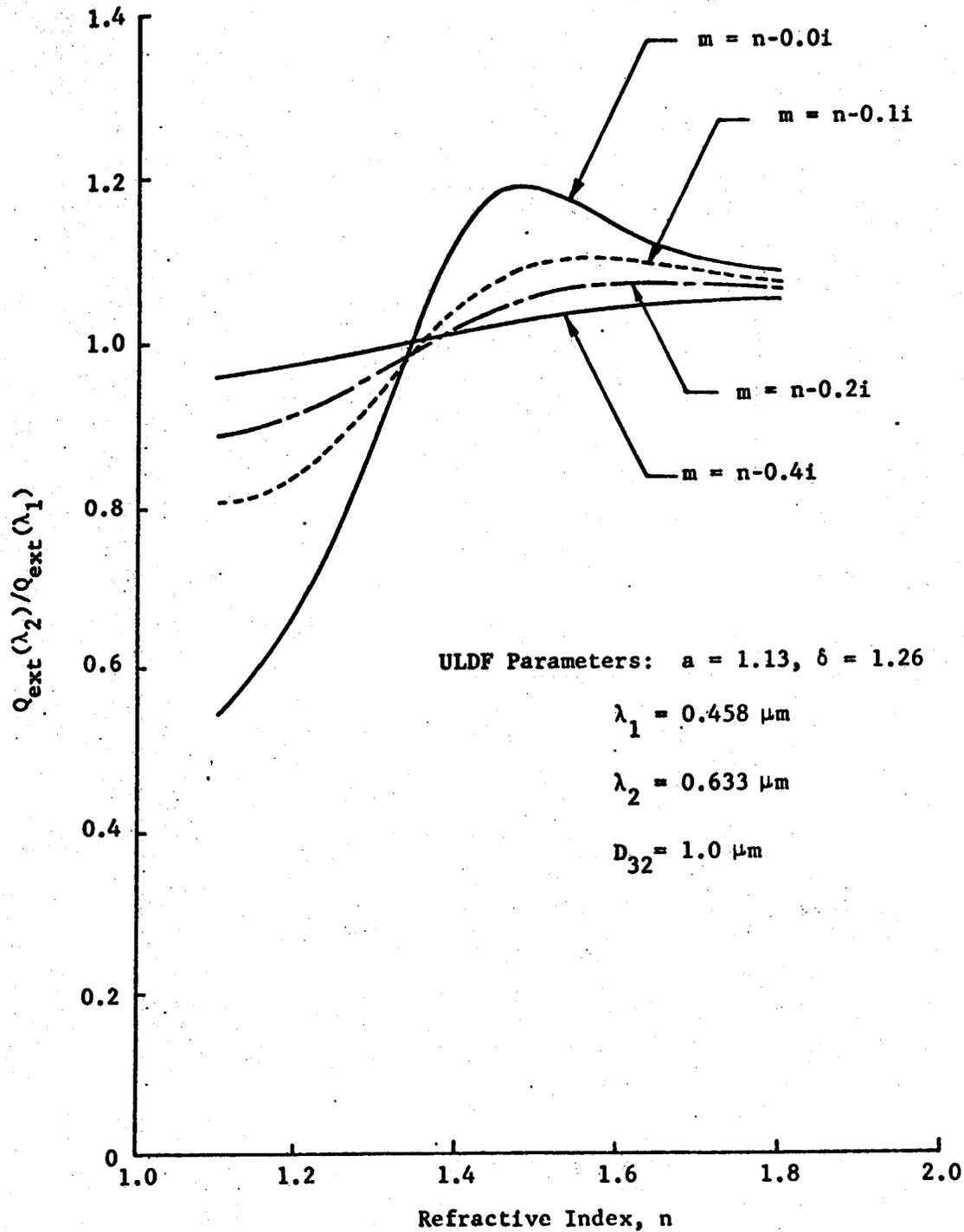


Figure 6. Effect of Absorption Index Upon Ratio of Extinction Efficiencies at Two Wavelengths.

III. TEST PROTOCOL

A. Sample Compositions

Tests have been conducted to determine the physical properties of the smoke produced during the burning of polyvinylchloride (PVC) and polypropylene samples specifically prepared for testing in this program. The chemical compositions of the PVC and polypropylene samples are listed in Tables I and II respectively. Testing with samples of known compositions provides the possibility of relating the measured physical and chemical characteristics of the smoke particulates to the presence of a particular additive in the test sample.

B. Test Conditions and Physical Properties Measured

Each of the PVC and polypropylene formulations listed in Tables I and II was tested under nonflaming conditions at a radiant heating rate of $5W/cm^2$. All samples were mounted horizontally and the CPTC ventilation gas was composed of room temperature air flowing at 425 liters per minute in all tests. In addition, the polypropylene samples (Table II) were tested in a ventilation gas at $100^{\circ}C$; all other CPTC conditions remaining the same. Finally, the sample dimensions are 75 mm x 75 mm (exposed surface) x 3.2 mm thick; corresponding to sample weights of approximately 25-30 grams for the PVC samples and 15-20 grams for the polypropylene samples.

For the test conditions characterized by room temperature ($25^{\circ}C$) ventilation gases, data are available for the following measured quantities: (1) particle size distribution; (2) particulate mass generated; (3) the evolution of the mean particle diameter with time; (4) the variation of the smoke optical density (at 458 nm) with time, and (5) the sample mass loss as a function of time. Where test conditions are characterized by high temperature ventilation gases, only in situ optical system data (items 3 and 4 above) are available,

Table I. Composition of PVC Samples

| Sample | PVC Resin | Lead Stabilizer | Plasticizer | | CaCO ₃ | Al ₂ O ₃ · 3H ₂ O | MoO ₃ | Sb ₂ O ₃ | Lubricants |
|--------|-----------|-----------------|----------------|-----------------------|-------------------|--|------------------|--------------------------------|------------|
| | | | 6-10 Phthalate | DI-Isodecyl Phthalate | | | | | |
| 1 | 100 | 5 | - | - | - | - | - | - | - |
| 2 | 100 | 5 | 45 | - | - | - | - | - | 1.5 |
| 3 | 100 | 5 | 45 | - | 50 | - | - | - | 1.5 |
| 4 | 100 | 5 | 45 | - | - | 50 | 5 | - | 0.5 |
| 5 | 100 | 5 | 45 | - | 50 | - | 5 | - | 1.5 |
| 6 | 100 | 5 | 45 | - | - | 50 | - | 5 | 0.5 |
| 7 | 100 | 5 | 45 | - | 50 | - | - | 5 | 1.5 |
| 8 | 100 | 7.4 | - | 30 | - | - | - | - | 0.4 |
| 9 | 100 | 7.4 | - | 30 | - | - | - | 2 | 0.4 |
| 10 | 100 | 5 | 45 | - | - | - | - | 5 | 1.5 |
| 11 | 100 | 5 | 45 | - | - | 50 | - | - | 1.5 |

TABLE II

POLYPROPYLENE SAMPLES

| <u>COMPONENT</u> | <u>Sample Number</u> | | | | | | |
|------------------|----------------------|----------|----------|----------|----------|----------|----------|
| | <u>1</u> | <u>2</u> | <u>3</u> | <u>4</u> | <u>5</u> | <u>6</u> | <u>7</u> |
| A | 100 | 67 | 67 | 60 | 66 | | |
| B | | 22 | 22 | | 22 | | |
| C | | 11 | | 13 | 11 | | |
| D | | | | 27 | | | |
| E | | | 11 | | | | |
| F | | | | | 1 | | |
| G | | | | | | 100 | |
| H | | | | | | | 100 |

| <u>Material</u> | <u>Chemical Description</u> | <u>Supplier</u> |
|-------------------------|---|---|
| A - Dypro 8621 PP resin | Medium melt flow, general purpose polypropylene resin | Arco Chemical Company |
| B - Chlorowax 70S | Chlorinated paraffin | Diamond Shamrock |
| C - Thermoguard S 711 | Modified antimony oxide (70% Sb_2O_3) | M & T Chemicals Company |
| D - Dechlorane plus 515 | Chlorinated cycloaliphatic | Hooker Chemical Company |
| E - Antimony oxide (KR) | Pure antimony oxide (Sb_2O_3) | Harshaw Chemical Company |
| F - CPE xo 2243-51 | Chlorinated polyethylene (46% chlorine) | Dow Chemical Company |
| G - Flamolin FR14228 | Not available | USI, Division of National Distillers and Chemical Corporation |
| H - Plaskon FR 1080 | Not available | Allied Chemical Company |

in addition to the sample weight loss measurements. The aerosol sampling system instrumentation cannot be operated at elevated temperatures.

IV. RESULTS OF NONFLAMING TESTS OF PVC SAMPLES WITH DIFFERENT ADDITIVES -

PHYSICAL PROPERTIES DATA

A. Low Temperature Tests at $5W/cm^2$

Tests of the eleven PVC samples (Table I) under nonflaming conditions in a room temperature ($25^{\circ}C$) ventilation gas (air) have been completed. Measurements have been obtained of the characteristics of the smoke produced under nonflaming conditions at $5W/cm^2$ radiant flux. The results of these tests are presented in Figures 7 through 15. Sample numbers indicated in these figures correspond to the compositions listed in Table I.

Figures 7 and 8 show the weight loss of seven PVC samples. In general, the samples which contained the lowest percentage of PVC resin and highest percentage of fillers produced the lowest weight loss rate during the test and left the greatest percentage of the original weight as a char.

The distributions of particle sizes as measured by the cascade impactor for the different PVC samples are shown in Figures 9 and 10. These plots also give an indication of the quantitative differences in the total particulate weight produced by the samples. All samples produced particles in sizes up to about 5 microns with a maximum in the distribution occurring between 0.9 and 2.0 microns. However, the samples which contained large amounts of $CaCO_3$ and $Al_2O_3 \cdot 3H_2O$ produced considerably lower quantities of particulates than the other PVC samples. This trend agrees with the results of Breden and Meisters⁴ who observed a noticeable reduction in specific optical density when $CaCO_3$ and $Al_2O_3 \cdot 3H_2O$ were added to polyester systems. Furthermore, the present data show that the addition of MoO_3 to the PVC's with fillers resulted in the lowest production of particulates. The addition of Sb_2O_3 to the plasticized PVC (Samples 6,7,9 and 10) did not produce a significant change in the quantity

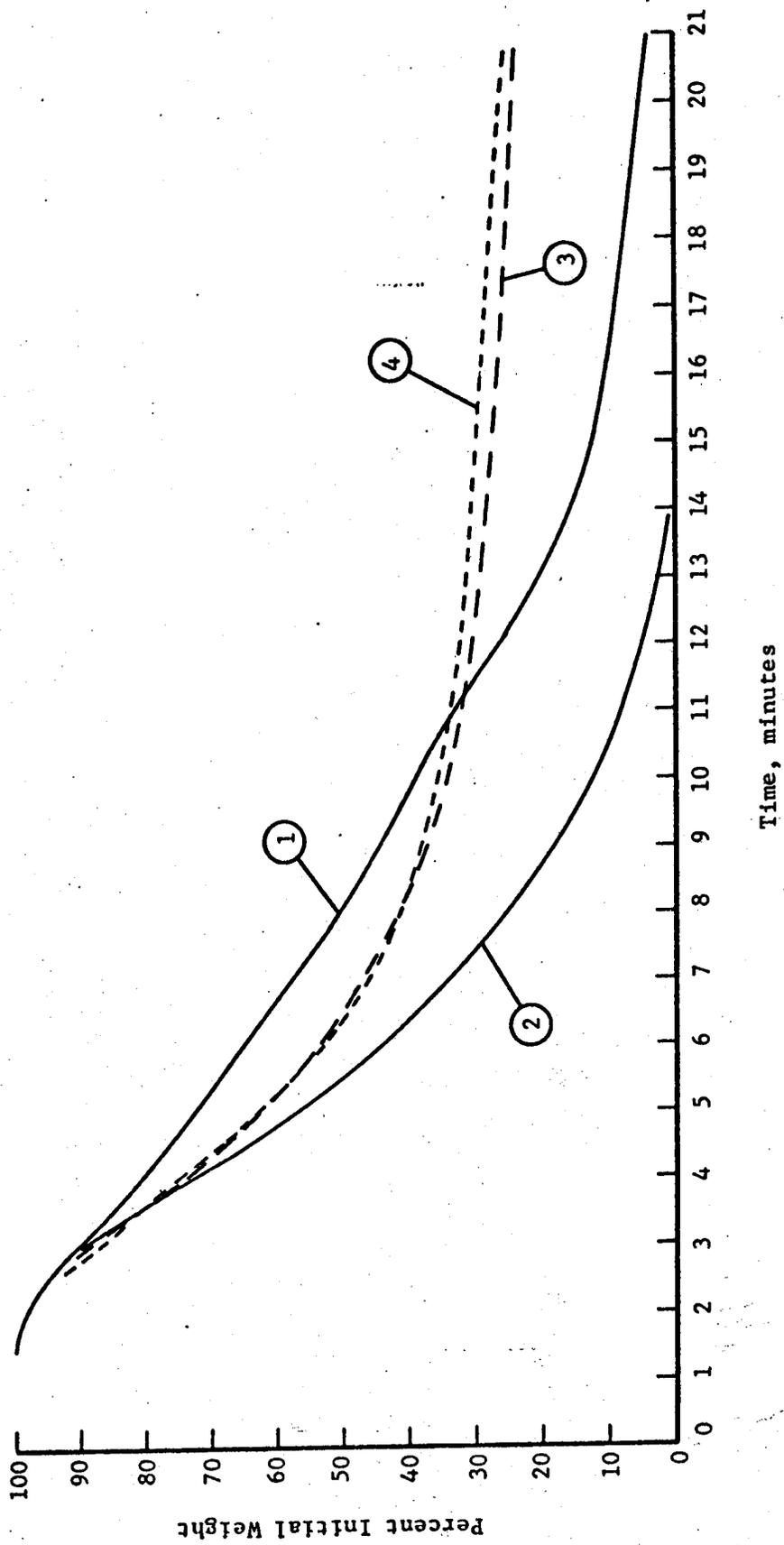


Figure 7. Effect of PVC Additives on Sample Weight Loss in Nonflaming Combustion at 5 Watts/cm².

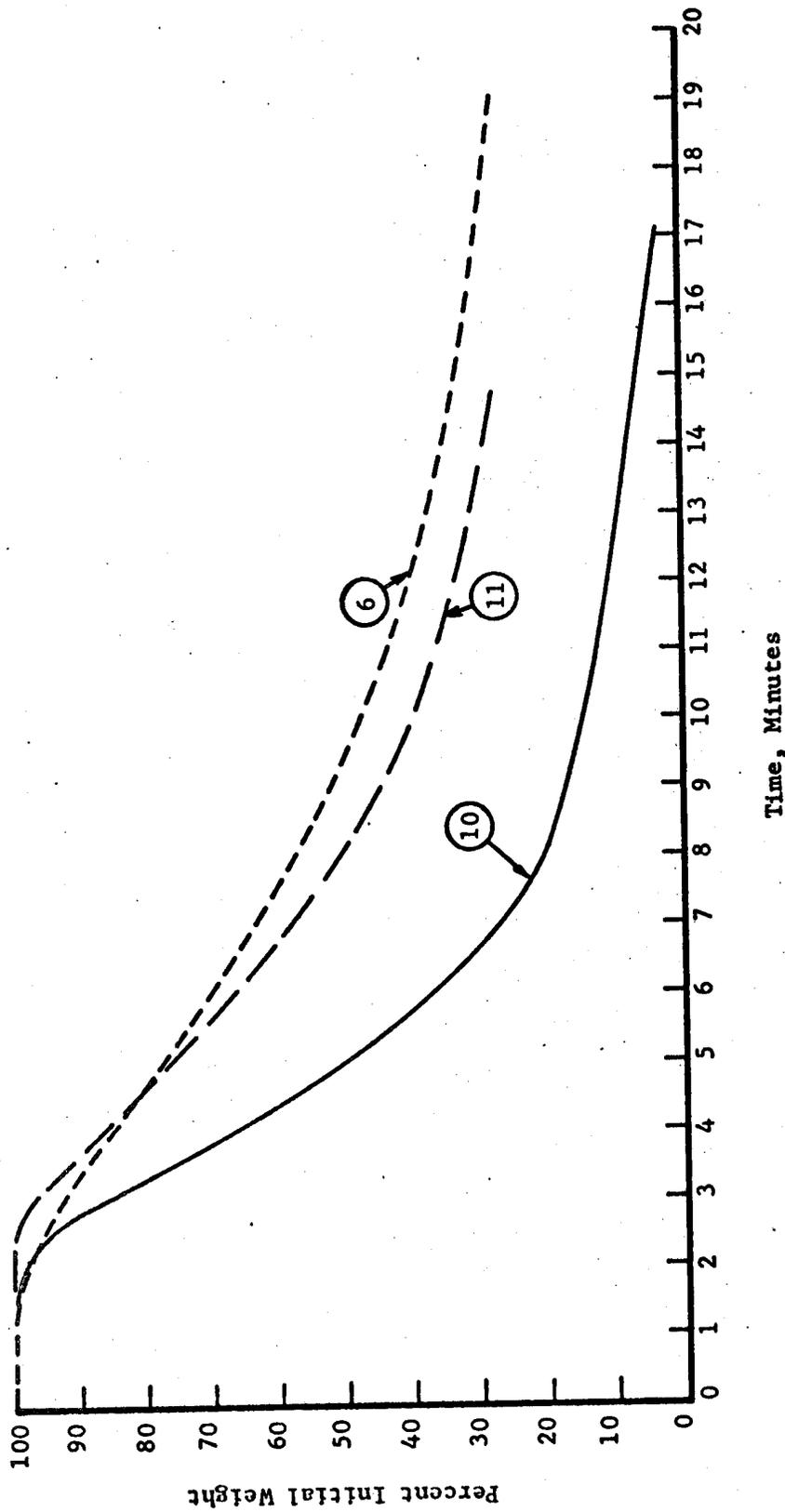


Figure 8. Effect of PVC Additives on Sample Weight Loss in Nonflaming Combustion at 5 W/cm^2 .

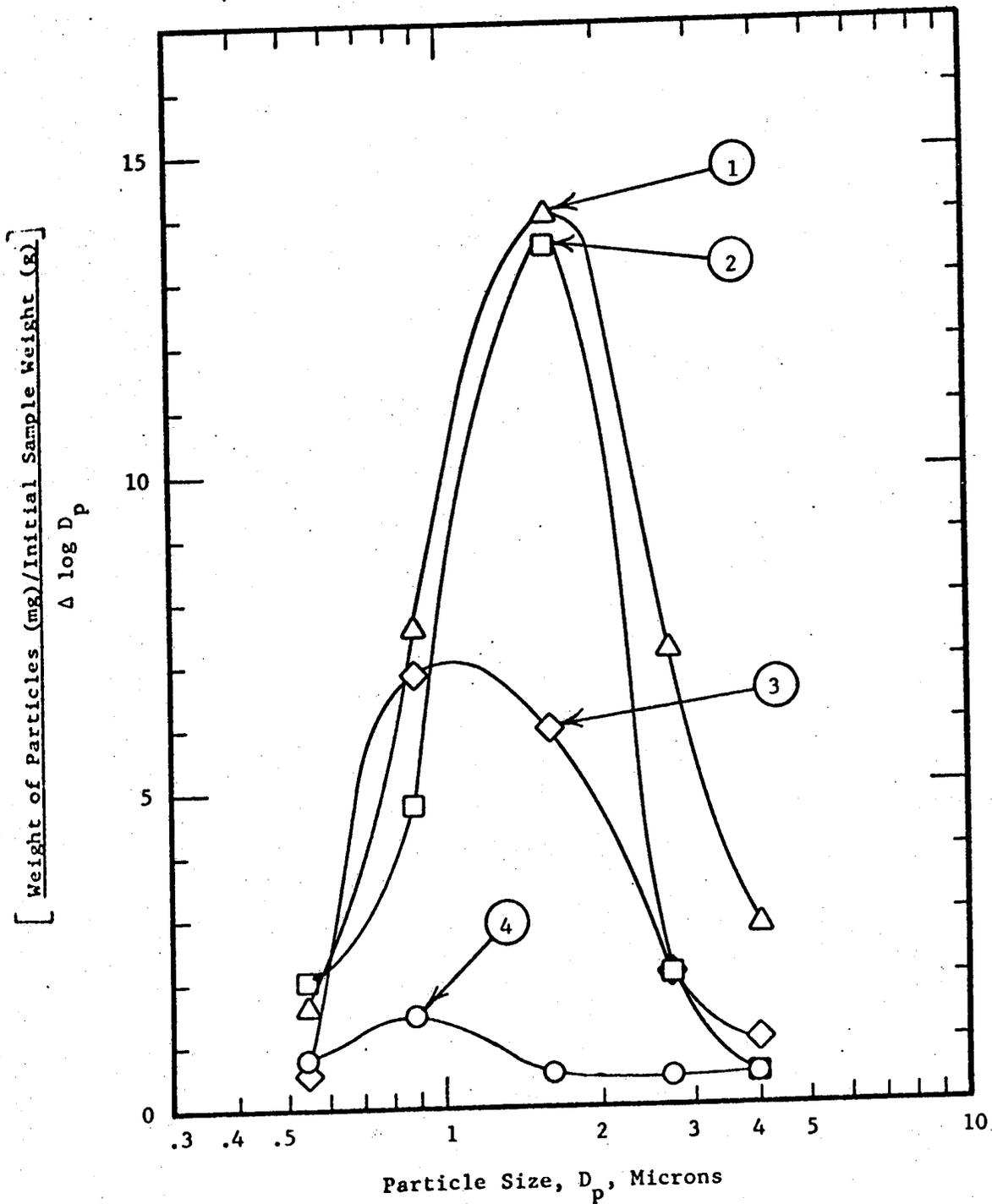


Figure 9. Effect of PVC Additives on Smoke Particle Characteristics in Nonflaming Combustion at 5 W/cm^2 .

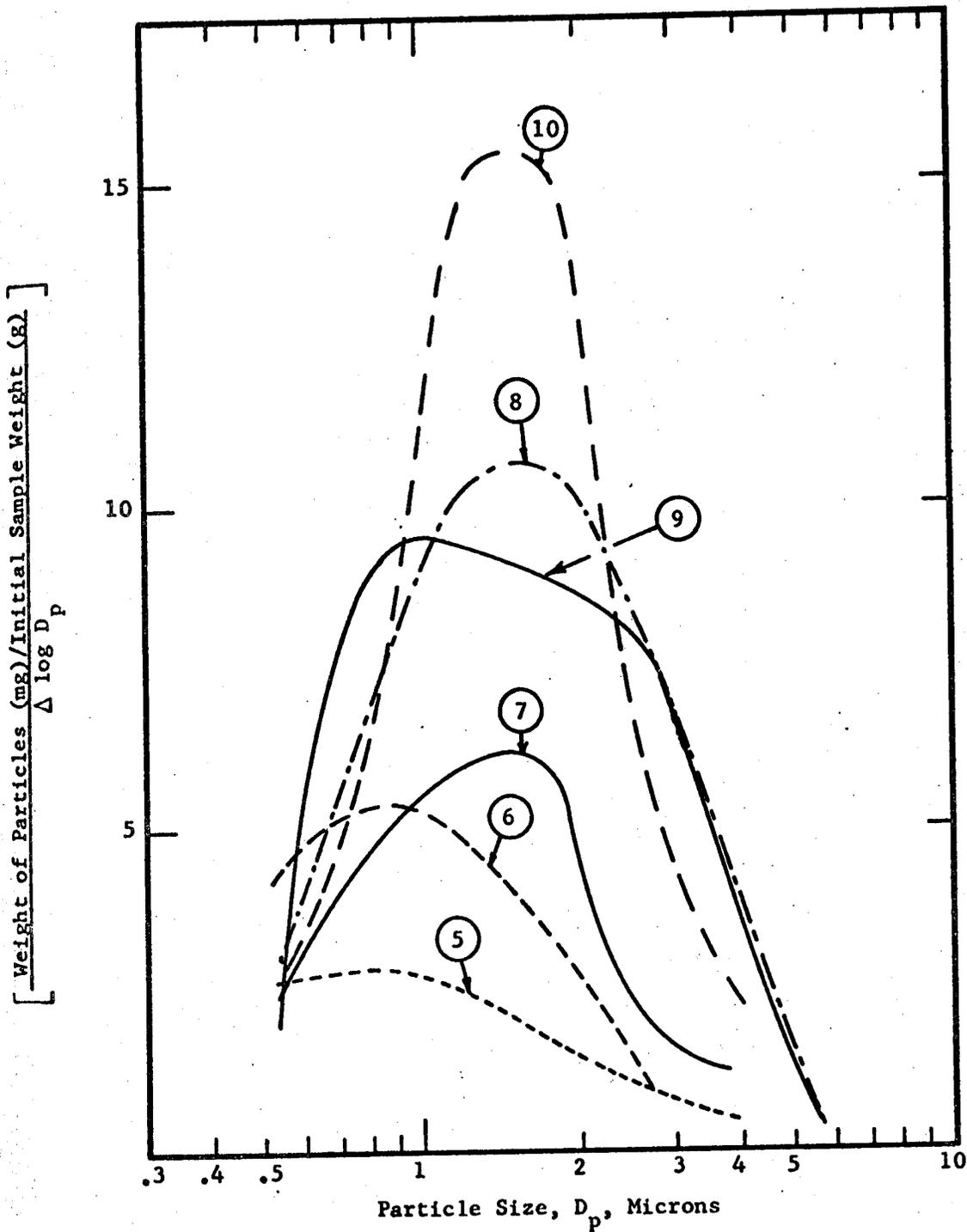


Figure 10. Effect of PVC Additives on Smoke Particle Characteristics in Nonflaming Combustion at 5 W/cm^2 .

or the size distribution of the particulates, when compared to the equivalent samples which do not contain Sb_2O_3 .

The time variations of the average smoke particle size during tests of six of the PVC samples are shown in Figures 11, 12 and 13. These data show that the compositions which have a sizable fraction of additives (2,5,6,8 and 10) tend to produce peak mean particle sizes between 1.4 and 1.6 micrometers earlier in the test ($t=1-4$ minutes), followed by a general decline in mean particle sizes for the remainder of the test. The samples containing the fillers CaCO_3 and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (nos. 5 and 6) show a more steady, rapid drop in particle sizes than samples 2, 8 and 10, which do not contain fillers. The latter compositions (2, 8 and 10) are characterized by a relatively stable period of particle diameters near 1.0 micrometers midway through the test followed by a steady decrease late in the test. In the case of the composition which contains only a stabilizer (No. 1), the particle sizes gradually increase during the first 8 minutes of the test, fluctuate near 1.0 micrometer midway through the test, and then gradually decrease for the remainder of the test.

Figures 14 and 15 provide smoke optical density data for the above-mentioned mix PVC compositions. Samples 2 and 10 produced the highest peak optical density levels; these samples were also characterized by relatively high particulate mass concentrations (Figures 9 and 10). Sample 8, which produced somewhat less total particulate mass than samples 2 and 10, had a lower peak optical density but produced considerable optical densities for a longer time period than most other samples. Finally, the purest PVC sample tested (No. 1) exhibited a different optical density behavior than the other samples, where the peak in optical density for sample 1 occurred relatively late in the test.

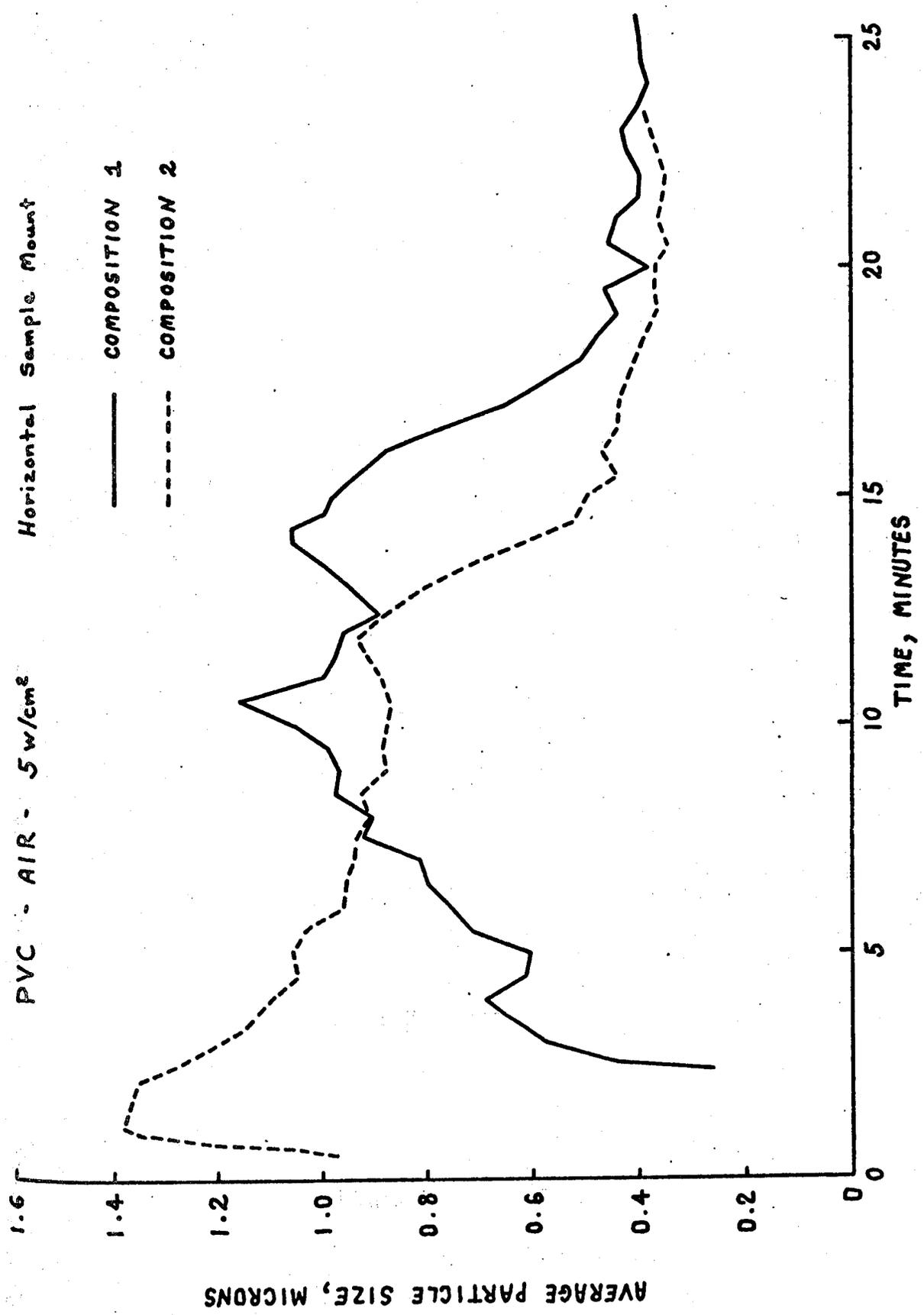


Figure 11. Effect of PVC Additives on Smoke Mean Particle Size in Nonflaming Combustion at 5 W/cm².

PVC - AIR - 5 W/cm²

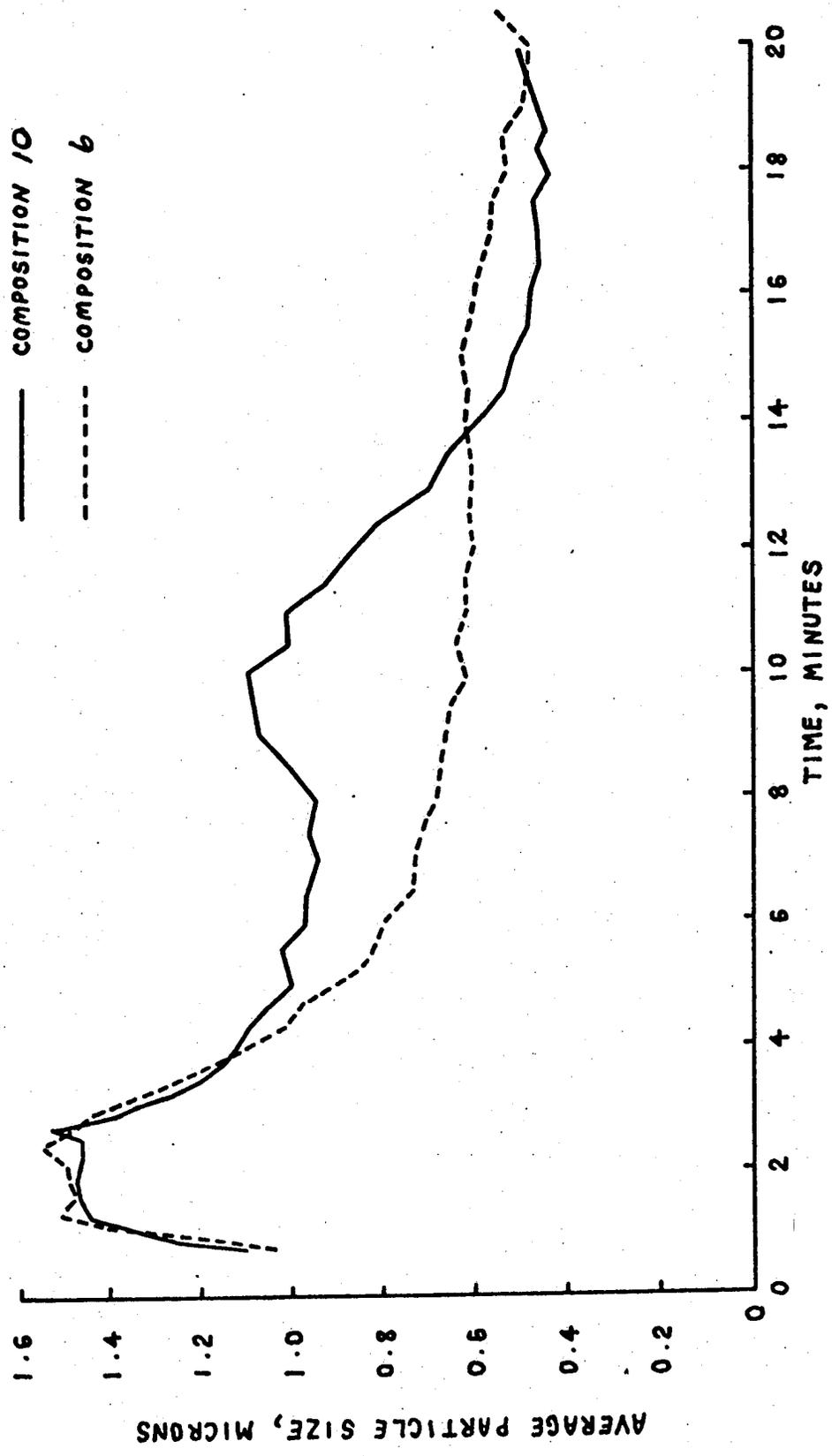


Figure 12. Effect of PVC Additives on Smoke Mean Particle Size in Nonflaming Combustion at 5 W/cm².

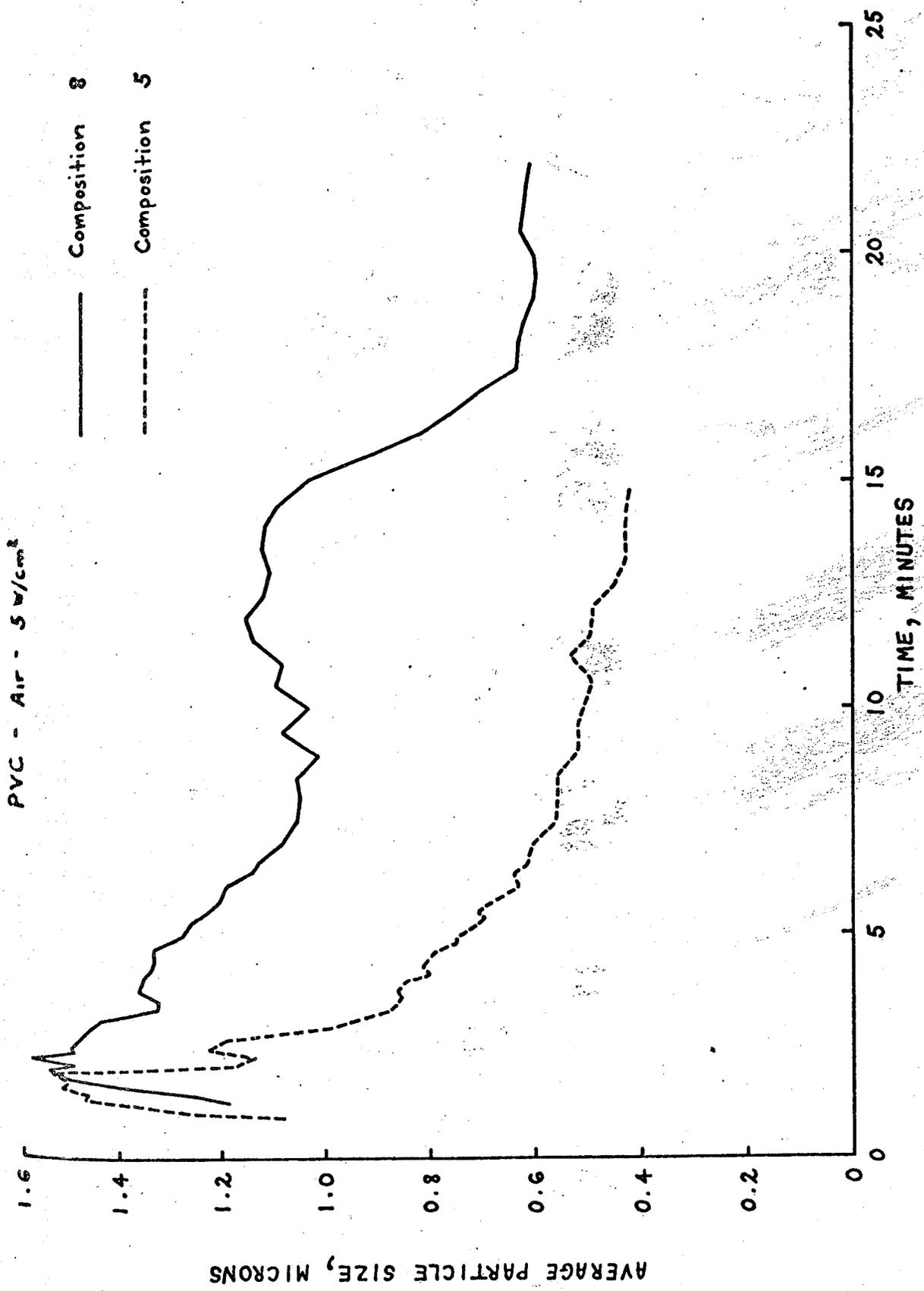


Figure 13. Effect of PVC Additives on Smoke Mean Particle Size in Nonflaming Combustion at 5 W/cm².

PVC - AIR - 5 W/cm²

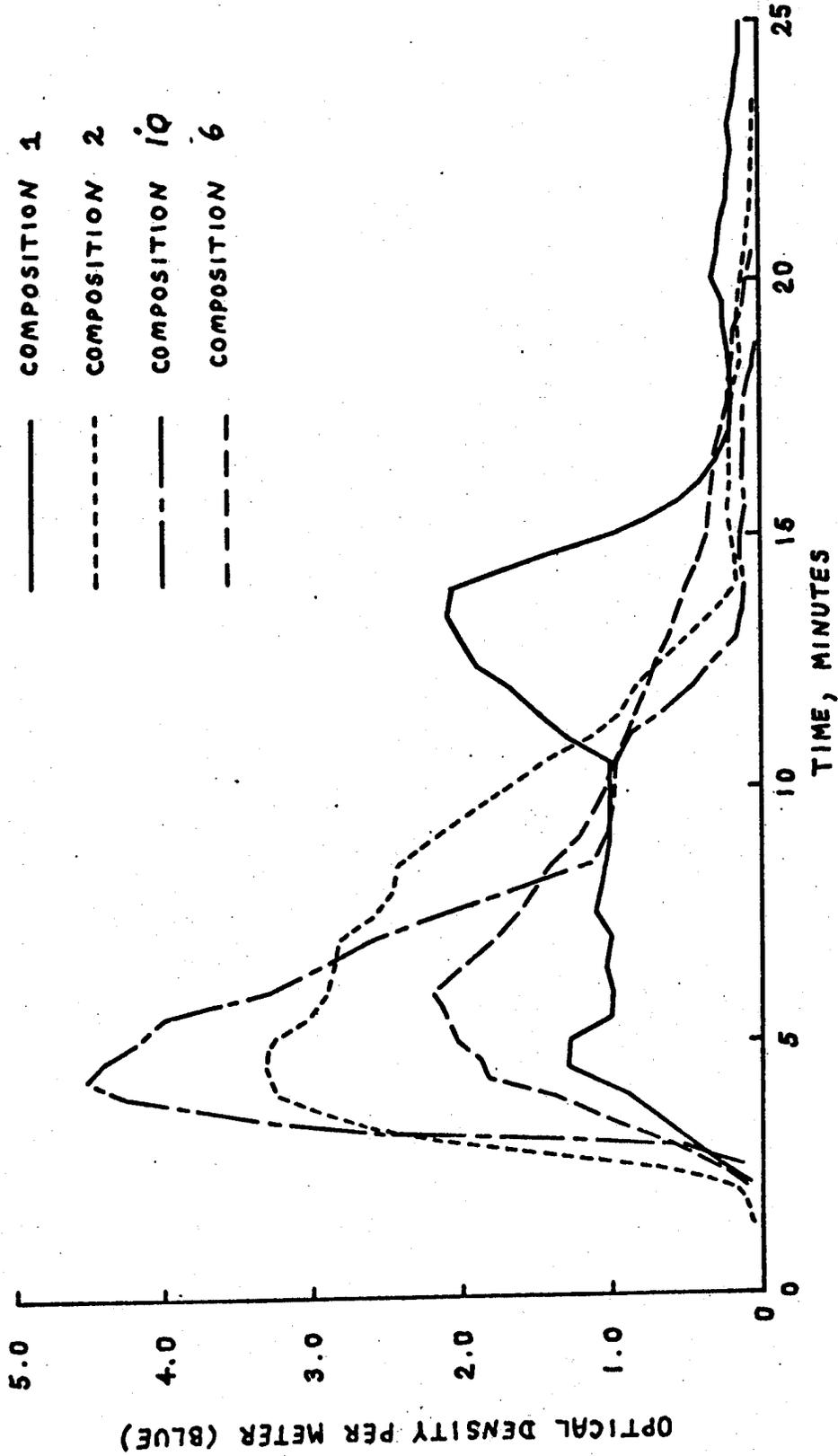


Figure 14. Effect of PVC Additives on Smoke Optical Density in Nonflaming Combustion at 5 W/cm².

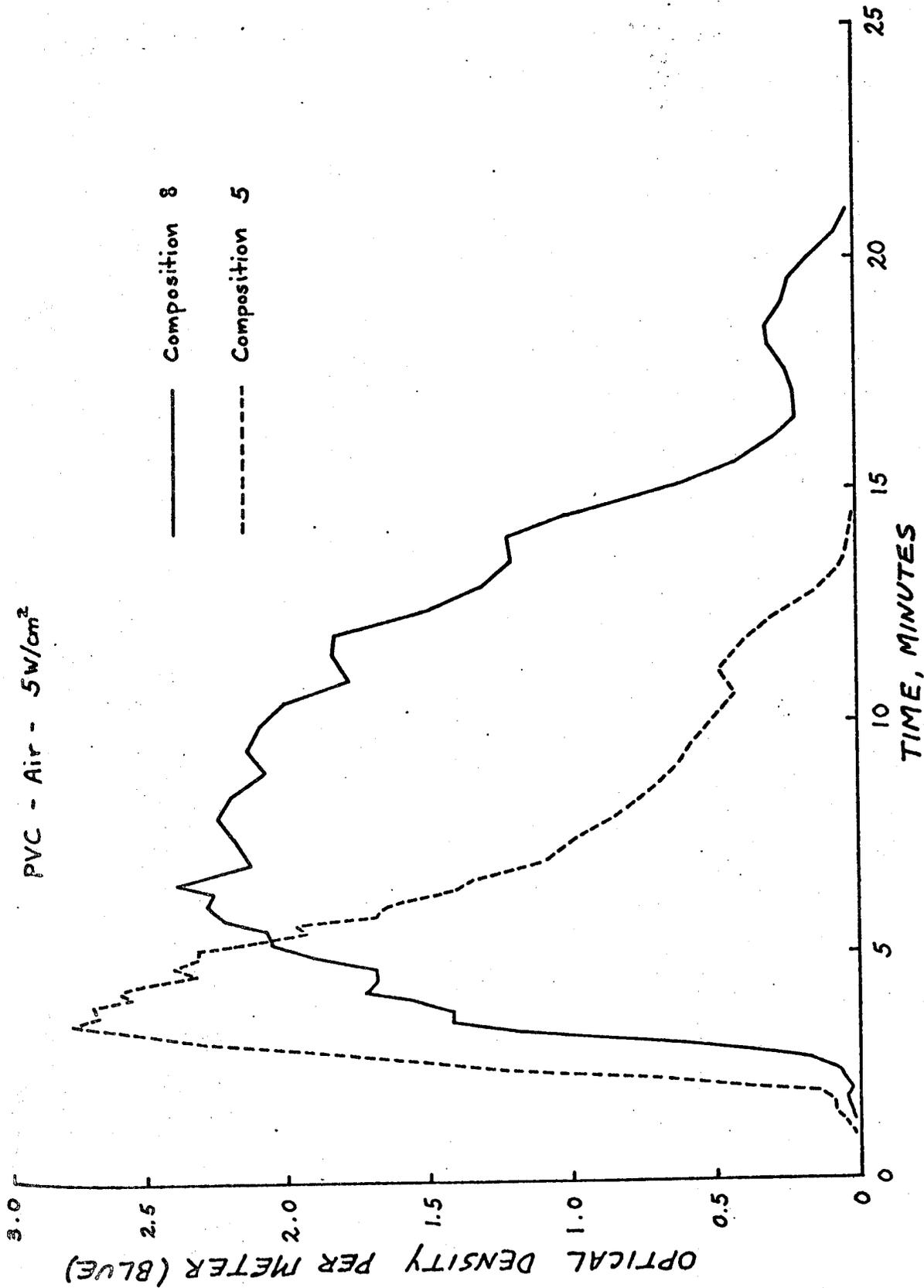


Figure 15. Effect of PVC Additives on Smoke Optical Density in Nonflaming Combustion at 5 W/cm².

8. Summary

In the low temperature nonflaming tests of different PVC compositions at W/cm^2 radiant flux, sample weight loss measurements show that the samples which are characterized by the lowest percentage of PVC resin and the highest percentage of fillers produced the lowest sample weight loss rate during tests and left the greatest percentage of the original sample weight as char. Cascade impactor data show that the samples which contain large amounts of the fillers CaCO_3 and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ produced considerably lower quantities of particulates than the other PVC's and that the addition of MoO_3 to the same samples containing fillers results in the lowest production of particulates. Particle size distribution peaks (also taken from cascade impactor data) for all of the PVC samples tested are near 1.0 micrometer in diameter.

The time resolved mean particle diameter plots show that the particle size trends during a test are influenced by whether or not the sample contains a large quantity of filler. In addition, smoke optical density data show that two samples which generated a relatively high total particulate mass, also produced the highest peak optical densities. In both the mean particle size and the optical density data, the trends observed for the simplest PVC sample (containing only a stabilizer) were different from the trends observed for all other samples.

V. RESULTS OF NONFLAMING TESTS OF POLYPROPYLENE SAMPLES WITH DIFFERENT ADDITIVES - PHYSICAL PROPERTIES DATA

A. Low Temperature Tests at $5W/cm^2$

Tests of the seven polypropylene samples (Table II) under nonflaming conditions in a room temperature ($25^{\circ}C$) ventilation gas (air) have been completed. Measurements have been obtained of the characteristics of the smoke produced under nonflaming conditions at $5W/cm^2$ radiant flux. The results of these tests are presented in Figures 16 through 22. Sample numbers indicated in these figures correspond to the compositions listed in Table II. Note also that samples 6 and 7 are commercially available samples for which the exact compositions are not known.

Figure 16 shows the sample weight loss data for the three polypropylene samples for which accurate force transducer measurements could be obtained. The tendency of polypropylene samples 1, 2, 3 and 4 to rapidly liquefy upon heating presented problems with the horizontal mount as presently designed and data was reduced for only the three samples shown. These measurements show that sample 7 had a lower weight loss rate than samples 5 and 6, where sample 7 was the only polypropylene sample which formed a char. Note also that sample 7 left the greatest fraction of the initial sample weight at the end of the test. Finally, it should be pointed out that in the test plotted for sample 6, flaming ignition was observed approximately $6\frac{1}{2}$ minutes into the test. Sample 4 also ignited once in three tests of that material, however no weight loss data could be obtained in any of the room temperature tests of composition 4. Samples 4 and 6 were the only samples which exhibited self-ignition during these nonflaming tests.

Particle size distribution data for nonflaming polypropylene smoke particulates are presented in Figures 17 and 18. These data show that samples

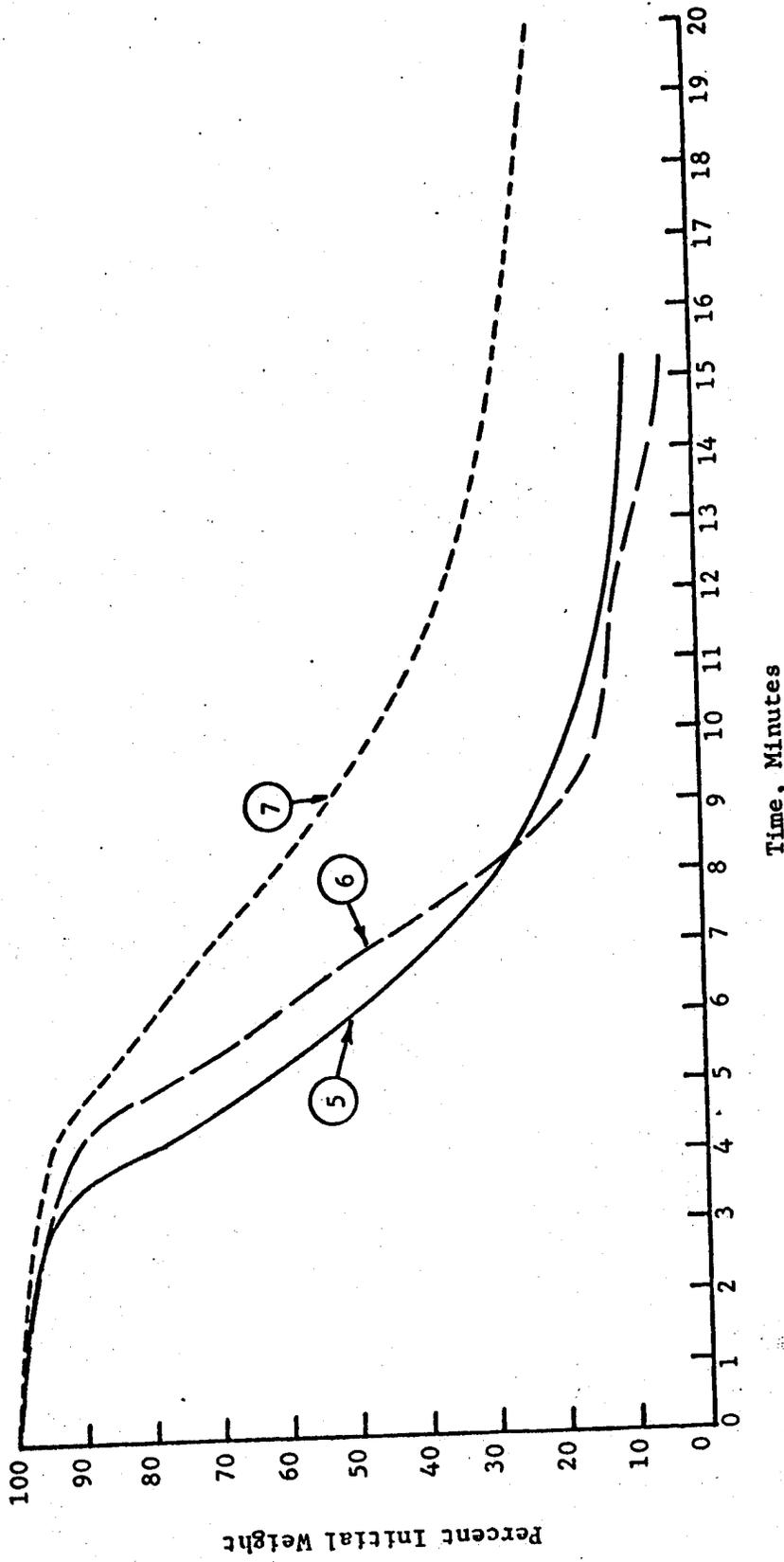


Figure 16. Effect of Polypropylene Fire Retardants on Sample Weight Loss in Nonflaming Combustion at 5 W/cm².

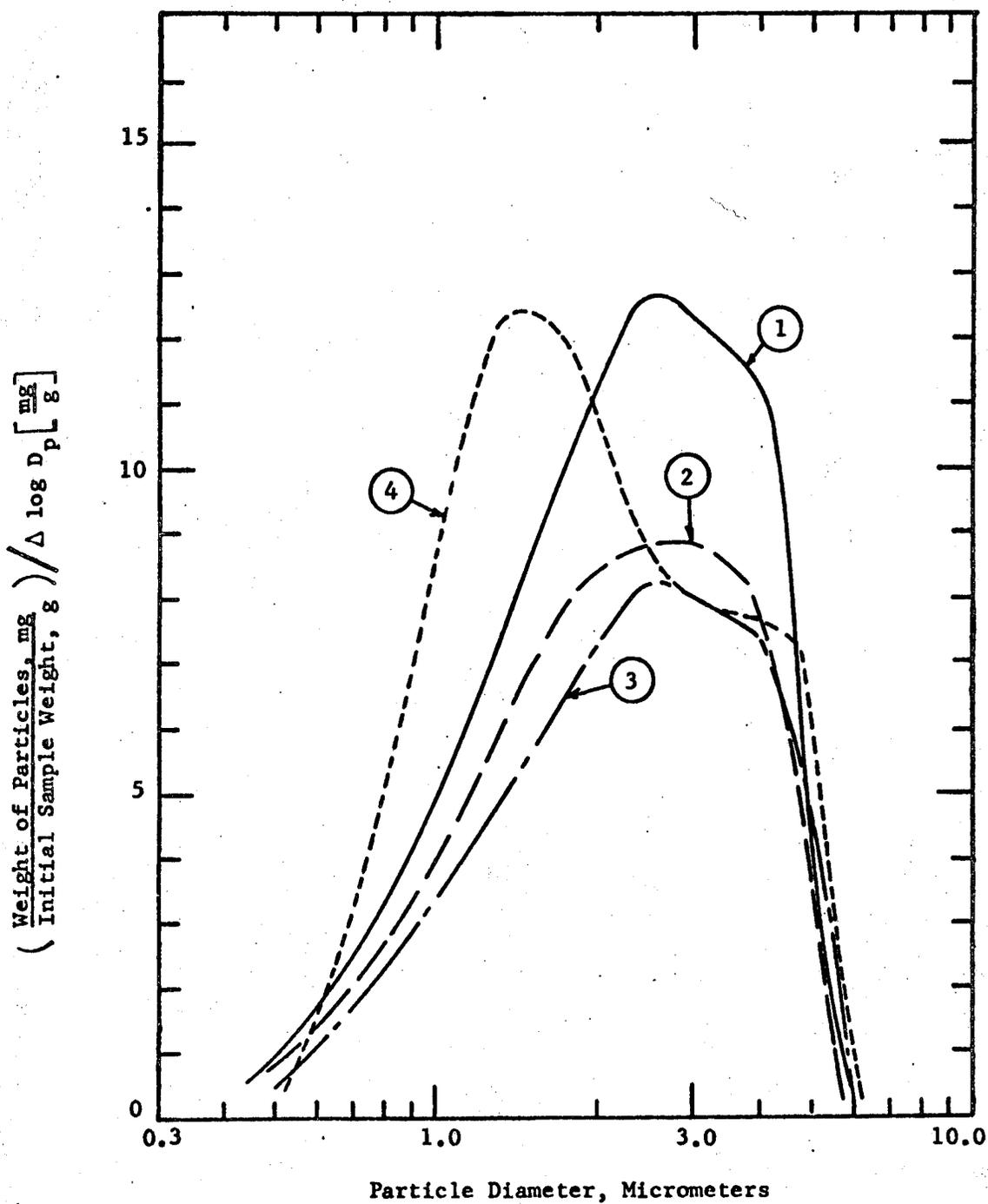


Figure 17. Effect of Polypropylene Fire Retardants on Smoke Particle Size Distribution in Nonflaming Combustion at 5 W/cm^2 .

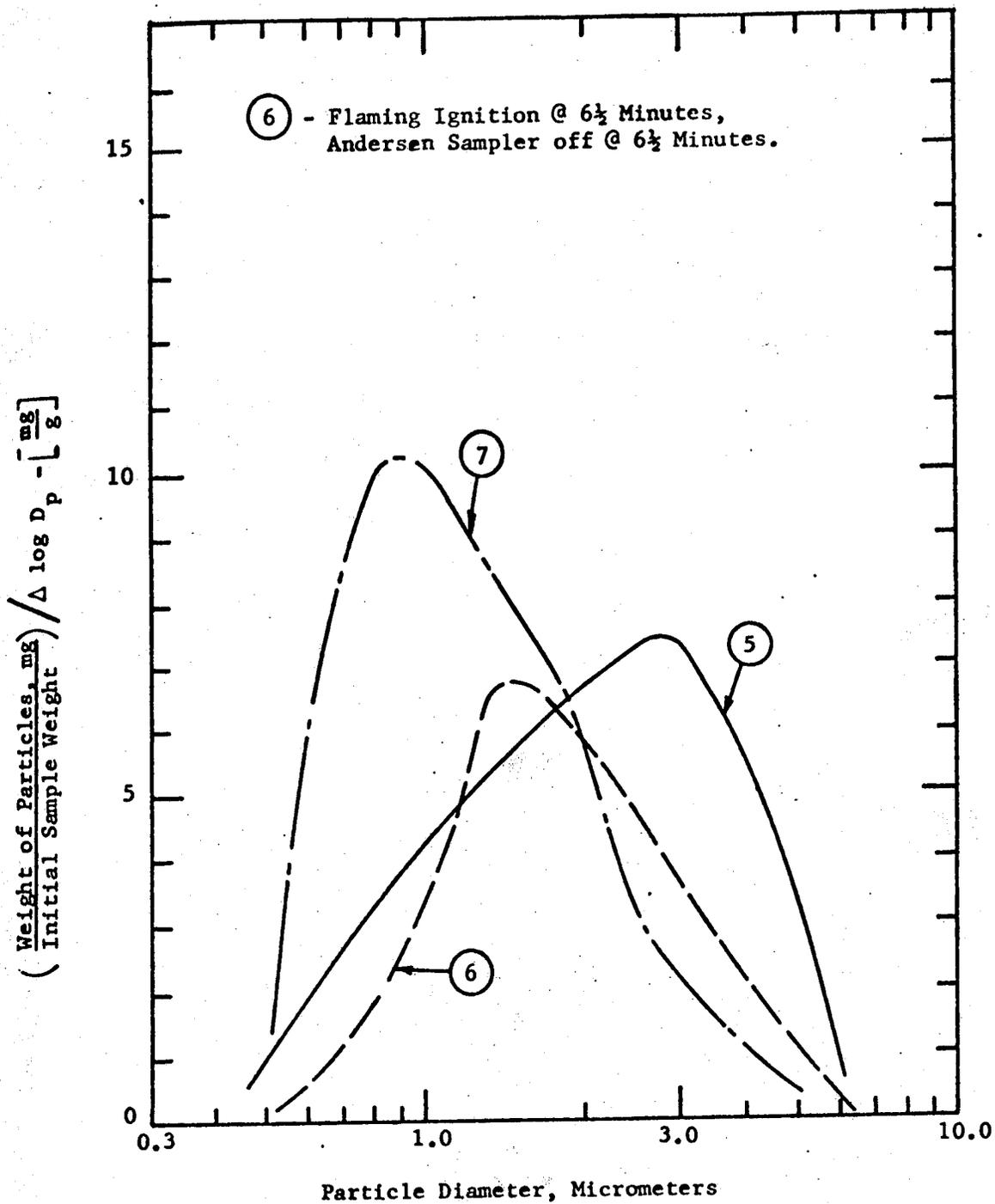


Figure 18. Effect of Polypropylene Fire Retardants on Smoke Particle Size Distribution in Nonflaming Combustion at 5 W/cm².

1, 2, 3 and 5 produced larger particles than the remaining samples, where particle size distribution peaks for those four samples fall between 2 and 4 micrometers in diameter. Those samples which produced the largest particles include the pure resin (No. 1) and the three compositions (2, 3 and 5) which contain the chlorinated paraffin fire retardant. The only sample which tends to form a char (No. 7), generated the greatest fraction of small particles that are below 1 micrometer in diameter. The peaks of the particle size distributions for the remaining samples 4 and 6 fall between the peaks of the distributions for samples 1, 2, 3 and 5, and sample 7. Note that the data plotted for sample 4 was taken from a test where no ignition was observed and the data for sample 6 taken during the period in that test prior to flaming ignition.

In terms of the total particulate mass generated, the lowest particulate masses per gram of initial sample weight were produced by the samples containing the chlorinated paraffin and by the char forming sample 7. Samples 3 and 5 generated the lowest particulate masses measured for the tests, with samples 2 and 7 producing somewhat greater amounts. The greatest total particulate masses generated were those measured for samples 1 and 4. Sample 6 cannot be compared on an equal basis since nonflaming conditions were not maintained during the entire period of the test of that composition.

An indication of the time variation of the average smoke particle sizes during nonflaming tests of the polypropylene is given in Figures 19 and 20. Note that the examples shown for samples 4 and 6 are cases where flaming ignition was observed during these tests. The data show that peak particle sizes of 1.5 - 1.6 micrometers in the nonflaming mode were reached by samples 1, 2, 3, 4 and 5. In addition, sample 7 shows the smallest overall mean particle sizes when compared to all other polypropylene samples. Moreover, these results

Polypropylenes - Air (25°C)
 Non-Flaming 5 W/cm²

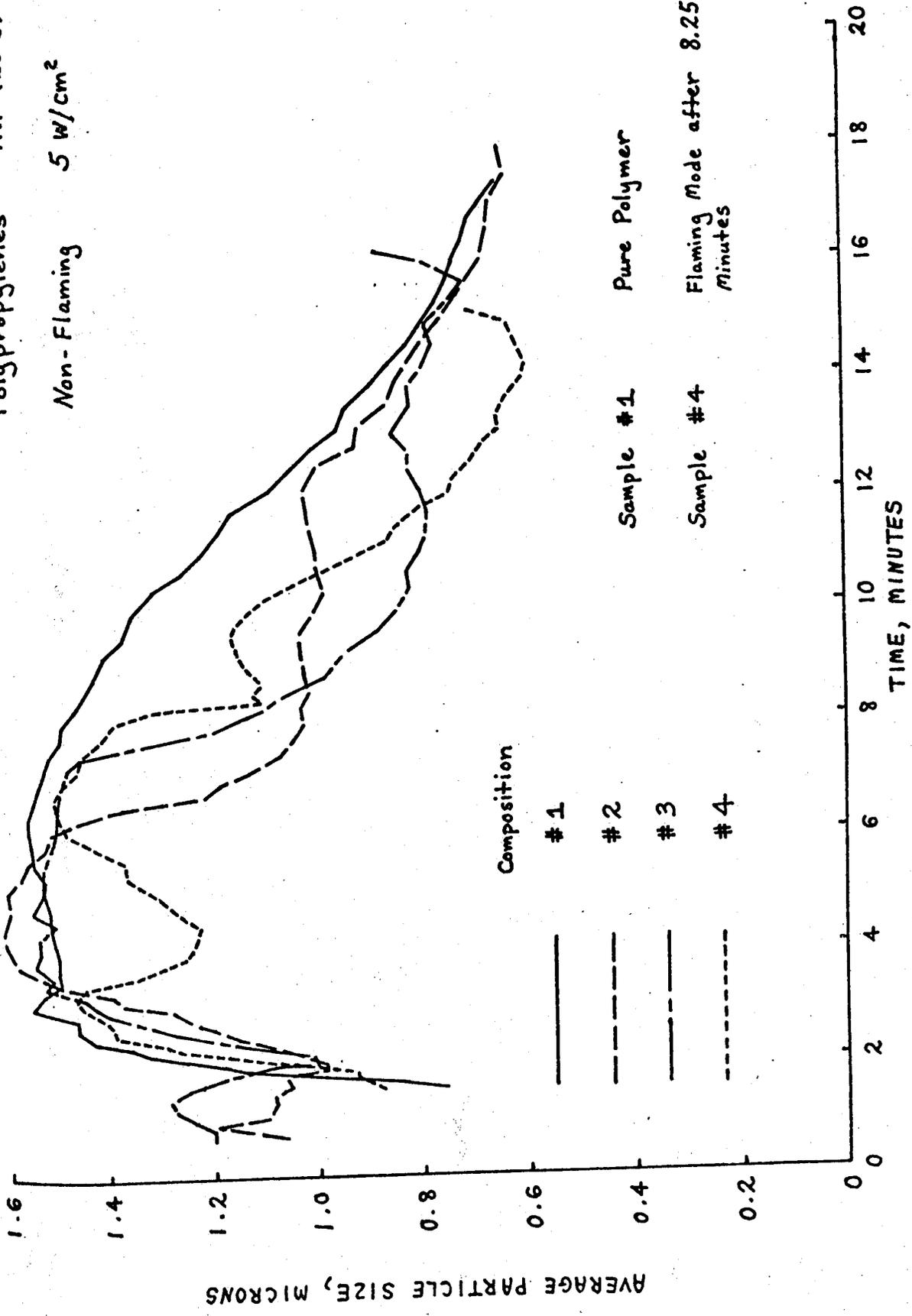


Figure 19. Effect of Polypropylene Fire Retardants on Smoke Mean Particle Size in Nonflaming Combustion at 5 W/cm².

Polypropylenes - Air (25°C)
Non-Flaming 5 W/cm²

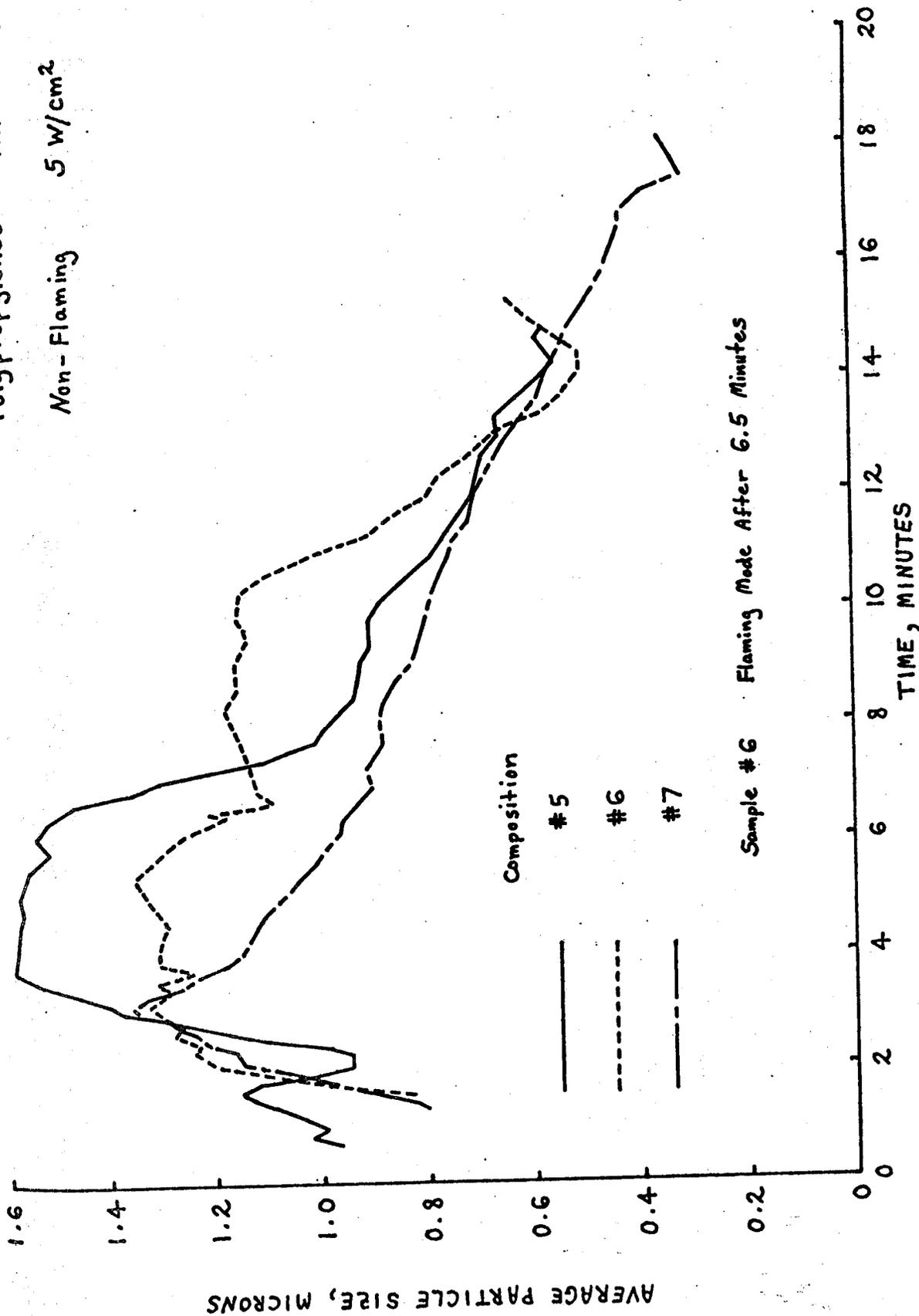


Figure 20. Effect of Polypropylene Fire Retardants on Smoke Mean Particle Size in Nonflaming Combustion at 5 W/cm².

are seen to be consistent with the cascade impactor data of Figures 17 and 18.

Any variation in the particle concentration and size distribution will also cause noticeable changes in the smoke optical density. Comparisons of such data for polypropylenes are presented in Figures 21 and 22. Peak optical densities are generally observed to be between 2/m. and 3/m. in the nonflaming mode, with the notable exception of sample 7. The highest optical density peaks were recorded for samples 4 and 6 after flaming ignition was observed in those tests. The fact that sample 7 produced the greatest overall optical density levels for nonflaming conditions may be due to the smaller particle sizes measured for that composition; where the optical density is roughly inversely proportional to the particle diameter for the range of particle sizes observed in these tests.

B. High Temperature Tests at $5W/cm^2$

Tests of the seven polypropylene samples (Table II) in a heated ($100^{\circ}C$) ventilation gas (air) have been completed. Measurements have been obtained of the characteristics of the smoke produced under initially nonflaming conditions at $5W/cm^2$ radiant flux. The results of these tests are presented in Figures 23 through 37. However, an important consequence of the high temperature test conditions just described is the fact that flaming ignition was observed during tests of all sample compositions. Thus, the test data presented in this section are characterized by a nonflaming-to-flaming transition in all plots. As mentioned previously, this series of tests has been limited to in situ optical system and force transducer measurements, since the aerosol sampling system instrumentation cannot be operated at elevated temperatures.

Figure 23 summarizes the weight loss data obtained for four polypropylene samples burned in the $100^{\circ}C$ ventilation gas. These curves show a rapid fall-off in sample weight beginning from three to five minutes into the test with a

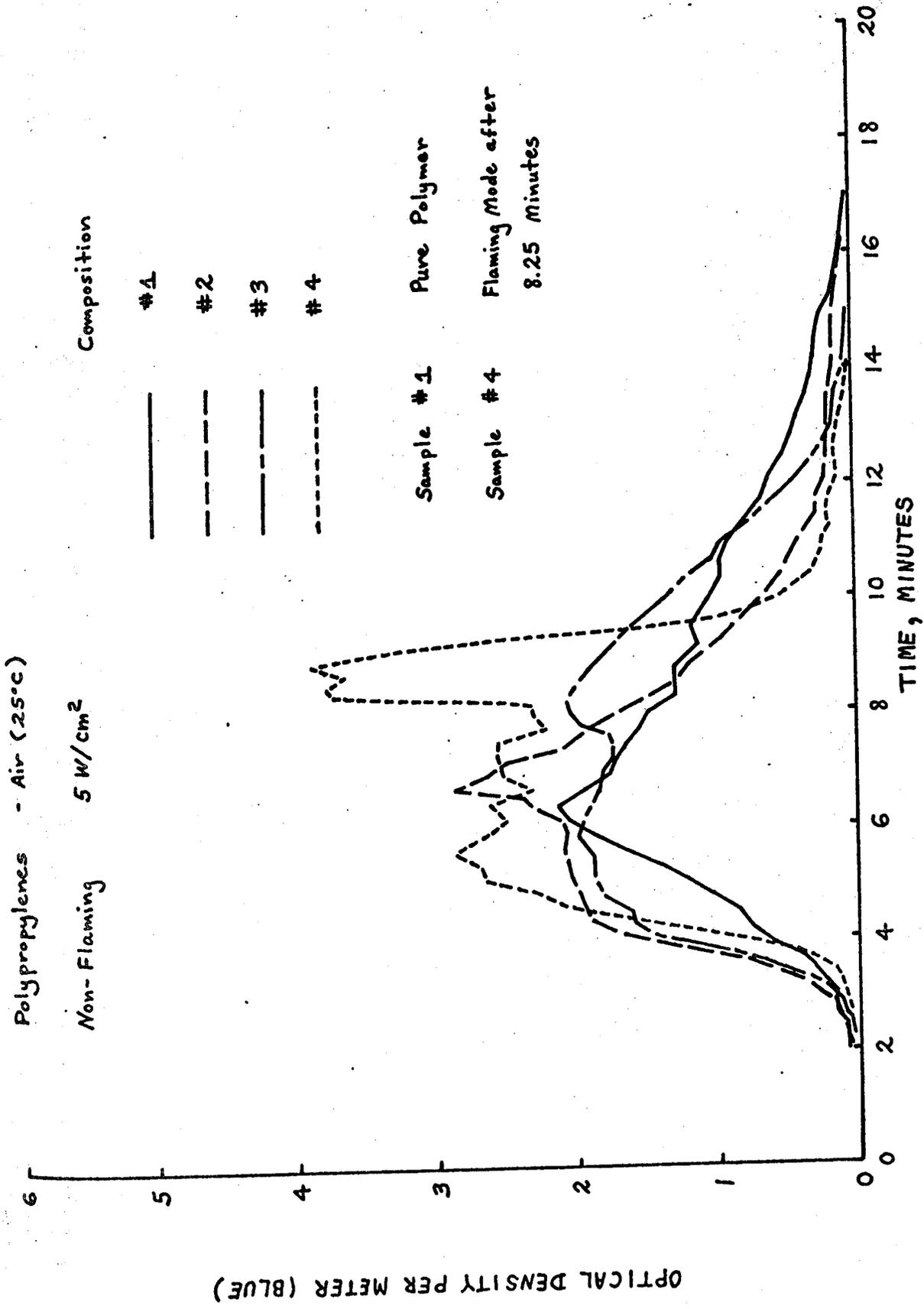


Figure 21. Effect of Polypropylene Fire Retardants on Smoke Optical Density in Nonflaming Combustion at 5 W/cm².

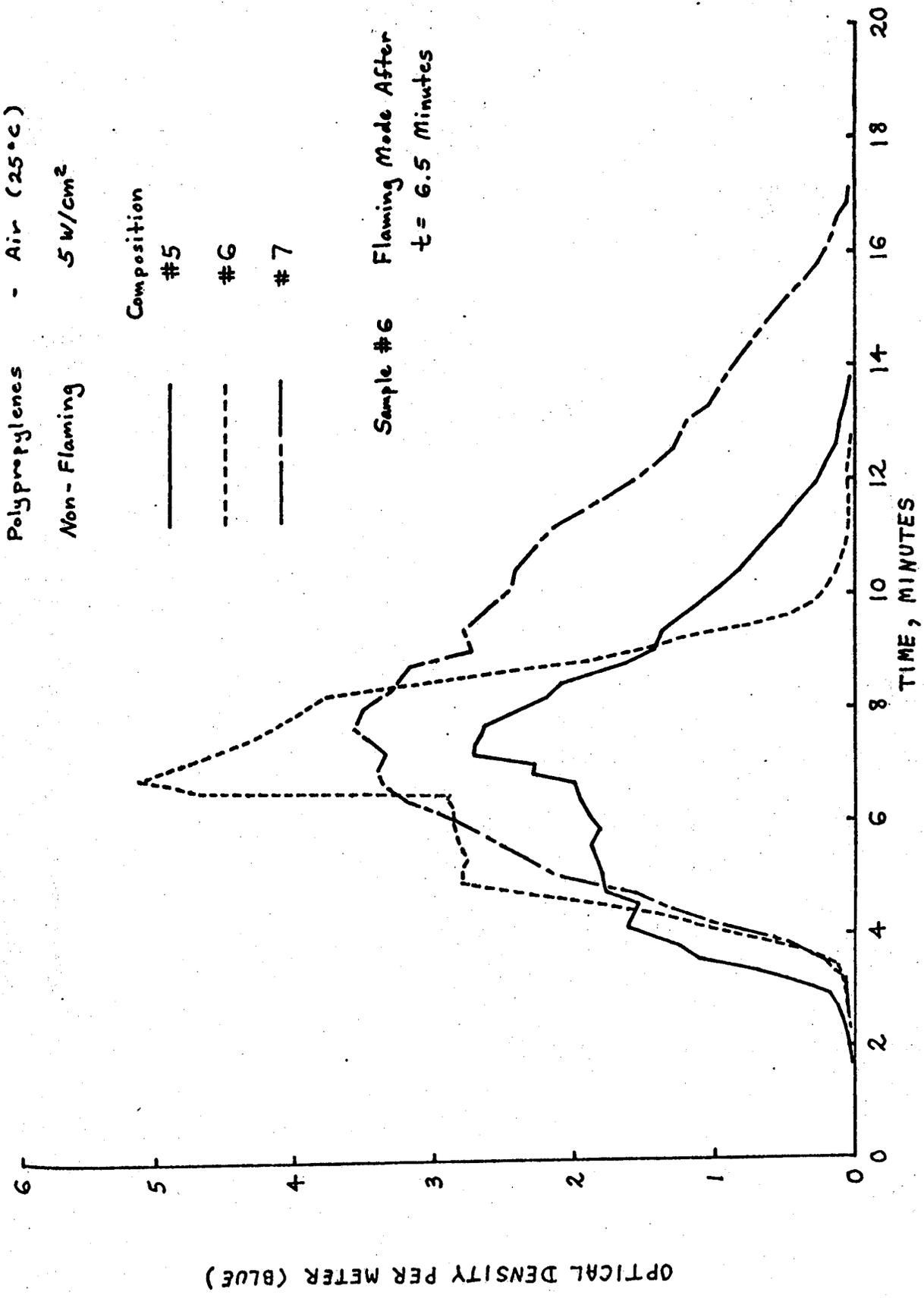


Figure 22. Effect of Polypropylene Fire Retardants on Smoke Optical Density in Nonflaming Combustion at 5 W/cm².

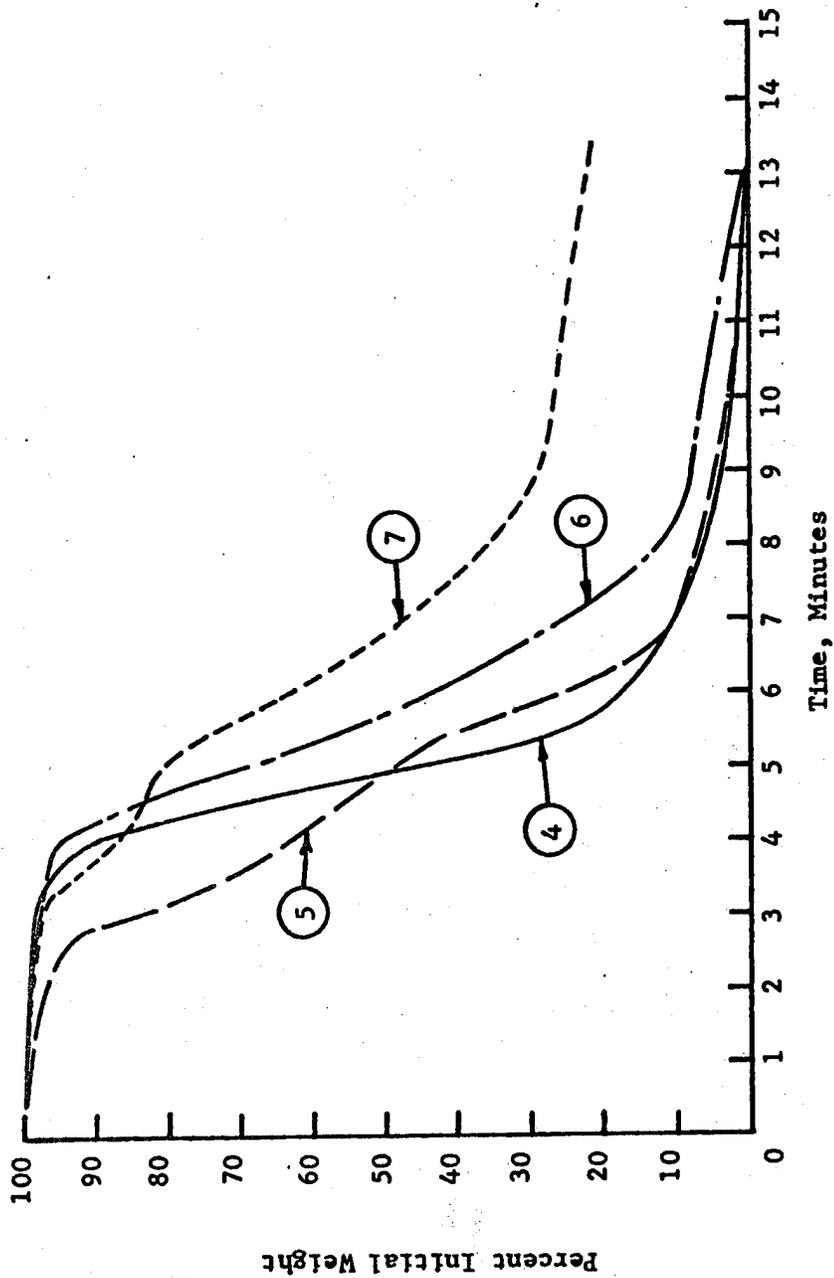


Figure 23. Effect of Polypropylene Fire Retardants on Sample Weight Loss in a 100°C Atmosphere at 5 W/cm².

leveling off by eight minutes into the test. The periods characterized by the greatest sample weight loss rates generally coincide with flaming ignition of the smoldering samples. Also, the weight loss rates observed in the heated ventilation gas are observed to be greater than the corresponding weight loss rates in room temperature tests.

Comparisons of smoke mean particle diameter behavior of two ventilation gas temperatures are presented for each polypropylene composition in Figures 24 through 30. These data show that particle sizes tend to be smaller in both nonflaming and flaming regimes at 100°C than the corresponding particle sizes measured in the tests in room temperature air. Composition 7 is an exception to this conclusion, where particle sizes after flaming transition are generally greater than the diameters measured under strictly nonflaming conditions at room temperature. As a result of the flaming transition observed for all seven compositions at 100°C the mean particle size decreased for samples 1, 2, 3 and 5 and increased for samples 4, 6 and 7. After ignition a stable period between 1.1 and 1.2 micrometers is observed for all samples.

Optical density behavior during high temperature tests are presented in Figures 31 through 37. In general, the optical densities are less in the nonflaming mode (prior to flaming ignition) at 100°C, and then peak rapidly after ignition at levels which are greater than those peak levels measured at room temperature. Composition 6 is observed to be an exception to these trends, where the optical density peaks are nearly the same at both environmental temperatures. Note that the data plotted for samples 4 and 6 in the room temperature case are from tests that resulted in flaming ignition. Finally, the highest peak optical density measured at 100°C was recorded for composition 4 with a value in blue light near 7/m.

Polypropylene #1

Non flaming 5 W/cm²

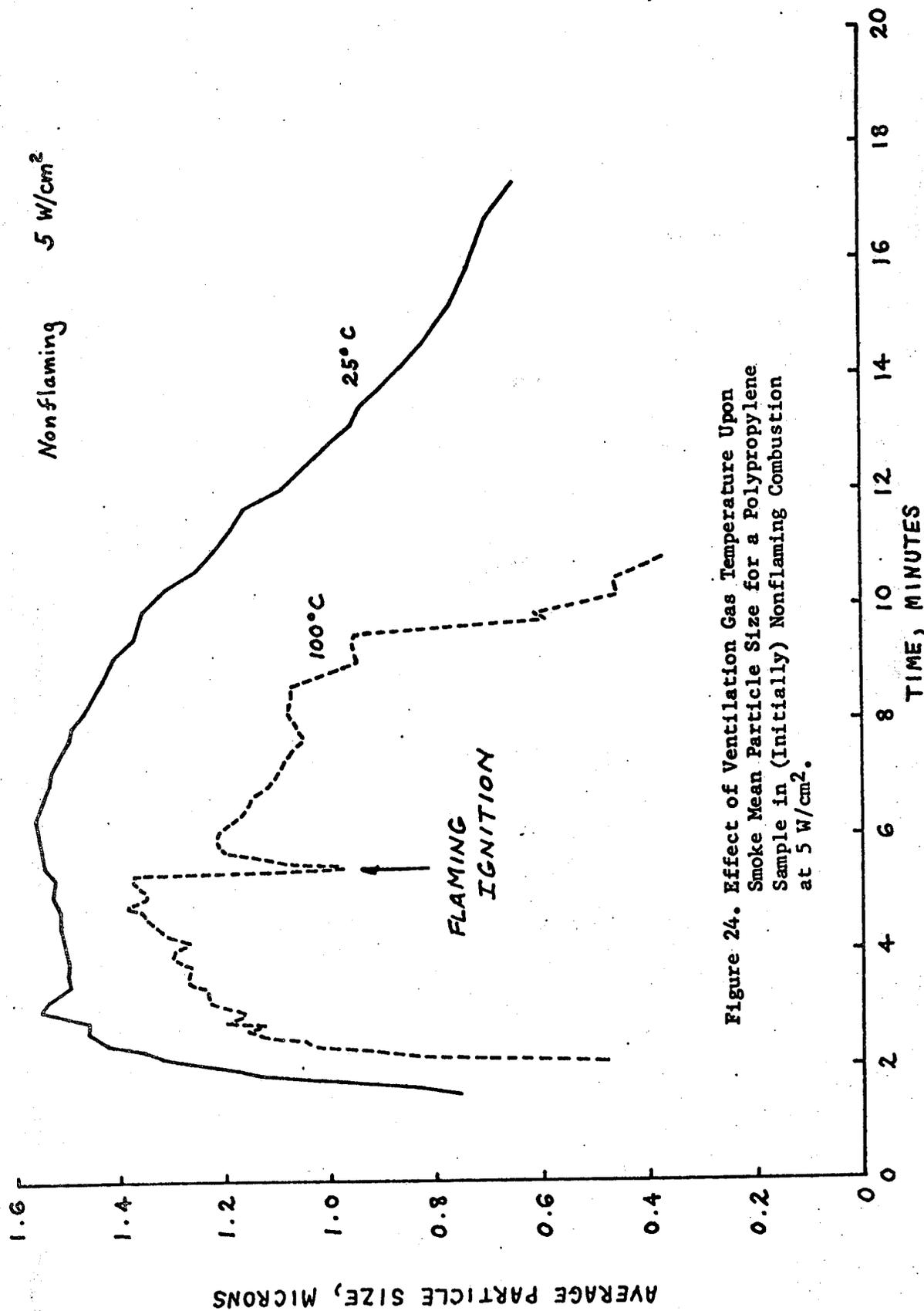


Figure 24. Effect of Ventilation Gas Temperature Upon Smoke Mean Particle Size for a Polypropylene Sample in (Initially) Nonflaming Combustion at 5 W/cm².

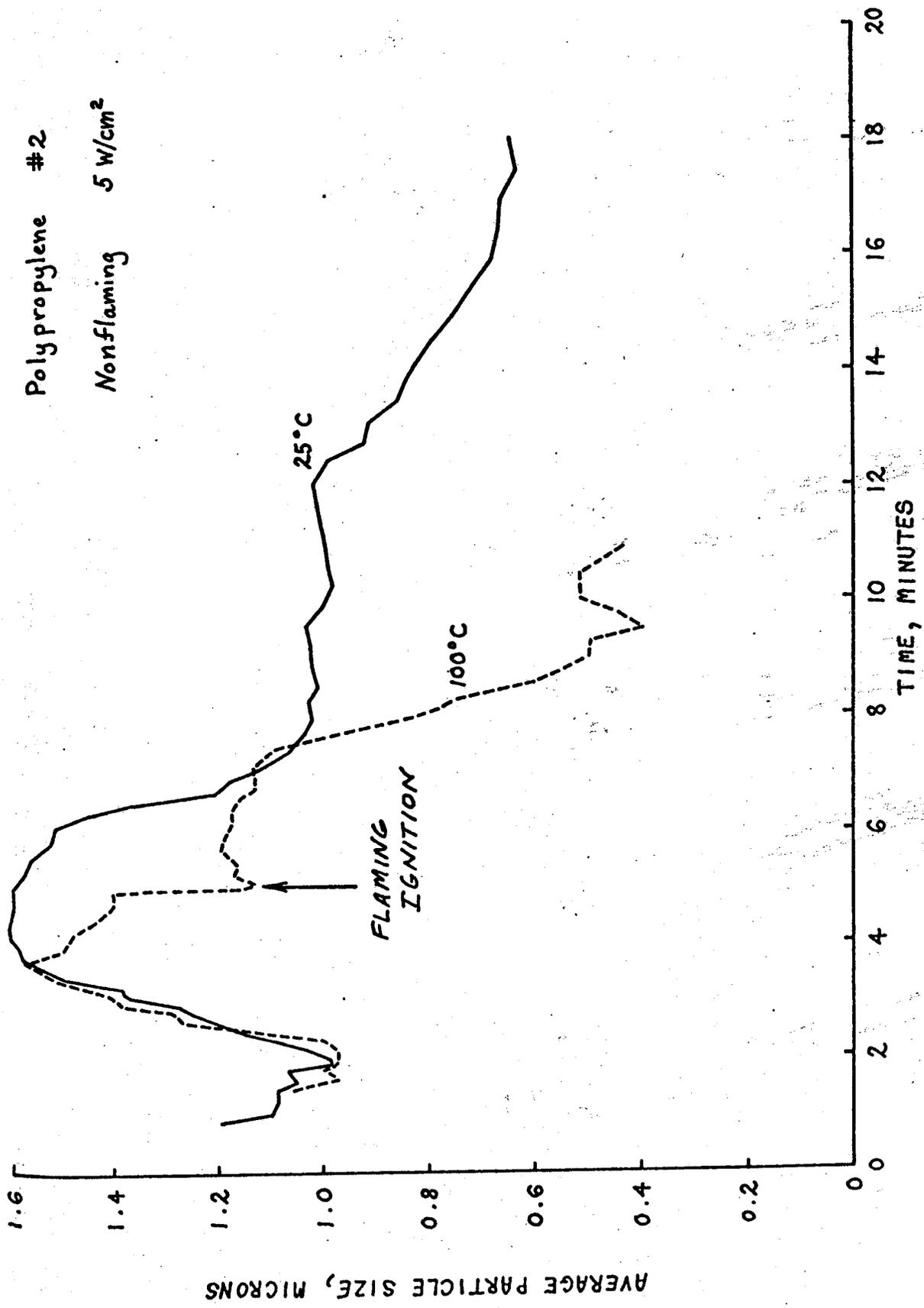


Figure 25. Effect of Ventilation Gas Temperature Upon Smoke Mean Particle Size for a Polypropylene Sample in (Initially) Nonflaming Combustion at 5 W/cm².

Polypropylene #3

Non-flaming 5 W/cm²

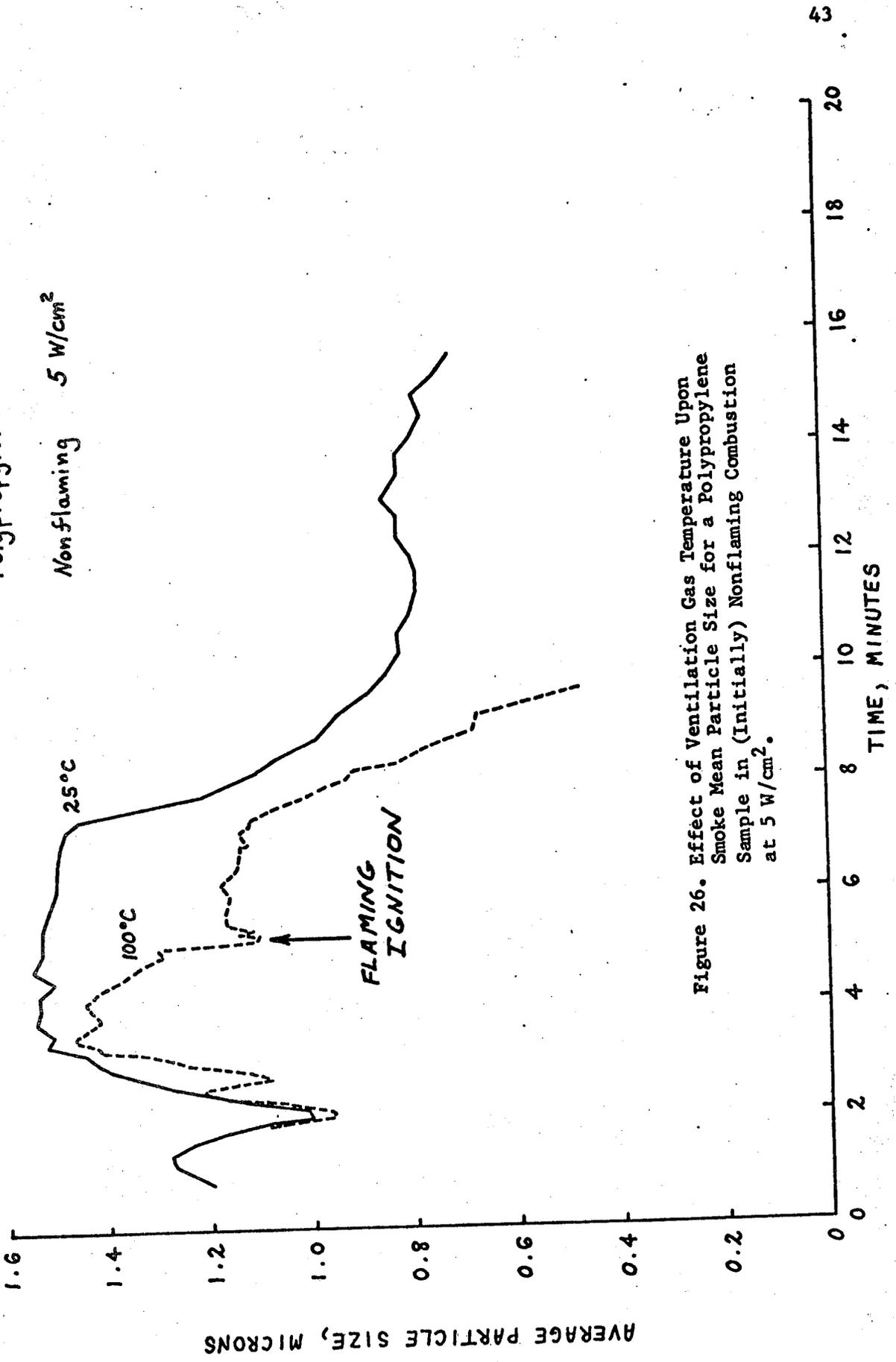


Figure 26. Effect of Ventilation Gas Temperature Upon Smoke Mean Particle Size for a Polypropylene Sample in (Initially) Nonflaming Combustion at 5 W/cm².

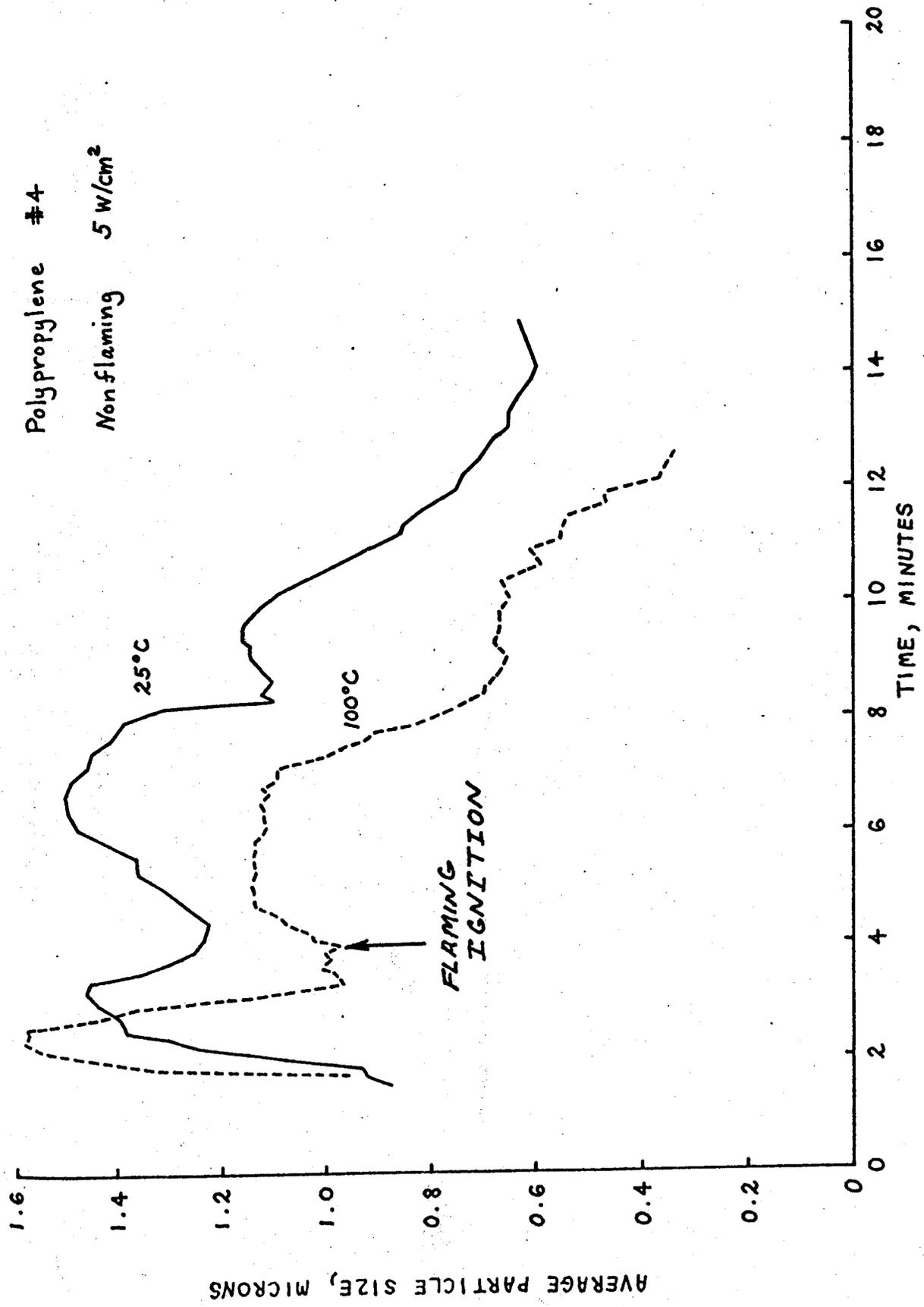


Figure 27. Effect of Ventilation Gas Temperature Upon Smoke Mean Particle Size for a Polypropylene Sample in (Initially) Nonflaming Combustion at 5 W/cm².

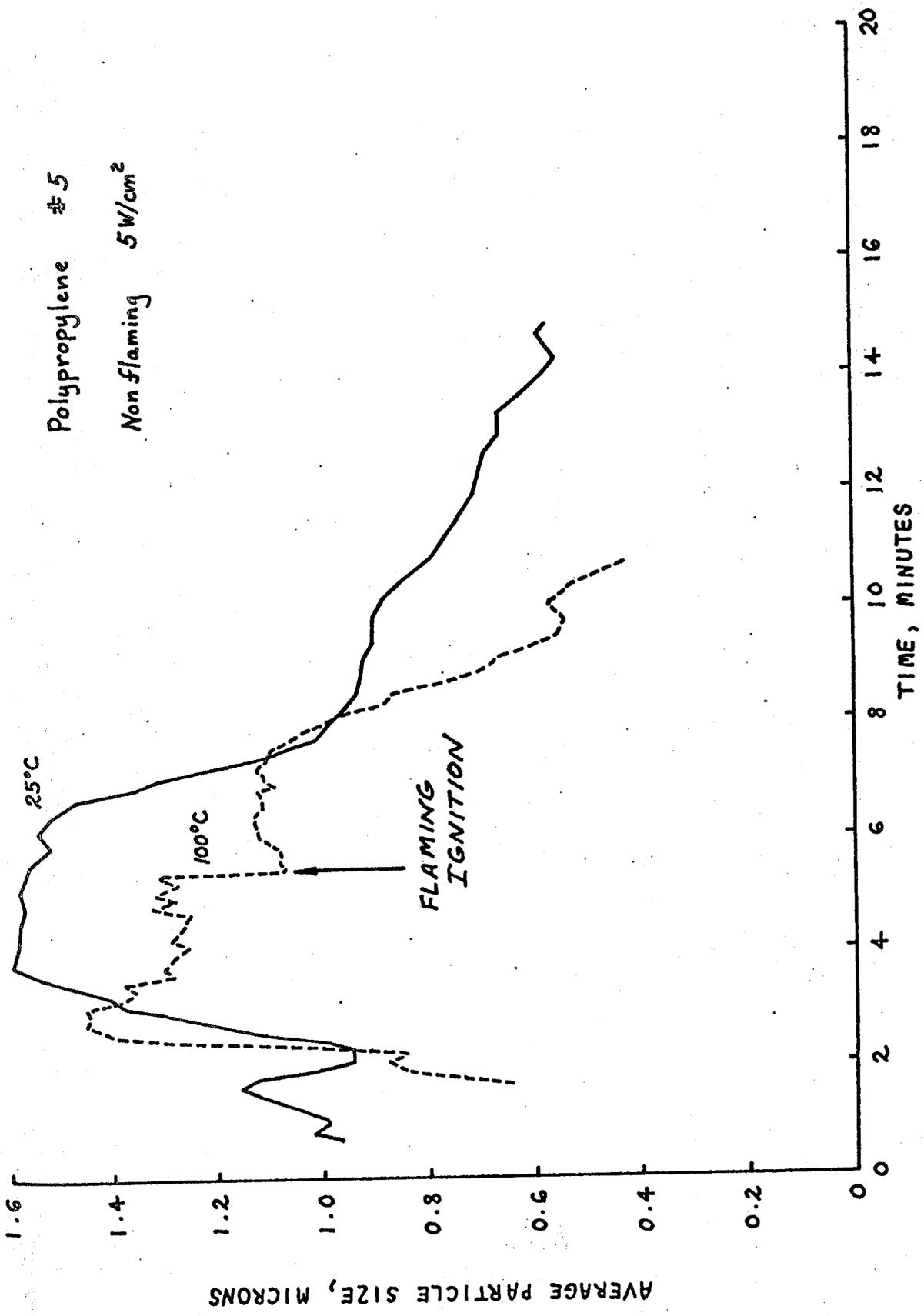


Figure 28. Effect of Ventilation Gas Temperature Upon Smoke Mean Particle Size for a Polypropylene Sample in (Initially) Nonflaming Combustion at 5 W/cm².

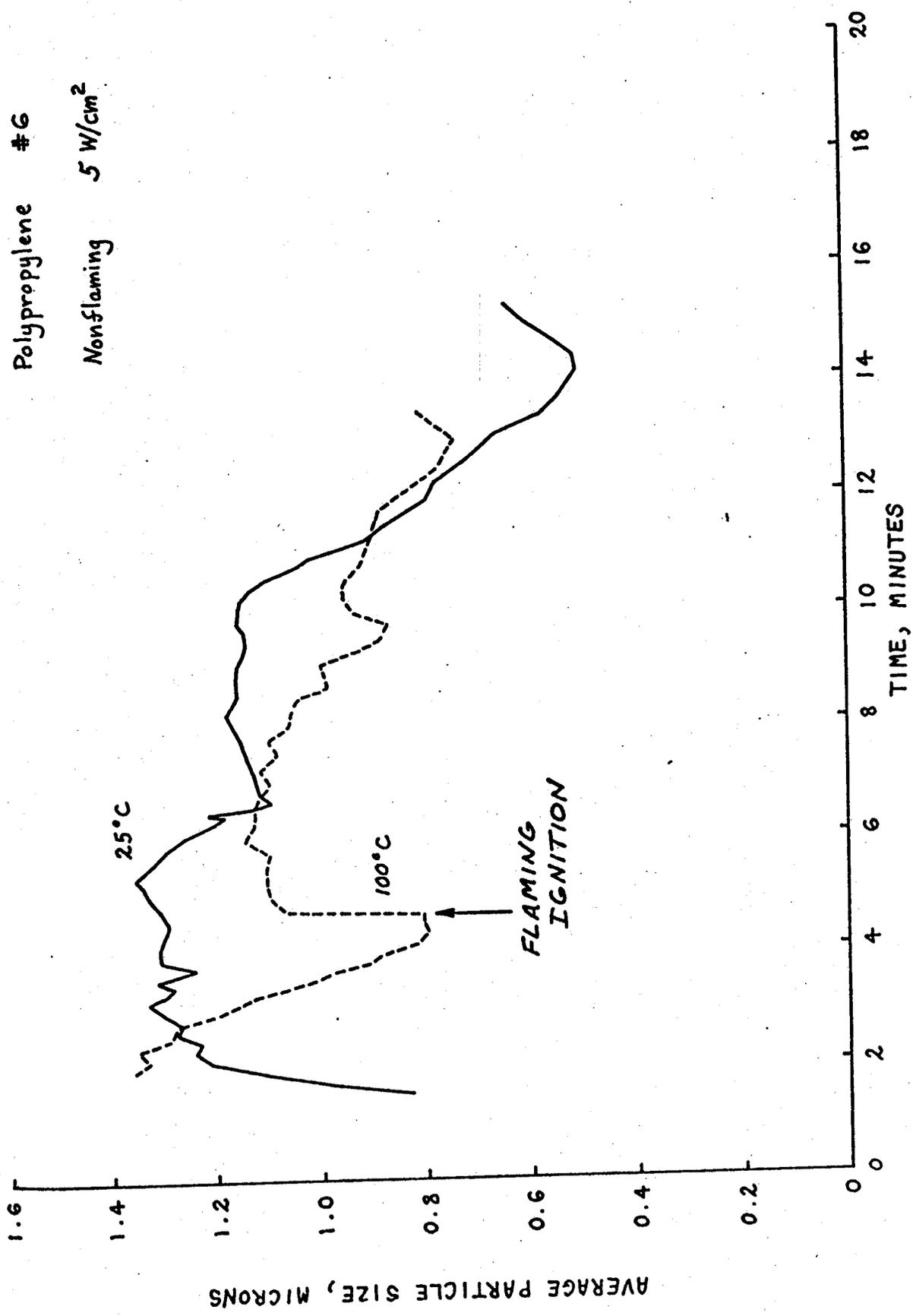


Figure 29. Effect of Ventilation Gas Temperature Upon Smoke Mean Particle Size for a Polypropylene Sample in (Initially) Nonflaming Combustion at 5 W/cm².

Polypropylene #7
Non-flaming 5 W/cm²

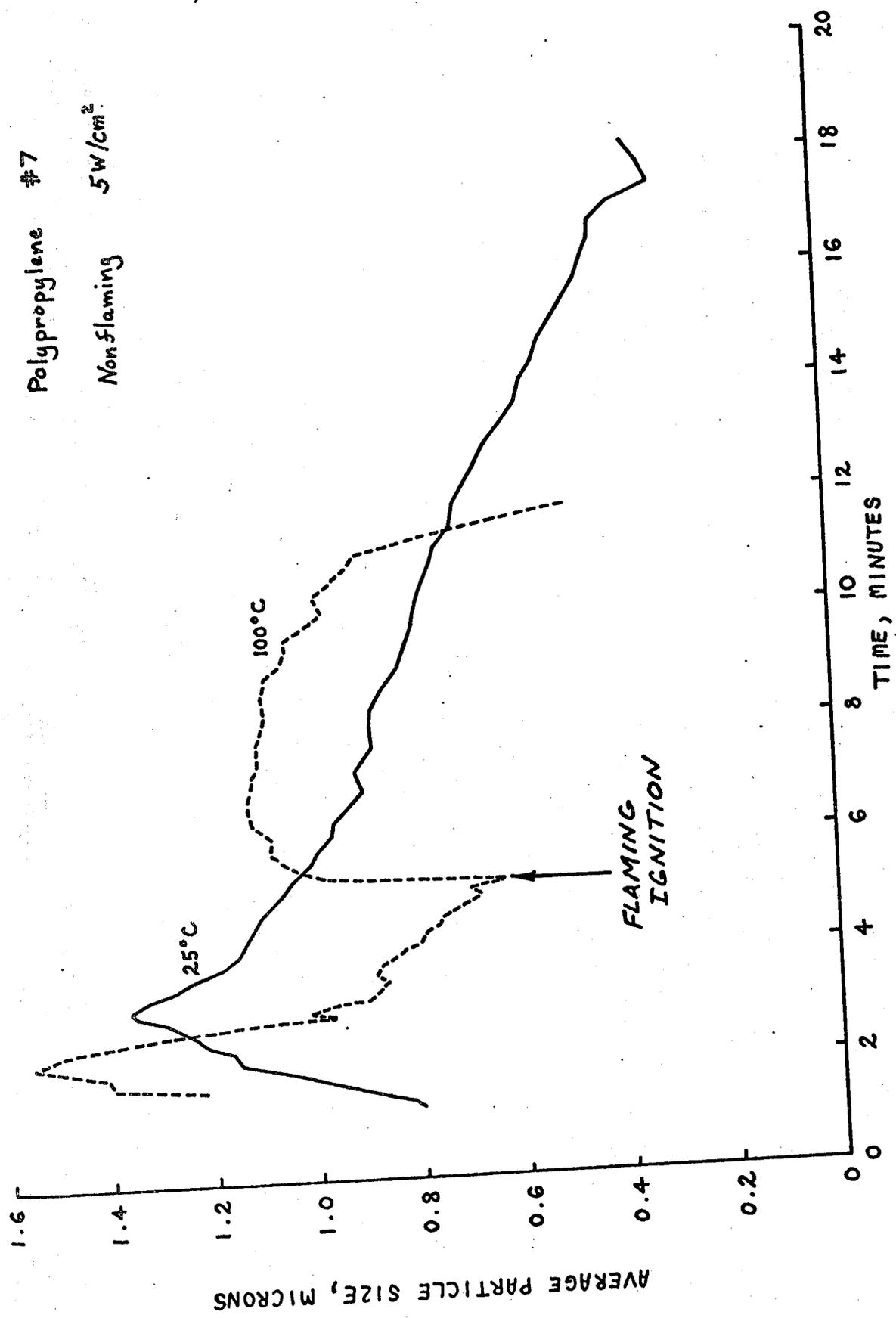
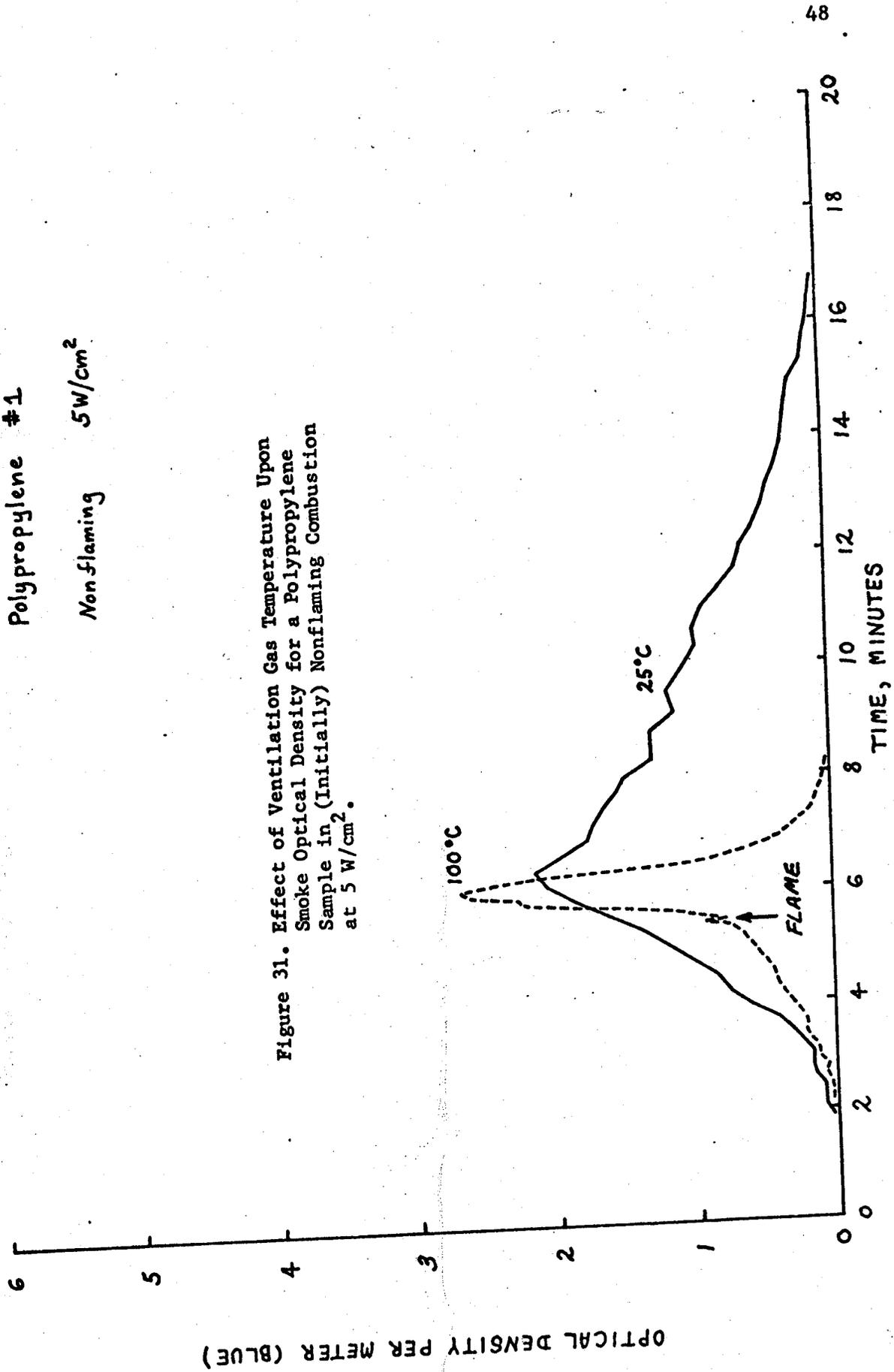


Figure 30. Effect of Ventilation Gas Temperature Upon Smoke Mean Particle Size for a Polypropylene Sample in (Initially) Nonflaming Combustion at 5 W/cm².

Polypropylene #1

Non flaming 5 W/cm²

Figure 31. Effect of Ventilation Gas Temperature Upon Smoke Optical Density for a Polypropylene Sample in₂ (Initially) Nonflaming Combustion at 5 W/cm².



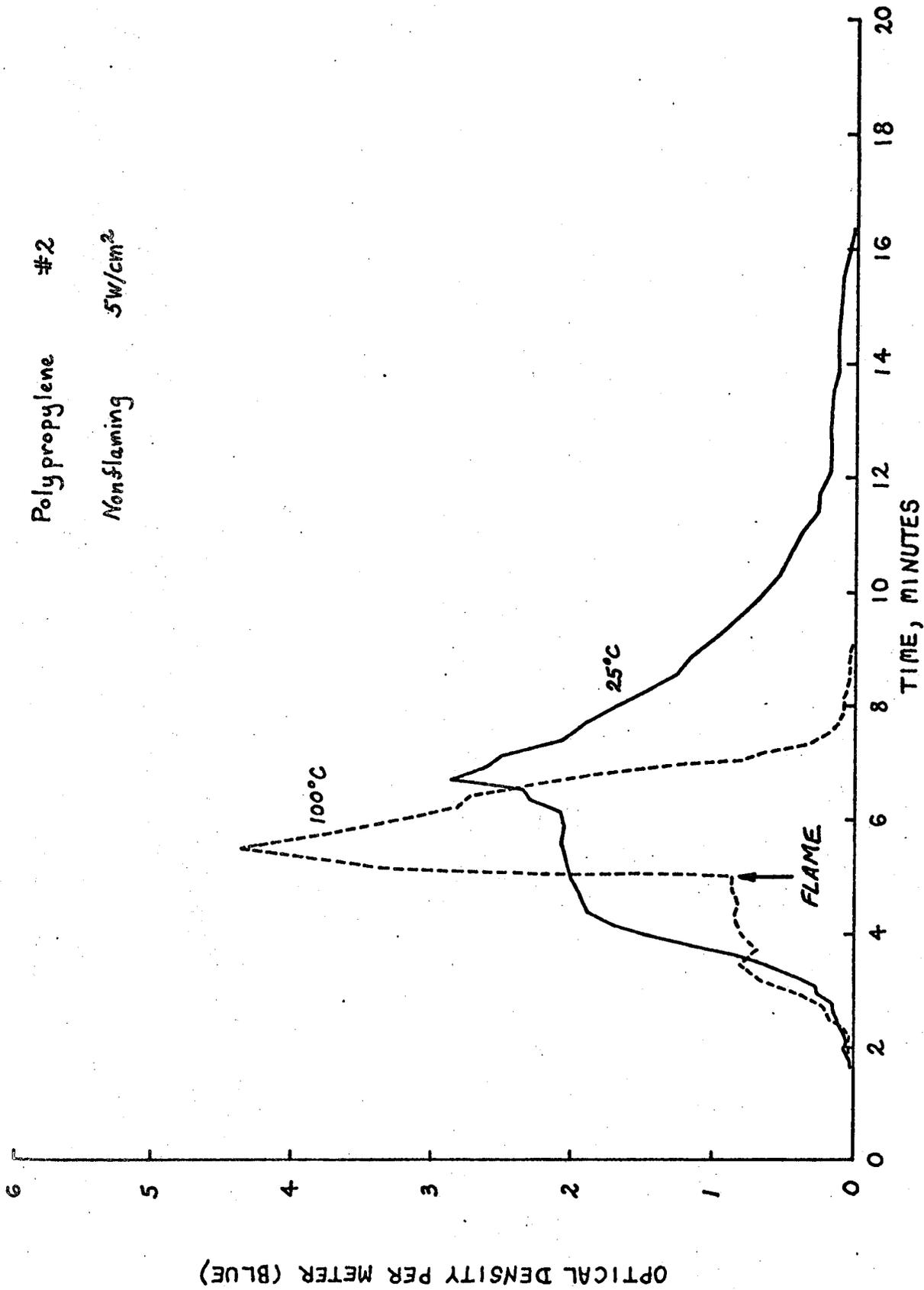


Figure 32. Effect of Ventilation Gas Temperature Upon Smoke Optical Density for a Polypropylene Sample in (Initially) Nonflaming Combustion at 5 W/cm².

Polypropylene #3

Nonflaming 5 W/cm²

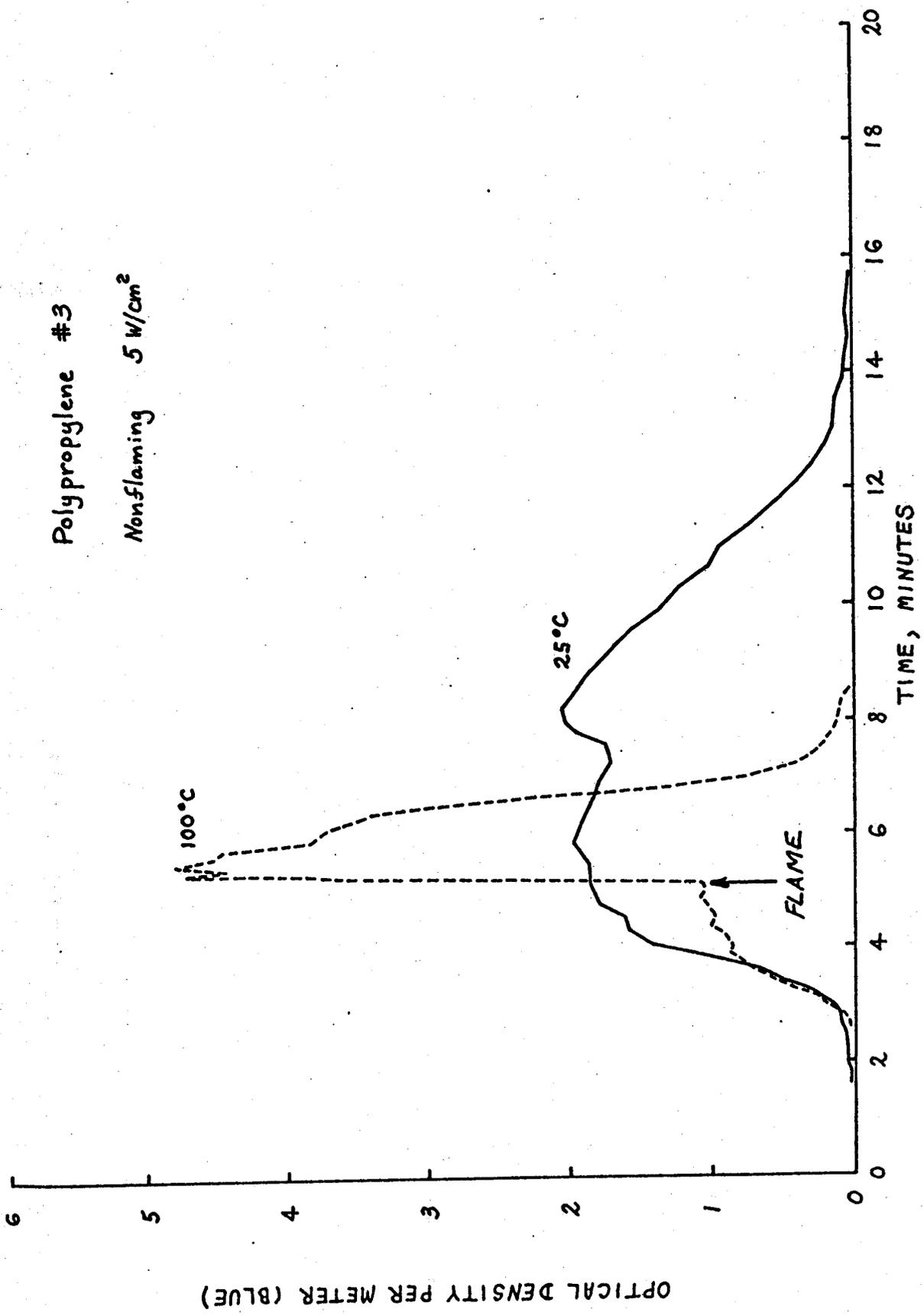


Figure 33. Effect of Ventilation Gas Temperature Upon Smoke Optical Density for a Polypropylene Sample in (Initially) Nonflaming Combustion at 5 W/cm².

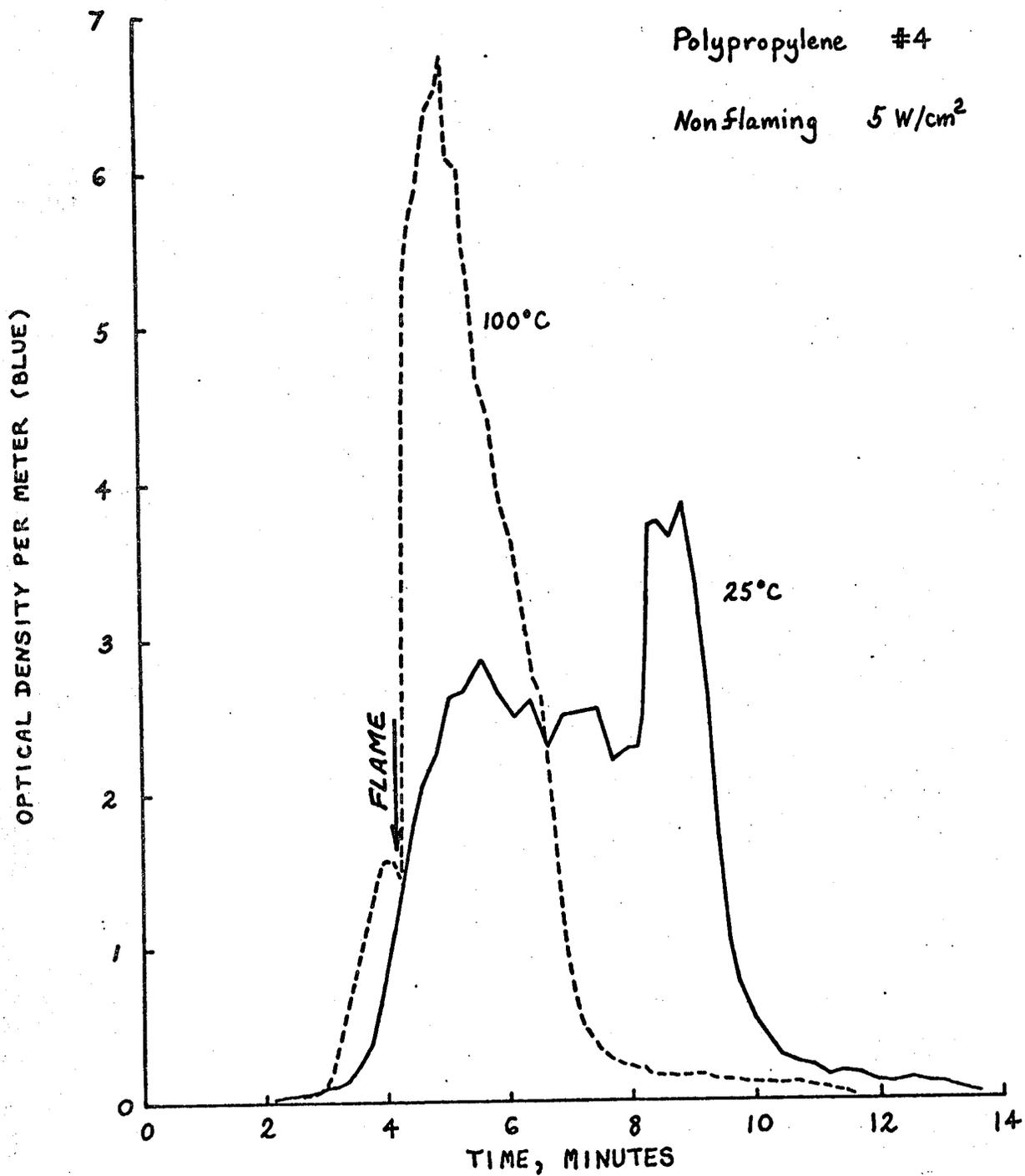


Figure 34. Effect of Ventilation Gas Temperature Upon Smoke Optical Density for a Polypropylene Sample in (Initially) Nonflaming Combustion at 5 W/cm².

Polypropylene #5
Nonflaming 5W/cm²

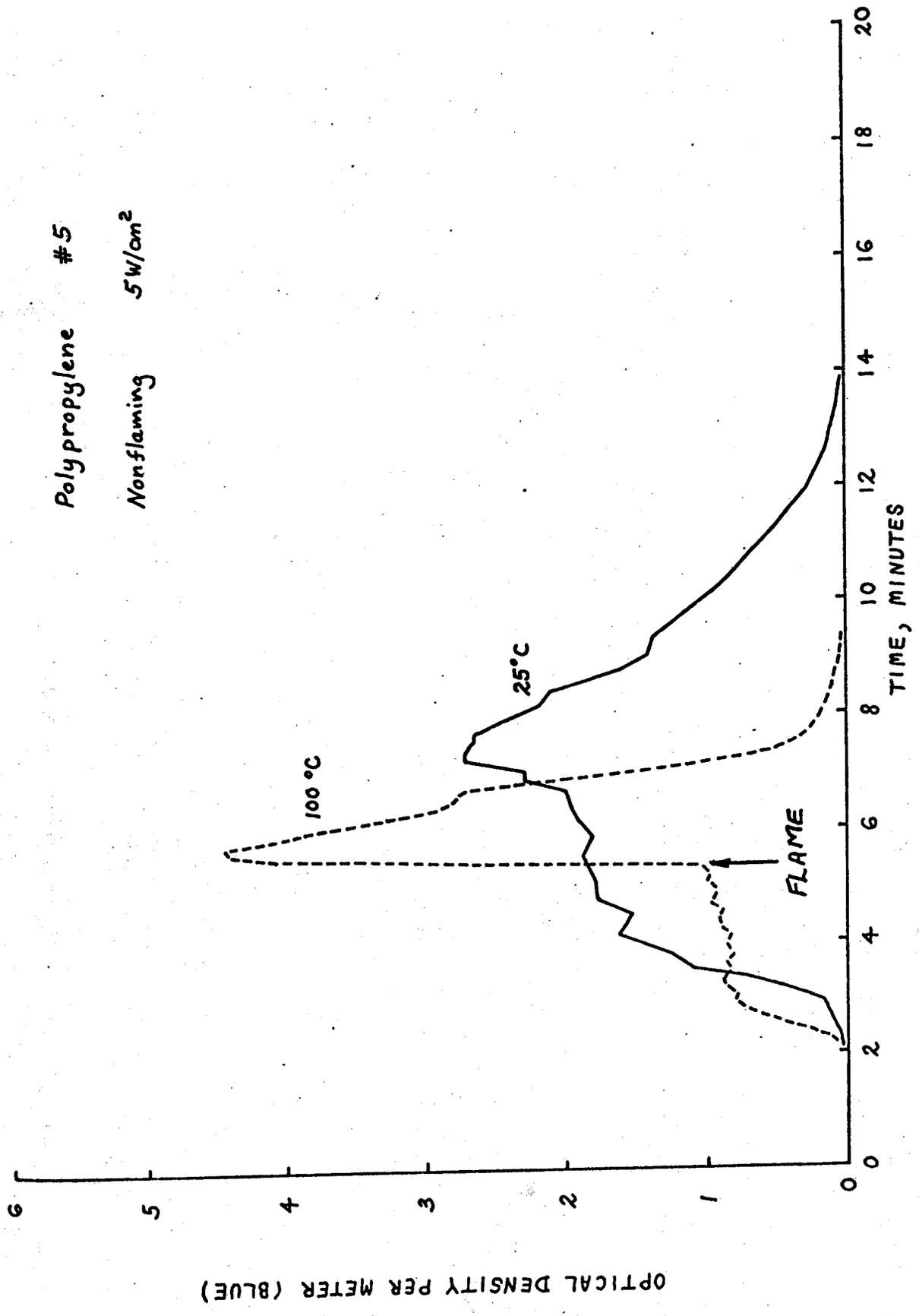


Figure 35. Effect of Ventilation Gas Temperature Upon Smoke Optical Density for a Polypropylene Sample in (Initially) Nonflaming Combustion at 5 W/cm².

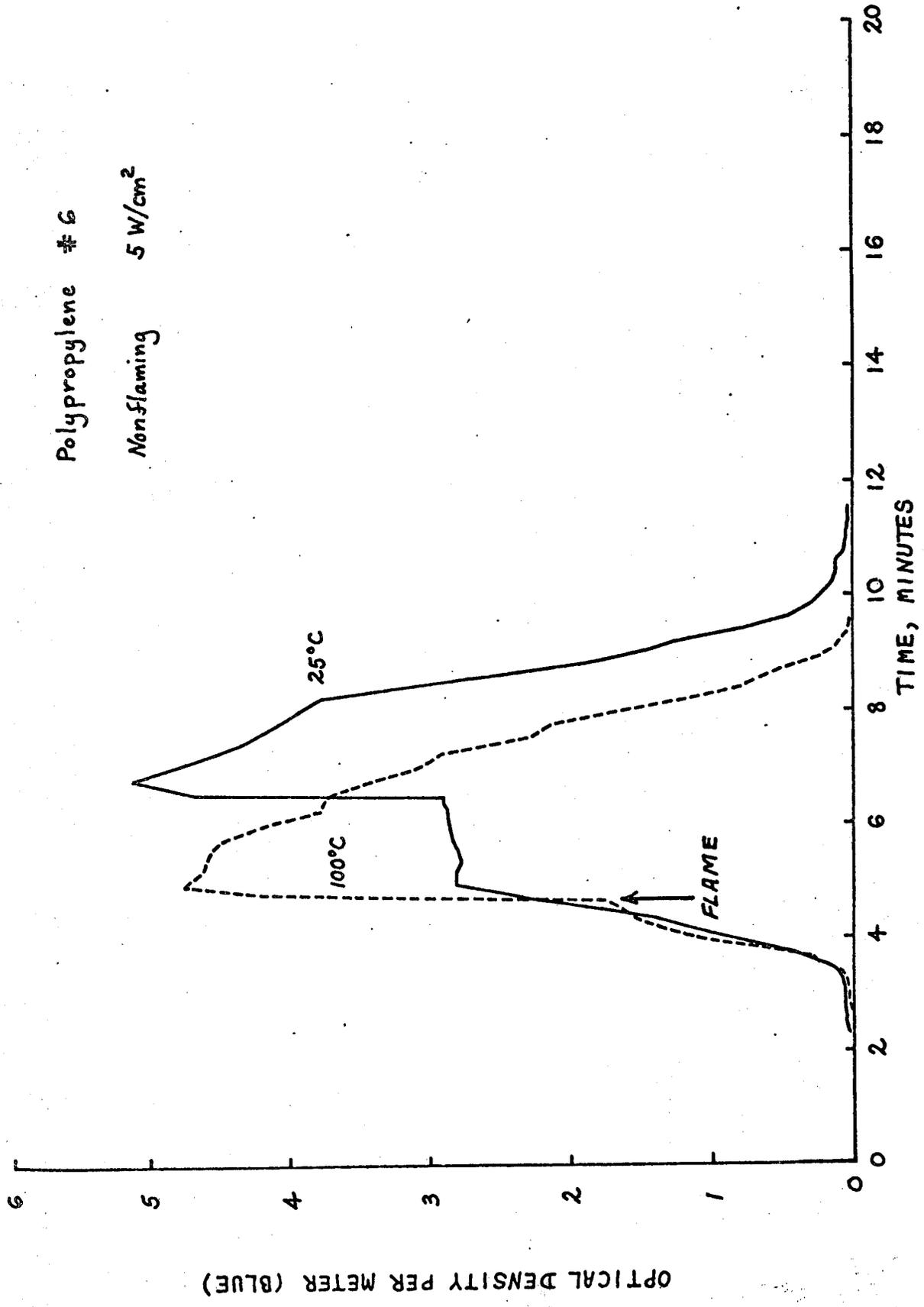


Figure 36. Effect of Ventilation Gas Temperature Upon Smoke Optical Density for a Polypropylene Sample in (Initially) Nonflaming Combustion at 5 W/cm².

Polypropylene #7

Nonflaming 5 W/cm²

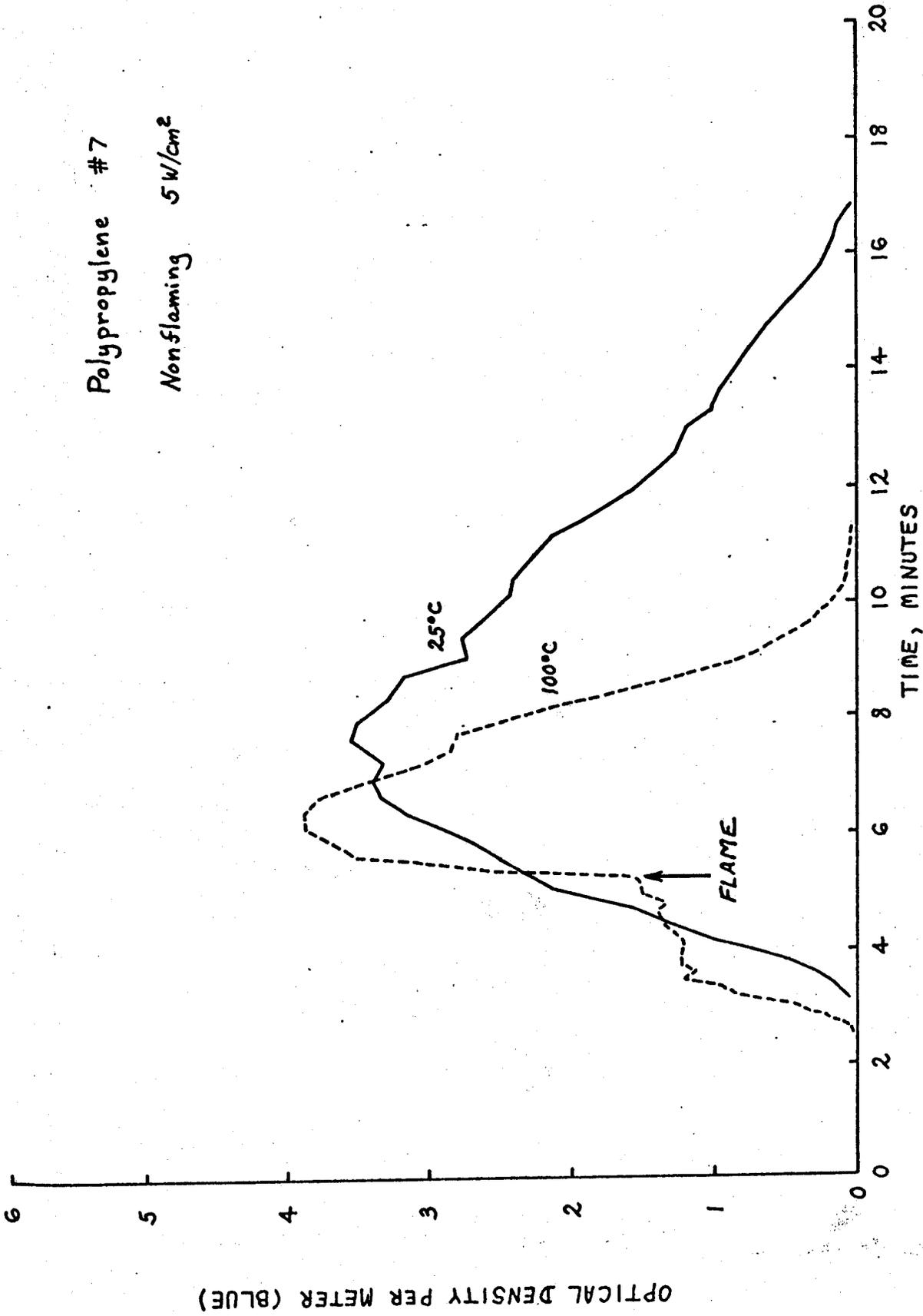


Figure 37. Effect of Ventilation Gas Temperature Upon Smoke Optical Density for a Polypropylene Sample in (Initially) Nonflaming Combustion at 5 W/cm².

C. Summary

In tests of seven polypropylene samples that were combusted (without an external ignition source) in room temperature ventilation gases, differences are observed in smoke properties among the different compositions. Sample weight loss data show that for the measurements which were obtained, the composition which tends to form a char exhibits the lowest weight loss rates and leaves the greatest fraction of sample weight at the end of the test. Also, two of the samples sustained spontaneous flaming ignition in the room temperature tests. Comparisons of particle size data for nonflaming conditions only, show that the pure resin and the compositions containing the chlorinated paraffin produced the greatest fraction of larger particle sizes. The char forming sample generated the greatest fraction of smaller particle sizes. Total particulate mass data show that under nonflaming conditions in room temperature air the samples containing the chlorinated paraffin as a fire retardant and the char forming sample produced the lowest particulate masses per gram of initial sample weight. Finally, time resolved optical measurements in the room temperature tests show measured peak mean particle diameters to be between 1.5 and 1.6 micrometers for most samples in the nonflaming mode and that the char forming sample which produced the smallest overall particle sizes generated the greatest overall (nonflaming) optical density levels.

Tests of polypropylene samples in the 100°C ventilation gas (air) were characterized by the spontaneous flaming ignition of all samples early in the tests. As a result, sample weight loss rates were greater at 100°C than in room temperature tests and the maximum weight loss rates coincide with the occurrence of flaming ignition. Particle size data show that mean particle diameters were generally smaller (with one exception) in both nonflaming and

flaming regions at 100°C than the particle sizes measured in room temperature tests. Also, the tendency of particle size to increase or decrease at the point of flaming ignition was dependent upon the particular polypropylene compositions. Finally, the highest optical density peaks measured in both room temperature and 100°C tests were observed shortly after flaming ignition for all samples.

VI. CATALOGING OF SMOKE PHYSICAL PROPERTIES DATA

In order to facilitate the use of smoke physical properties data by researchers who are dealing with the toxicological aspects of smoke or the effects of properties such as particle size on the response of smoke detectors, the National Bureau of Standards has requested that data which have been previously obtained in this smoke research program be catalogued in a single document. These cataloging efforts were subsequently initiated during the last quarter of the grant year.

The quantities which have been agreed upon (in consultation with NBS personnel) for systematic cataloging are as follows:

- (i) fraction of sample weight loss that becomes particulate matter;
- (ii) total particulate mass concentration;
- (iii) total particulate number concentration;
- (iv) mass median diameter;
- (v) geometric standard deviation;
- (vi) maximum optical density per meter; and
- (vii) volume-surface mean particle diameter (D_{32}) at maximum optical density.

In addition, cumulative probability plots of the "fraction of particles with diameter less than D_p "versus "log D_p " are being compiled. These plots, in addition to the above-listed physical properties, for data obtained through October 1, 1977 will be submitted in a separate formal report to NBS; which is to be completed on or about January 1, 1978.

VII. MODELING OF SMOKE PRODUCTION OF SOLID MATERIALS

Development of an analytical model capable of describing certain "smoking" characteristics of different solid materials is underway. Specifically, a one-dimensional model describing the smoldering decomposition with charring of a slab of polymeric material of finite thickness has been considered. The model is depicted in Figure 38. The face of the "sample" is subjected to a known incident heat flux and both the solid and gas phase properties are described. Thus far, fundamental equations have been formulated to describe the solid phase decomposition, the theoretical behavior of the solid-gas phase and the transport of the volatile, condensable products of thermal degradation.

The sample material is described during the decomposition process by the porosity, ϵ ; which is defined as the local volume fraction of material which is occupied by the gas/vapor phase. Thus, the material sample will be characterized by regions which range from the primary solid decomposition reaction zone to a very porous char structure closest to the sample surface. The developed governing equations with associated assumptions are shown in Table III.

In order to obtain solutions to the developed conservation equations and boundary conditions an iterative solution procedure based upon the method of quasi-linearization has been applied, and a computer program which utilizes an implicit finite differencing scheme has been written. The differencing algorithm is the "box-scheme" method first utilized by Keller⁵ and then by Kansa;⁶ and the resulting coefficient matrix is solved by a block tri-diagonal inversion routine. The program is presently designed to calculate gas density, solid porosity, gas velocity and gas-solid temperature. Debugging of the program has been completed and refinements in the computation schemes have been carried out. Examples of calculated time-resolved porosity, temperature, pressure and velocity profiles are given in Figures 39-42 for a model polymeric material decomposing under the influence of an incident heat flux.

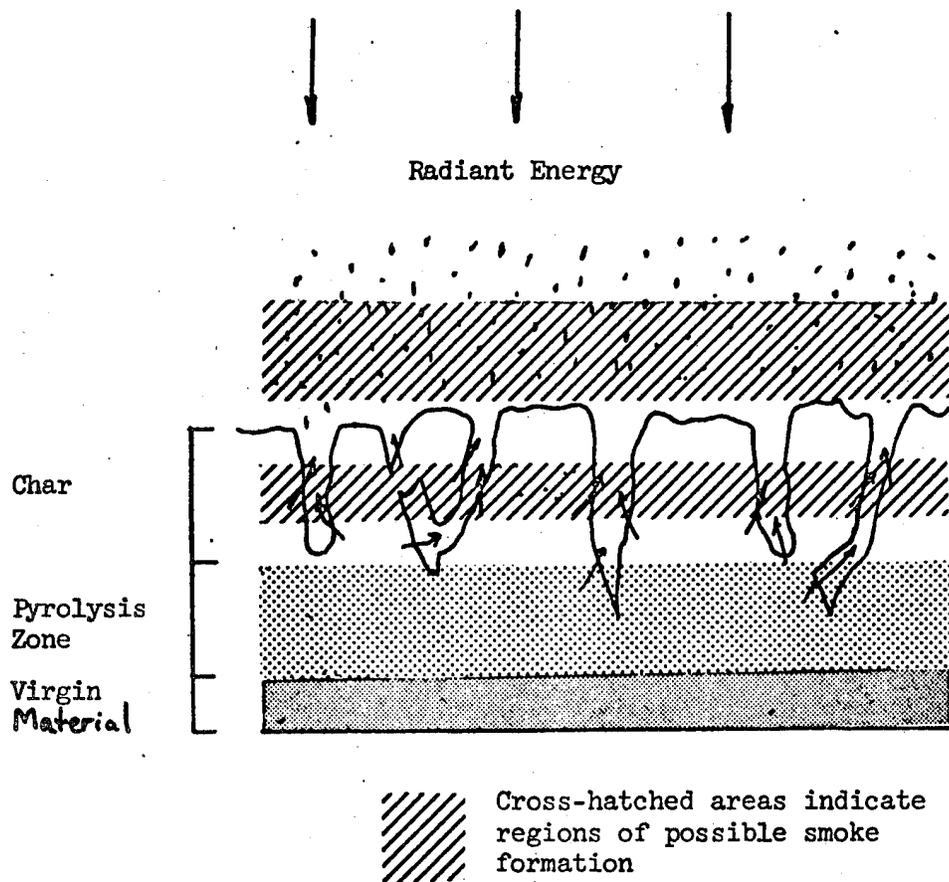


Figure 38. Description of the Investigated Theoretical Model.

Table III. Governing Equations and Assumptions

Gas Phase Continuity

$$\pi_1 \frac{\partial(\epsilon \rho_g')}{\partial t'} + \pi_1 \pi_2 \frac{\partial(\epsilon \rho_g' u')}{\partial x'} = \frac{\partial \epsilon}{\partial t'}$$

Solid Decomposition

$$\frac{\partial \epsilon}{\partial t'} = (\epsilon_{\text{char}} - \epsilon) \exp\left[-\bar{E}_s \left(\frac{1}{T'} - 1\right)\right]$$

Gas Phase Momentum (includes Darcy's drag)

$$\frac{\partial(\epsilon \rho_g' T')}{\partial x'} = -\epsilon u'$$

Energy

$$\begin{aligned} \pi_1 \pi_2 \epsilon \rho_g' u' \frac{\partial T'}{\partial x'} + \pi_3 \frac{\partial[(1-\epsilon)T']}{\partial t'} + \pi_1 \epsilon \rho_g' \frac{\partial T'}{\partial t'} \\ + T' \frac{\partial \epsilon}{\partial t'} = \pi_4 \frac{\partial\left\{(1-\epsilon)k_s' \frac{\partial T'}{\partial x'}\right\}}{\partial x'} + \pi_5 \frac{\partial\left(\epsilon \frac{\partial T'}{\partial x'}\right)}{\partial x'} \\ + \bar{H} \frac{\partial \epsilon}{\partial t'} \end{aligned}$$

Assumptions

1. One-dimensional analysis
2. Solid and gas phase are in thermal equilibrium
3. Solid decomposition represented by global Arrhenius rate equation
4. No gas phase chemical reactions

Note: Primed (') quantities are dimensionless, where x , t , ρ_g , u and T have been non-dimensionalized by L , τ , ρ_{g0} , u_0 and T_0 .

Table III. Governing Equations (continued)

Energy Balance at Front Surface of Sample

$$\begin{aligned}
 & -\pi_1 (1 - \epsilon_w) k'_{s_w} \left(\frac{\partial T'}{\partial x'} \right) \Big|_{w_+} + \pi_2 \epsilon_w \rho'_{g_{w_+}} u'_{w_+} T'_{w_+} \\
 & + \epsilon_w \rho'_{g_{w_+}} \left(\frac{u'^3_{w_+}}{2} \right) - \pi_5 \epsilon_w \left(\frac{\partial T'}{\partial x'} \right) \Big|_{w_+} = \\
 & + \pi_2 \rho'_{g_{w_-}} u'_{w_-} T'_{w_-} + \rho'_{g_{w_-}} \left(\frac{u'^3_{w_-}}{2} \right) - \pi_3 T'^4_{w_+} + \pi_4 \\
 & - \pi_5 \frac{\partial T'}{\partial x'} \Big|_{w_+}
 \end{aligned}$$

Energy Balance at Rear Surface of Sample

$$-\pi_1 (1 - \epsilon_b) k'_{s_b} \left(\frac{\partial T'}{\partial x'} \right) \Big|_b = \pi_3 T'^4_b + \pi_6 [T'_b - 1]$$

Definitions

$$\pi_1 = \frac{\rho_{g_0}}{\rho_s}$$

$$\pi_4 = \frac{\sigma k_{s_0}}{\rho_s L^2 c_{p_g}}$$

$$\pi_2 = \frac{\sigma u_0}{L}$$

$$\pi_5 = \frac{\sigma k_g}{\rho_s L^2 c_{p_g}}$$

$$\pi_3 = \frac{c_{p_s}}{c_{p_g}}$$

Table III. Governing Equations (continued)

Definitions (continued)

$$\Gamma_1 = \frac{k_{s_0} T_0}{\rho_{g_0} L u_0^3}$$

$$\Gamma_2 = \frac{c_{p_g} T_0}{u_0^2}$$

$$\Gamma_3 = \frac{a_c T_0^4 \sigma}{\rho_{g_0} u_0^3}$$

$$\Gamma_4 = \frac{a_c \dot{q}_{rad}}{\rho_{g_0} u_0^3}$$

$$\Gamma_5 = \frac{k_g T_0}{\rho_{g_0} L u_0^3}$$

$$\Gamma_6 = \frac{T_0 h_{conv}}{\rho_{g_0} u_0^3}$$

$$\tau = [A_p \exp(-\bar{E}_s)]^{-1}$$

$$u_0 = \frac{P_0}{L \Phi}$$

$$\bar{E}_s = \frac{E_s}{RT_0}$$

$$\bar{H} = \frac{H}{c_{p_g} T_0}$$

Table III. Governing Equations (continued)

Nomenclature

| | |
|------------------------|--------------------------------------|
| ϵ | - porosity |
| ϕ | - Darcy's constant |
| ρ | - density |
| σ | - Stefan-Boltzmann constant |
| τ | - characteristic time |
| A | - frequency factor |
| a | - adsorptivity/emissivity |
| c | - specific heat |
| E | - activation energy |
| H | - heat of reaction |
| h_{conv} | convective heat transfer coefficient |
| k | - thermal conductivity |
| L | - sample thickness |
| p | - pressure |
| \dot{q}_{rad} | radiant heat flux |
| R | - universal gas constant |
| T | - temperature |
| u | - gas velocity |
| u_0 | - characteristic velocity |
| x | - distance |

Subscripts

| | |
|-----|-------------------------------|
| w | - sample front surface |
| b | - sample back surface |
| s | - solid |
| g | - gas |
| o | - ambient (initial) condition |
| $+$ | - solid phase side |
| $-$ | - gas phase side |

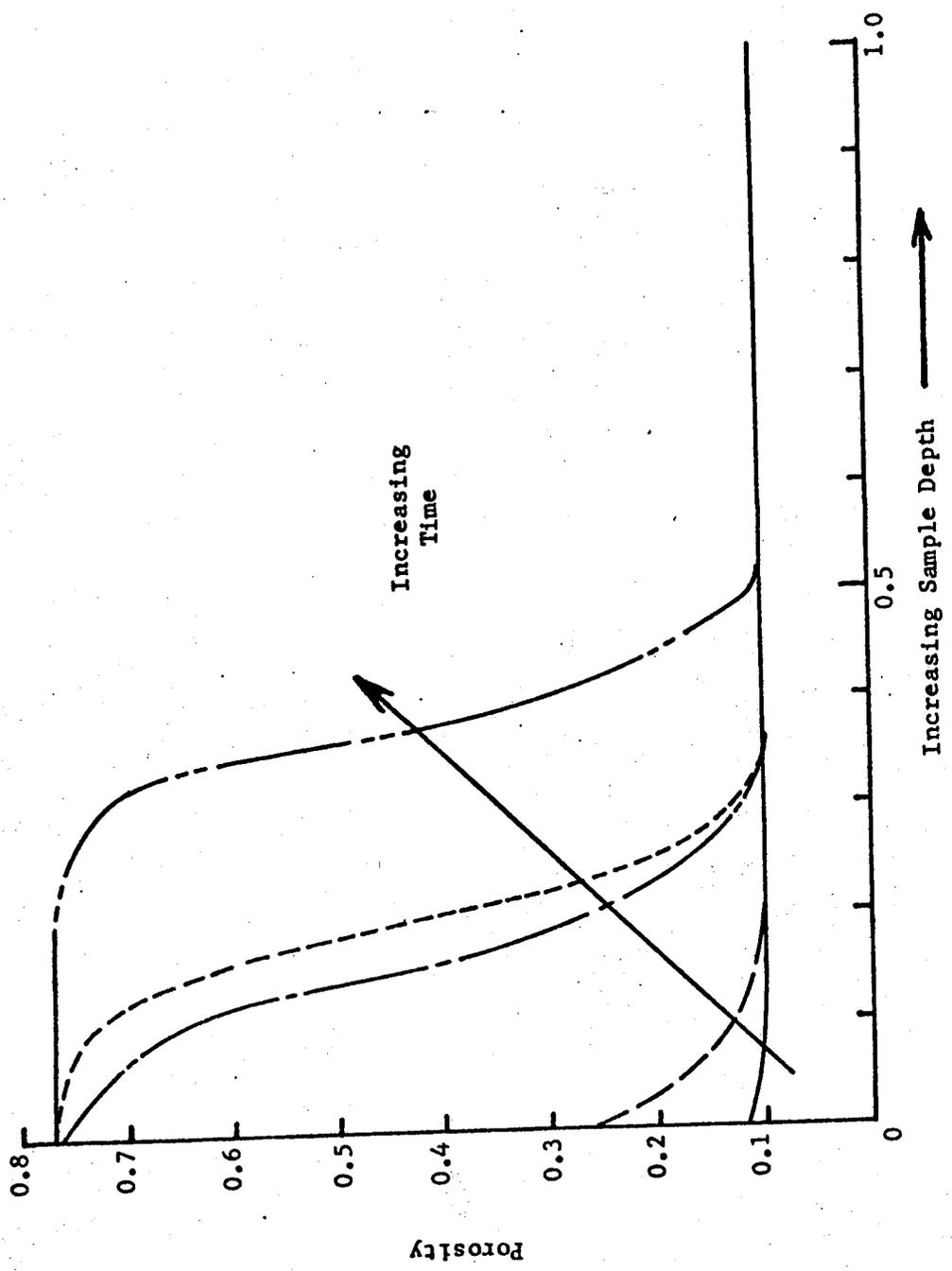


Figure 39. Time History of the Material Porosity Within a Charring, Degrading Sample.

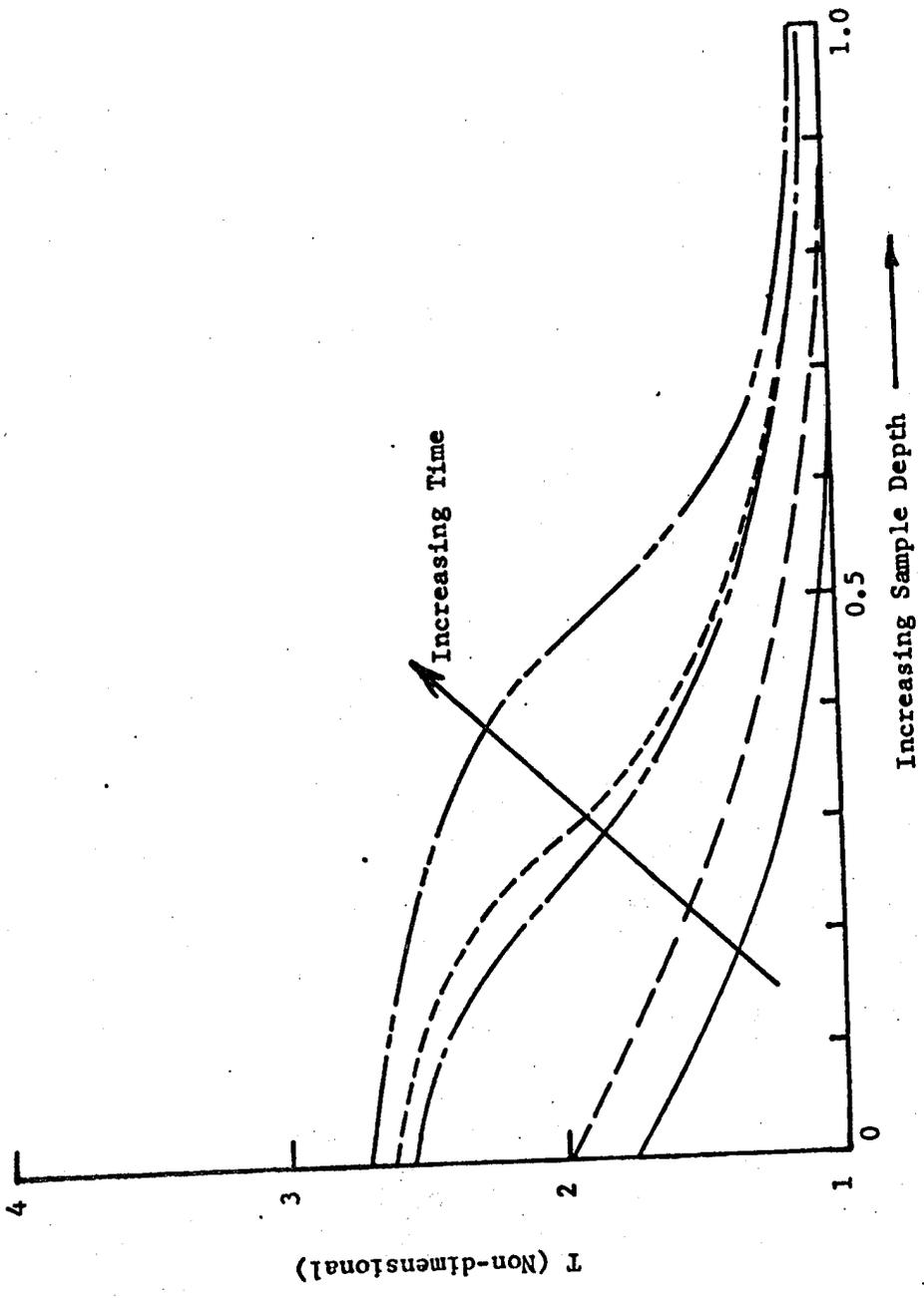


Figure 40. Time History of the Temperature Profile Within a Charring, Degrading Sample.

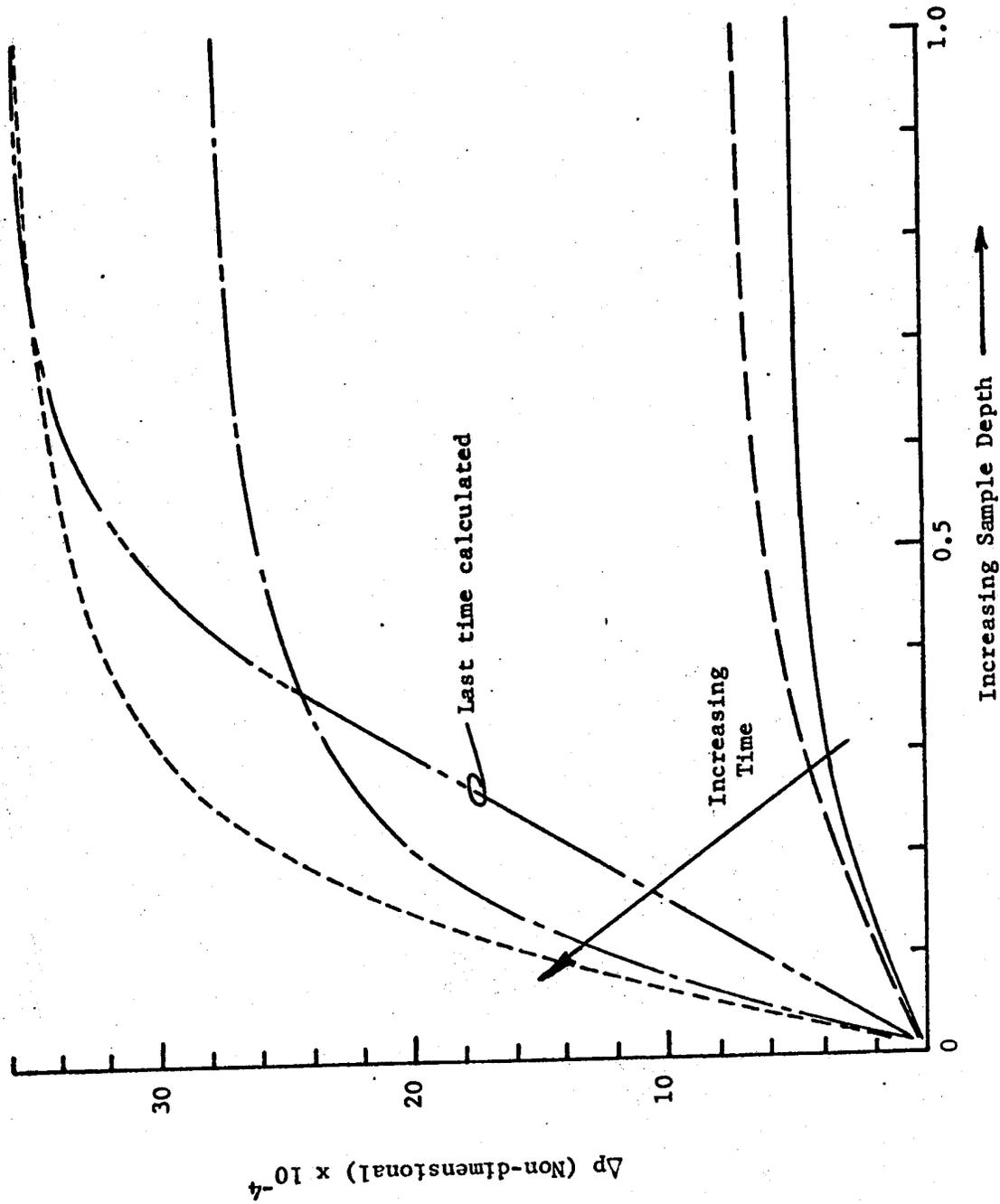


Figure 41. Time History of the Pressure Profile Within a Charring, Degrading Sample.

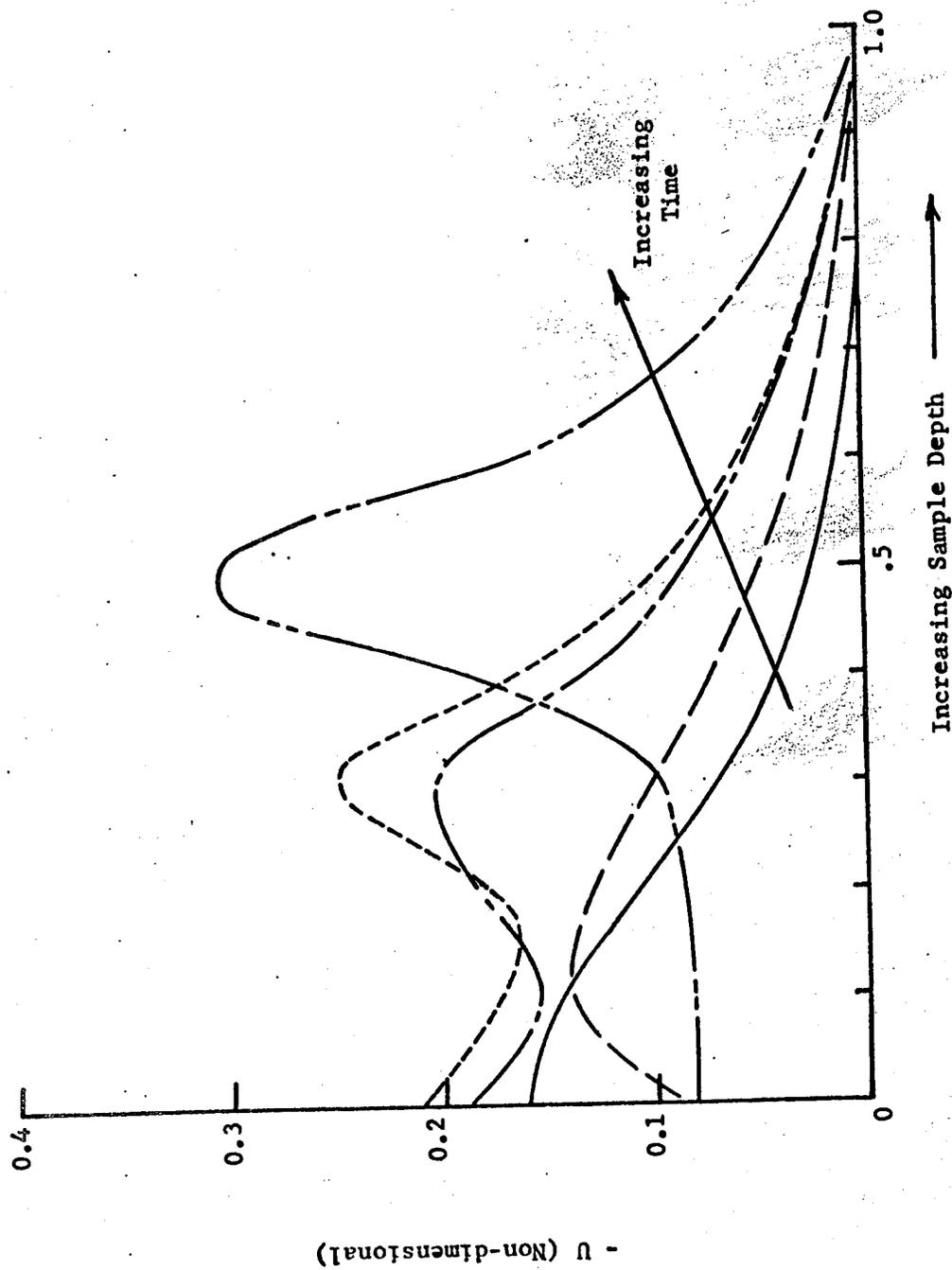


Figure 42. Time History of the Velocity Profile Within a Charring, Degrading Sample.

In view of the complexities associated with such a modeling problem, actual smoke formation processes have not been included in the preliminary model. Therefore, efforts in the forthcoming grant year will be directed toward the addition of smoke formation processes. Specifically, there is evidence to indicate that the smoke produced under nonflaming conditions consists primarily of condensible liquid compounds, and the model will be designed to investigate this hypothesis through the inclusion of two condensation mechanisms: (1) condensation resulting from homogeneous nucleation and (2) condensation resulting from the presence of heterogeneous condensation nuclei. These processes will be included both within the interior region of the sample and beyond the heated surface of the sample. It is anticipated that the predictions resulting from the model will then determine the relative importance of the two mechanisms, in addition to the primary goal of evaluating the validity of the smoke-formation-by-condensation hypothesis.

VIII. CHEMICAL ANALYSIS OF SMOKE PARTICULATES

The chemical analysis efforts have focused on two primary objectives:

(i) the analysis of compounds important because of their high toxicity and
(ii) the analysis of compounds important in determining the mechanisms of the smoke formation process. In the first category, compounds of prime interest are the low molecular weight compounds adsorbed onto the particulates which are known to possess acute toxicity (such as HCl, HCN and certain aldehydes). A sample collection and separation scheme has been developed which involves the thermal desorption of these compounds from the particulates in a stream of dry helium, then collection and concentration of the compounds with a packed trap. The volatile compounds are then thermally released for analysis by GC retention time and GC/MS. Recently work has begun on a micro-preparative GC scheme for the pre-separation of low molecular weight compounds, prior to identification by GC retention time and GC/MS. By this means, it is hoped to achieve effective "clean-up" of the complex mixture of organic compounds in the molecular weight range of approximately 44-120.

In the second category, the emphasis has been on obtaining thorough pre-separation of the complex particulate material prior to the analytical step, in order to obtain reliable compound identification. Considerable progress has been made in this direction in the analysis of the high molecular weight compounds found in the particulates. However, the very complex nature of the organic mixture and the very similar nature of many of the compounds, such as the presence of mixtures of isomers or of the members of homologous series, has made separation and identification of the studied particulates a difficult task.

A. PVC Smoke Particulates

A general scheme for the analysis of particulates collected from burning PVC samples under nonflaming conditions has been developed, which has provided good separation of the components of the complex mixture and has enabled many compounds to be identified by GC/MS. The efficiency of the system is a very great improvement on what has been achieved previously, and many compounds which were only partly resolved before have now been more fully resolved.

Essentially the scheme involves the dissolution of soluble components of the particulates in CH_2Cl_2 , filtering and removal of acidic components from the clear filtrate by washing with dilute aqueous NaOH. Following drying with MgSO_4 , and evaporation of the solvent under N_2 , the sample is injected into a high pressure liquid chromatographic system for preliminary separation. A reversed phase is used for the separation (μ Bondapak C_{18}) (see Figure 43) which produces partial resolution of the mixture. The effluents from the column are collected as six fractions, using as solvents methanol/ H_2O (75:25) for the first five cuts and pure methanol for the final cut. Repetitive separation and collection is carried out until sufficient quantities of each collected fraction are adequate for subsequent GC/MS analysis. The gas chromatographic separation of the first four of these fractions (Figures 45-48) shows greatly enhanced separation and very greatly reduced background signal compared to the mixture prior to HPLC separation (Figure 44). Fractions 5 and 6 contain high molecular weight polymeric material which is not readily resolvable by gas chromatography, and which is better examined by infra-red and ultra-violet absorption studies.

An optimum gas chromatographic packed column configuration has been developed (Ultrapond 100/120 mesh packing on a 3m length, 2mm i.d. glass column)

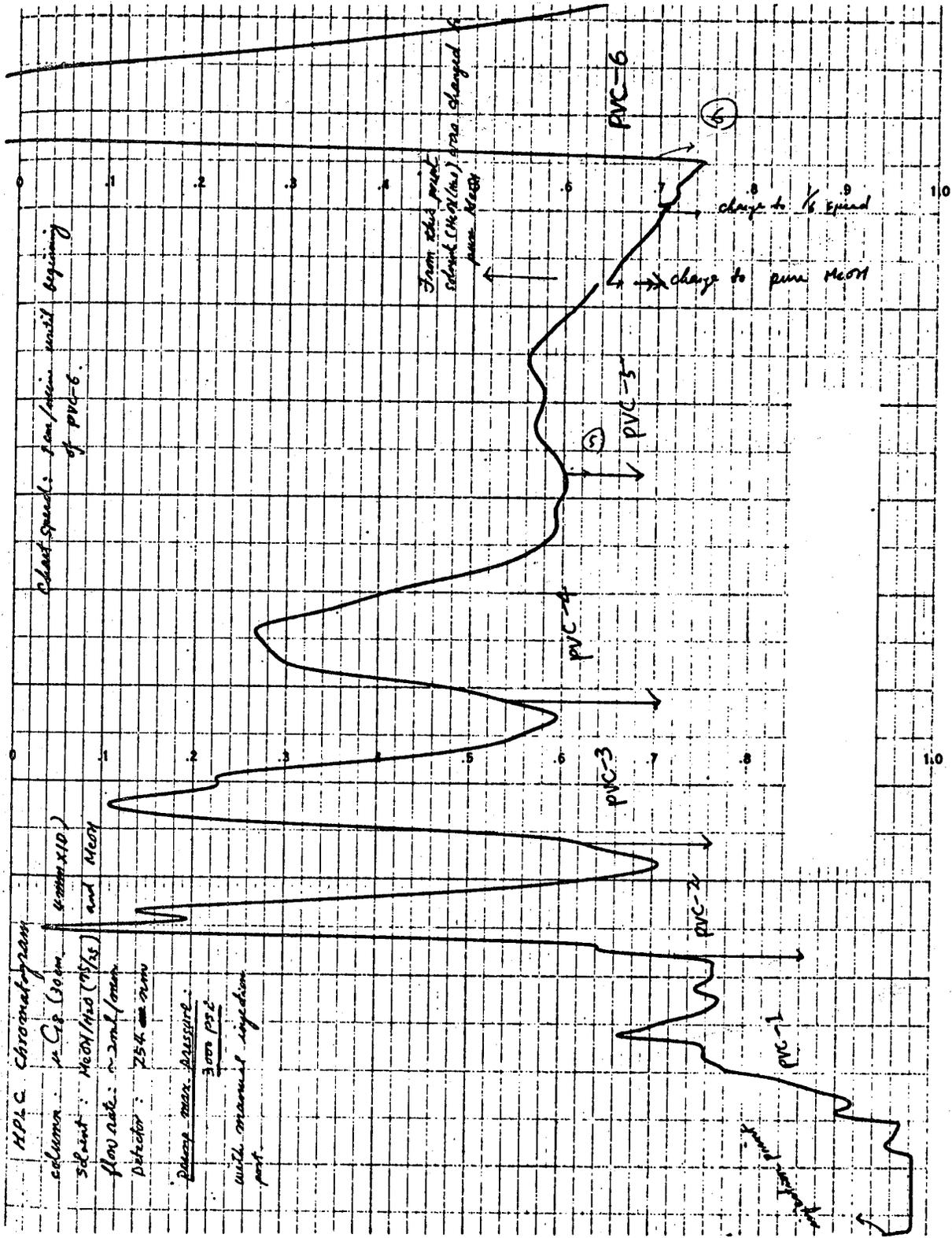


Figure 43. High Pressure Liquid Chromatogram.

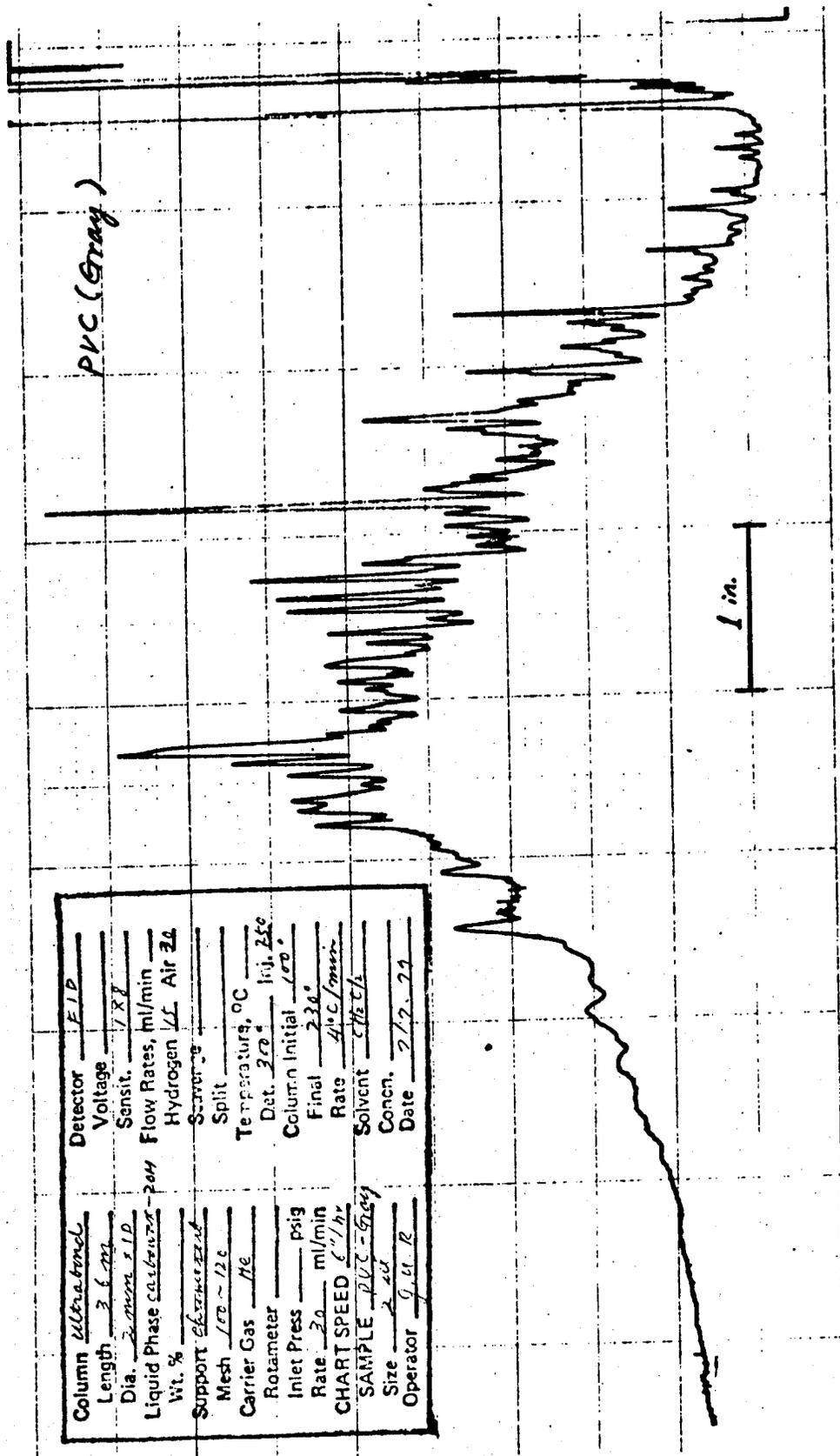


Figure 44. Gas Chromatographic Separation of PVC Smoke Particulates. Mixture prior to HPLC separation.

PVC - 1

| | |
|----------------------------------|--|
| Column <u>Alkylated</u> | Detector <u>FID</u> |
| Length <u>2.6 m</u> | Voltage <u>1 X 8</u> |
| Dia. <u>2 mm ID</u> | Sensit. <u>1 X 8</u> |
| Liquid Phase <u>Carbowax-20M</u> | Flow Rate, ml/min <u>Hyrogen 1.5 Air 2.0</u> |
| Wt. % <u>Chromosorb</u> | Support <u>Chromosorb</u> |
| Mesh <u>100-120</u> | Split <u>Temperature, °C</u> |
| Carrier Gas <u>He</u> | Det. <u>300</u> Inj. <u>250</u> |
| Rotameter _____ | Column Initial <u>100</u> |
| Inlet Press _____ psig | Final <u>230</u> |
| Rate <u>30</u> ml/min | Rate <u>4°C/min</u> |
| CHARISPEED <u>6"/hr</u> | Solvent <u>CH₂Cl₂</u> |
| SAMPLE <u>PVC-1</u> | Concn. _____ |
| Size <u>3 cc</u> | Date <u>7/16/77</u> |
| Operator <u>J. H. B.</u> | |

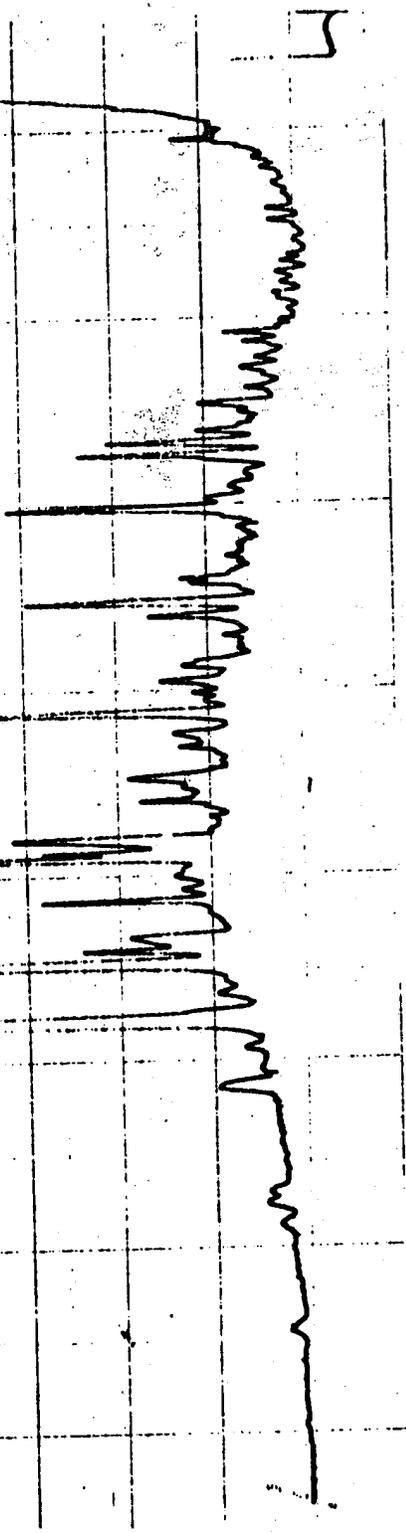


Figure 45. Gas Chromatographic Separation of PVC Smoke Particulates.

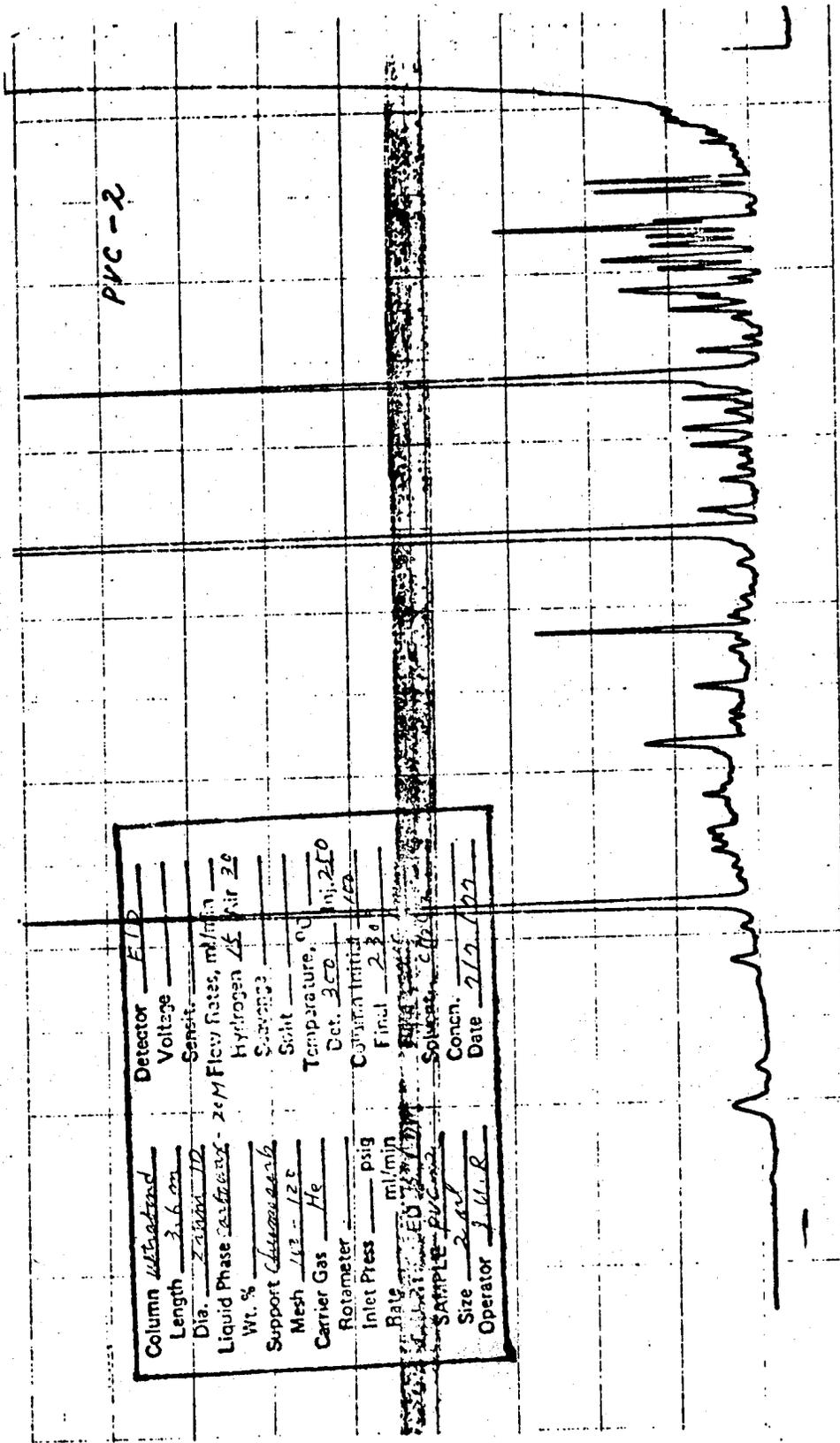


Figure 46. Gas Chromatographic Separation of PVC Smoke Particulates.

PVC-3

| | |
|----------------------------------|------------------------------------|
| Column <u>U-tube</u> | Detector <u>FID</u> |
| Length <u>36 in</u> | Voltage <u>1 X 1</u> |
| Dia. <u>2 mm x 10</u> | Sensit. <u>1 X 1</u> |
| Liquid Phase <u>Carbowax-20M</u> | Flow Rates, ml/min <u>—</u> |
| Wt. % <u>—</u> | Hydrogen <u>1.5</u> Air <u>2.0</u> |
| Support <u>Chromasorb</u> | Screening <u>—</u> |
| Mesh <u>100-120</u> | Split <u>—</u> |
| Carrier Gas <u>He</u> | Temperature, °C |
| Rotameter <u>—</u> | Det. <u>200</u> Inj. <u>210</u> |
| Inlet Press <u>—</u> psig | Column Initial <u>100</u> |
| Rate <u>30</u> ml/min | Final <u>230</u> |
| CHART SPEED <u>6"/hr</u> | Rate <u>400/minute</u> |
| SAMPLE <u>PVC-3</u> | Solvent <u>ethyl eth.</u> |
| Size <u>3.50</u> | Concn. <u>—</u> |
| Operator <u>J. L. R.</u> | Date <u>7/6/77</u> |

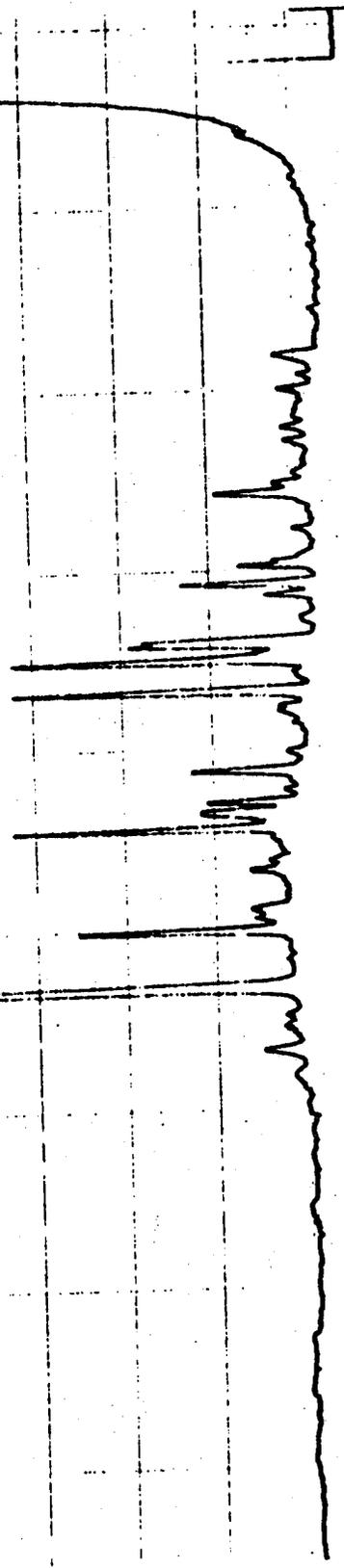


Figure 47. Gas Chromatographic Separation of PVC Smoke Particulates.

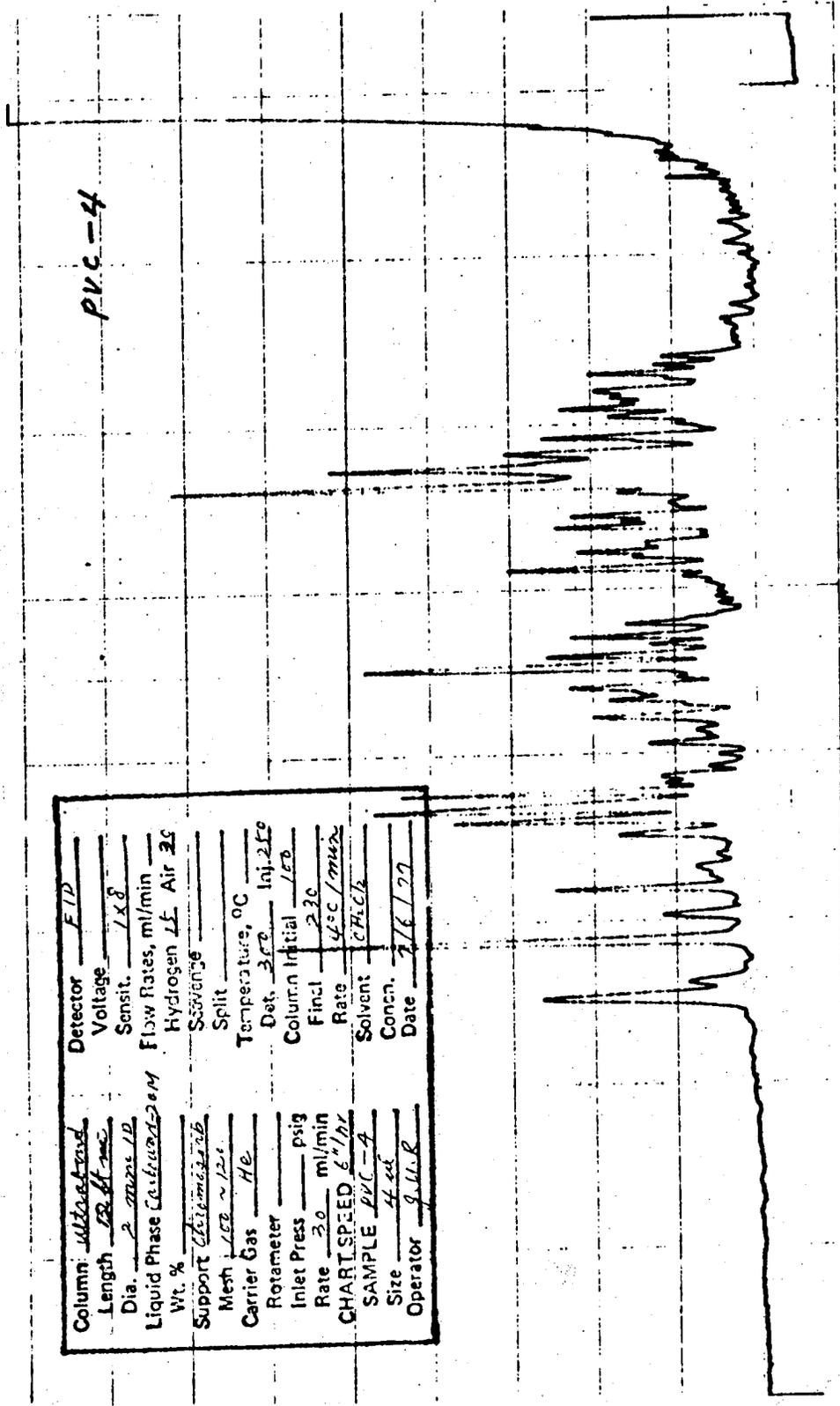
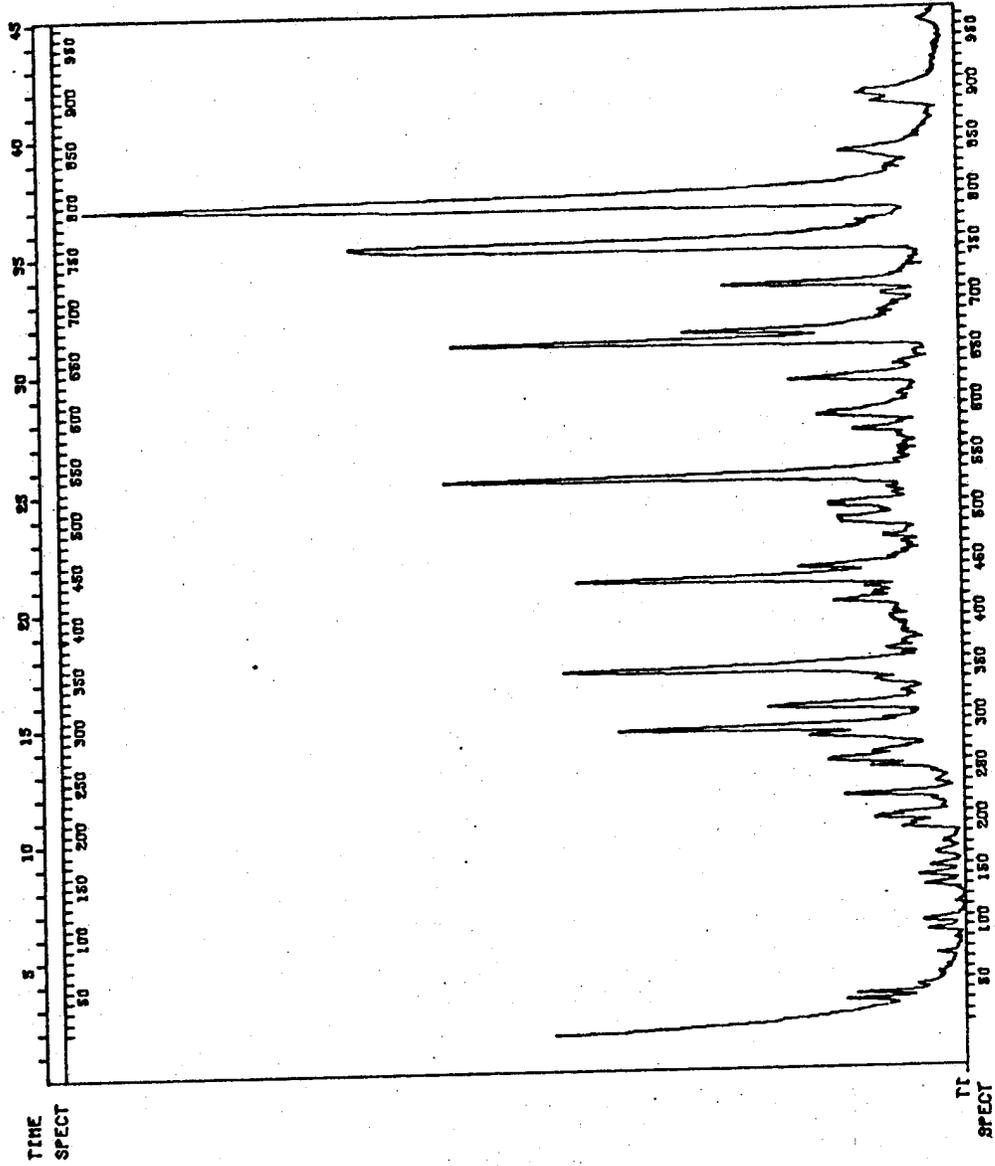


Figure 48. Gas Chromatographic Separation of PVC Smoke Particulates.

for the pre-mass-spectral separation. This column provides good reliable performance for the separation prior to MS identification. However, capillary column separation, which will be attempted in future work, may improve the separation even further. Partial identification of the column effluents has been achieved by mass spectral comparison with reference data files, but further confirmatory work has to be carried out using UV and IR absorption techniques and GC retention times in comparison with authentic reference materials before unequivocal assignments can be made.

In the process of MS identification, use has been made of single ion chromatograms (monitoring M^+ ions, base peaks and some important fragmented ions in the mass spectra). The total and single ion chromatograms shown in Figures 49-63 represent the chromatograms of collected fractions separated by HPLC (see Figure 43). Figures 49-51 represent cut # 1, Figures 52-54 represent cut # 2, Figures 55-59 represent cut # 3 and Figures 60-63 represent cut # 4. The deterioration in gas chromatographic resolution as the later HPLC cuts are examined is clear. The final cuts (Nos. 5 and 6) give very little useful information, and are not shown here. The single ion chromatograms of three of the PVC samples (FRN. Nos. 5029, 5010, 5011, 5025 and 5026 (Figures 49-59) show the complex isomeric nature of many of the compound peaks. M^+/e :142 (methylnaphthalenes), 156 (dimethylnaphthalenes and/or ethylnaphthalenes), 166 (fluorene), and 178 (phenanthrene and anthracene) are observable. With PVC sample FRN No. 5011, phenanthrene and anthracene were partly resolved (see Figure 53). Phthalates (at M^+/e 149) appear in all chromatograms; however, identification by mass spectrometry alone will probably not be adequate to identify phthalates because of the similarity of the mass spectra of such homologous series. Note also that PVC sample # 4 (Figures 60-63) shows an even more complex pattern of compounds than the first



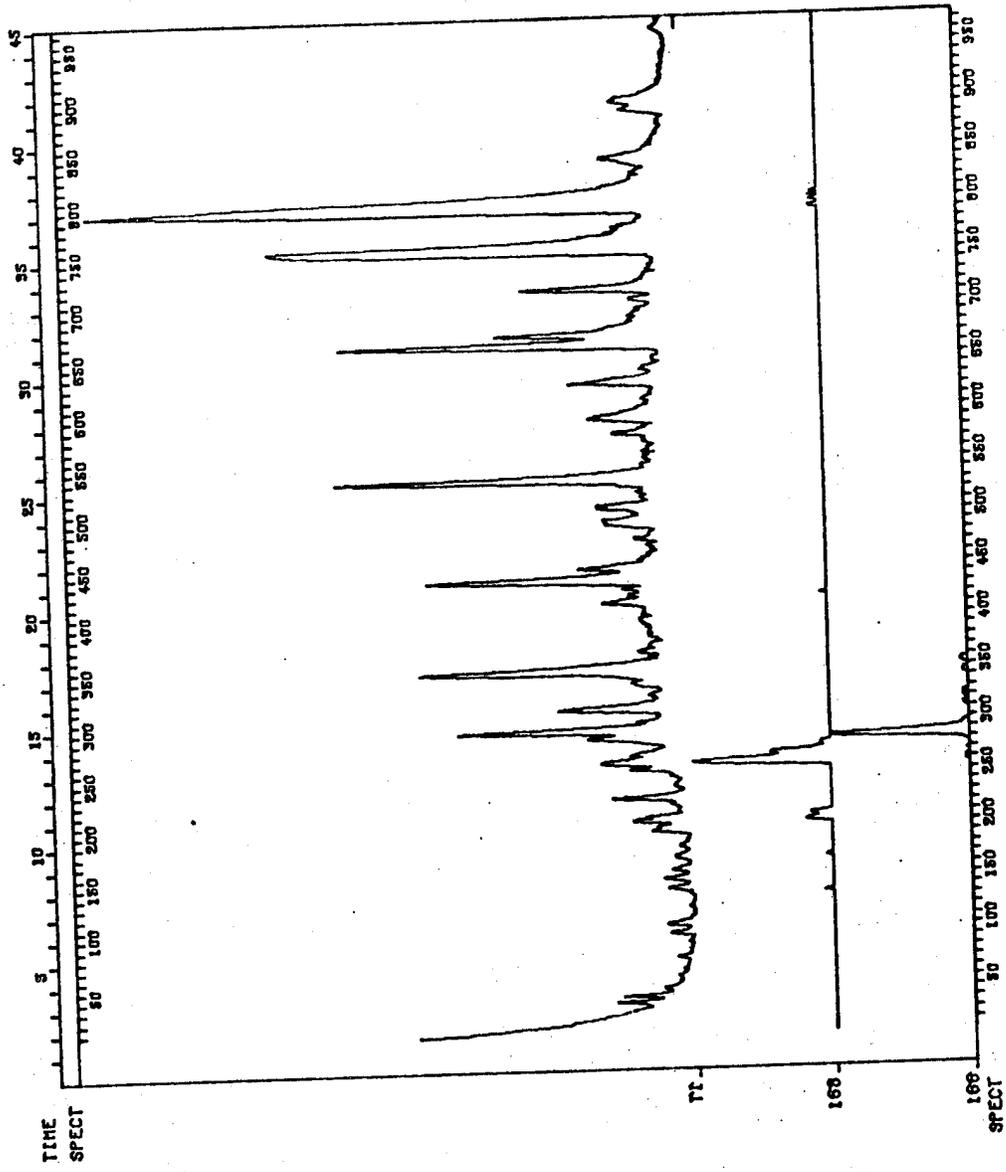
SAMPLE 5029
 50 < M < 300

PVC-1 IN CH2CL2, 10FT ULTR, HE=30ML/M, T1=100.4C, T2=240.0T, F1=25

9/21/77, J.V.: RME

STARTING MASS 50

Figure 49. Total Ion Chromatogram for PVC Smoke Particulates.



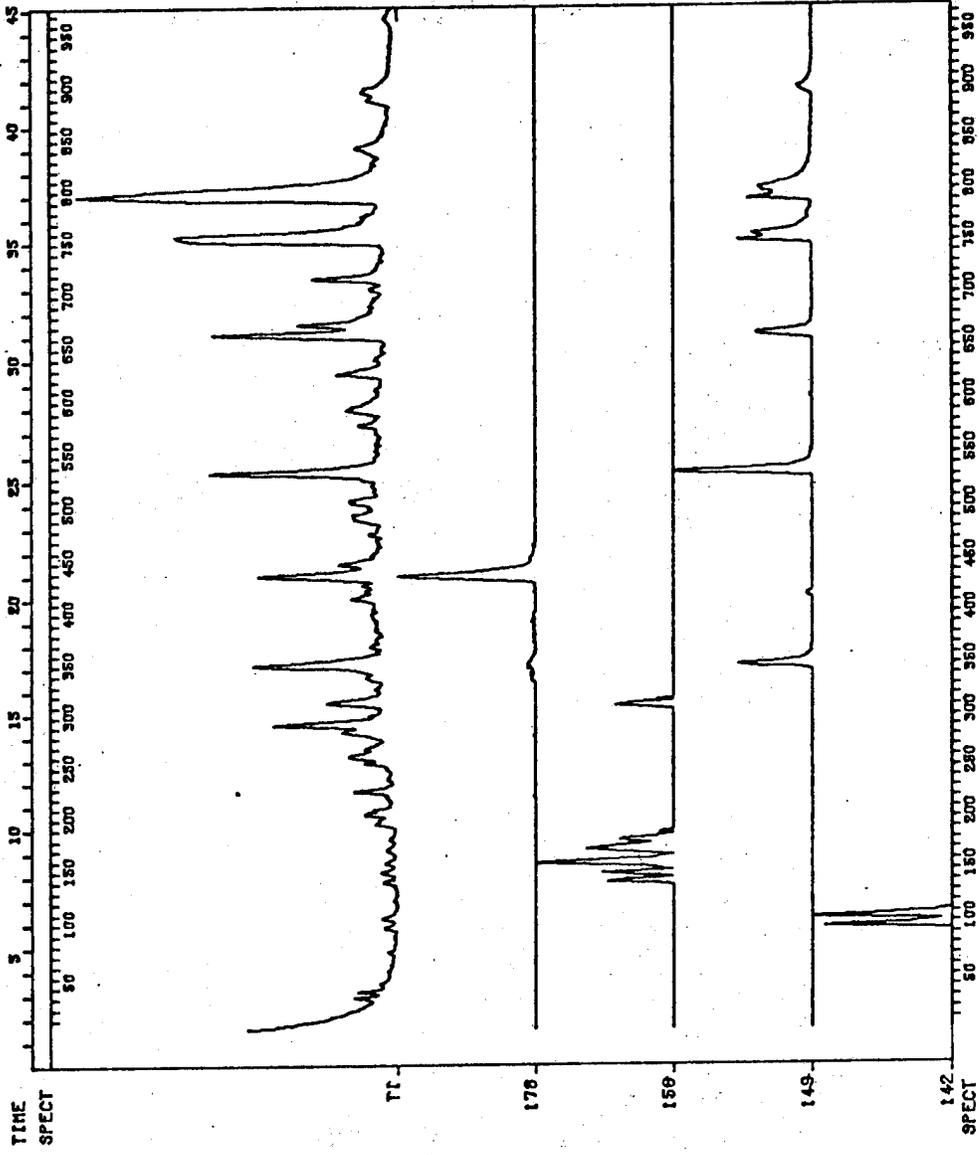
SAMPLE 5029
 50 < M < 300

PVC-1 IN CH2CL2, ICFI UL.F8.HE=30HL/M, F1=100.4C, F2=240.1F=25

8/21/77, J.V.-RHEE

STARTING MASS 50

Figure 50. Single and Total Ion Chromatograms for PVC Smoke Particulates.



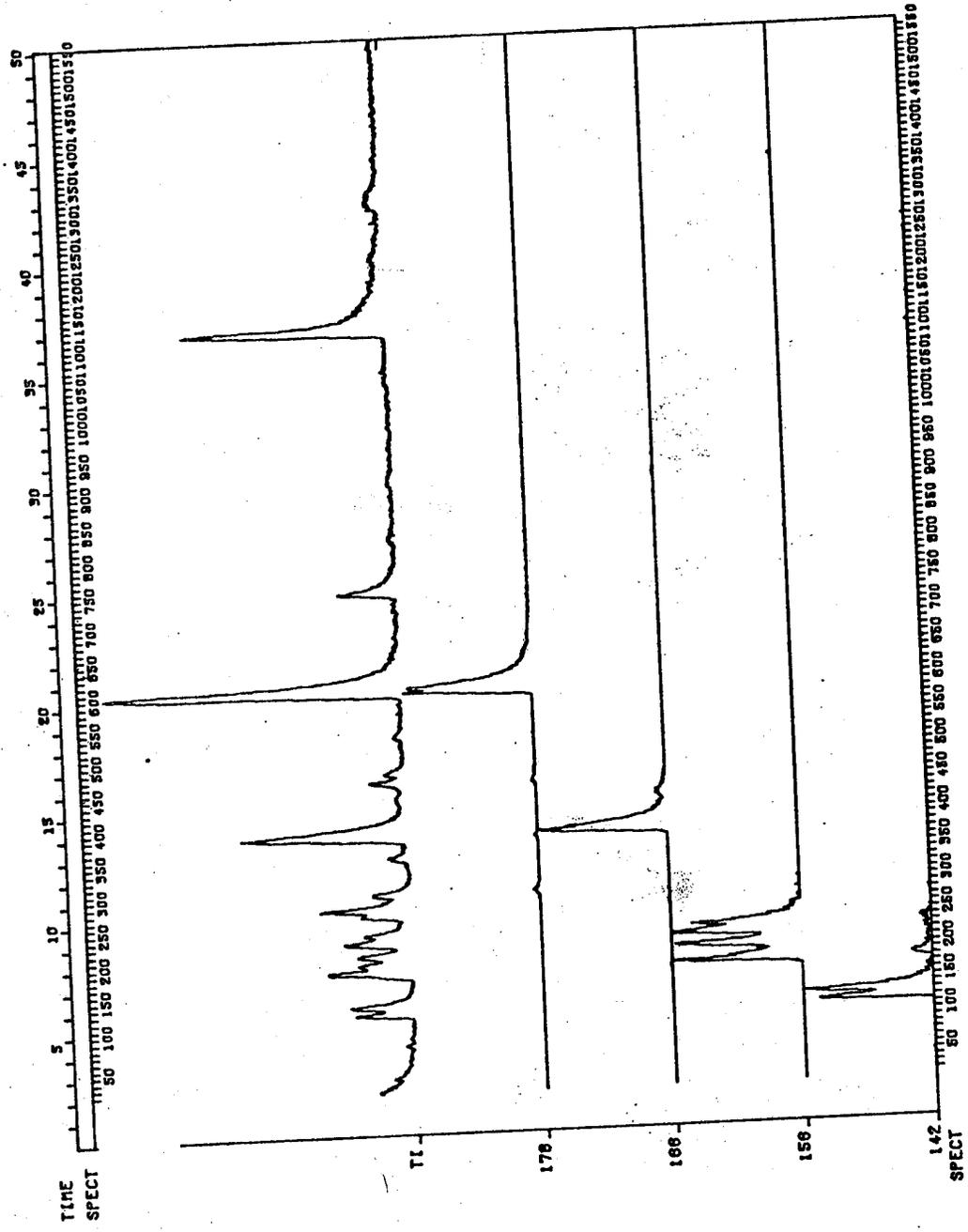
SAMPLE 5029
 50 < M < 300

PVC-1 IN CH2CL2, 10FT ULTB, HE=30ML/M, T1=100, FC, T2=240, T1=25

9/21/77, J.U. RHEE

STARTING MASS 50

Figure 51. Single and Total Ion Chromatograms for PVC Smoke Particulates.



PVC-2 IN CH2CL2
 T1=100, 2MIN, T2=230, 18
 STARTING M93 50

Figure 52. Single and Total Ion Chromatograms for PVC Smoke Particulates

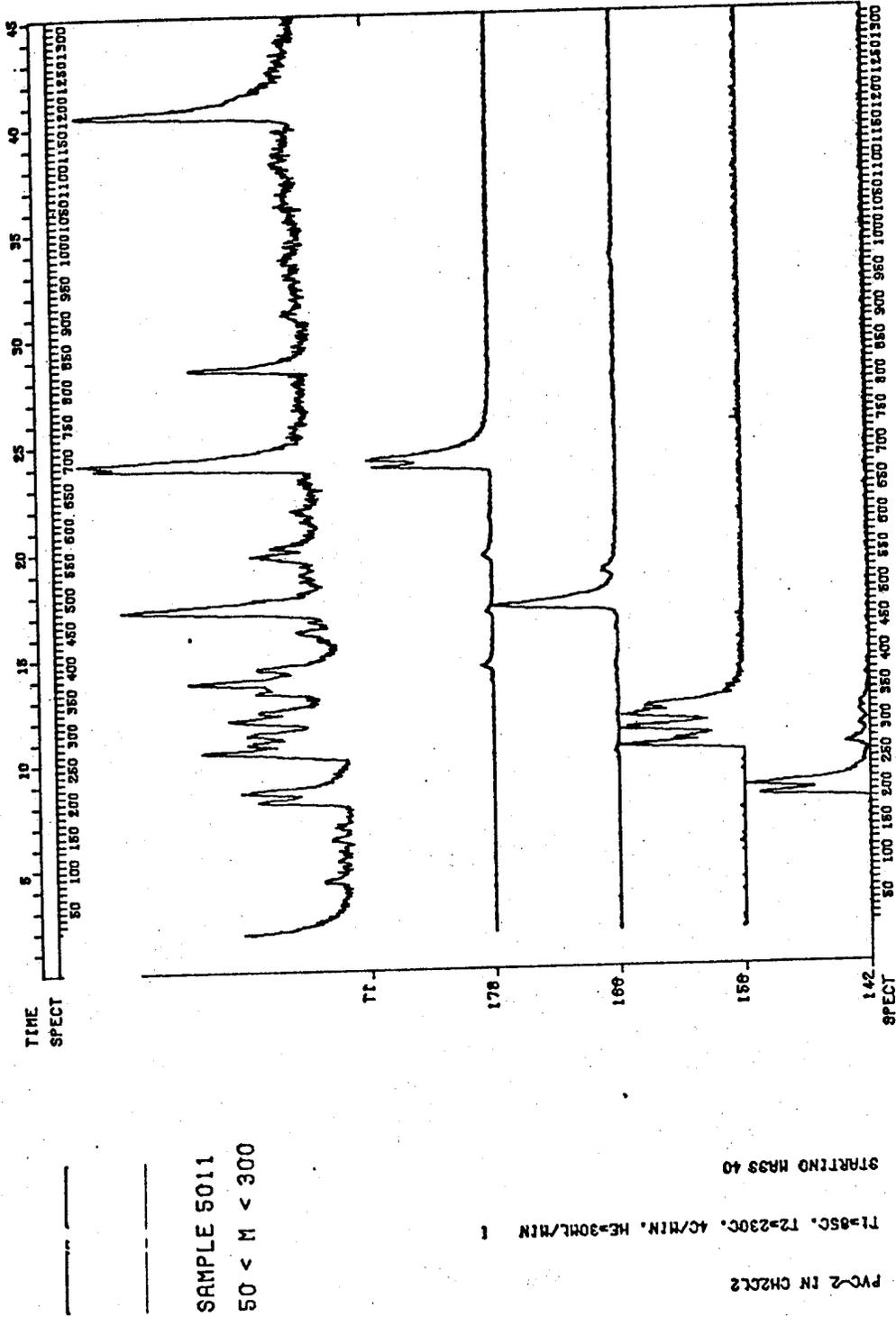
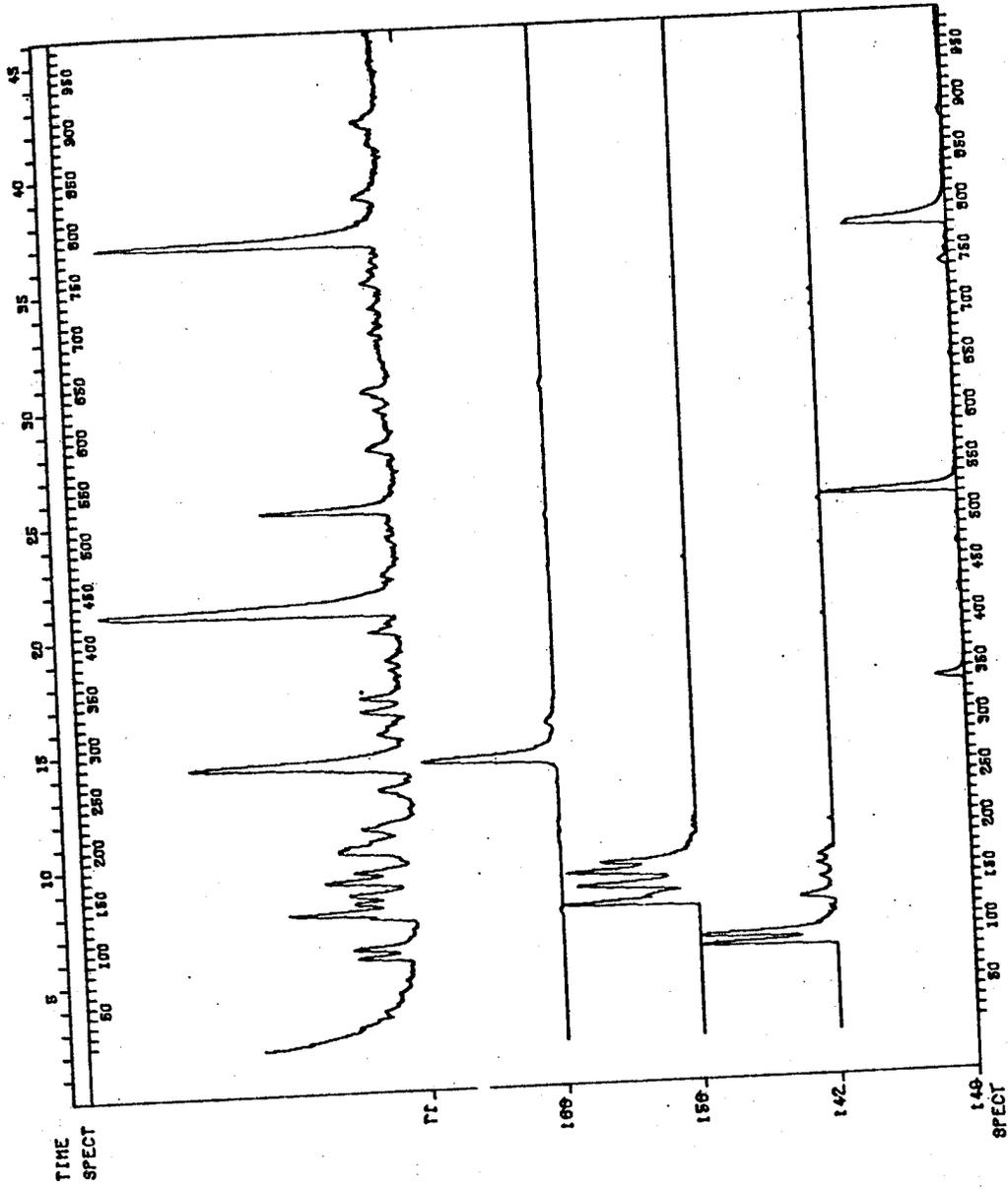


Figure 53. Single and Total Ion Chromatograms for PVC Smoke Particulates



PVP-2 IN CH2CL2, F1=100, 40/H, F2=240, HE=30NL/II, 10FT ULTB9
 5/19/77
 STARTING MASS 50
 SAMPLE 5026
 50 < M < 300

Figure 54. Single and Total Ion Chromatograms for PVC Smoke Particulates.

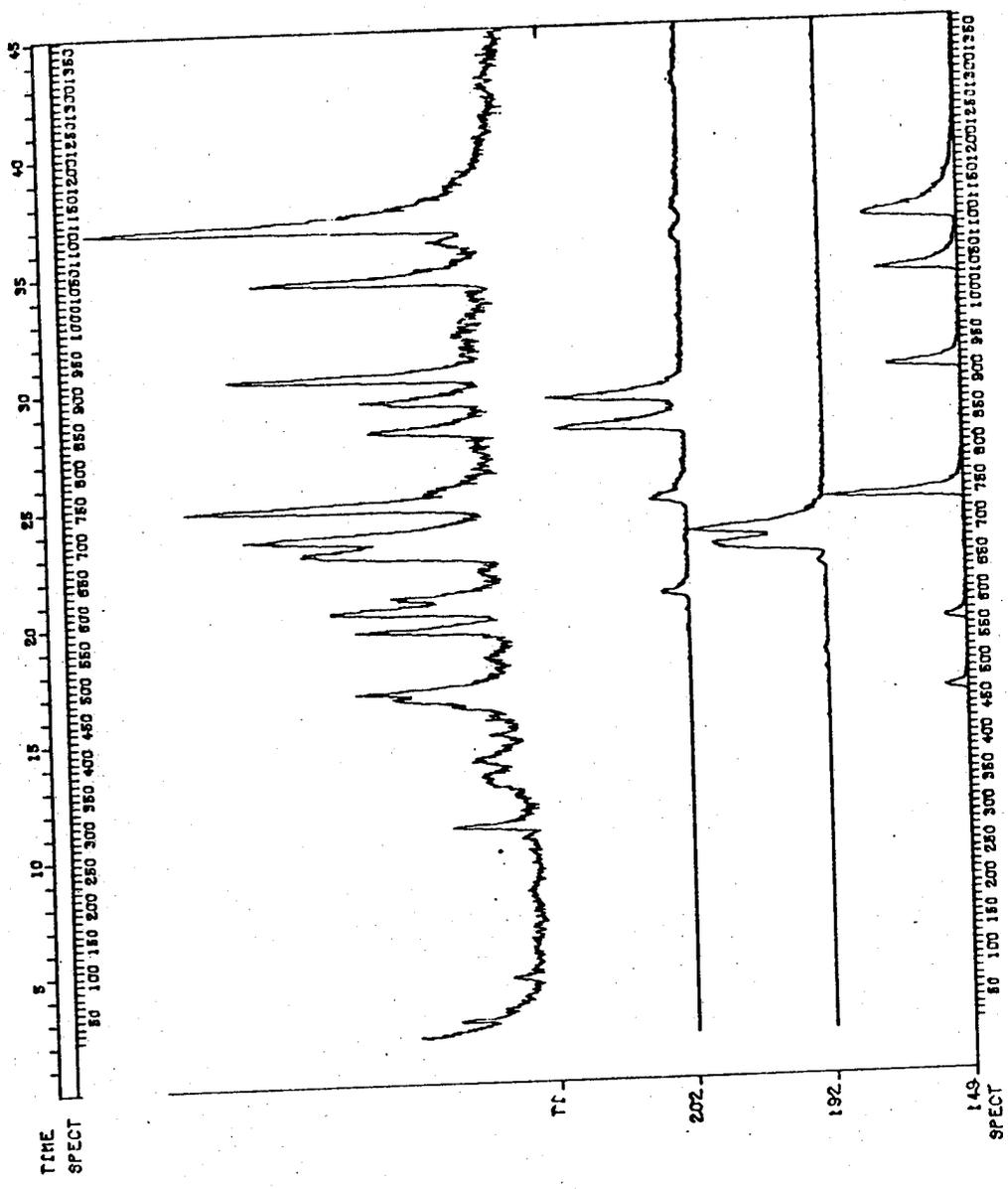
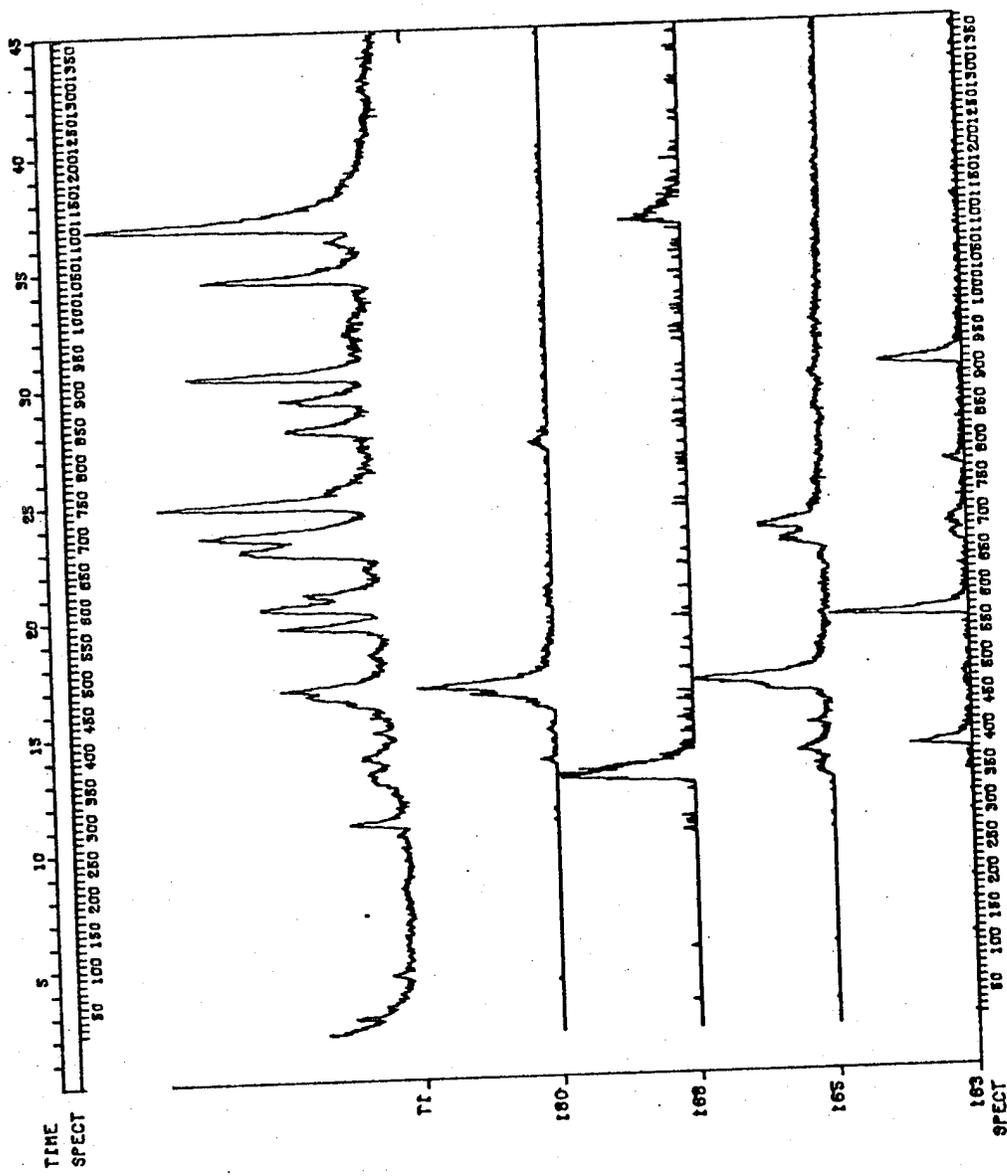


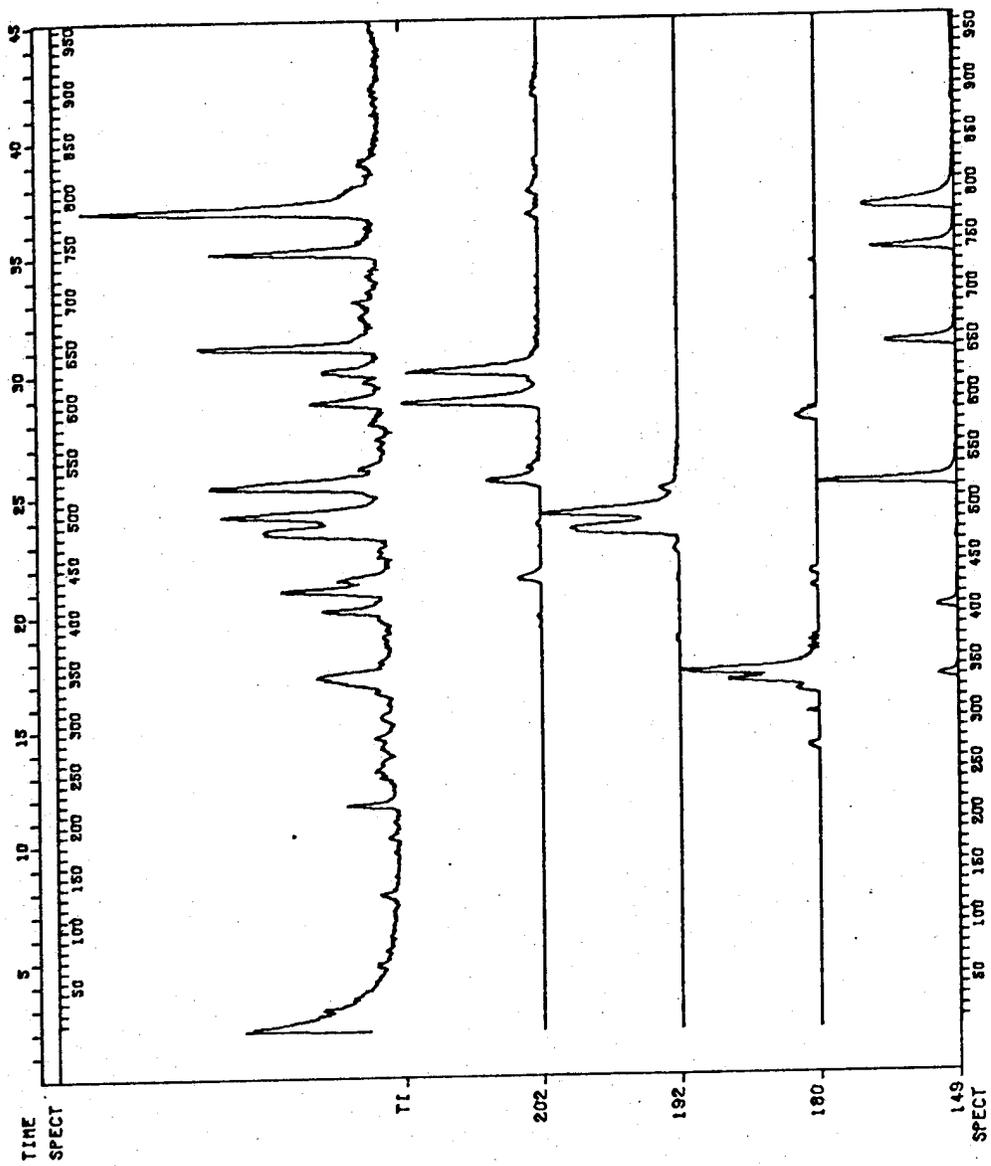
Figure 55. Single and Total Ion Chromatograms for PVC Smoke Particulates



PVC-3 IN CH2CL2, 4/18/77
 T1=100C, 4C/MIN, T2=230C, HE=30ML/MIN 2
 STARTING M93 50

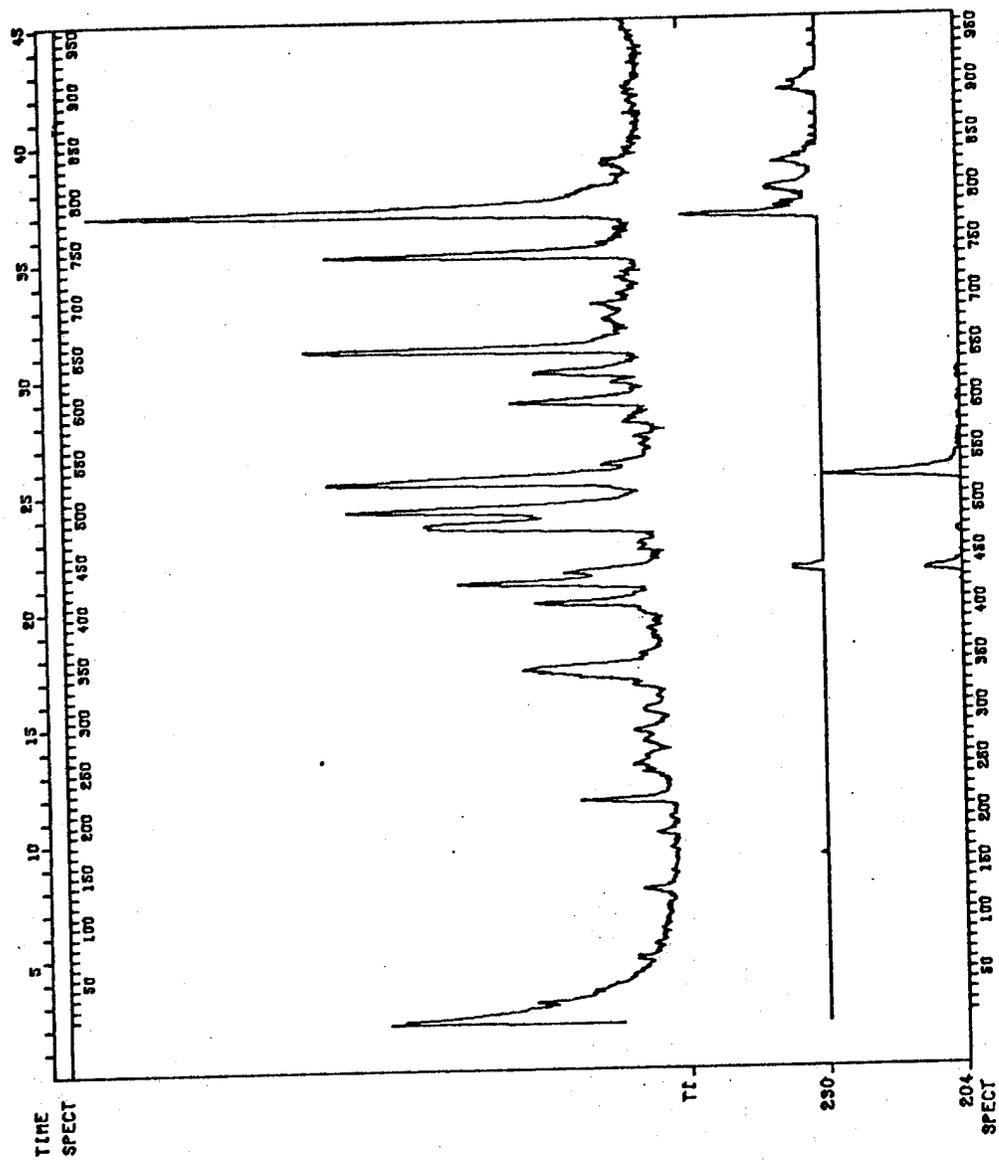
SAMPLE 5025
 50 < M < 300
 50 < M < 300

Figure 56. Single and Total Ion Chromatograms for PVC Smoke Particulates



PVC-3 IN CH2CL2, T1=100, 4C/M, T2=250, HE=30ML/M, FT-250, DT
 9/18/77
 STARTING MASS 50
 SAMPLE 5025
 50 < M < 300

Figure 57. Single and Total Ion Chromatograms for PVC Smoke Particulates.



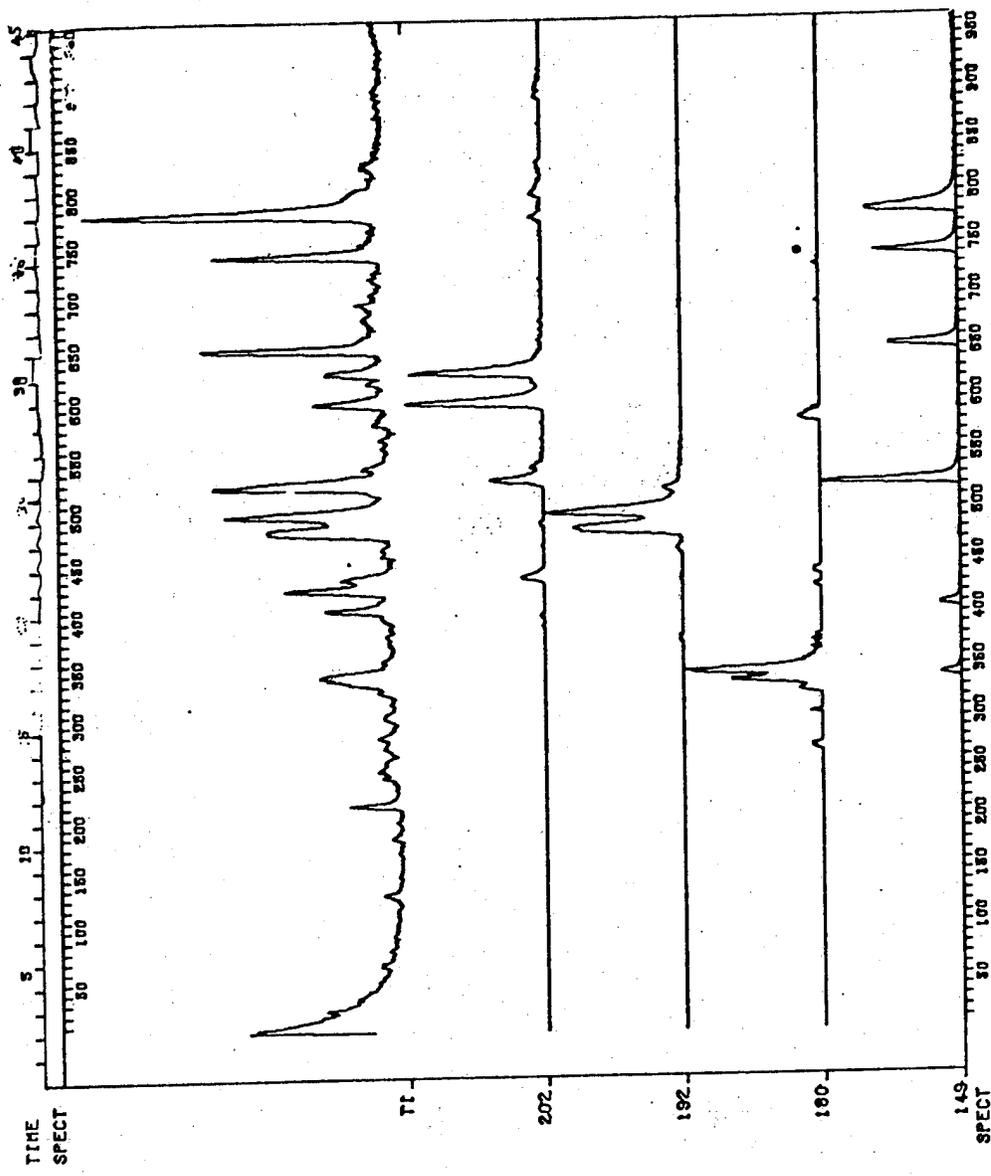
SAMPLE 5025
 50 < M < 300

PVC-3 IN CH2CL2, T1=100, 4C/M, T2=250, HE=30ML/N, FT-250, DT

9/19/77

STARTING MASS 50

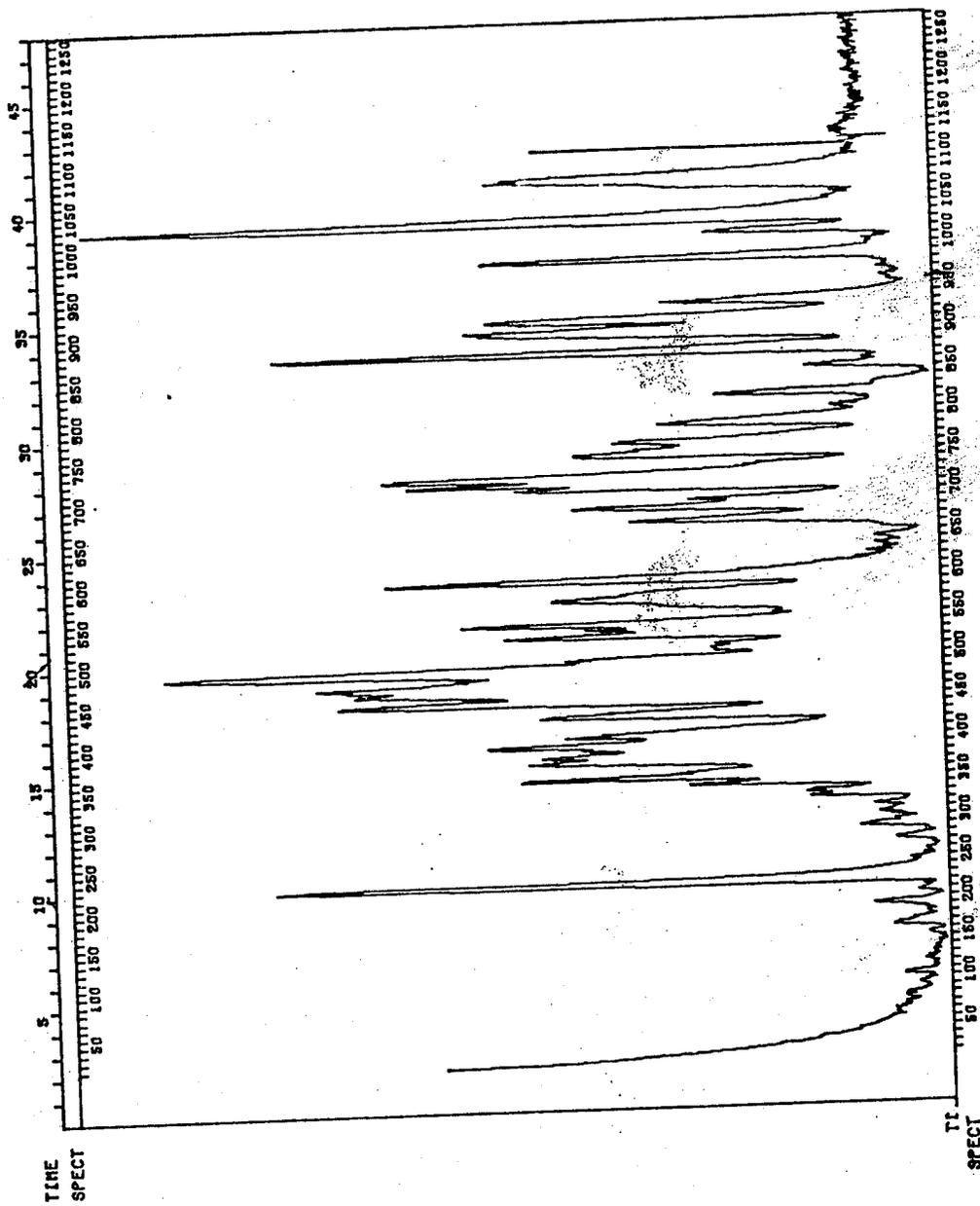
Figure 58. Single and Total Ion Chromatograms for PVC Smoke Particulates.



SAMPLE 5025
 50 < M < 300

PVC-3 IN CH2CL2, T1=100, 4C/N, T2=250, HE=30NL/M, T1-250, 01
 8/19/77
 STARTING MASS 50

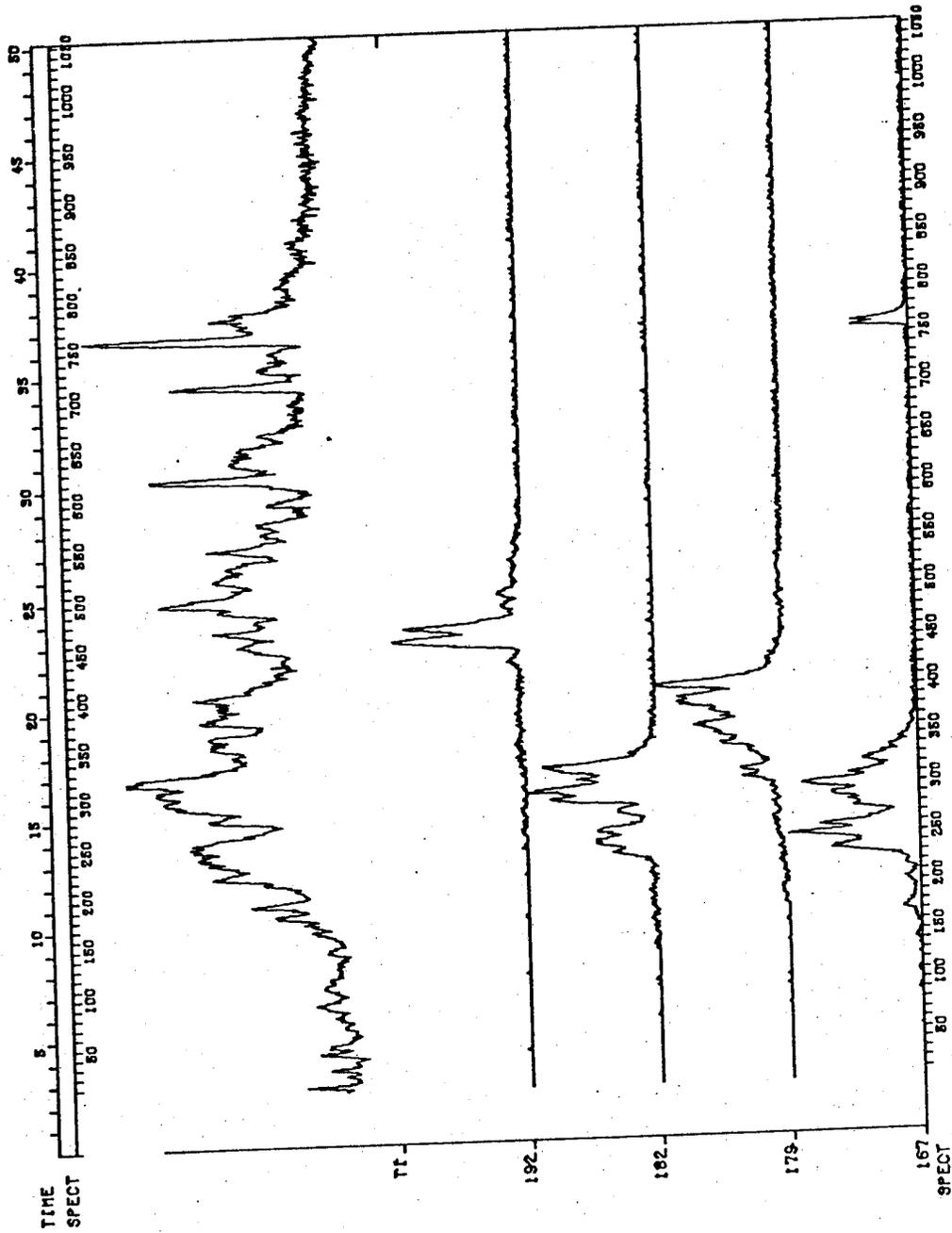
Figure 59. Single and Total Ion Chromatograms for PVC Smoke Particulates.



PVC-4 IN CH2CL2. 9/8/77
 T1=100.4C/MIN. T2=250. DT=300.ME
 STARTING MASS 50

SAMPLE 5011
 50 < M < 300

Figure 60. Total Ion Chromatogram for PVC Smoke Particulates.



SAMPLE 5029
 50 < M < 300

PVC-4 CH2CL2 BY LC. 4/20/77
 T1=100C, T2=240C, 4C/MIN, HE=0.2,
 STARTING MASS 50

Figure 61. Single and Total Ion Chromatograms for PVC Smoke Particulates

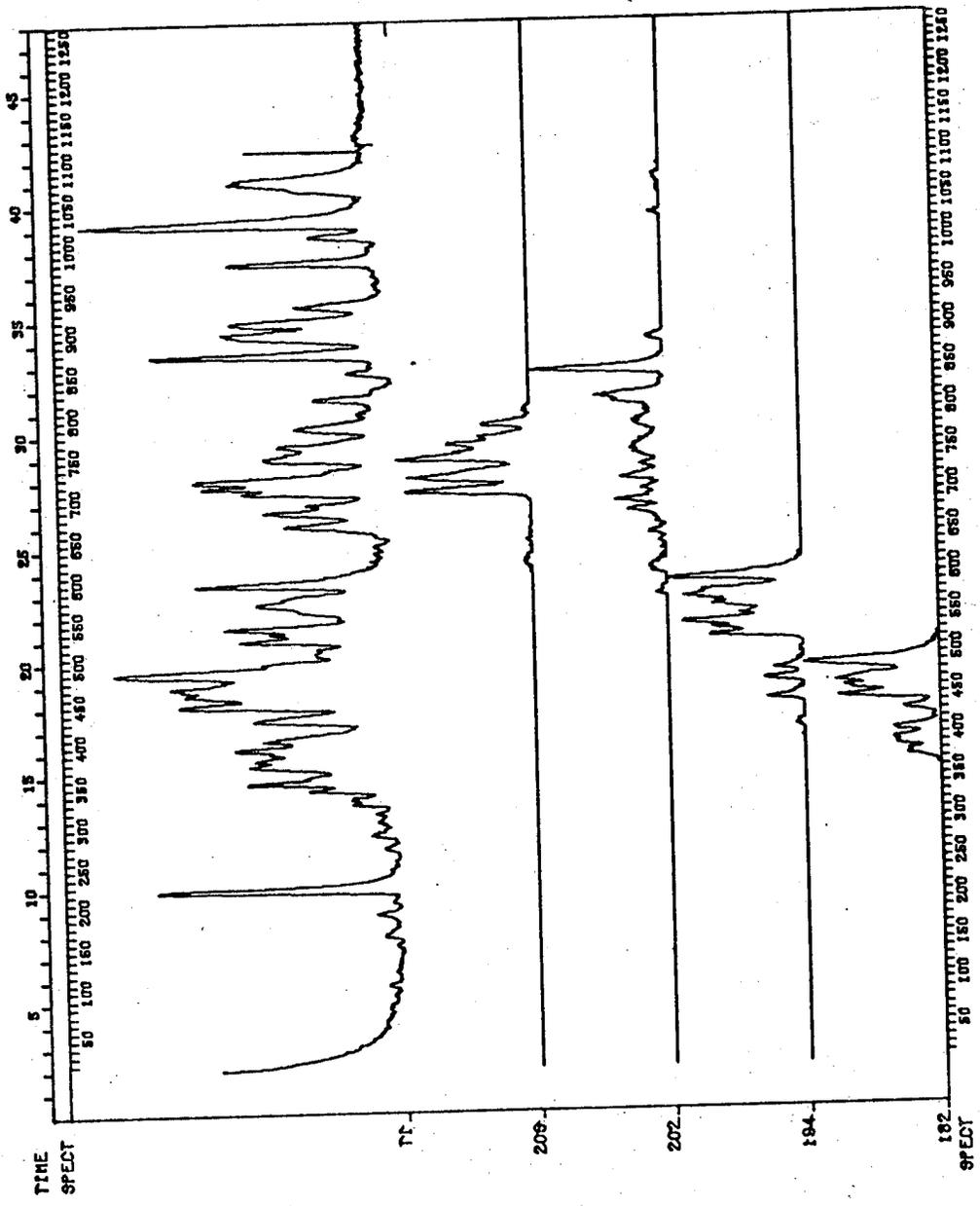
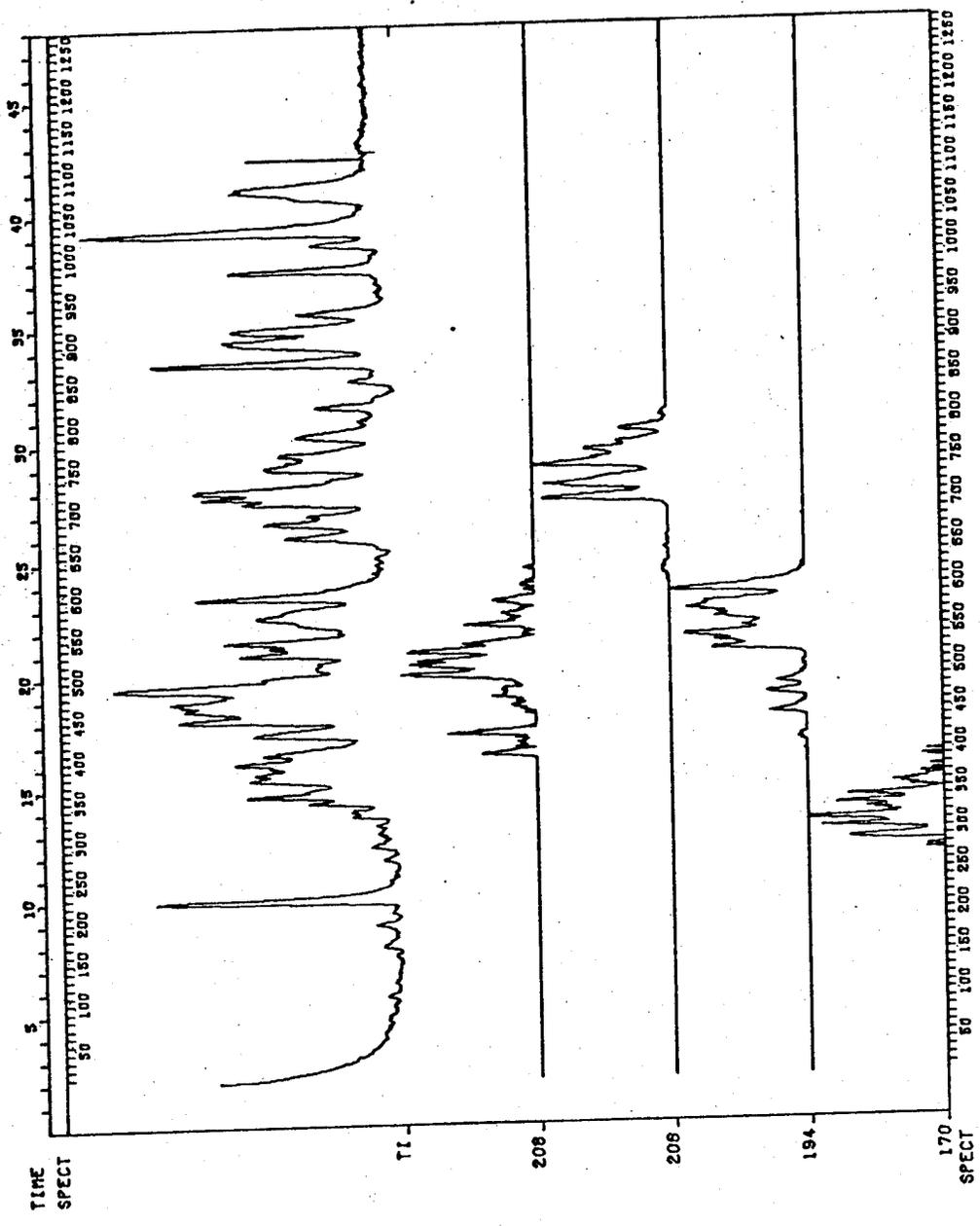


Figure 62. Single and Total Ion Chromatograms for PVC Smoke Particulates.



SAMPLE 5011
 50 < M < 300

PVC-4 IN CH2CL2, 9/6/77
 T1=100, C/M/N, T2=250, T1=250, DT=300, ME=
 STARTING MASS 50

Figure 63. Single and Total Ion Chromatograms for PVC Smoke Particulates.

three cuts.

B. Summary

To summarize the chemical analysis data; it has been possible to achieve very good separation of PVC particulates by HPLC and GC and also to identify many of the compounds by GC/MS. While further confirmatory work is necessary by IR and UV analysis and by comparison of data with that from reference materials, a good working scheme has been developed for the higher molecular weight components of the particulates.

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