no action

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 1/18/78

Project Title: "Investigation of the Properties of the Combustion Products Generated by Building Fires."

Project No: E-16-647

Project Director: Dr. B. T. Zinn

Sponsor: Products Research Committee; The Society of the Plastics Industry, Inc.

Agreement Period: From 1/1/78 Until 12/31/78

Type Agreement: Research Agreement dated 1/10/78

Amount:

$37,908	(PRC - E-16-647)
3,416	(GIT - E-16-324)
$41,324	TOTAL

Reports Required: Quarterly Progress Reports, Final Report

Sponsor Contact Person (s):

Technical Matters

Contractual Matters
(thru OCA)

Lowell R. Perkins, Executive Director
Products Research Committee
c/o John W. Lyons
Bldg. 225, Room B-142
National Bureau of Standards
Washington, D. C. 20234

Defense Priority Rating: N/A

Assigned to: Aerospace Engineering (School/Laboratory)

COPIES TO:

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- Division Chief (EES)
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- Project Code (GTRI)
- Other

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION

Date: 3/19/79

Project Title: Investigation of the Properties of the Combustion Products Generated by Building Fires.

Project No: E-16-647/G-33-633

Project Director: Dr. B. T. Zinn/Dr. R. F. Browner

Sponsor: Products Research Committee - The Society of the Plastics Industry, Inc.

Effective Termination Date: 1/31/79

Clearance of Accounting Charges: 1/31/79 (Fixed Price)

Grant/Contract Closeout Actions Remaining:

x Final Invoice ~~and Closing Documents~~
_ Final Fiscal Report
_ Final Report of Inventions
_ Govt. Property Inventory & Related Certificate
_ Classified Material Certificate
_ Other ____________

Assigned to: Aerospace Engineering/Chemistry (School/Laboratory)

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Library, Technical Reports Section
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Other ____________

CA–4 (1/79)

E 16-647

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
AEROSPACE ENGINEERING

404-894-3000

DANIEL GUGGENHEIM SCHOOL
OF AERONAUTICS

To: Products Research Committee

From: Ben T. Zinn, Regents' Professor; Principal Investigator

Subject: Quarterly Progress Report for PRC Research Project No. RP-77-UU-4: Investigation of the Properties of the Combustion Products Generated by Building Fires; for the period January 1, 1978 to March 31, 1978.

This quarterly report describes the efforts conducted under PRC Research Project No. RP-77-U-4 during the period January 1, 1978 to March 31, 1978, in the School of Aerospace Engineering, Georgia Institute of Technology. Progress which has been made to date is described according to the tasks which were set forth in the revised research proposal. Note that since the detailed quarterly reports submitted during the previous grant year required a considerable expenditure of time in preparation, the quarterly reports for this grant year will be of a more concise nature in order to more productively utilize the personnel assigned to the project. All data which are reviewed in these reports will be documented in detail in the final report. Other contributing personnel were Drs. C. P. Bankston, R. F. Browner, E. A. Powell, J. C. Liao, T. K. Joseph and Mr. R. O. Gardner.

TASK A. Determination of the Effect of Substrate Polymer Structure on Smoke Characteristics.

Tests have been initiated in the Combustion Products Test Chamber (CPTC) for the purpose of analyzing the effect of cellular polymer structure on the smoking characteristics of foam materials. The four foams selected from the PRC standard sample bank for study are: flexible polyurethane foam (GM-21), rigid polyurethane foam (GM-29), rigid trimer foam (GM-31), and expanded polystyrene (GM-47). Room temperature (25°C) tests (horizontal mount) of each of these materials have been conducted under nonflaming conditions and flaming tests at room temperature are presently underway. Preliminary analysis of the nonflaming data (Table 1) shows that three of the foams produced less than 10 percent of the sample weight loss as smoke particulates, while one sample (GM-47) exceeded 10 percent. Also, the mass median diameters calculated from cascade impactor data show that the polystyrene (GM-47) produced the largest particle sizes and the rigid trimer generated extremely small particles. Analysis of these data and the forthcoming flaming data will continue with the aim of correlating smoke properties with the substrate polymer characteristics.

TASK B. Determination of the Effect of Additives on Smoke Characteristics.

Tests of the four fire retarded foam compositions (GM-23, GM-31, GM-43 and GM-49) which correspond to the non-fire retarded compositions studied in Task A will be initiated during the next quarter. Results can then be compared with the results of tests of the non-fire retarded samples in order to correlate the effects of fire retardants on smoke characteristics.

TASK D. Chemical Analysis of Smoke Particulates.

A new analytical technique has been developed for the purpose of separating, identifying and quantitating the amounts of polynuclear aromatic hydrocarbons (PAH) in smoke particulates (see Table 2). This analytical technique has been applied to the smoke particulates generated by a fire-retarded flexible polyurethane foam (GM-23) combusted under nonflaming conditions at 5 W/cm^2 in air in the CPTC. The results for this material show that no detectable amounts of PAH are present in the smoke particulates generated under the stated conditions. Efforts are currently underway to develop a scheme for the analysis of the "non-PAH" fraction which is present in polyurethane smoke particulates.

A small (approximately 1.5 liters in volume) combustion chamber and sampling system have been assembled for the accurate analysis of toxic gases adsorbed on smoke particulates. Combustion is carried out under continuous ventilation and samples are heated by a Nichrome coil. The smoke particulates are trapped by a 47 mm glass fiber filter and the gases desorbed by heating are collected in a cold-trap. Collected gases are then introduced directly into a Gas Chromatograph/Mass Spectrometer System for analysis and identification. Checkout and calibration of this new facility is presently underway and testing will begin during the next quarter.

Table 1.

Preliminary Smoke Properties Data

Nonflaming Conditions - 5 W/cm^2

	Γ	D_{MMD}	Char Residue- % Initial Sample Weight
GM-21	.064	1.23	T
GM-29	.070	0.82	39.0
GM-41	.047	0.26	62.0
GM-47	.114	1.84	T

Γ = Fraction of sample weight loss converted to smoke particulates

D_{MMD} = Mass median diameter

T = Trace quantity

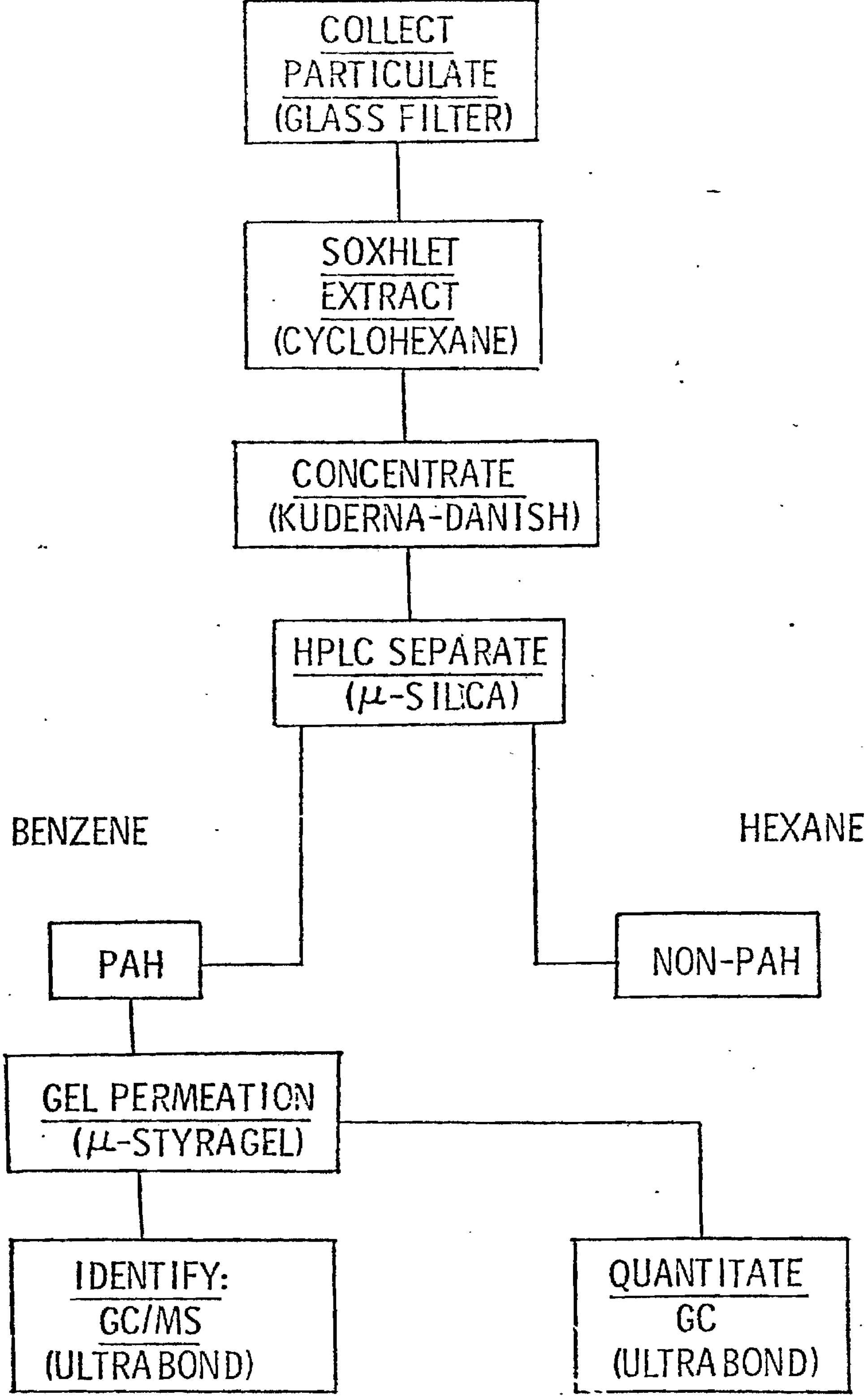

COLLECT PARTICULATE (GLASS FILTER)
SOXHLET EXTRACT (CYCLOHEXANE)
CONCENTRATE (KUDERNA-DANISH)
HPLC SEPARATE (μ-SILICA)
BENZENE
HEXANE
PAH
NON-PAH
GEL PERMEATION (μ-STYRAGEL)
IDENTIFY: GC/MS (ULTRABOND)
QUANTITATE GC (ULTRABOND)

Table 2.

E-16-647

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
AEROSPACE ENGINEERING

404-894-3000

DANIEL GUGGENHEIM SCHOOL
OF AERONAUTICS

To: Products Research Committee

From: Ben T. Zinn, Regents' Professor; Principal Investigator

Subject: Quarterly Progress Report for PRC Research Project No. 75-115: Investigation of the Properties of the Combustion Products Generated by Building Fires; for the period April 1, 1978 to June 30, 1978.

This quarterly report describes the efforts conducted under PRC Research Project No. 75-115 during the period April 1, 1978 to June 30, 1978, in the School of Aerospace Engineering, Georgia Institute of Technology. Progress which has been made to date is described according to the tasks which were set forth in the revised research proposal. Other contributing personnel were Drs. C. P. Bankston, R. F. Browner, E. A. Powell, T. K. Joseph and Mr. R. O. Gardner.

TASK A. Determination of the Effect of Substrate Polymer Structure on Smoke Characteristics.

Tests have been carried out in the Combustion Products Test Chamber (CPTC) for the purpose of analyzing the effect of cellular polymer structure on the smoking characteristics of foam materials. The four foams selected from the PRC standard sample bank for study are: flexible polyurethane foam (GM-21), rigid polyurethane foam (GM-29), rigid trimer foam (GM-31), and expanded polystyrene (GM-47). Room temperature (25°C) tests (horizontal mount) of each of these materials have been conducted under flaming conditions. Analysis of these data (Table 1) shows that GM-29 and GM-47 have the greatest tendency to smoke, where GM-29 also exhibited the highest peak optical density. The flexible urethane foam (GM-21) generated the least amount of smoke and the rigid trimer (GM-41) generated a relatively moderate amount of particulates. Particle sizes are in the one micron range with the polystyrene foam generating the largest particles. Samples which tend to leave a measurable fraction of the initial weight as char (GM-29 and GM-41), left less residue in the flaming case than in the nonflaming case. The corresponding data for nonflaming conditions are presented in Table 2; comparisons of smoking tendencies and particle diameters show that differences in particulate properties between flaming and nonflaming conditions depend upon the individual material considered.

TASK B. Determination of the Effect of Additives on Smoke Characteristics

The four fire retarded foam compositions (GM-23, GM-31, GM-43 and GM-49) which correspond to the non-fire retarded compositions studied in Task A have been procured and studies of these materials have been initiated. Some delays in the test program have slowed progress on this Task; however, flaming and nonflaming tests at room temperature of the four materials will be completed as soon as possible in the next quarter. These results will then be compared with the results of Task A in order to study the effects of fire retardants on smoke characteristics.

TASK D. Chemical Analysis of Smoke Particulates.

An analytical scheme for the separation and identification of the "non-PAH" fraction of polyurethane smoke particulates has been developed (see Fig. 1). The analysis (using GC/MS) of these products in an effort to identify the various classes of compounds which are present is now underway.

The recently developed small combustion chamber and sampling system (Fig. 2) has been utilized for the collection and analysis of volatiles produced during the combustion of a flexible polyurethane foam (GM-21). Volatiles in both the gas phase (Fig. 3) and those which are absorbed on the particulates (Fig. 4) are being analyzed using this system. Pyrolysis of the polyurethane is carried out in air and is initiated by a Nichrome coil connected to a power supply. The particulates are collected on the glass fiber filter and the gas phase is collected in the Porapak-R trap at -70°C. Collected gases are then backflushed directly into a GC/MS system for analysis. The particulates are then heated to 50°C and the volatiles are desorbed under a flow of 40 ml./min He for 25 min. and collected in the trap. The volatiles are then injected into the GC/MS system as before. Using this method, comparisons will be made of the differences in types and quantities of volatiles which are found in the gas phase and absorbed on the particulates. Analysis of the separated compounds (figures 3 and 4) is presently underway using a GC/MS system equipped with both Chemical Ionization and Electron Impact Ionization sources.

Table 1.

Preliminary Smoke Properties Data

Flaming Conditions - 5 W/cm^2

	Γ	D_{32}	OD	Char Residue-%Initial Weight
GM-21	<.01	0.94	0.45	T
GM-29	.085	0.94	4.69	15.1
GM-41	.060	1.10	2.15	37.4
GM-47	.085	1.22	1.27	T

Γ = Fraction of sample weight loss converted to smoke particulates

D_{32} = Volume-surface mean particle diameter at maximum optical density

OD = Maximum optical density at 458 nm.

T = Trace quantity

Table 2.

Preliminary Smoke Properties Data

Nonflaming Conditions - 5 W/cm^2

	Γ	D_{MMD}	D_{32}	OD	Char Residue- % Initial Weight
GM-21	.064	1.23	0.96	0.94	T
GM-29	.070	0.82	1.06	0.58	39.0
GM-41	.047	0.26	0.66	0.15	62.0
GM-47	.114	1.84	1.14	0.06	T

Γ = Fraction of sample weight loss converted to smoke particulates

D_{MMD} = Mass median diameter

D_{32} = Volume-surface mean particle diameter at maximum optical density

OD = Maximum optical density at 458 nm

T = Trace quantity

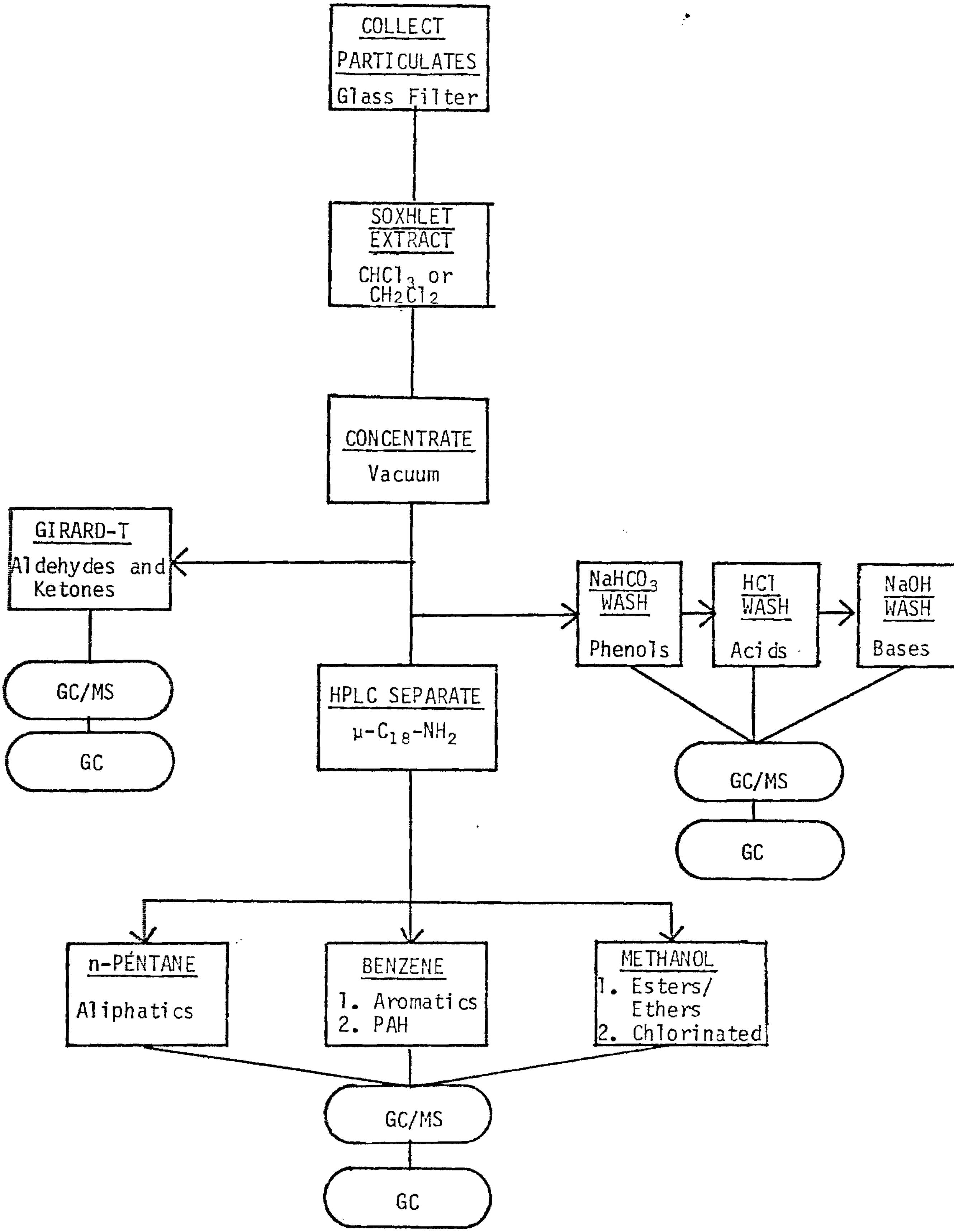


Figure 1. Methodology for Chemical Analysis of Smoke Particulates

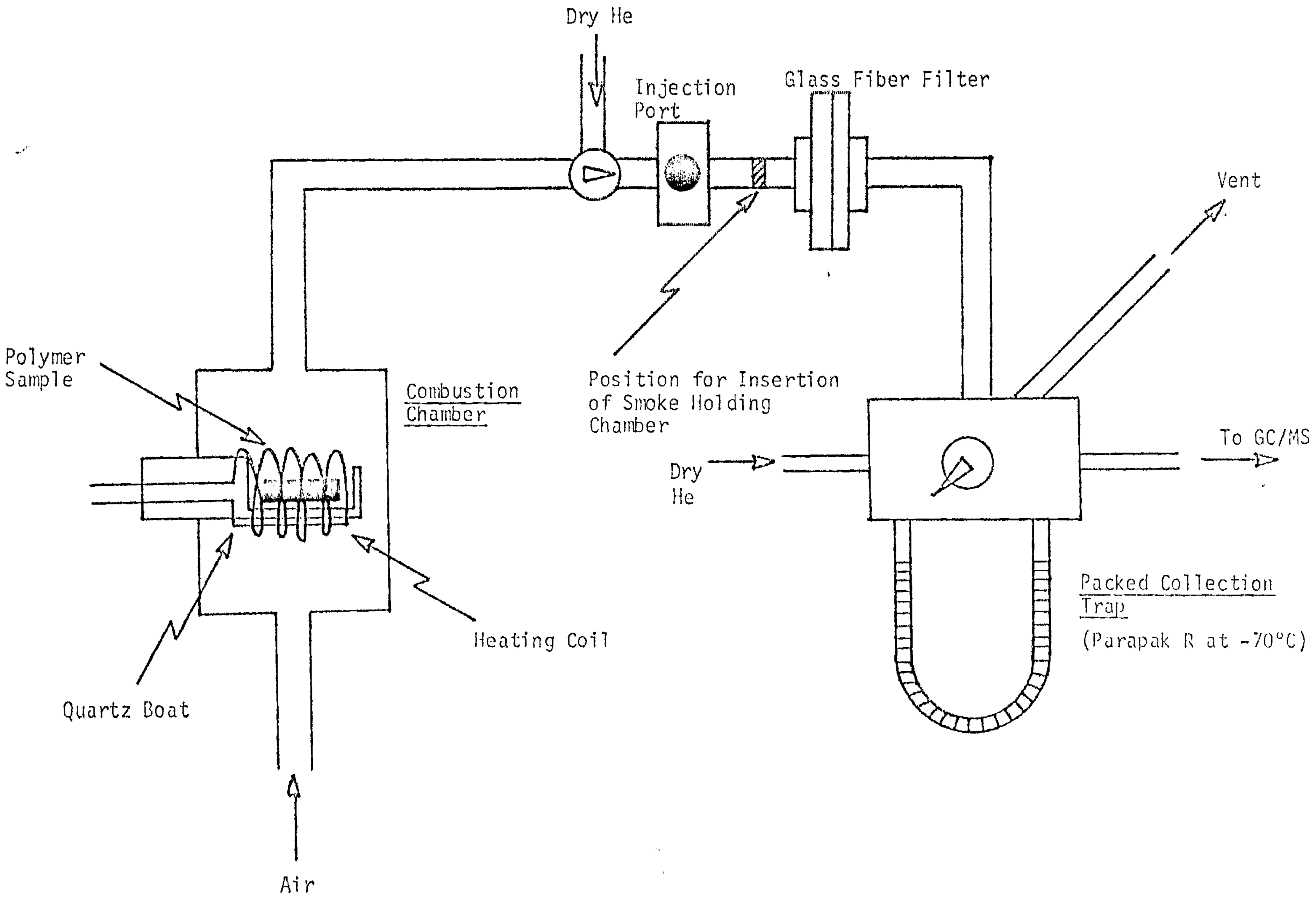
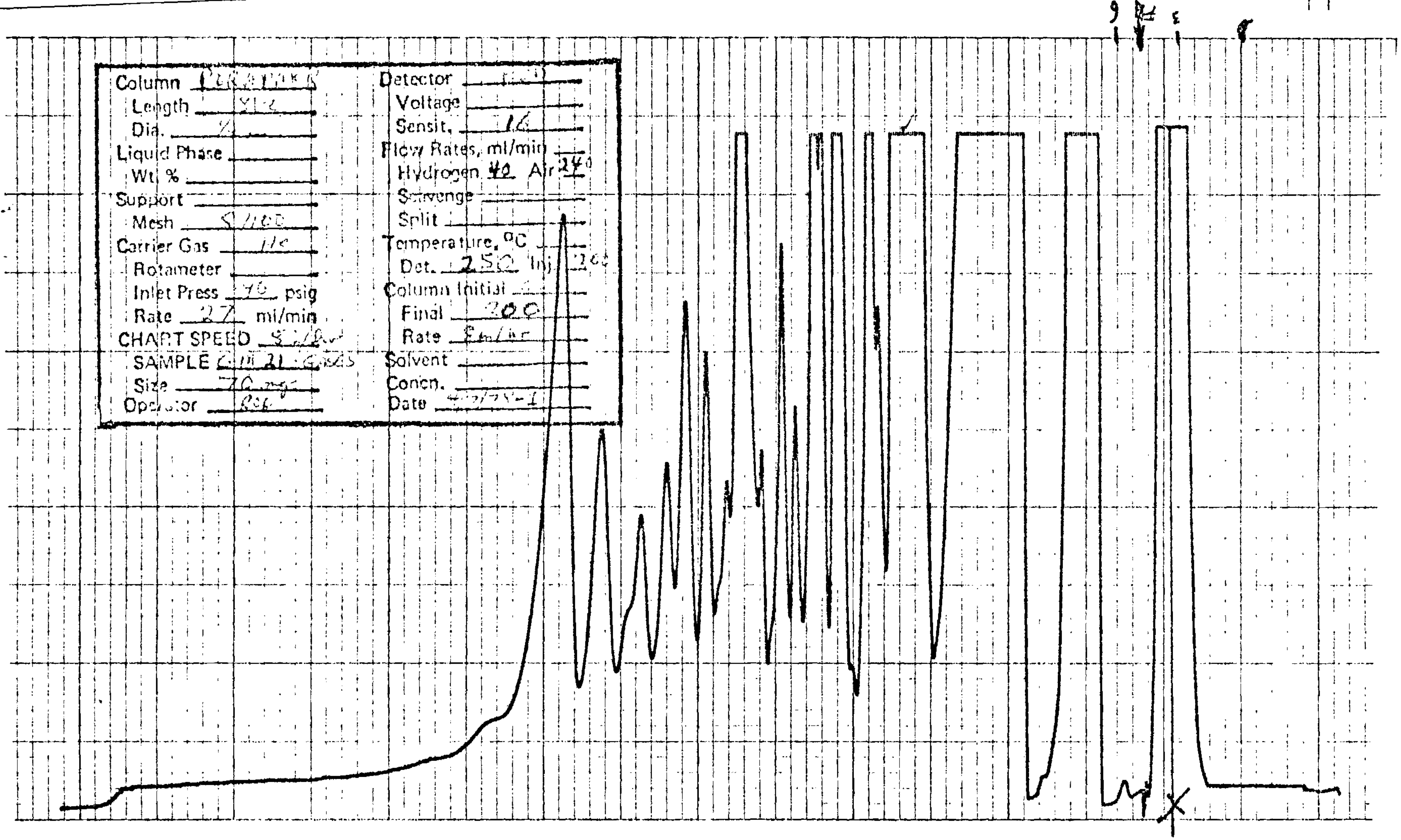


Figure 2. Apparatus for Particulates Collection/
Volatiles Release.



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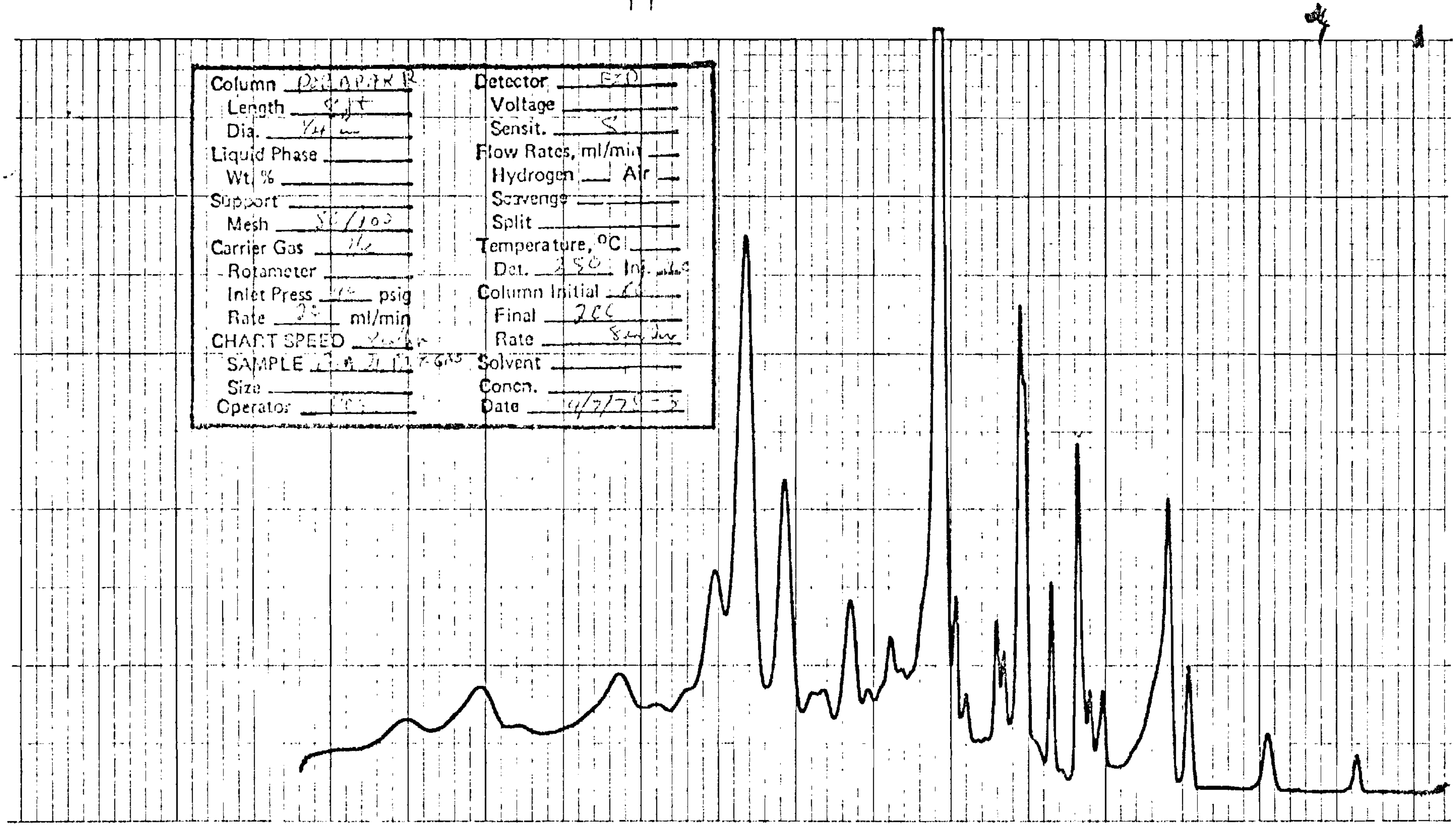
Length [illegible]
Dia. ¼
Liquid Phase
Wt %
Support
Mesh 80/100
Carrier Gas He
Rotameter
Inlet Press 70 psig
Rate 27 ml/min
CHART SPEED [illegible]
SAMPLE GM 21 GASES
Size 70 mg
Operator [illegible]

Detector FID
Voltage
Sensit. 16
Flow Rates, ml/min
Hydrogen 40 Air 240
Scavenge
Split
Temperature, °C
Det. 250 Inj. 200
Column Initial [illegible]
Final 200
Rate [illegible]
Solvent
Concn.
Date [illegible]

POLYURETHANE

GAS PHASE PYROLYSIS PRODUCTS

FIGURE 3.



Column PORAPAK R
Length 8 ft
Dia. 1/4 in
Liquid Phase
Wt. %
Support
Mesh 80/100
Carrier Gas [illegible]
Rotameter
Inlet Press [illegible] psig
Rate [illegible] ml/min
CHART SPEED [illegible]
SAMPLE [illegible]
Size
Operator [illegible]

Detector FID
Voltage
Sensit. 5
Flow Rates, ml/min
Hydrogen Air
Scavenge
Split
Temperature, °C
Det. 250 Inj. [illegible]
Column Initial [illegible]
Final 200
Rate [illegible]
Solvent
Concn.
Date [illegible]

POLYURETHANE

VOLATILES DESORBED FROM PARTICULATES

FIGURE 4.

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
AEROSPACE ENGINEERING

404-894-3000

DANIEL GUGGENHEIM SCHOOL
OF AERONAUTICS

To: Products Research Committee

From: Ben T. Zinn, Regents' Professor; Principal Investigator

Subject: Quarterly Progress Report for PRC Research Project No. 75-115: Investigation of the Properties of the Combustion Products Generated by Building Fires; for the period July 1, 1978 to Sept. 30, 1978.

This quarterly report describes the efforts conducted under PRC Research Project No. 75-115 during the period July 1, 1978 to Sept. 30, 1978, in the School of Aerospace Engineering, Georgia Institute of Technology. Progress which has been made to date is described according to the tasks which were set forth in the revised research proposal. Other contributing personnel were Drs. R. F. Browner, M. Pasternak, E. A. Powell, T. K. Joseph and Mr. R. O. Gardner.

TASK A. Determination of the Effect of Substrate Polymer Structure on Smoke Characteristics.

Further tests have been carried out in the Combustion Products Test Chamber (CPTC) for the purpose of analyzing the effect of cellular polymer structure on the smoking characteristics of foam materials exposed to high environmental temperatures. The four foams selected from the PRC standard sample bank for study are: flexible polyurethane foam (GM-21), rigid polyurethane foam (GM-29), rigid trimer foam (GM-41), and expanded polystyrene (GM-47). The results of room temperature tests ($25^{o}C$) of each of these materials (horizontal mount) have previously been reported for both flaming and non-flaming conditions. During this report period nonflaming high temperature tests have been conducted in which the samples were exposed to the same 5 W/cm^2 radiant flux and the ventilation air (flow rate of 283 ℓ/min) was preheated to 200°C. The results of these tests are compared with the corresponding room temperature tests in Table 1. Since the sampling system cannot be operated at elevated temperatures, values of Γ were not obtained in these tests. Based on optical density, raising the ambient temperature to 200°C gave a large (GM-21 and GM-29) to moderate (GM-41) decrease in the amount of smoke produced by the polyurethane foams under nonflaming conditions, while little effect of high temperature was obtained for the polystyrene foam (GM-47). Increasing the environmental temperature gave a moderate increase in the mean particle diameter D_{32} for GM-29 and GM-41, a slight increase in D_{32} for GM-21, and a slight decrease in D_{32} for GM-47. Samples which leave a measurable fraction of the initial weight as char (GM-29 and GM-41) left less residue in the 200°C environment than in the room temperature one. Corresponding high temperature data for flaming combustion of each of these materials will be obtained in October.

TASK B. Determination of the Effect of Additives on Smoke Characteristics.

High temperature nonflaming tests of the four fire retarded foam compositions (GM-23, GM-31, GM-43 and GM-49), which correspond to the non-fire retarded compositions studied in Task A, have been conducted. The results of these tests are presented in Table 2. Surprisingly, the fire retarded flexible foam (GM-23) spontaneously ignited (i.e., without the aid of a pilot flame) after only 1.4 minutes of exposure to the radiant source and the 200°C environment, while the non-fire retarded material (GM-21) did not exhibit flaming combustion under the same conditions. The optical density given in Table 2 for GM-23 is the maximum value obtained during nonflaming combustion (which occurred just before ignition), and the D_{32} value given corresponds to this optical density value. Comparing the corresponding data in Tables 1 and 2 shows that the addition of fire retardants has little effect on the peak optical density of the smoke obtained from these four materials under high temperature nonflaming conditions. On the other hand, a moderate effect of fire retardants upon the mean particle diameter was observed for each material; in each case a decrease in D_{32} was obtained. The flexible and rigid polyurethane foams with fire retardant (GM-23 and GM-31) left considerably more char residue than the corresponding non-fire retarded materials (GM-21 and GM-29), while the fire retarded rigid trimer foam (GM-43) left slightly less char than the non-fire retarded material (GM-41). During the remaining quarter of this project each of the fire retarded materials will be tested under flaming conditions at 200°C, followed by room temperature tests (with particulate sampling) under both flaming and nonflaming conditions.

TASK D. Chemical Analysis of Smoke Particulates.

The methodology for the determination of the "non-PAH" fraction of polyurethane smoke particulates and of volatiles, in the gas phase and those absorbed on the particulates, was described in the last report. Standards have been employed in order to test the validity and efficiency of these methods.

Analysis of the polyurethane samples is presently underway. Compounds present are being identified by GC/MS/computer system equipped with both chemical ionization and electron impact ionization sources and by comparison of GC retention times. For example, acrolein (m/e = 56) was indicated by GC/MS to be present in the gas phase of GM-21 and this was confirmed by comparing GC retention times using Porapak-R as the column and flame ionization detector gas chromatography. Similar determination of other compounds of interest is presently occurring and the final list of compounds found will be in the final report.

Table 1.

Preliminary Smoke Properties Data

Nonflaming Conditions - 5 W/cm^2

Material	D_{32}		OD		Char Residue % Initial Weight	
	25°C	200°C	25°C	200°C	25°C	200°C
GM-21	0.96	1.02	1.42	0.27	T	1.2
GM-29	1.05	1.52	0.87	0.14	39.0	17.7
GM-41	0.67	1.06	0.23	0.10	62.0	41.3
GM-47	1.17	1.04	0.09	0.07	T	T

D_{32} = Volume-surface mean particle diameter at maximum optical density

OD = Maximum optical density at 458 nm

T = Trace quantity

Table 2.

Preliminary Smoke Properties Data for Fire Retarded Materials

Nonflaming Conditions - 5 W/cm^2 - 200°C

Material	D_{32}	OD	Char Residue % Initial Weight
GM-23	0.65*	0.29*	5.1
GM-31	1.36	0.21	27.8
GM-43	0.80	0.10	38.3
GM-49	0.90	0.05	T

* = Value just before flaming ignition (OD rose to 0.59 during flaming phase)

D_{32} = Volume-surface mean particle diameter at maximum optical density

OD = Maximum optical density at 458 nm

T = Trace quantity

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

B. T. Zinn, Regents' Professor
C. P. Bankston, Research Engineer
R. F. Browner, Assistant Professor
E. A. Powell, Assistant Professor
T. K. Joseph, Post Doctoral Fellow
J. C. Liao, Post Doctoral Fellow
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School of Aerospace Engineering
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Atlanta, GA 30332

Final Report of Products Research Committee Project
for the period
January 1, 1978 to December 31, 1978

ABSTRACT

This report describes the research conducted under a Products Research Committee project entitled "Investigation of the Properties of the Combustion Products Generated by Building Fires." The objective of this study is to determine the physical and chemical properties of smoke produced by burning four cellular polymers obtained from the Products Research Committee sample bank. The four materials studied are: (1) flexible and (2) rigid polyurethane foams, (3) rigid trimer foam, and (4) expanded polystyrene foam. Both fire-retarded and non-fire-retarded formulations of these materials have been burned under a variety of conditions simulating actual fire situations. Measurements have been made of smoke particle size distributions, total smoke particulate mass generated, smoke mean particle diameter, smoke optical density and sample weight loss. Results show that the measured smoke characteristics are dependent upon the ventilation gas temperature at which samples are burned under both flaming and nonflaming conditions. Also, differences between flaming and nonflaming combustion are observed in the trends of the measured quantities as environmental temperature changes. Differences in smoke properties are also noted among the four substrate polymer compositions considered. Finally, the presence of a fire retardant additive affects the physical characteristics of the smoke generated under all of the test conditions considered.

TABLE OF CONTENTS

I. INTRODUCTION

This report describes the efforts conducted under a Products Research Committee research project during the period January 1, 1978 to December 31, 1978. The subject grant is entitled "Investigation of the Properties of the Combustion Products Generated by Building Fires." The objectives of this program during the past year have been: (1) continued 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 cellular-polymer building and furnishing materials; (2) determination of the dependence of the properties of smoke generated by the combustion of these materials on the temperature of the chamber atmosphere and the type of burning (i.e., flaming or non-flaming); and (3) determination of the dependence of smoke and gaseous products generated by burning cellular polymers on the type and amount of fire retardant chemical additives found in those polymers.

To pursue the objectives outlined above, the efforts of this research project have been divided into three major categories or tasks. Task A is concerned with the determination of the effect of the substrate polymer structure upon its smoking properties; Task B deals with the determination of the effect of fire retardant additives on the smoking characteristics of particular substrate polymers; and Task C is concerned with the chemical analysis of smoke particulates generated under non-flaming and flaming conditions.

This program has been directed by Dr. Ben T. Zinn in the School of Aerospace Engineering of the Georgia Institute of Technology. Other contributing personnel include Drs. C. P. Bankston, R. F. Browner, T. K. Joseph, J. C. Liao, M. Pasternak and E. A. Powell. Also assisting was Mr. R. O. Gardner, Graduate Research Assistant.

II. 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/cm^2); (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 measurement of scattered blue laser light ($\lambda = 0.458\ \mu m$) at forward angles of 5^{o} and 15^{o} provide time-resolved data describing the average size of the smoke particles. Measurements of transmitted red ($\lambda = 0.633\ \mu m$) and blue laser lights provide the optical densities of the smoke at these two wavelengths. For nonabsorbing particles (usually produced by nonflaming combustion) the transmitted light measurements along with the mean particle size measurements also yield the refractive index and volume concentration of the smoke particles. For absorbing particles (i.e., soot) measurements of 90^{o}-scattered light intensities parallel to and perpendicular to the plane of polarization of the incident light beam provide additional data necessary to determine the complex refractive index of the smoke particles. Details of the optical system are available in References 2, 3, and 4.

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. A new gas chromatograph/mass spectrometer system has been obtained which has chemical ionization capabilities. The GC/MS system is equipped with a computerized data acquisition and analysis system that records the total-ion chromatograms and the mass spectra.

III. TEST PROTOCOL

A. Sample Compositions.

In Task A four different cellular plastic materials obtained from the Products Research Committee sample bank were tested for the purpose of analyzing the effect of the particular cellular polymer structure on the smoking characteristics of foam materials. The four materials which were studied are: flexible polyurethane foam (GM-21), rigid polyurethane foam (GM-29), rigid trimer foam (GM-41), and expanded polystyrene foam (GM-47). The flexible polyurethane foam (GM-21) consists of 68% glycerine based polyoxypropylene and ethylene glycol (3500 molecular weight) and 24% toluene diisocyanate (2, 4 isomer 80%, 2, 6 isomer 20%) with small amounts of blowing agents, catalysts, and stabilizers. The rigid polyurethane foam (GM-29) is a fluorocarbon blown polymeric isocyanate, while the rigid trimer foam (GM-41) is a rigid isocyanurate foam which contains some polyurethane. These four materials contain no fire retardant additives.

In Task B the four classes of cellular plastics considered in Task A were extended to include the equivalent fire-retarded foam materials, which were also obtained from the Products Research Committee sample bank. In this manner, the effects of the fire retardants on smoke formation were evaluated for each standard reference foam material. The four corresponding fire retarded samples which were tested are: flexible polyurethane foam (GM-23), rigid polyurethane foam (GM-31), rigid trimer foam (GM-43), and expanded polystyrene foam (GM-49). The fire retardant additive used in these materials is a chlorinated phosphonate ester.

B. Test Conditions and Physical Properties Measured.

Each of these materials was first tested at room temperature (25°C) under both flaming and nonflaming conditions at a radiant heating rate of 5 W/cm^2. Next the same materials were tested under both flaming and nonflaming conditions at the same radiant flux in a ventilation gas which had been preheated to 200°C. These conditions were selected as representative of a range of environmental extremes which may be encountered in actual fire situations. In the flaming tests, the pyrolysis products generated by exposure of the sample to the radiant flux were ignited by a small propane pilot flame. In all tests the samples were mounted horizontally and the CPTC ventilation gas consisted of air flowing at a volumetric rate (before heating) of 283 liters per minute. Due to the decrease in density of the ventilation air during heating, the volumetric flow rate of the heated air during the 200°C tests was 449 liters per minute. Finally, the sample dimensions are 75 mm x 75 mm (exposed surface) x 7 mm thick; corresponding to sample weights of approximately 2.5 - 3.5 grams for the polyurethane samples and 1.1 - 1.4 grams for the polystyrene samples.

For the test conditions characterized by room temperature (25°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 wavelengths of 0.458 μm and 0.633 μm) 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, in addition to the sample weight loss measurements. The aerosol sampling system instrumentation cannot be operated at elevated temperatures.

IV. DETERMINATION OF THE EFFECT OF SUBSTRATE POLYMER STRUCTURE ON SMOKE CHARACTERISTICS.

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

Tests of flexible polyurethane foam (GM-21), rigid polyurethane foam (GM-29), rigid trimer foam (GM-41), and expanded polystyrene foam (GM-47) under nonflaming conditions in room temperature (25°C) ventilation air have been completed. Measurements have been obtained of the characteristics of the smoke produced under nonflaming conditions at 5 W/cm^2 radiant flux. The results of these tests are presented in Figures 1 through 7 and are summarized in Table 1.

Figure 1 shows the weight loss for the rigid polyurethane foam (GM-29). Most of the mass loss occurred during the first four minutes of exposure to the radiant heat flux and nearly forty percent of the initial weight remained as char. The flexible polyurethane foam (GM-21) and the expanded polystyrene foam (GM-47) left virtually no char residue, while the rigid trimer foam (GM-41) left the greatest amount of char, over sixty percent of its initial weight (Table 1). The mass loss rates of the flexible polyurethane foam (GM-21) and the rigid trimer foam (GM-41) were comparable to that of the rigid polyurethane foam (GM-29), but the expanded polystyrene foam (GM-47) lost mass at a much lower rate, requiring about 20 minutes for complete pyrolysis.

Smoke particle size distributions which were obtained with the cascade impactor are shown in Figure 2. This instrument furnishes the distribution of particulate weight over the aerodynamic size range of 0.43 to 11 microns. The smoke is sampled continuously over the entire

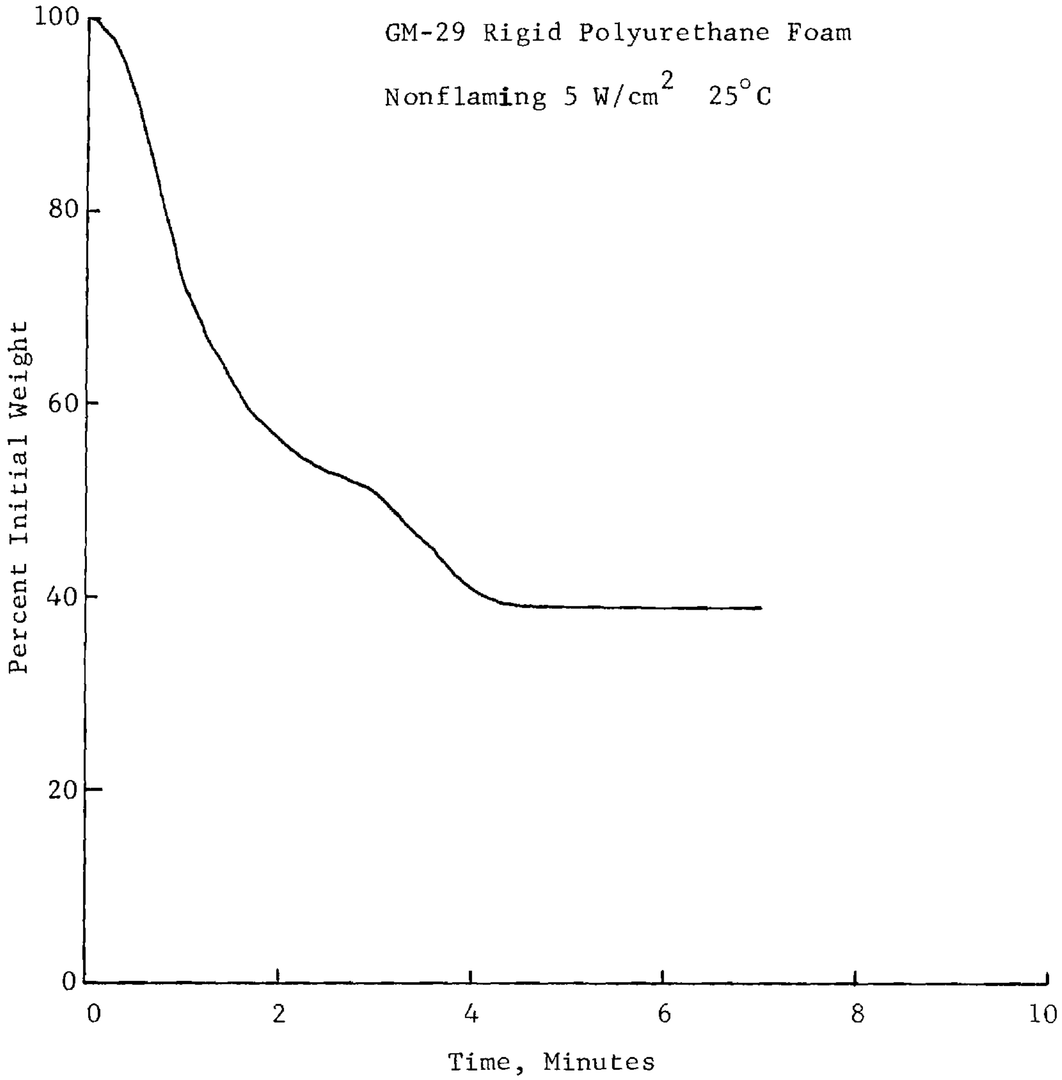


Figure 1. Sample Weight Loss in Nonflaming Combustion in Room Temperature Air for Rigid Polyurethane Foam Exposed to 5 W/cm^2 Radiant Flux.

test time; thus the resulting size distribution is an integrated distribution for the entire test. These size distributions are presented as cumulative type curves which are generated by plotting the percentage of particulate weight having particle diameters less than a given particle size versus the particle size on log-normal probability type paper[5]. For each of the cellular polymers tested the cumulative size distribution data have been reasonably represented by a straight line, which indicates that the mass-size distribution is approximately log-normal. This implies that the number and surface-size distributions are also log-normally distributed with the same standard deviation[5].

The cumulative size distribution curves in Figure 2 show that the largest smoke particles are produced by the expanded polystyrene foam (GM-47) with a mass median diameter (D_{MMD}) of 1.8 microns, while the smallest particles are produced by the rigid trimer foam (GM-41) with a D_{MMD} of 0.26 microns. The mass median diameter is readily obtained from the cumulative probability plots in Figure 2; fifty percent of the sampled particulates (by mass) are composed of particles of diameters less (or greater) than the mass median diameter[5]. The standard deviations (σ) of the smokes produced by these polymers are in the range 2.2 - 4.2 microns. The standard deviation is the square root of the second moment about the mean particle diameter, and it is an indication of the relative spread of particle diameters about the mean diameter. Since the data shown approximately follows a log-normal distribution, the values of σ calculated from the cumulative probability plots gives a general indication of the dispersity of the data thus

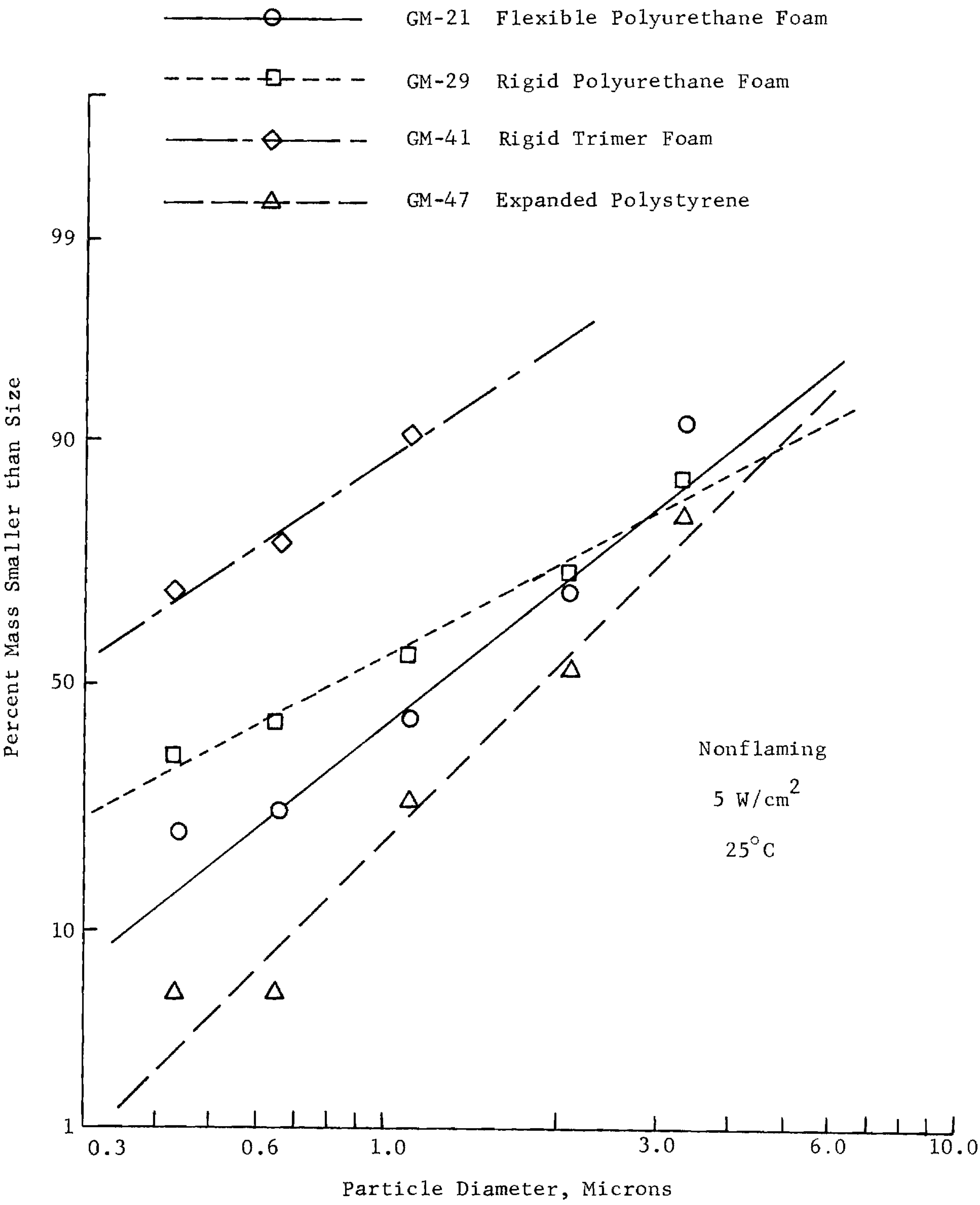


Figure 2. Smoke Particle Size Distributions for Four Cellular Polymers Generated Under Low Temperature Nonflaming Conditions.

providing a reasonable basis for comparisons. Values of D_{MMD} and σ taken from Figure 2 are presented in Table 1.

Additional data were also taken with the Whitby Electrical Aerosol Analyzer. This instrument provides time resolved particle volume distributions for particle diameters between 0.05 and 1.0 micron with a time resolution of about 1.5 minutes. Electrical analyzer data for three cellular polymers are presented in Figures 3 and 4 as plots of particle volume percent versus particle diameter (log scale). Here particle volume percent is given by $\frac{1}{4}$ $(\Delta V/V)/\Delta(\log D_p)$ where ΔV is the volume of particles in the size range described by Δ $(\log D_p)$ and V is the total particulate volume. For a log-normal distribution the bell-shaped volume (mass) size distribution curve is symmetrical, and it peaks at the mass-median diameter D_{MMD}. For asymmetrical distributions (not log-normal) the peak corresponds to the most probable diameter which differs from the mass-median diameter.

Volume size distributions obtained with the Whitby aerosol analyzer are presented in Figure 3 for the rigid polyurethane foam (GM-29) and the rigid trimer foam (GM-41). For both materials the size distribution curves shift toward smaller particle sizes as the test proceeds, indicating significant variations in particle size with time during a test. Also the departure of the size distribution from a log-normal distribution increases with time as revealed by the increasing asymmetry of the curves. This latter effect is especially noticeable for the rigid polyurethane foam (GM-29) which apparently exhibits a bimodal distribution after about five minutes. (The second peak occurs

Nonflaming 5 W/cm^2 25°C

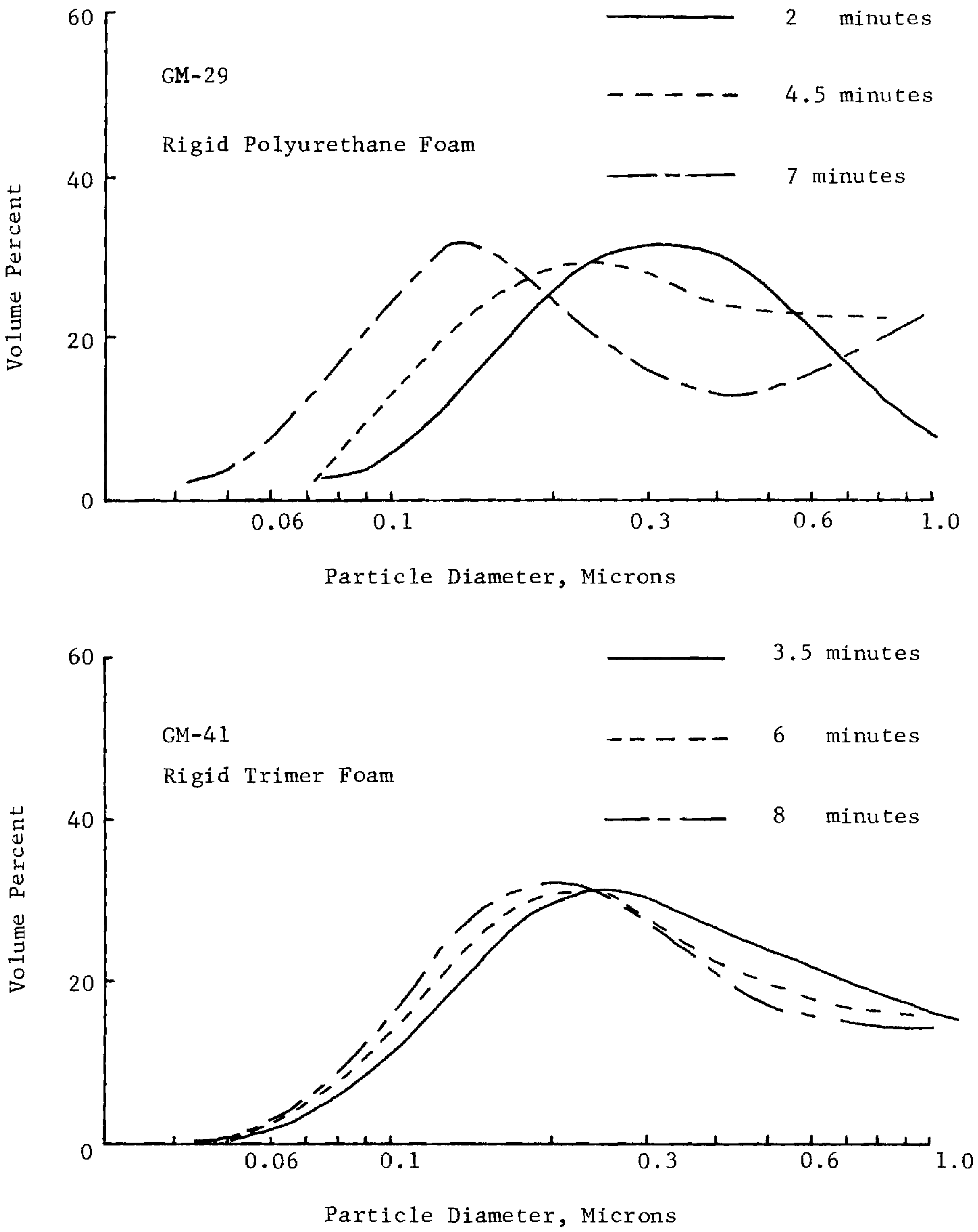


Figure 3. Time Resolved Particle Size Distributions for Two Cellular Polymers Generated Under Low Temperature Nonflaming Conditions.

above 1.0 micron which is above the range of the Whitby analyzer). A strongly asymmetrical or bimodal distribution for GM-29 is consistent with the mass-median diameter of 0.82 micron obtained from the cascade impactor measurements which is larger than the most probable diameter (0.15 - 0.3 microns) obtained with the Whitby analyzer. For the rigid trimer foam (GM-41) the departures from a log-normal distribution are much less, and the most probable diameters obtained with the Whitby analyzer (0.2 - 0.25 microns) are in good agreement with the mass-median diameter of 0.26 micron obtained from the cascade impactor data.

Figure 4 shows time-resolved volume size distributions obtained with the Whitby analyzer for the expanded polystyrene foam (GM-47). For this material there is little variation in particle size distribution with time. The Whitby data obtained during the middle of the test (between 11 and 18 minutes) is consistent with the mass median diameter of 1.8 microns obtained with the cascade impactor. For the initial and final stages of the test the Whitby data indicates a reduction in the numbers of particles with diameters greater than 0.5 micron.

Plots of the volume-surface mean diameter (D_{32}) versus time obtained with the in situ optical system are shown in Figures 5 and 6 for the four cellular polymers studied. Figure 5 shows that for the flexible polyurethane foam (GM-21), the rigid polyurethane foam (GM-29), and the rigid trimer foam (GM-41) burning under nonflaming conditions in room temperature ventilation air, D_{32} increases rapidly to a peak between 1.2 and 1.6 microns followed by a more gradual decline. Of

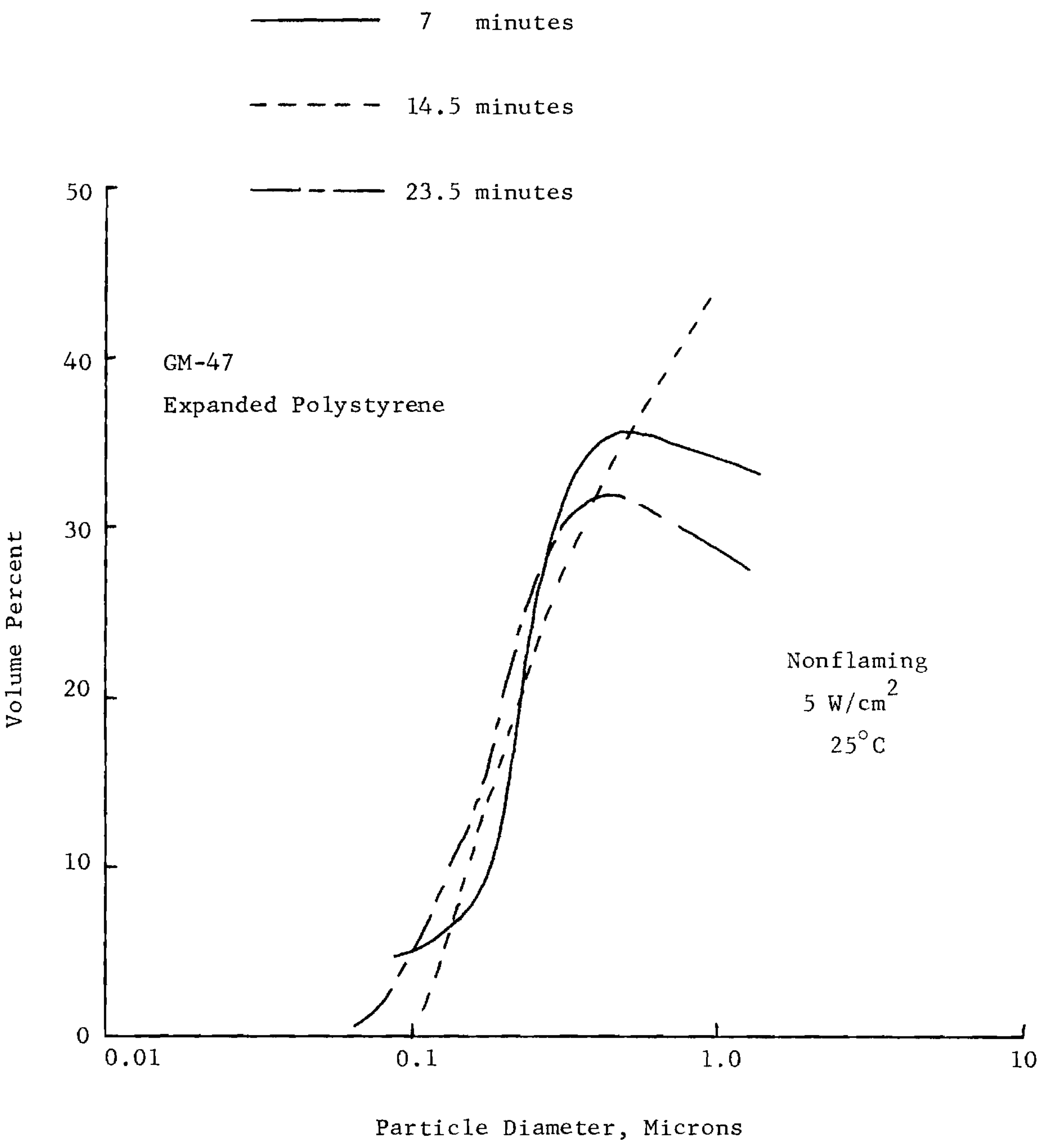


Figure 4. Time Resolved Particle Size Distributions for Expanded Polystyrene Generated Under Low Temperature Nonflaming Conditions.

these three chemically similar materials, the flexible polyurethane foam (GM-21) produces the largest particles initially ($D_{32} = 1.6$ microns) with a decline in D_{32} to about 0.9 micron after about three minutes. Both the rigid polyurethane foam (GM-29) and the rigid trimer foam (GM-41) exhibit an initial D_{32} peak of about 1.2 microns; subsequently D_{32} for the GM-29 foam levels off at about 0.7 micron while D_{32} for the GM-41 foam continues to decrease to less than 0.2 micron after eight minutes. Figure 6 shows the variation in D_{32} with time for the expanded polystyrene foam (GM-47). For this material D_{32} reaches a maximum of about 1.3 microns during the first five minutes followed by a very slow decline to about 1.0 micron during the remaining 15 minutes.

Because of the wide variations in mean particle diameter during the course of a test, a characteristic value of D_{32} for each material was selected as a basis for comparison among the various polymers studied. Since mean particle diameter is an important factor in determining the light obscuring properties of smoke, the value of D_{32} selected was taken at the time of maximum optical density during each test. These D_{32} values are presented in Table 1.

Optical densities per meter (OD) in blue light ($\lambda = 0.458\ \mu m$) for low temperature, nonflaming tests of the four cellular polymers are presented in Figure 7. The smoke optical density per unit optical path length is defined as follows:

$$OD = \frac{\log_{10} \frac{I_o}{I}}{L}$$

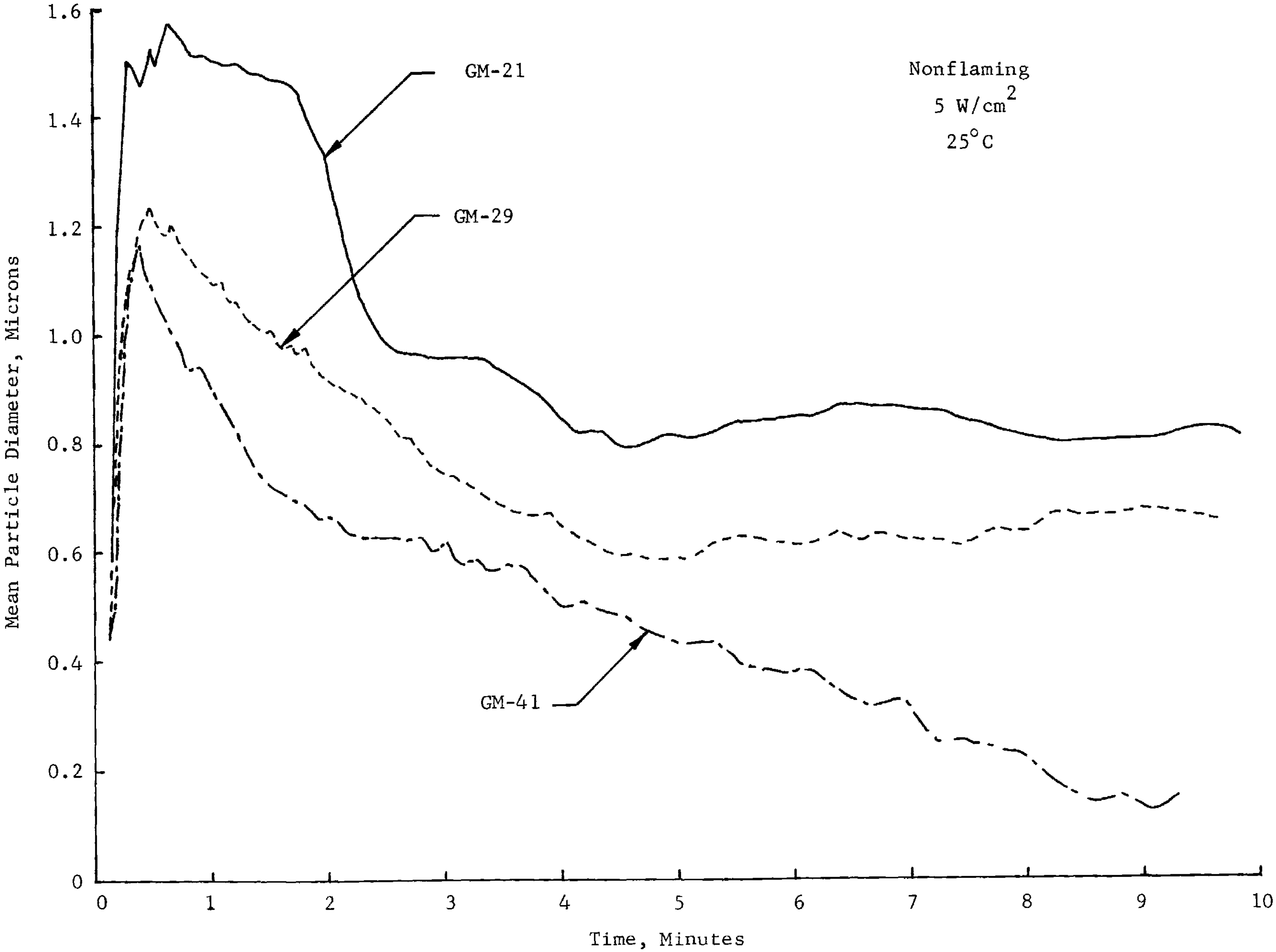


Figure 5. Smoke Mean Particle Size for Three Cellular Polyurethanes in Nonflaming Combustion in Room Temperature Air.

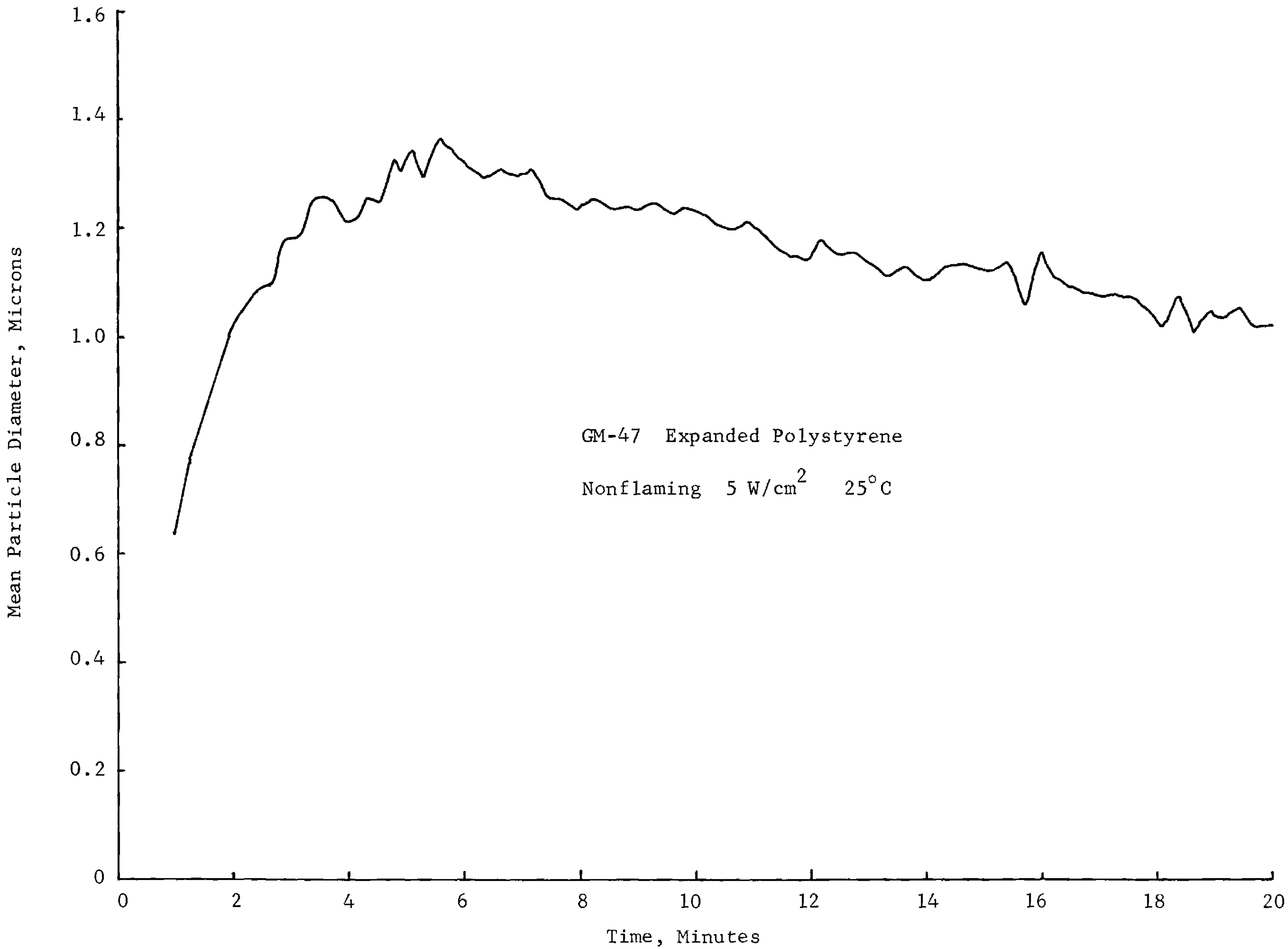


Figure 6. Smoke Mean Particle Size for Expanded Polystyrene in Nonflaming Combustion in Room Temperature Ventilation Air.

where I_o is the incident light intensity, I is the light intensity transmitted through the smoke, and L is the optical path length (0.114 meter for the CPTC). Figure 7 reveals that the optical density curves vary widely among the four materials tested. The flexible polyurethane foam (GM-21) produces the largest peak optical density (1.4 per meter) of the four polymers tested under nonflaming conditions. The rigid polyurethane foam (GM-29) yields a considerably smaller peak OD of 0.9 per meter followed by the rigid trimer foam (GM-41) which produces a peak OD of only 0.2 per meter. These three materials all produce significant light obscuration only during the initial six minutes of the test. The expanded polystyrene foam (GM-47) produces the least light obscuration of the four polymers tested, with a peak optical density of less than 0.1 per meter. Furthermore the GM-47 foam requires about 12 minutes to reach its maximum optical density, in contrast to three minutes or less for the other materials. Values of the peak optical densities in red and blue light and the corresponding time at which the peak OD occurs are given in Table 1 for each of the four cellular polmers investigated.

The smoke properties data for nonflaming combustion of the four cellular substrate polymers in room temperature air are summarized in Table 1. In addition to the data already discussed, Table 1 includes values of Γ, the fraction of sample weight loss converted to smoke particulates (the remaining fraction of the sample weight loss is converted to gaseous combustion products). The values of Γ can be used as a criterion for ranking the smoking tendency of these materials. Thus the expanded polystyrene foam (GM-47) has the greatest smoking tendency

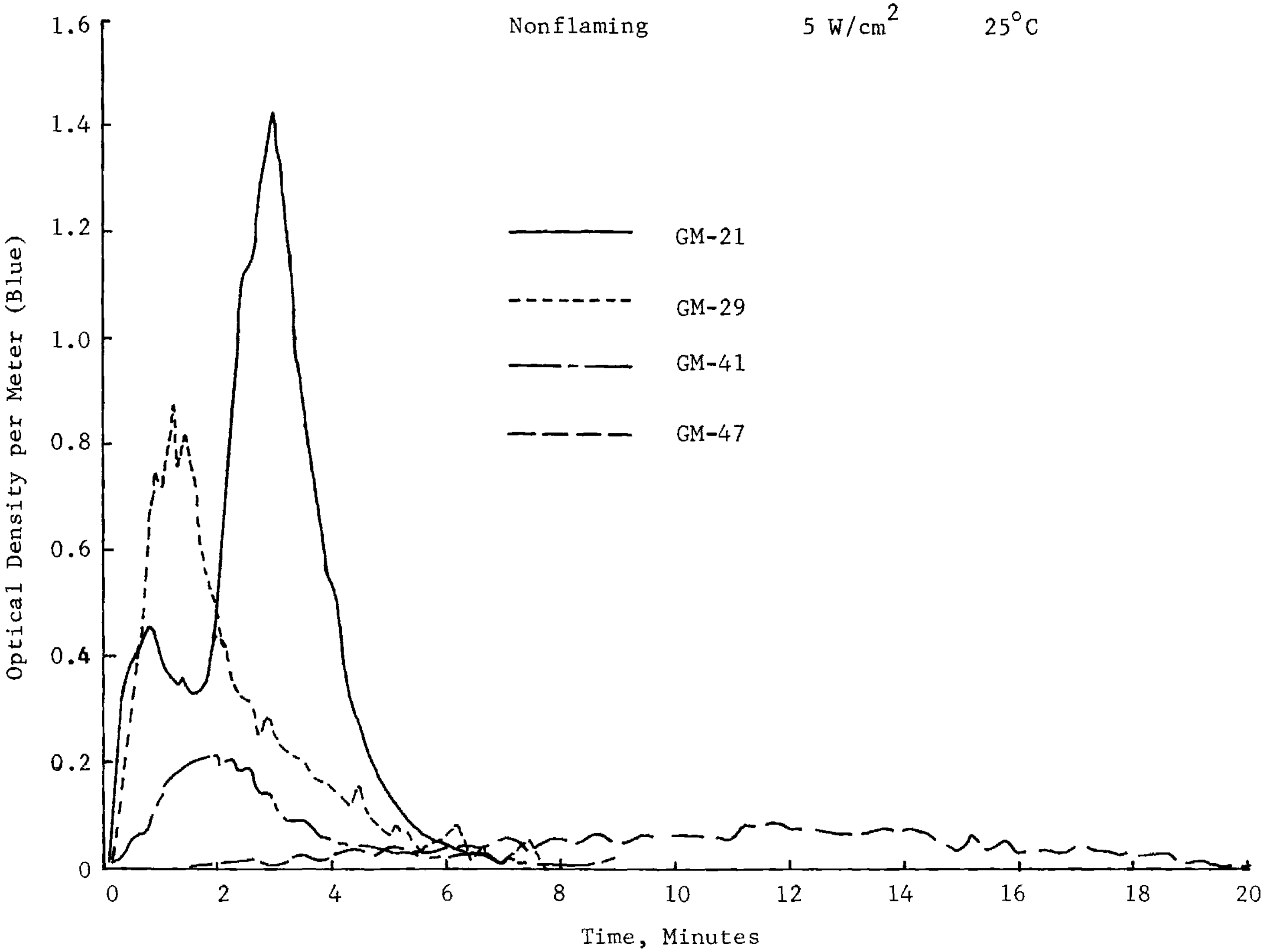


Figure 7. Optical Densities for Four Cellular Polymers in Nonflaming Combustion in Room Temperature Ventilation Air.

of the four polymers tested under nonflaming conditions; the rigid polyurethane foam (GM-29) and the flexible polyurethane foam (GM-21) are ranked second and third according to their Γ values. The rigid trimer foam (GM-41) produces the least amount of smoke of the four cellular plastics tested.

Peak optical density, OD_{max}, can also be used to rank the smoking tendency of these materials. However, the relative ranking of the four cellular materials tested under nonflaming conditions using OD_{max} as a ranking criterion is considerably different from that obtained on the basis of Γ. The greatest differences in the smoke rankings based on Γ and OD_{max} occur for the expanded polystyrene foam (GM-47) which ranks highest in smoking tendency according to Γ but lowest in smoke production according to OD_{max}. This is a consequence of the much lower mass loss rate obtained with the expanded polystyrene foam than with the other materials. In a ventilated test chamber such as the CPTC the particulate volume concentration and hence the optical density is proportional to the sample mass loss rate, thus the low mass loss rate of the polystyrene foam leads to low optical densities in spite of the higher Γ values obtained. In addition the flexible polyurethane foam (GM-21) exhibits a greater OD_{max} than the rigid polyurethane foam (GM-29) even though a smaller fraction of its total mass loss is converted to particulates. In this case the opposite rankings of smoking tendency are due to the greater total mass loss of the GM-21 foam in which virtually all of the sample is converted to combustion products, while the GM-29 foam leaves about 40% of its initial mass as char.

Table 1

Smoke Properties Data - Nonflaming Conditions - 5 W/cm^2 - 25°C

Material	Γ	D_{MMD} (μm)	σ (μm)	OD_{max}		D_{32} (μm)	Time to Peak OD (min)	Char Residue % Initial Weight
				Blue	Red			
GM-21	.064	1.23	2.56	1.42	1.17	0.96	3.0	T
GM-29	.070	0.82	4.21	0.87	0.87	1.05	1.2	39.0
GM-41	.047	0.26	3.09	0.23	0.19	0.68	1.9	62.0
GM-47	.114	1.84	2.17	0.09	0.06	1.17	11.7	T

Γ = Fraction of sample weight loss converted to smoke particles.

D_{MMD} = Mass median diameter.

σ = Geometric standard deviation.

OD_{max} = Maximum optical density in blue (.458 μm) and red (.633 μm) light at a volumetric flow rate of 283 liters/minute.

D_{32} = Volume-surface mean particle diameter at maximum optical density.

T = Trace quantity.

Particle size data obtained with the in situ optical system can be readily compared with the corresponding sampling data by means of Table 1. For the flexible polystyrene foam (GM-21) and the expanded polystyrene foam (GM-47) the volume-surface mean diameter D_{32} obtained from the light scattering measurements is smaller than the mass median diameter D_{MMD} obtained from the cascade impactor data, while D_{32} is larger than D_{MMD} for the rigid polyurethane foam (GM-29) and the rigid trimer foam (GM-41). Such differences are expected, however, since (1) the two mean diameters are defined differently and (2) the D_{32} values are determined instantaneously while the D_{MMD} values are integrated averages for the entire test. In view of these differences the particle sizes obtained by the optical system and the sampling system are seen to be in good agreement.

B. Low Temperature Flaming Tests at 5 W/cm^2.

The same four cellular polymers were also tested under *flaming* conditions in room temperature (25°C) air. In each case the pyrolysis products generated by exposure of the sample to the 5 W/cm^2 radiant flux were ignited by a small propane pilot flame. The results of these tests are presented in Figures 8 through 10 and are summarized in Table 2.

Weight loss data for the flexible polyurethane foam (GM-21), the rigid trimer foam (GM-41), and the expanded polystyrene foam (GM-47) obtained under flaming conditions are given in Figure 8. Most of the mass loss occurs during the flaming phase of combustion which occurs during the first two minutes after initial exposure for these three

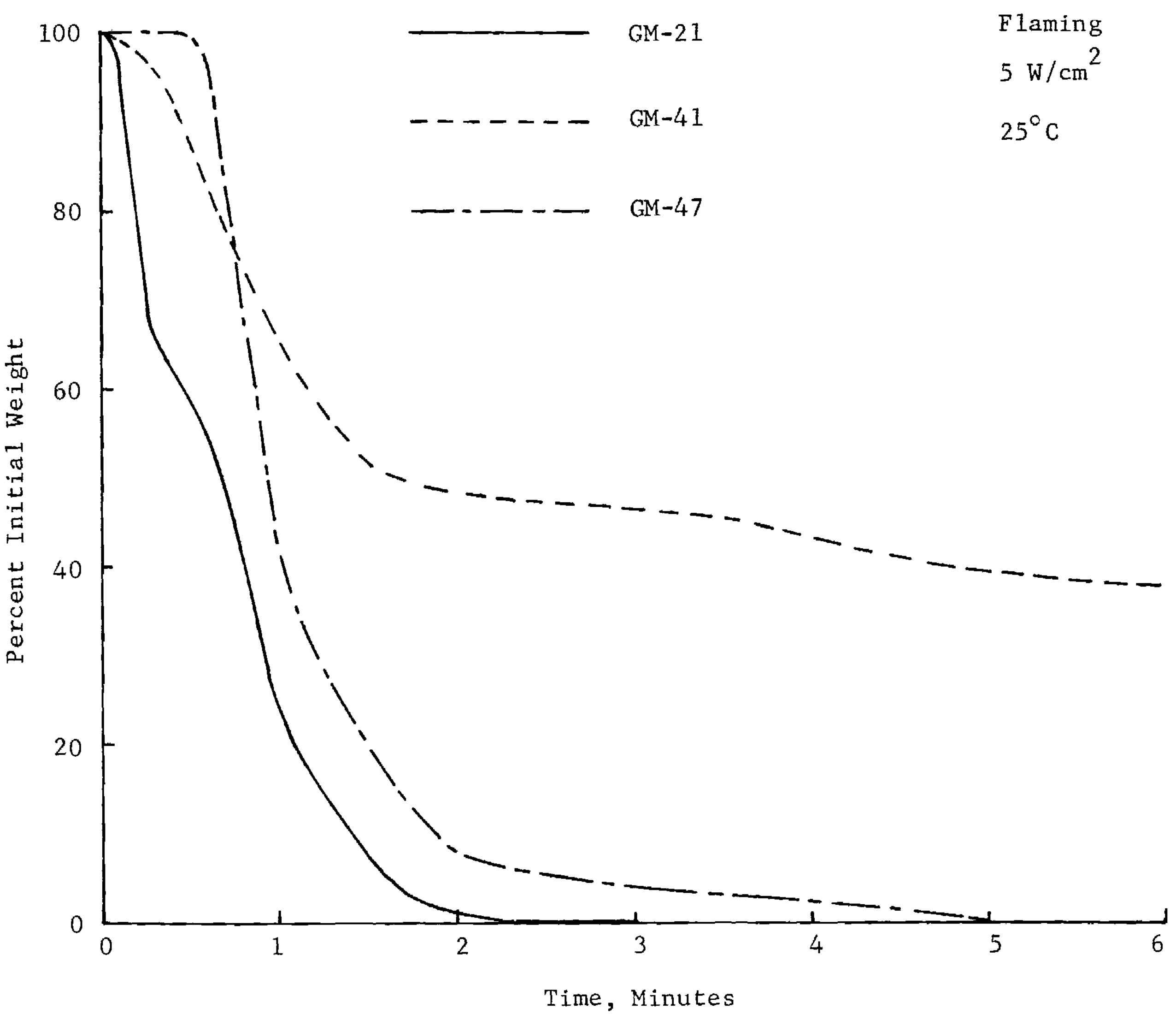


Figure 8. Sample Weight Loss in Flaming Combustion in Room Temperature Air for Three Cellular Polymers.

materials. For each of these materials the mass loss rates under flaming combustion are greater than those obtained under nonflaming conditions. For the char forming polymers (GM-29 and GM-41), the amount of char residue (in percentage of initial weight) remaining after completion of flaming combustion was approximately half of that obtained under nonflaming combustion (Table 2). In contrast to the nonflaming case, the mass loss rate of the expanded polystyrene foam (GM-47) for flaming combustion was comparable to those obtained for the other three materials.

No particle size distributions are available for the four cellular polymers tested under flaming conditions. For the flexible polyurethane foam (GM-21) the quantities of smoke particulates collected on the cascade impactor plates were too small for reliable size distribution measurements. For the other materials the large sooty particulates produced during flaming combustion tended to clog the lower stages of the cascade impactor rendering the particle size data unreliable. Furthermore most of the particles generated by these polymers during flaming combustion were too large (greater than one micron in diameter) to be measured with the Whitby Electrical Aerosol Analyzer. For determination of Γ, particulates were collected by two filters connected in series. These Γ values are given in Table 2.

Figure 9 shows the variation of smoke mean particle diameter D_{32} with time for the four cellular plastics burning under flaming conditions in room temperature air. After a brief ignition period, mean particle diameters were relatively constant during the entire period of flaming combustion. These sizes ranged from about 0.9 micron for the flexible polyurethane foam (GM-21) to about 1.2 microns for the expanded polystyrene foam (GM-47). The spike in the D_{32} curve for the rigid trimer foam (GM-41) at four minutes occurred when the char curled up to allow direct impingement of the pilot flame upon the sample. Values of D_{32} at maximum optical density for flaming combustion are presented in Table 2 along with the corresponding non-flaming values. For the flexible and rigid polyurethane foams (GM-21 and GM-29) somewhat smaller particles are produced under flaming conditions, while the expanded polystyrene foam (GM-47) tends to produce slightly larger particles under flaming conditions. In contrast to the other materials tested, flaming rigid trimer foam (GM-41) produces particles with an average diameter considerably larger than the particles produced by the same material under nonflaming conditions.

Optical densities in blue light are shown in Figure 10 for the same materials burning under flaming conditions in room temperature air. Each of the cellular polymers tested exhibits a strongly peaked optical density curve with the maximum OD occurring during the period of flaming combustion when the mass loss rate is the highest. The rigid polyurethane foam (GM-29) produces by far the densest smoke of the four polymers tested, with a maximum OD of 7 per meter. The rigid trimer foam (GM-41) and the expanded polystyrene foam (GM-47) produce moderate light obscuration with peak optical densities of 3.2 per meter and 1.9 per meter respectively. The flexible polyurethane foam (GM-21) produces the least light attenuation with an OD_{max} of only 0.7 per meter. The

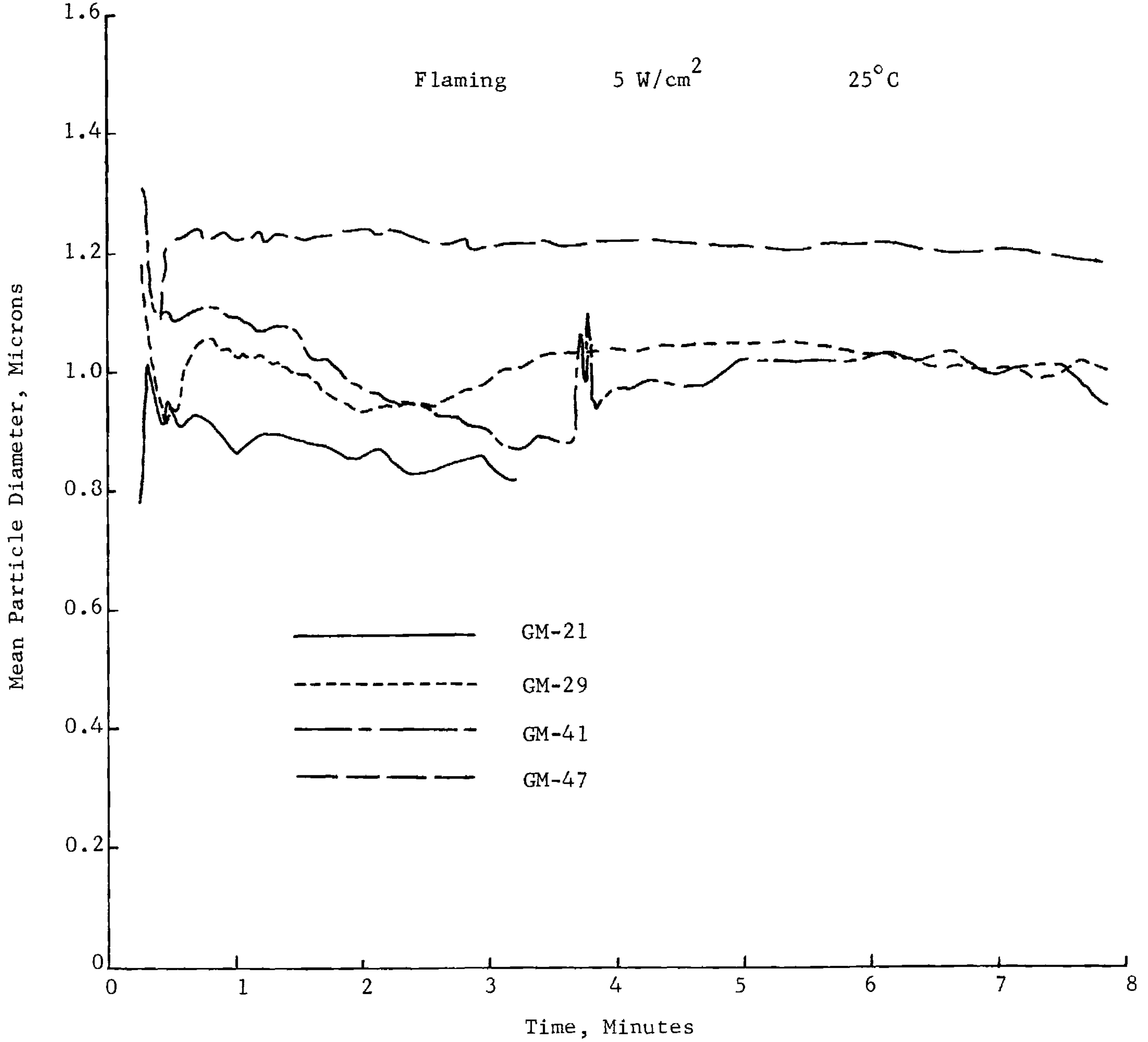


Figure 9. Smoke Mean Particle Diameter for Four Cellular Polymers in Flaming Combustion in Room Temperature Ventilation Air.

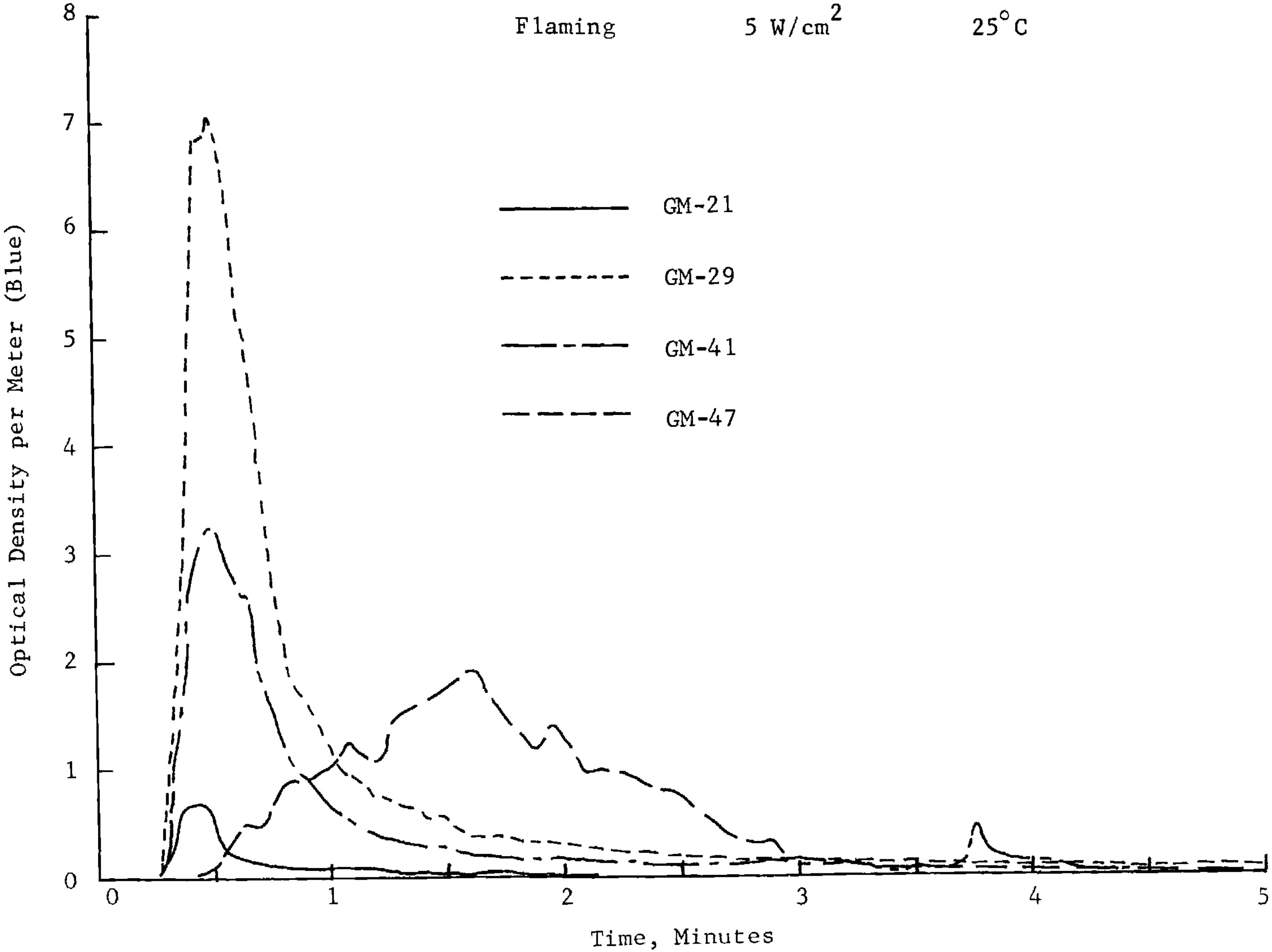


Figure 10. Optical Densities for Four Cellular Polymers in Flaming Combustion in Room Temperature Ventilation Air.

expanded polystyrene foam (GM-47) requires more than three times longer to reach maximum optical density (1.6 minutes) than the other materials (0.5 minutes). Optical densities in red light were also obtained (Table 2), and they are significantly smaller than the optical densities in blue light for each material tested.

Smoke properties data for the four cellular substrate polymers obtained under flaming conditions are summarized in Table 2. In order to facilitate comparisons with the nonflaming data, the smoke properties data obtained under nonflaming conditions are also presented in Table 2. From the tabulated values of Γ and the amount of char residue, it is seen that the rigid polyurethane foam (GM-29) and the rigid trimer foam (GM-41) generate considerably more total smoke by mass under flaming conditions than under nonflaming conditions, while the expanded polystyrene foam (GM-47) produces less total particulate mass under flaming conditions. These three materials all yield much greater optical densities under flaming conditions than under nonflaming conditions; these OD_{max} values are much greater than expected from considerations of the total particulate mass alone. This result can be understood by considering the differing optical properties of the smoke particles generated by flaming and nonflaming combustion. The smoke particulates are predominately liquid droplets in nonflaming tests, while the particles generated under flaming conditions are "sooty" agglomerates which absorb as well as scatter light. Furthermore, the particulates are generated over a shorter period of time during the flaming tests which tends to increase the particle volume concentration and thus

Table 2. Smoke Properties Data - Room Temperature Air - 5 W/cm^2

Material	Type of Combustion	Γ	OD_{max}		D_{32} (μm)	Time to Peak OD (min)	Char Residue % Initial Weight
			Blue	Red			
GM-21	F	<.01	0.68	0.52	0.94	0.5	T
	NF	.064	1.42	1.17	0.96	3.0	T
GM-29	F	.085	7.03	4.98	0.93	0.5	15.1
	NF	.070	0.87	0.87	1.05	1.2	39.0
GM-41	F	.060	3.23	2.44	1.09	0.5	37.4
	NF	.047	0.23	0.19	0.68	1.9	62.0
GM-47	F	.085	1.90	1.50	1.23	1.6	T
	NF	.114	0.09	0.06	1.17	11.7	T

Γ = Fraction of sample weight loss converted to smoke particles.

OD_{max} = Maximum optical density in blue (.458 μm) and red (.633 μm) light at a volumetric flow rate of 283 liters/minute.

D_{32} = Volume-surface mean particle diameter at maximum optical density.

T = Trace quantity.

the optical density. These considerations also explain why the smoke optical density for flaming combustion of the flexible polyurethane foam (GM-21) is only moderately smaller than the corresponding nonflaming value, even though the total particulate mass generated under flaming conditions is much smaller than that produced under nonflaming conditions.

C. High Temperature Tests at 5 W/cm^2.

Both flaming and nonflaming tests of the four cellular plastics were also conducted in ventilation air which was preheated to 200°C. Sample mass loss rates, mean particle diameters, and optical densities obtained at 200°C are compared with the corresponding room temperature (25°C) data in Figures 11 through 20. Peak optical densities and volume-surface mean diameters for both room temperature and 200°C tests are shown in Tables 3 (nonflaming) and 4 (flaming) along with the Γ values for the low temperature tests. Since the sampling system could not be operated at the elevated temperatures, Γ values, particle size distributions, and the mass median diameters are not available for the 200°C tests.

Figure 11 shows sample mass loss data for three of the cellular polymers obtained under nonflaming conditions at 200°C. Room temperature data is also included for the rigid polyurethane foam (GM-29) which shows that increasing the ventilation air temperature to 200°C results in a substantial increase in the mass loss rate and a significant reduction in the percentage of the initial weight remaining as char. The other materials also exhibit greater pyrolysis rates in the heated

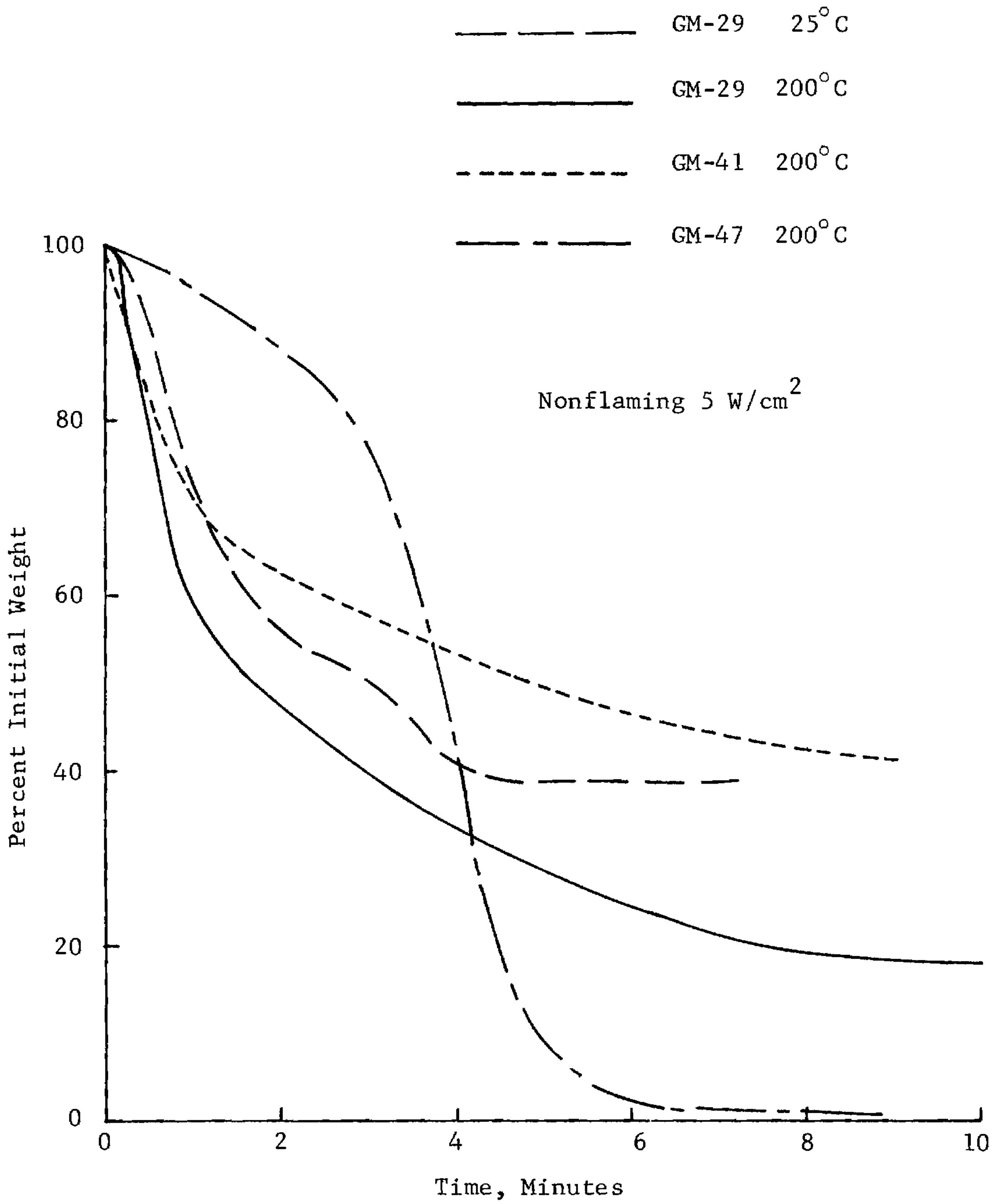


Figure 11. Effect of Ventilation Gas Temperature Upon Sample Weight Loss for Polyurethane and Polystyrene Cellular Polymers Under Nonflaming Conditions.

ventilation air than at room temperature. Furthermore the rigid trimer foam (GM-41) also leaves considerably less char in the 200°C tests than at room temperature. Mass loss data obtained under flaming conditions at 200°C are compared with the corresponding room temperature data in Figure 12. The data shown for the flexible polyurethane foam (GM-21) and the rigid trimer foams (GM-41) indicates that the effect of environmental temperature upon mass loss rate and amount of char produced is smaller for flaming combustion than for nonflaming combustion. These effects of ventilation air temperature upon mass loss are due to the presence of convective heat transfer to the sample (or at least reduced convective heat loss) in the higher temperature environment. The primary mode of heat transfer to the sample surface is radiation from the radiant heat source and the flame, which heats the sample surface and causes pyrolysis to occur. The reduced convective cooling of the sample surface in the hotter atmosphere has a smaller effect upon surface temperature and hence pyrolysis rate in the flaming case because of the additional radiant flux from the flame (i.e., the percent increase in the <u>net</u> heat flux is smaller in the flaming case).

The effects of elevated environmental temperature upon the variation of the mean particle diameter D_{32} with time for each of the cellular polymers tested are shown in Figures 13 through 16 for both nonflaming and flaming combustion. For the GM-21 flexible polyurethane foam (Figure 13), increasing the ventilation gas temperature to 200°C yields a moderate decrease in D_{32} for nonflaming combustion and a moderate increase in D_{32} for flaming combustion. In the high temperature

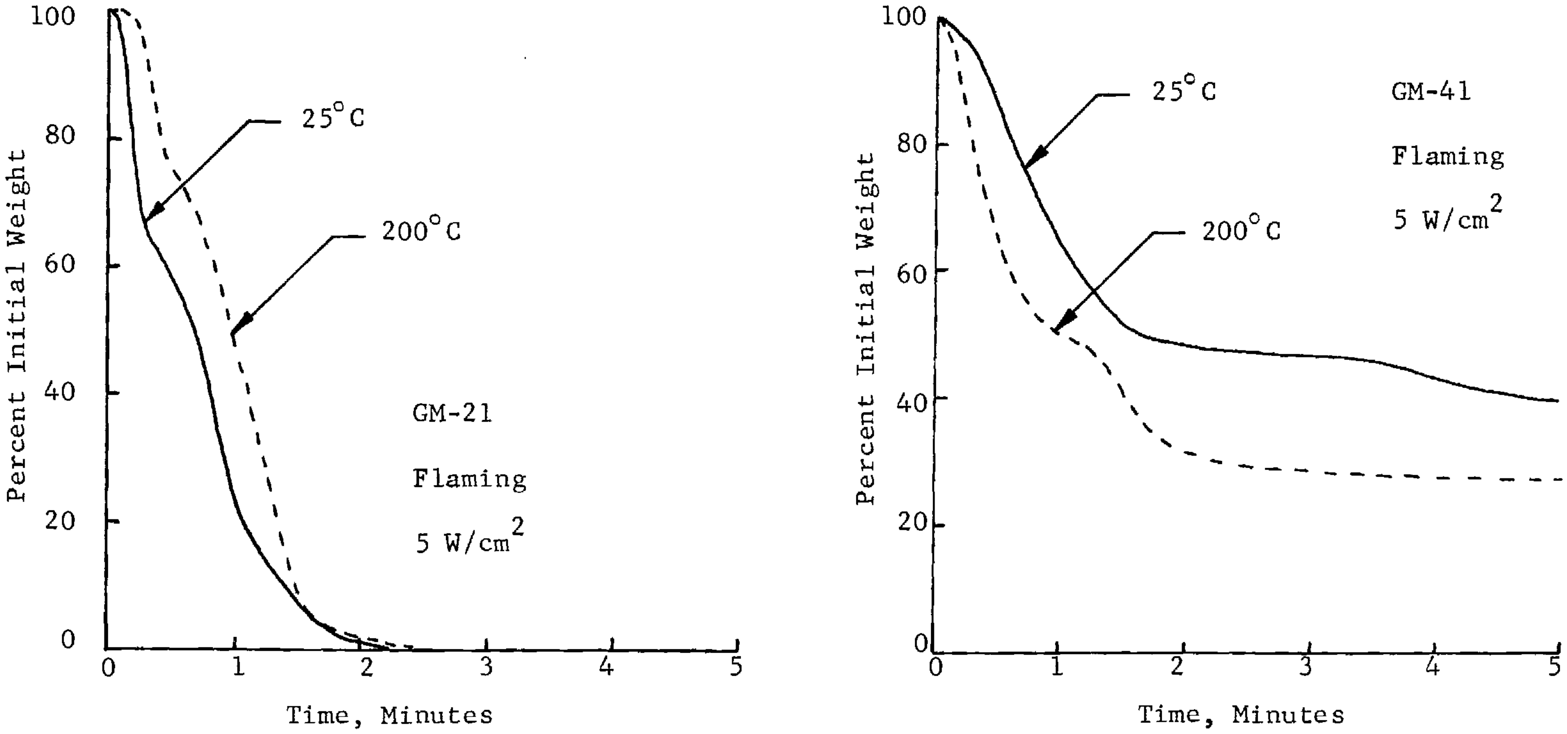
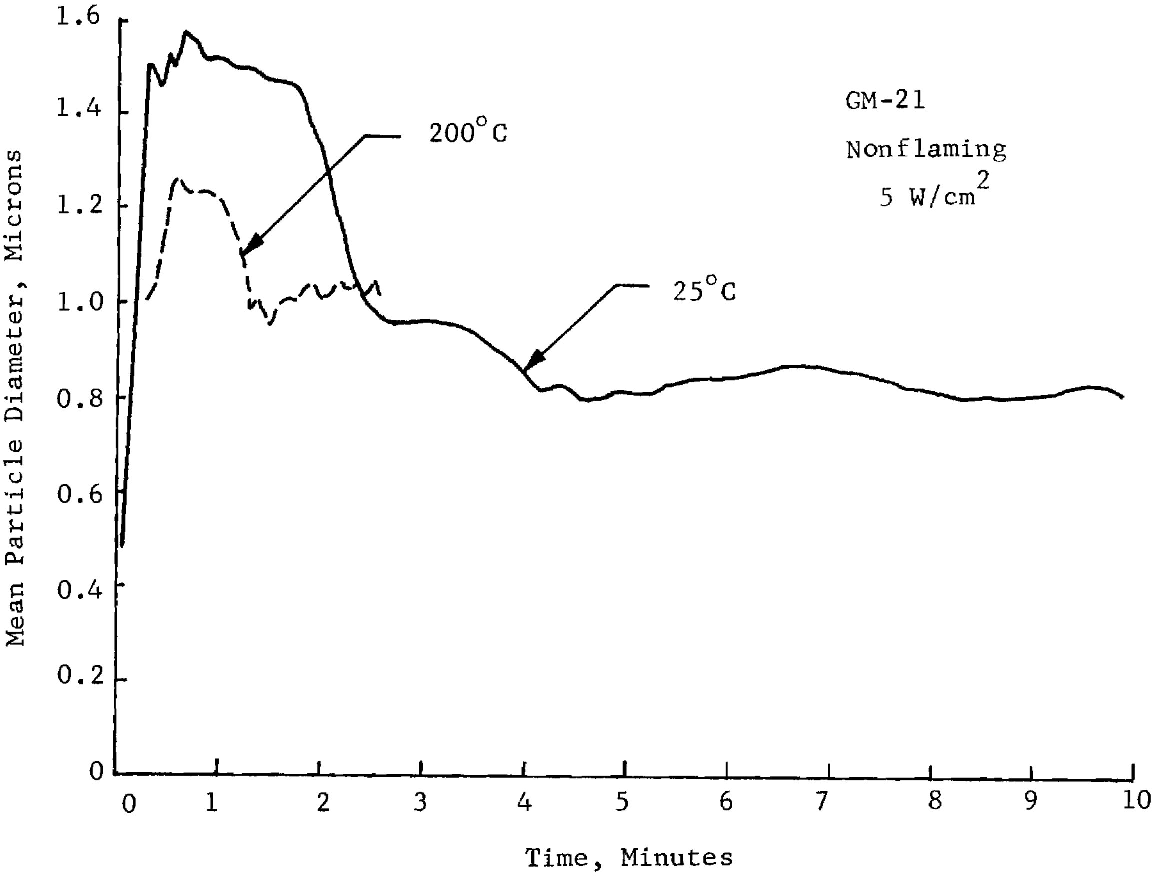


Figure 12. Effect of Ventilation Gas Temperature Upon Sample Weight Loss for Two Cellular Polyurethanes Under Flaming Conditions.

nonflaming test of GM-21, the sample spontaneously ignited about midway through the test, giving a sudden drop in mean particle size. For nonflaming combustion of the GM-29 rigid polyurethane foam (Figure 14) and the GM-41 rigid trimer foam (Figure 15) the effect of environmental temperature on mean particle size is opposite to that observed for GM-21; that is, larger particles are produced in the 200°C tests than in the room temperature tests. For flaming tests of GM-29 (Figure 14) and GM-41 (Figure 15), as in the case of GM-21, moderate increases in D_{32} are obtained by increasing the ventilation air temperature. Relative to the 25°C test, the GM-47 expanded polystyrene foam (Figure 16) exhibits smaller particles over a much shorter time in the 200°C nonflaming tests, while very little effect of environmental temperature upon D_{32} is observed in the flaming tests of GM-47.

The effect of ventilation air temperature on the characteristic mean particle size corresponding to maximum smoke optical density is seen from the data in Tables 3 and 4. For the rigid polyurethane foam (GM-29) and the rigid trimer foam (GM-41) burning under nonflaming conditions (Table 3), the characteristic mean particle size obtained at 200°C is roughly 50% larger than that obtained at 25°C. For these two materials under nonflaming conditions the peak optical density occurs while D_{32} is rapidly decreasing in both the low and high temperature environments. The characteristic values of D_{32} given in Table 3 for nonflaming combustion of the flexible polyurethane foam (GM-21) appear to contradict the D_{32} curves shown in Figure 13. This discrepancy can be explained by noting that: (1) at 200°C the



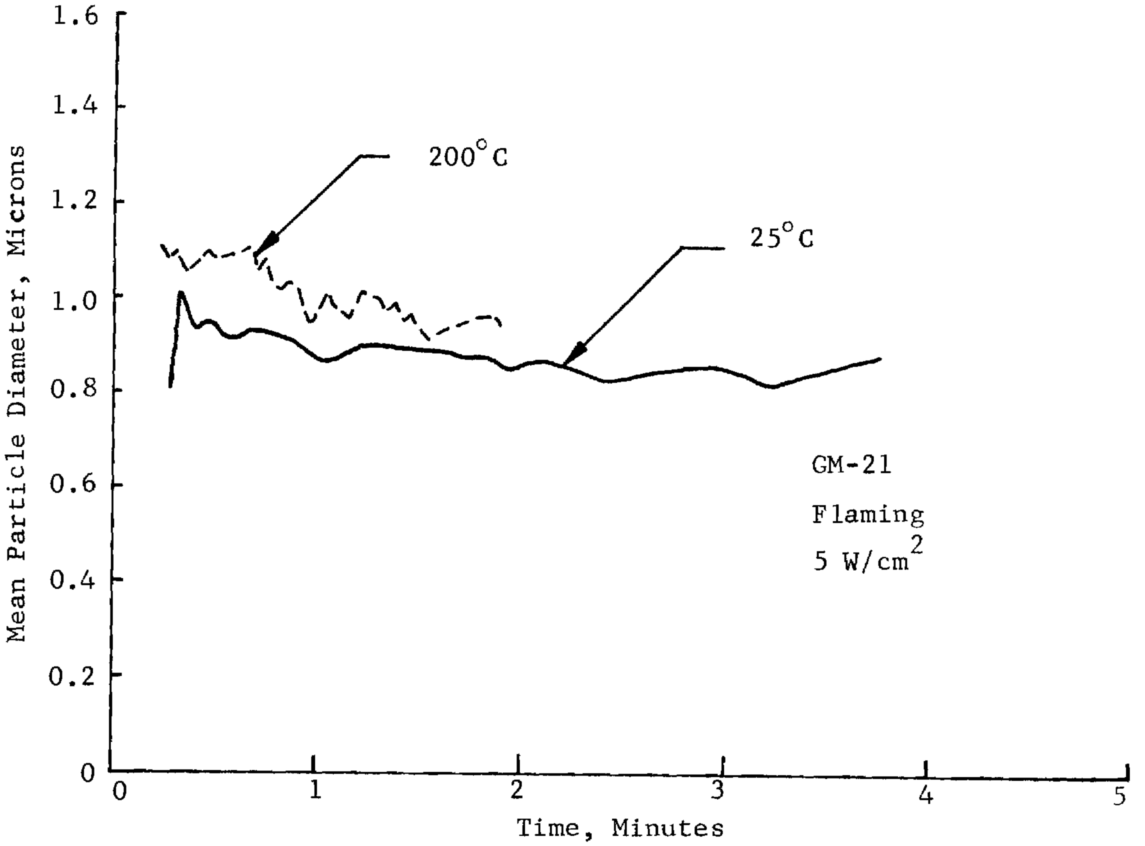


Figure 13. Effect of Ventilation Gas Temperature Upon Smoke Mean Particle Size for Flexible Polyurethane Foam.

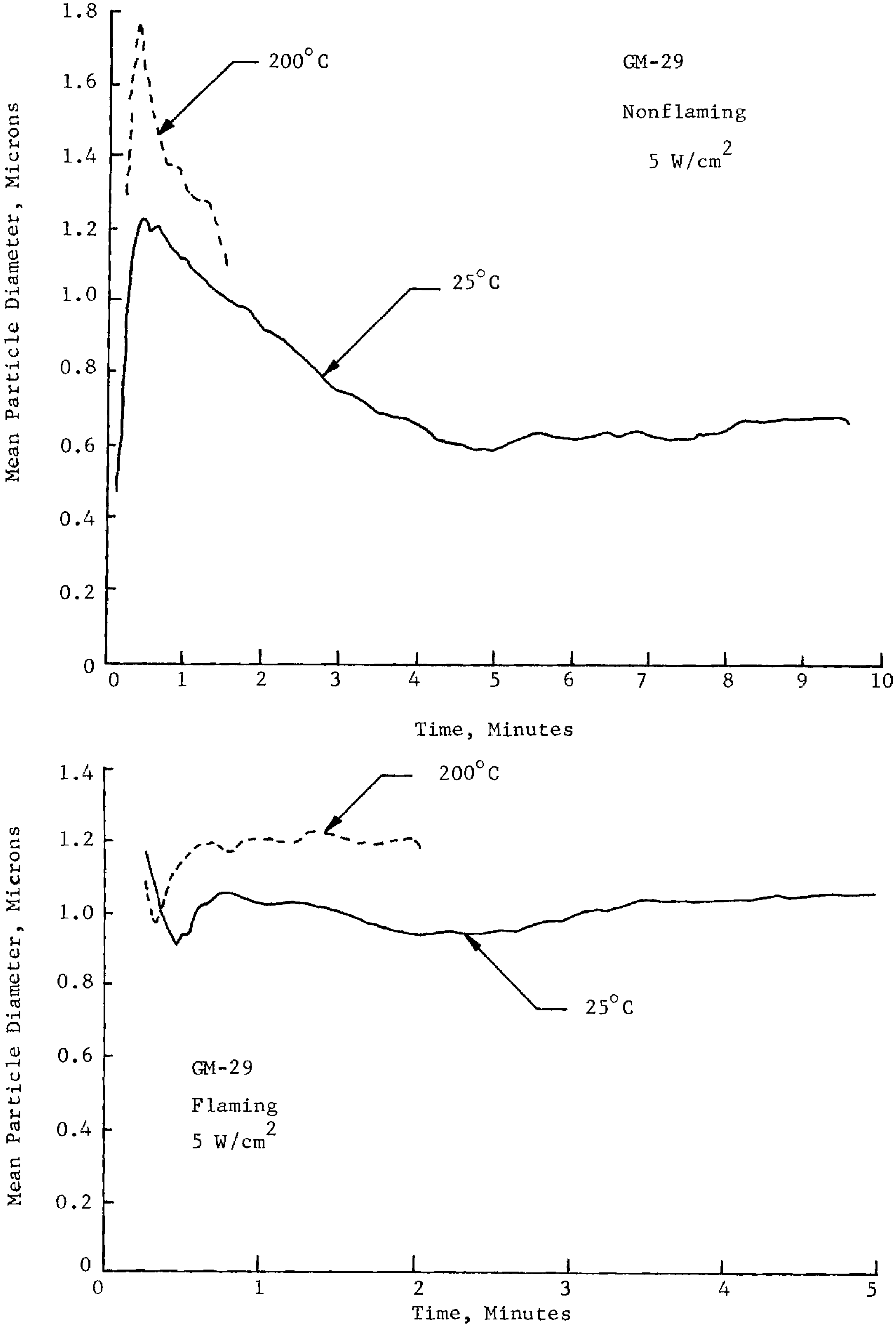


Figure 14. Effect of Ventilation Gas Temperature Upon Smoke Mean Particle Size for Rigid Polyurethane Foam.

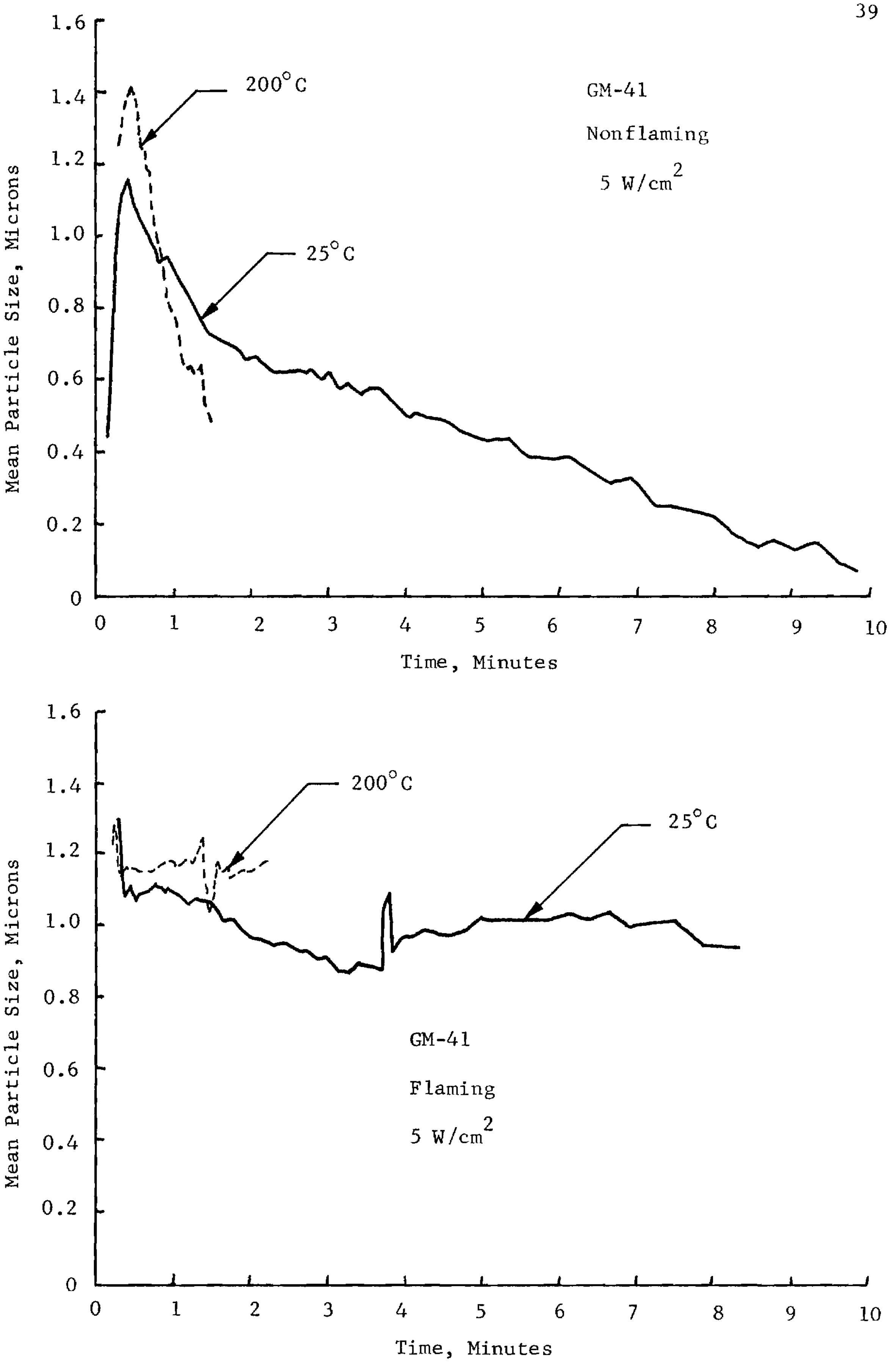
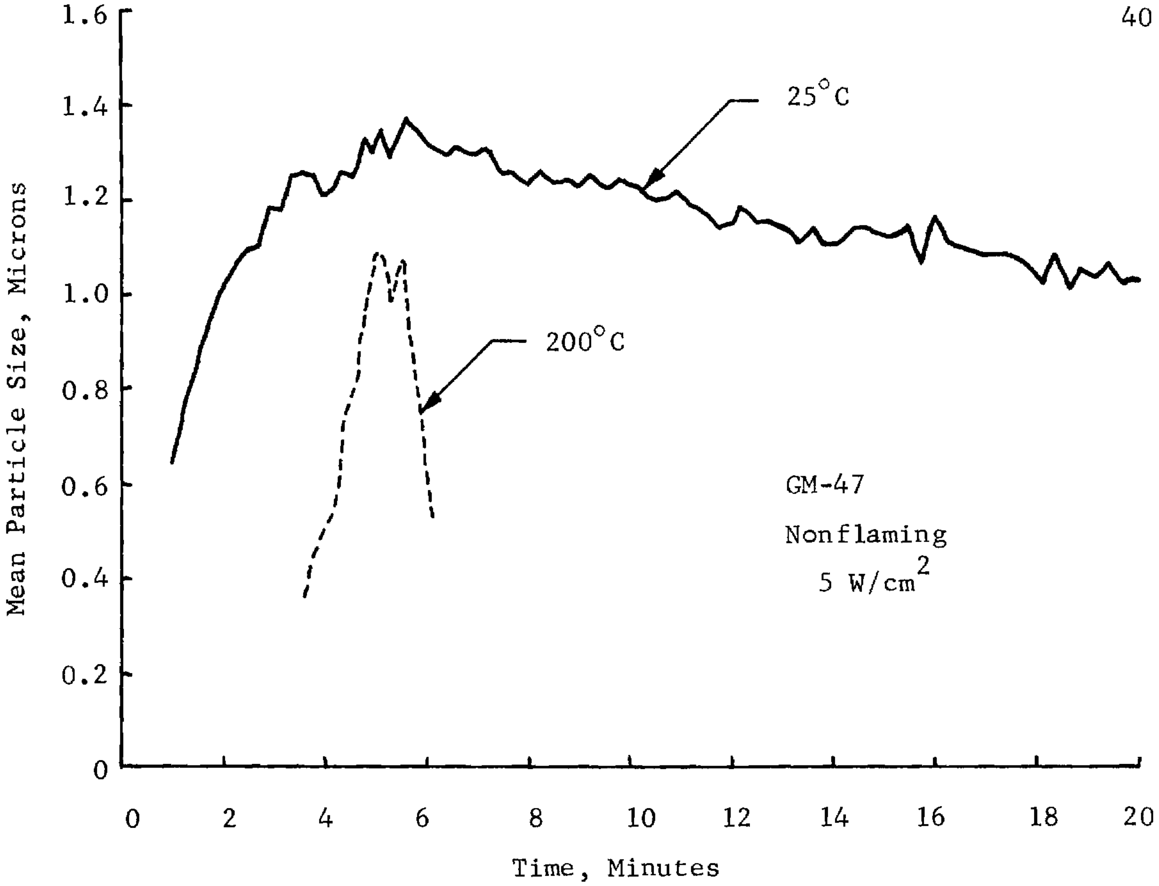


Figure 15. Effect of Ventilation Gas Temperature Upon Smoke Mean Particle Size for Rigid Trimer Foam.



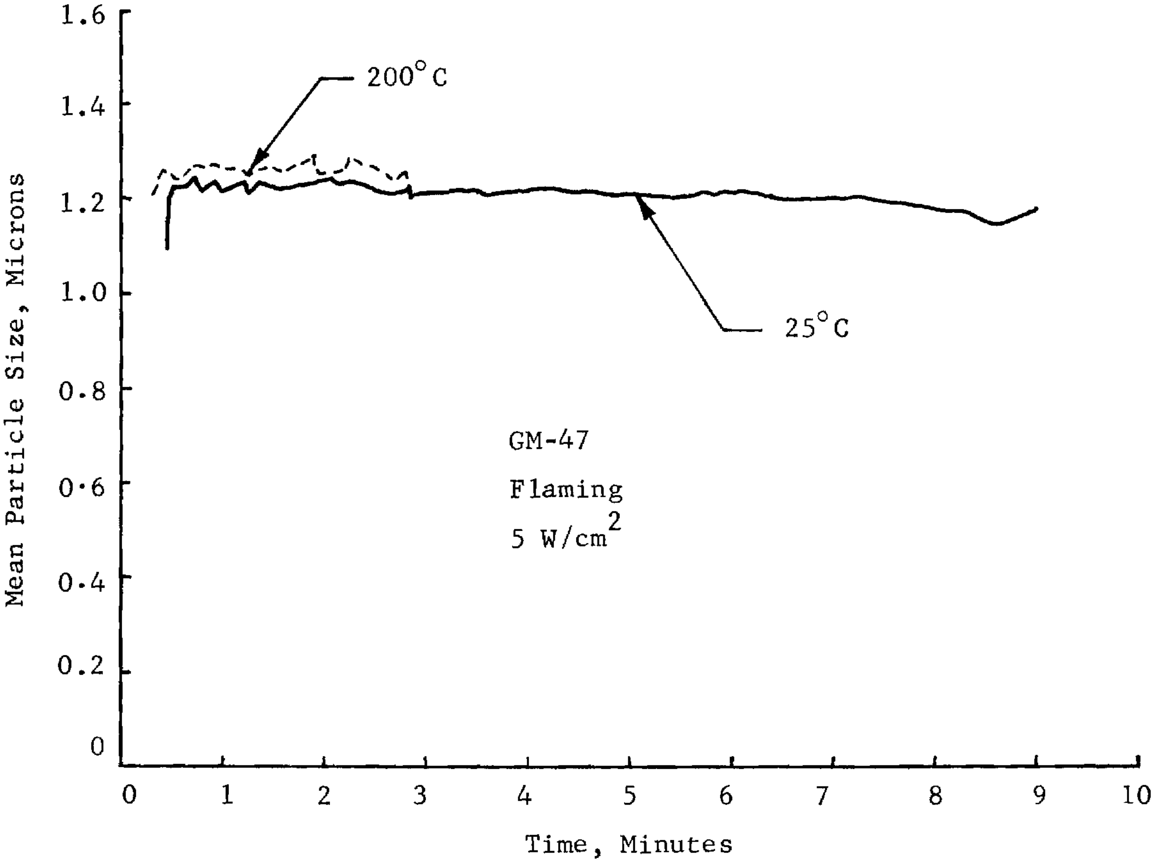


Figure 16. Effect of Ventilation Gas Temperature Upon Smoke Mean Particle Size for Expanded Polystyrene.

peak optical density (before spontaneous ignition) occurs early in the test while D_{32} is near its maximum value and (2) at 25°C the peak optical density occurs later in the test when D_{32} is much smaller than its maximum value. In the case of flaming combustion (Table 4), the characteristic mean particle diameters for all four materials tested are slightly larger in the 200°C tests than in the room temperature tests.

The time variations of the optical density in blue light (0.458 μm) are presented in Figures 17 through 20 for both flaming and nonflaming tests of each of the substrate polymers in both 200°C and room temperature environments. Under nonflaming conditions the two polyurethane foams (Figure 17 and 18) and the rigid trimer foam (Figure 19) exhibit a large decrease in the peak optical density as a result of the increase in environmental temperature to 200°C. For nonflaming combustion of the expanded polystyrene foam (Figure 20) the peak optical density is about the same at both temperatures. For all four materials tested under nonflaming conditions, the peak optical density occurs much earlier and the period of significant light obscuration is much shorter at 200°C than at 25°C. Under flaming conditions the effect of environmental temperature upon optical density is much less than that observed for nonflaming combustion. For the flexible polyurethane foam (Figure 17) the optical density curve for flaming combustion at 200°C is nearly identical to the corresponding room temperature curve. For flaming tests of the other three materials, the maximum optical density obtained at 200°C is about half of the OD_{max} obtained at room temperature. Part of the decrease in optical density is due to the increased dilution of the smoke by the higher volumetric flow rate of the hot venti-

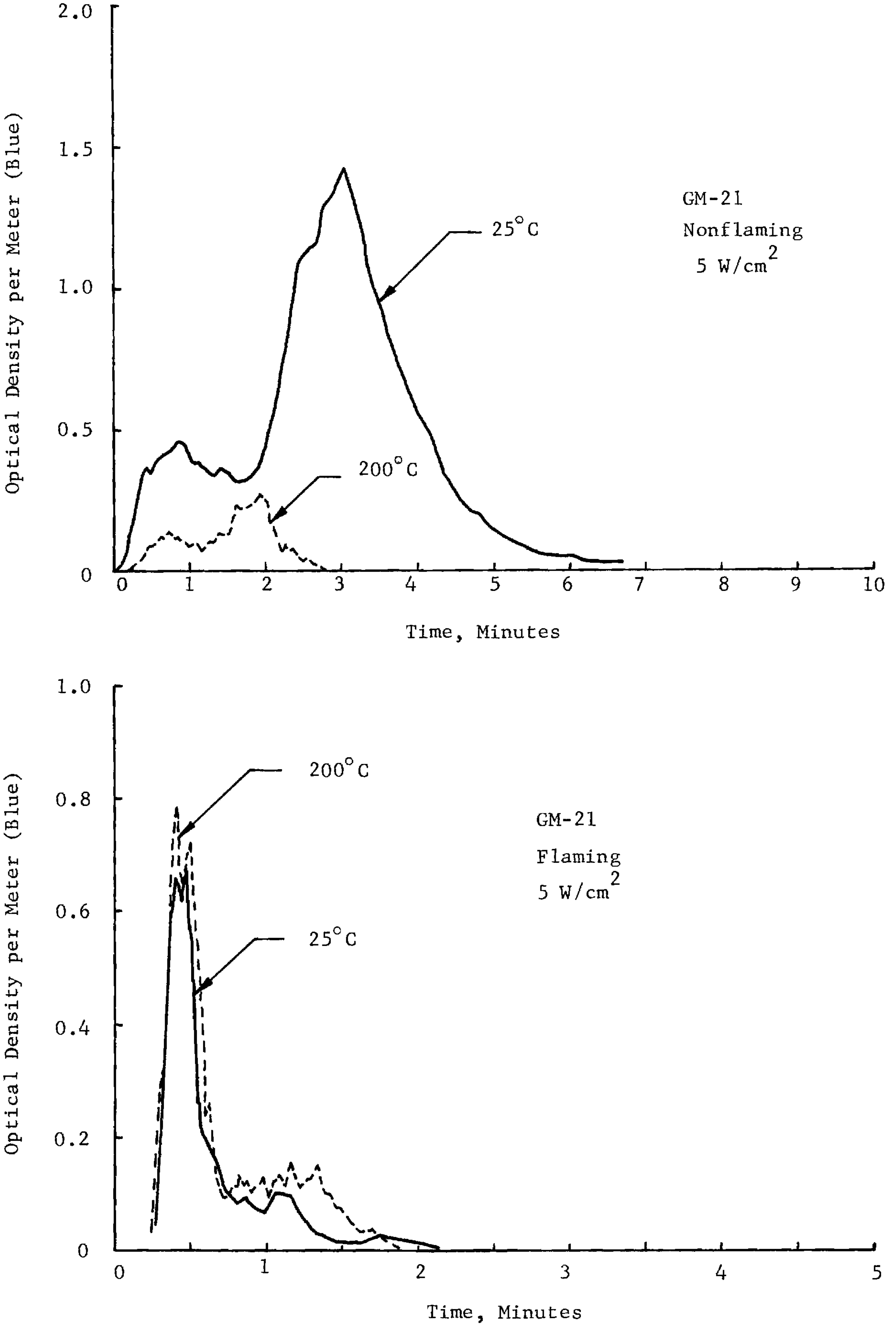


Figure 17. Effect of Ventilation Gas Temperature Upon Smoke Optical Density for Flexible Polyurethane Foam.

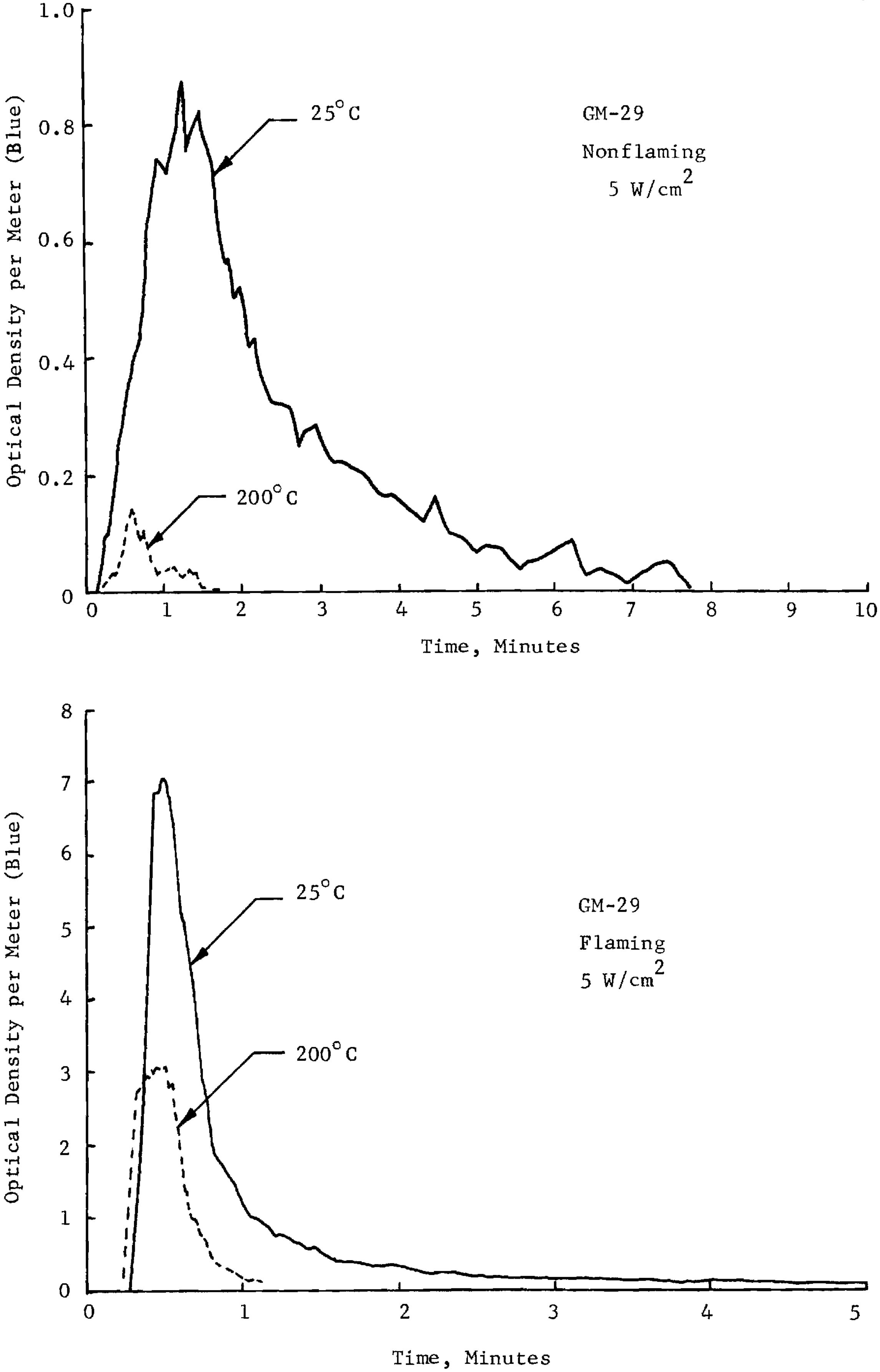


Figure 18. Effect of Ventilation Gas Temperature Upon Smoke Optical Density for Rigid Polyurethane Foam.

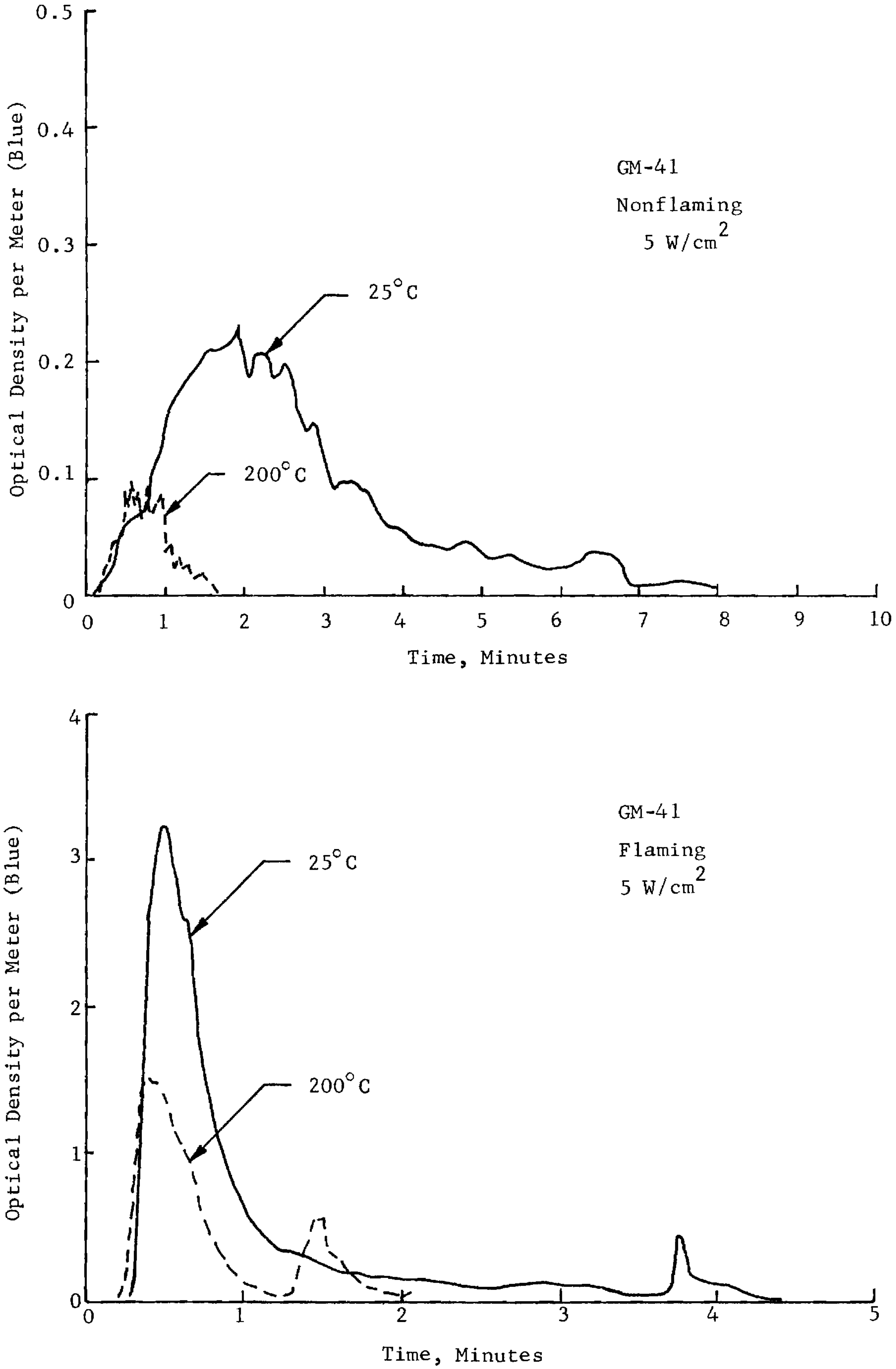
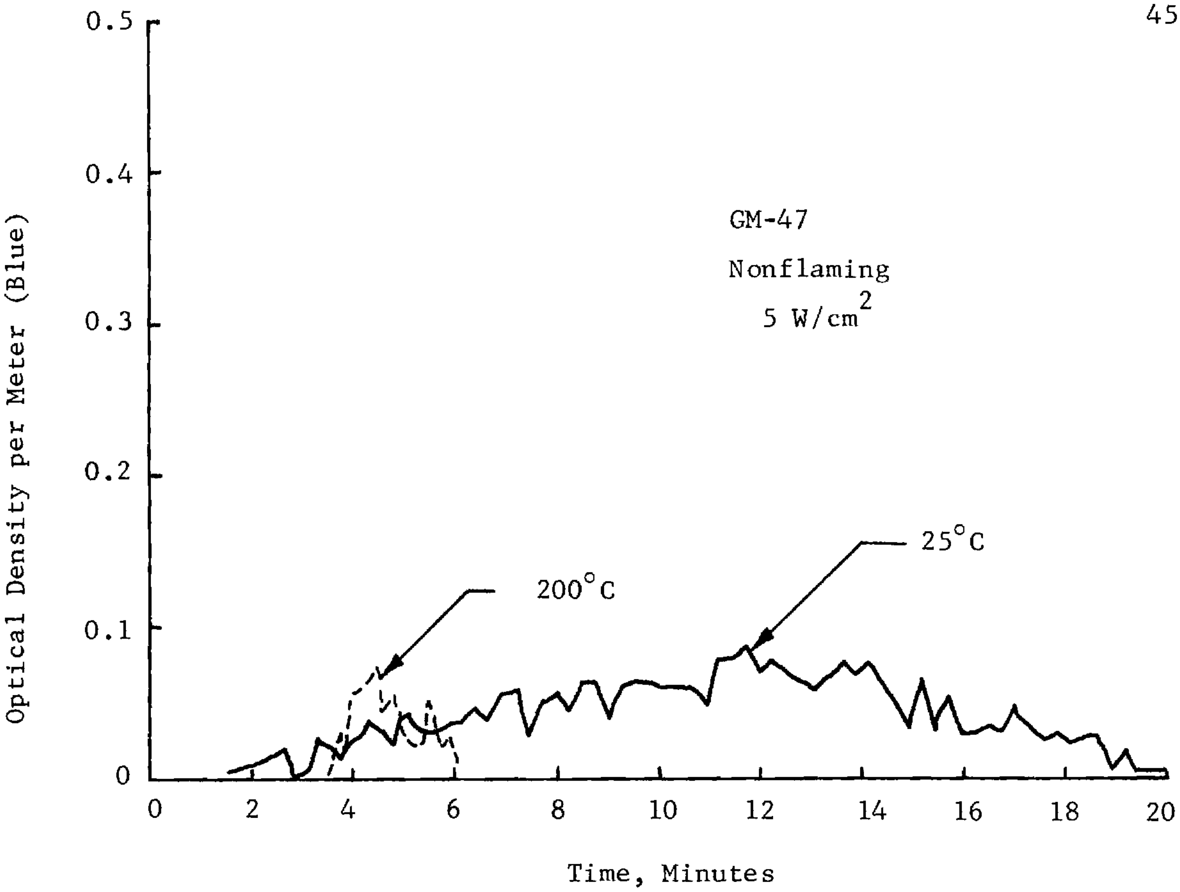


Figure 19. Effect of Ventilation Gas Temperature Upon Smoke Optical Density for Rigid Trimer Foam.



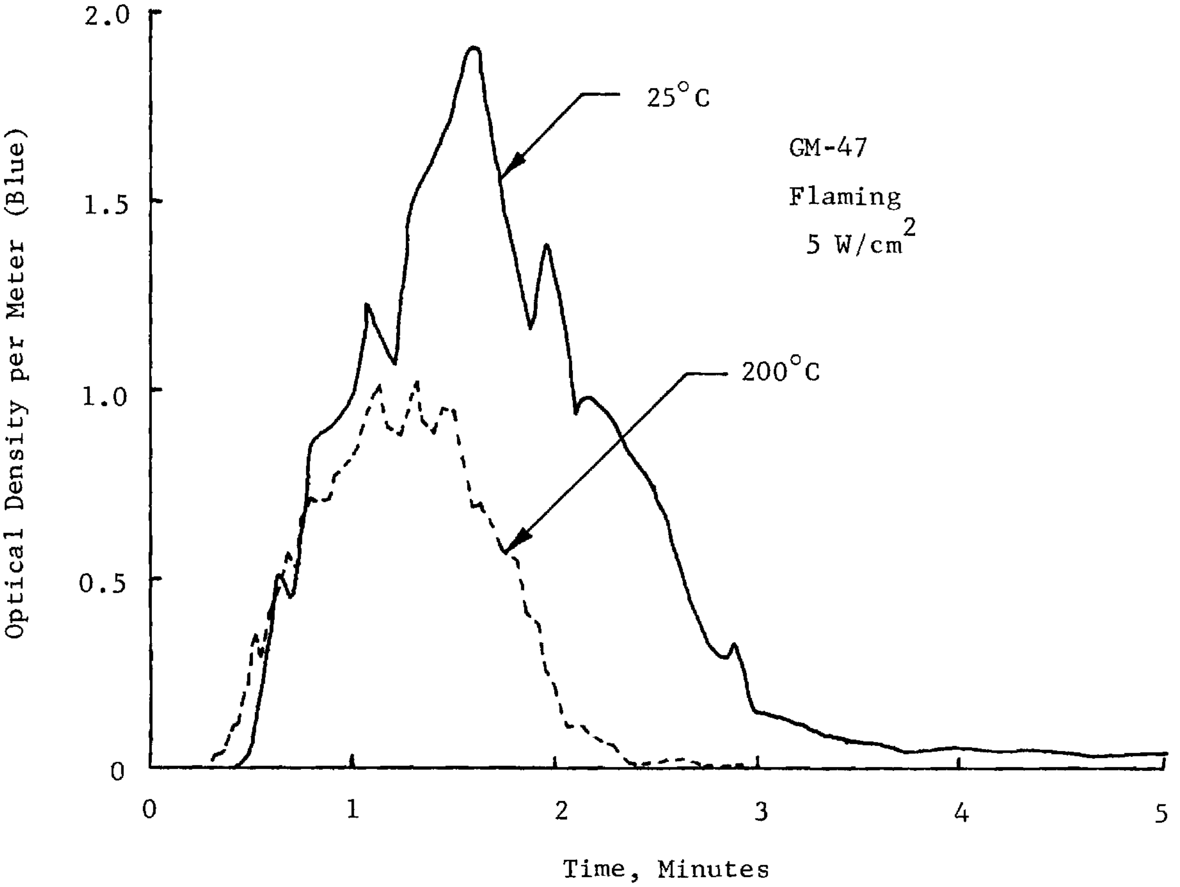


Figure 20. Effect of Ventilation Gas Temperature Upon Smoke Optical Density for Expanded Polystyrene.

lation air. (The flow rate of the ventilation air before heating was the same for both high and low temperature tests). In order to eliminate this dilution effect, the 200°C optical density data presented in Tables 3 and 4 has been corrected to the same volumetric flow rate as the 25°C data. Except for the flexible polyurethane foam, the corrected optical densities indicate that under flaming combustion increasing the environmental temperature yields moderate decreases in the peak optical density obtained under constant volumetric flow rate conditions (Table 4). This result is opposite to the behavior observed in previous flaming tests of several non-cellular polymers (polystyrene, polyvinyl chloride, polypropylene, polyethylene, and polymethylmethacrylate) which gave moderate increases in OD_{max} at elevated environmental temperatures[6]. For nonflaming combustion of the expanded polystyrene foam the corrected optical densities indicate a moderate increase in OD_{max} due to increased ventilation air temperature.

For flaming combustion the OD_{max} data in Table 4 shows that the smokiness ranking of the four cellular polymers according to optical density is the same at high temperature as at room temperature. In order of decreasing OD_{max} these materials are ranked as follows: (1) GM-29 rigid polyurethane foam, (2) GM-41 rigid trimer foam, (3) GM-47 expanded polystyrene foam, and (4) GM-21 flexible polyurethane foam. On the other hand Table 3 shows that for nonflaming combustion at 200°C all four materials produce about the same low value of optical density (0.12 - 0.22 per meter) and can not be clearly ranked. For low temperature nonflaming conditions these same materials appear in Table 3 in order of decreasing optical density.

Although the parameter Γ could not be measured for the high temperature tests, the effect of elevated temperature upon Γ for flaming combustion can be estimated from the optical density and weight loss data. Since mean particle size and refractive index (for soot particles) do not change greatly with increased ventilation air temperature, a decrease in optical density at 200°C indicates a lower volume concentration of smoke particles at the higher temperature. In a ventilated system the smoke volume concentration is proportional to the mass rate of production of particulates which is the product of Γ and the total mass loss rate of the sample. If the volume concentration is lower while the total mass loss rate is moderately higher at 200°C than at room temperature, then the fraction of the mass loss converted to particulates (Γ) at 200°C must be significantly smaller than the corresponding room temperature value. Thus Γ apparently decreases with increasing environmental temperature for the GM-29 rigid polyurethane foam, the GM-41 rigid trimer foam, and the GM-47 expanded polystyrene foam under flaming conditions. By a similar argument, it appears that Γ increases with increasing environmental temperature for flaming combustion of the GM-21 flexible polyurethane foam. In the case of nonflaming combustion (Table 3) the larger effect of environmental temperature upon D_{32} and possibly refractive index lead to difficulties in estimating Γ in the manner described above. However, the large decreases in OD_{max} with increasing ventilation gas temperature

Table 3. Smoke Properties Data - Nonflaming Conditions - 5 W/cm^2

Material	Temperature °C	Γ	OD_{max} Blue	OD_{max} Red	D_{32} (μm)	Time to Peak OD (min)	Char Residue % Initial Weight
GM-21	25	.064	1.42	1.17	0.96	3.0	T
	200	-	0.21	0.11	1.23	0.7	1.2
GM-29	25	.070	0.87	0.87	1.05	1.2	39.0
	200	-	0.22	0.11	1.52	0.6	17.7
GM-41	25	.047	0.23	0.19	0.68	1.9	62.0
	200	-	0.15	0.06	1.06	0.7	41.3
GM-47	25	.114	0.09	0.06	1.17	11.7	T
	200	-	0.12	0.06	1.04	4.7	T

Γ = Fraction of sample weight loss converted to smoke particulates

OD_{max} = Maximum optical density in blue (.458 μm) and red (.633 μm) light at a volumetric flow rate of 283 liters/minute.

D_{32} = Volume-surface mean particle diameter at maximum optical density.

T = Trace quantity.

Table 4. Smoke Properties Data - Flaming Conditions - 5 W/cm^2

Material	Temperature °C	Γ	OD_{max}		D_{32} (μm)	Time to Peak OD (min)	Char Residue % Initial Weight
			Blue	Red			
GM-21	25	<.01	0.68	0.52	0.94	0.5	T
	200	-	1.24	0.95	1.08	0.4	T
GM-29	25	.085	7.03	4.98	0.93	0.5	15.1
	200	-	4.86	3.87	1.11	0.5	17.5
GM-41	25	.060	3.23	2.44	1.09	0.5	37.4
	200	-	2.39	1.89	1.17	0.4	27.2
GM-47	25	.085	1.90	1.50	1.23	1.6	T
	200	-	1.61	1.33	1.26	1.3	T

Γ = Fraction of sample weight loss converted to smoke particulates.

OD_{max} = Maximum optical density in blue (.458 μm) and red (.633 μm) light at a volumetric flow rate of 283 liters/minute.

D_{32} = Volume-surface mean particle diameter at maximum optical density.

T = Trace quantity.

observed for nonflaming combustion of the polyurethane foams (GM-21 and GM-29) probably are due to a corresponding decrease in Γ.

D. Summary and Discussion.

Low temperature tests of flexible and rigid polyurethane foams, rigid trimer foam, and expanded polystyrene foam indicate the effects of the chemical structure of the substrate polymer upon its smoking characteristics. These results show that the expanded polystyrene foam has a greater fraction of its pyrolysis products converted to smoke particulates under nonflaming conditions than the other materials, while the flexible polyurethane foam yields the greatest optical density. The variety of mean particle diameter and optical density variations observed under nonflaming conditions results from differences in chemical structure of the various polymers studied which yield different mixtures of condensible pyrolysis products. For example, polystyrene should produce the greatest concentration of the wax-like, aromatic tars that dominate nonflaming pyrolysis products due to the readily available phenyl groups.[7] The similarities in particle sizes and the wide range of optical densities obtained under flaming conditions indicate that: (1) the chemical structure of the substrate polymer is not a major factor in determining the particle size characteristics of the sooty smokes produced by flaming combustion and (2) the chemical composition of the substrate polymer is important in determining the rate of production of smoke particulates under flaming combustion.

The results of this study show that the type of combustion (i.e., flaming or nonflaming) is an important factor in determining the physical characteristics of smoke. For the rigid polyurethane and trimer foams, more total smoke by mass is generated under flaming conditions than under nonflaming conditions, and for all materials except the flexible polyurethane foam peak optical densities are much greater in the flaming tests. Mean particle sizes obtained in flaming tests tend to be larger or smaller than those measured under nonflaming conditions depending upon the material tested. Sample mass loss rates are consistently higher under flaming conditions than under nonflaming conditions. Finally, the order of ranking the smoking tendencies of the four cellular polymers tested (with either Γ or optical density as a ranking criterion) depends upon the type of combustion. These differences are presumably due to the fact that the thermal environments and pyrolysis products are different in the flaming and nonflaming cases. Consequently, the smoke formation processes in flaming combustion follow a different route of particle formation, where the particles are found to be "sooty" in nature, than in the nonflaming situation. More specifically, assuming that the properties of the initial pyrolysis products of the polymer are similar in both situations, much of the pyrolysis products that follow the condensation route in the nonflaming situation undergo further reactions in the flaming case, resulting in a lower fraction of the total mass loss converted to soot particulates (i.e., flexible polyurethane foam and expanded polystyrene foam). For materials which generate considerably larger particles in the flaming case (i.e., rigid trimer foam), the rapid generation of pyrolysis products probably results in fuel-rich conditions during the burning of these materials. In many cases the soot thus formed is composed of long chainlike agglomerates. In contrast, the smoke collected in nonflaming tests consists of a complex mixture of tarry, liquid organic compounds which contains little or no soot.

This study also shows that the temperature of the immediate surroundings of a burning polymer is an important factor in determining the characteristics of the smoke produced. High temperature tests of the flexible polyurethane foam under flaming and nonflaming conditions have produced the same opposite trends observed previously for several non-cellular polymers.[6] In flaming tests of this material, higher ventilation gas temperatures result in greater smoke optical densities and larger smoke particles, while in nonflaming tests, higher temperatures result in lower smoke densities and smaller particles. For the other three cellular polymers under flaming conditions, however, higher ventilation gas temperatures result in lower optical densities although the smoke particles are still larger than those produced in the low temperature tests. For nonflaming tests of the rigid polyurethane and trimer foams, increasing the environmental temperature reduces the optical density but increases the mean particle size. Measured data also show that the increased environmental temperature in the high temperature tests results in increased weight loss rates for both modes of combustion that imply increased supply of pyrolysis products by the polymer to the gas phase. Since the oxygen supply remains fixed, the excess fuel may result in increased particle concentration in the flaming case where the particles are presumably generated within the flame (i.e., flexible polyurethane foam). In contrast, condensation processes are probably the dominating particulate formation mechanisms in the non-flaming case and increased environmental temperatures will tend to hinder the condensation step and the associated particulate formation (i.e., the polyurethane and trimer foams).

The validity of the conjectures outlined in this section will have to be verified or modified from the results of future studies.

V. EFFECT OF FIRE RETARDANT ADDITIVES ON SMOKE CHARACTERISTICS

Tests of the equivalent fire retarded materials corresponding to the four polymers investigated in Task A were conducted under Task B. These fire retarded materials are flexible polyurethane foam (GM-23), rigid polyurethane foam (GM-31), rigid trimer foam (GM-43), and expanded polystyrene foam (GM-49),all of which contain the same fire retardant, a chlorinated phosphonate ester. Each of the fire retarded materials was exposed to the same test conditions as the non-fire-retarded materials; that is, flaming and nonflaming tests at room temperature and at 200°C.

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

Sample weight loss data for room temperature tests of the four fire retarded (FR) materials are shown in Figure 21 for nonflaming combustion. For the rigid polyurethane foam (GM-31) the data for the non-fire-retarded material (GM-29) is shown for comparison. For this material the addition of fire retardant results in a lower mass loss rate and a larger amount of char residue. For the fire retarded materials under nonflaming conditions, the flexible polyurethane foam (GM-23) exhibits the most rapid weight loss while the expanded polystyrene foam (GM-49) yields the lowest mass loss rate. In contrast to the corresponding non-fire-retarded polymers which leave little or no char under nonflaming conditions, the fire retarded flexible polyurethane foam (GM-23) and expanded polystyrene foam (GM-49) leave an appreciable fraction of their original weight (13% and 26% respectively) as char residue. In nonflaming tests, the rigid trimer foam

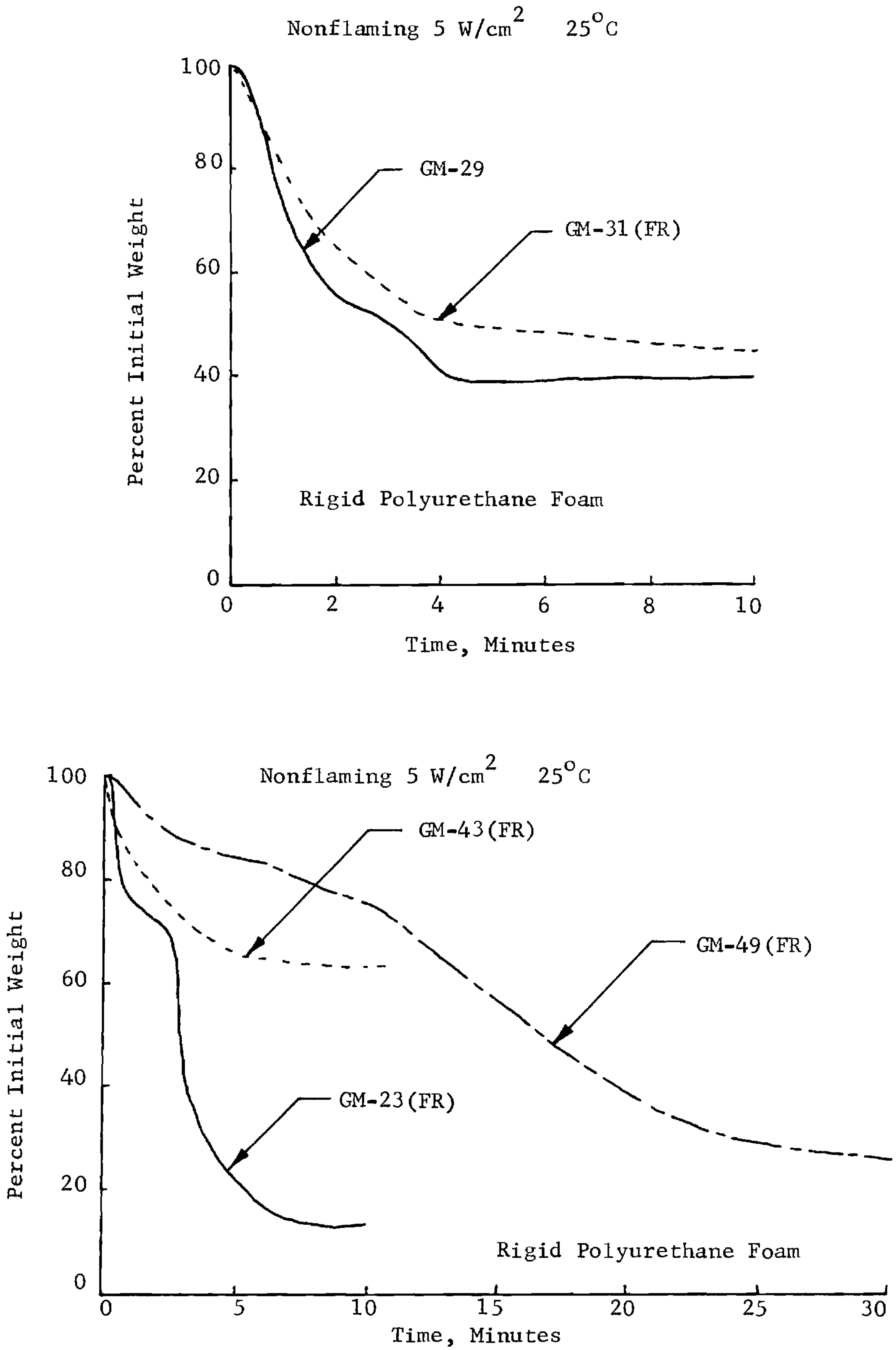


Figure 21. Sample Weight Loss for Four Fire Retarded Cellular Polymers under Low Temperature Nonflaming Conditions.

(GM-43) yields only slightly more char residue than its non-fire-retarded counterpart (Table 5).

Figure 22 shows weight loss data for the rigid trimer foam (GM-43) burning under flaming conditions along with the data for the equivalent non-fire-retarded material. For flaming tests of this material,adding the fire retardant results in a considerably lower mass loss rate and significantly larger amount of char residue. Addition of fire retardants also increases the amount of char yield for flaming flexible polyurethane foam (GM-23), while the fire retarded rigid polyurethane foam (GM-31) yields slightly less char than its non-fire-retarded equivalent (GM-29) under flaming conditions (Table 6). The fire retarded expanded polystyrene foam does not ignite in the room temperature atmosphere under 5 W/cm^2 radiant flux.

Smoke particle size distributions obtained with the cascade impactor for the four fire retarded materials tested under nonflaming conditions in room temperature ventilation air are shown in Figure 23. As discussed previously, this data is presented as cumulative log-normal probability plots in which log-normal distributions are represented by straight lines. For the fire retarded flexible and rigid polyurethane foams (GM-23 and GM-31) the larger particles depart from the log normal distribution, and two straight lines are used to represent this data. The size distributions for the other two fire retarded materials are well represented by a single straight line and are thus approximately log normal. Mass median diameters (D_{MMD}) and standard deviations (σ) derived from these data are given in Table 5.

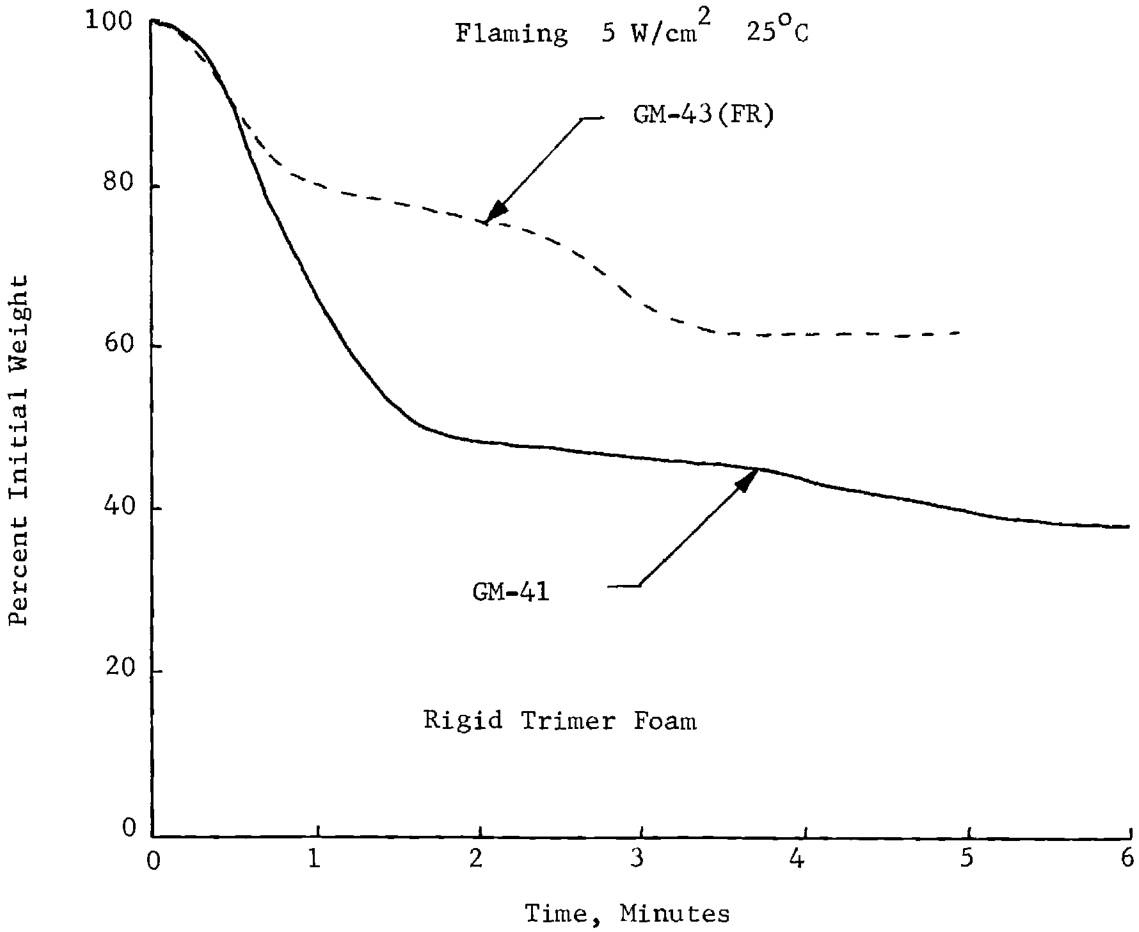


Figure 22. Effect of Fire Retardants Upon Sample Weight Loss for Rigid Trimer Foam Under Low Temperature Flaming Conditions.

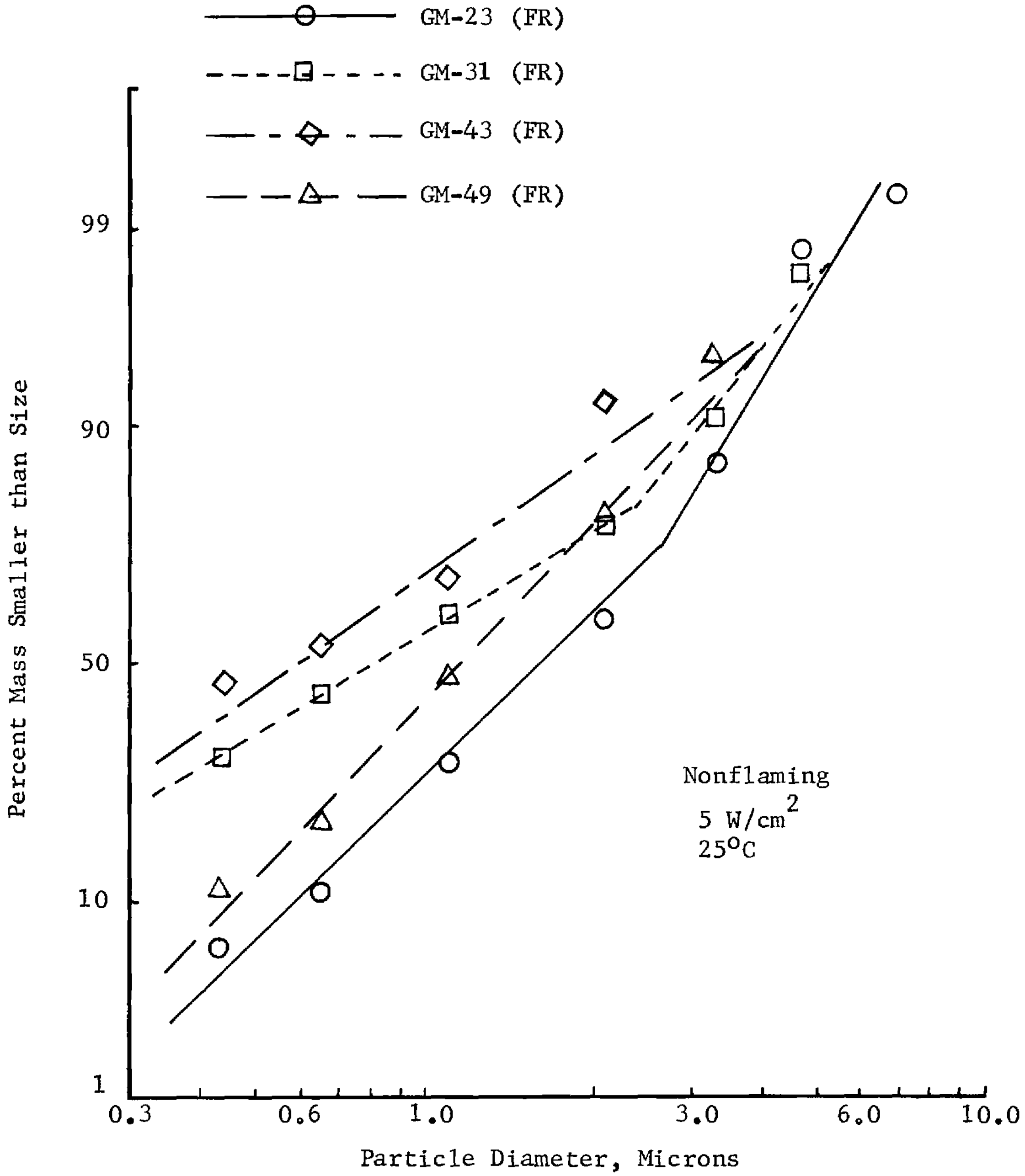


Figure 23. Smoke Particle Size Distributions for Four Fire Retarded Cellular Polymers Generated Under Low Temperature Nonflaming Conditions.

For the fire retarded materials, the largest particles are produced by the flexible polyurethane foam (GM-23) with a mass median diameter of 1.6 microns, while the rigid trimer foam (GM-43) produces the smallest particles with a D_{MMD} of 0.6 microns. For these same two materials, the mass median diameters are substantially greater than those obtained for the equivalent non-fire-retarded materials. In contrast, addition of fire retardants has little effect on D_{MMD} for the rigid polyurethane foam and considerably reduces D_{MMD} for the expanded polystyrene foam. For each of the fire-retarded materials the standard deviations are slightly smaller than those obtained for the corresponding non-fire-retarded materials. For the same reasons as discussed previously for the non-fire-retarded materials, particle size distributions are not available for the fire retarded materials under flaming conditions.

The time-variation of the volume-surface mean particle diameter D_{32} is given in Figures 24 through 27 for both flaming and nonflaming tests of the four fire retarded cellular polymers studied. In each D_{32} versus time plot, data for both fire-retarded and non-fire-retarded materials are presented.

For nonflaming combustion of the flexible polyurethane foam (Figure 24), the addition of fire retardant substantially reduces the mean particle size of the smoke generated during the first two minutes of the test while having little effect on D_{32} for the remainder of the test. For nonflaming tests of the rigid polyurethane foam (Figure 25) and the rigid trimer foam (Figure 26), fire retardants appear to have little effect on mean particle size, although the fire-retarded rigid trimer foam produces measurable smoke over a much shorter time than its non-fire-retarded counterpart. For the expanded polystyrene foam (Figure 27), the evolution of D_{32} with time is slower and the mean particle size is somewhat smaller for the fire-retarded material. Characteristic mean particle diameters, D_{32}, obtained at the time of maximum optical density during the nonflaming tests of the fire-retarded and non-fire-retarded polymers are given in Table 5. The addition of fire retardant results in a small decrease in the characteristic value of D_{32} for the flexible polyurethane foam and the expanded polystyrene foam while having only a slight effect on the characteristic particle size for the rigid polyurethane foam, and the rigid trimer foam. Except for the flexible polyurethane foam, the effect of fire retardants upon mean smoke particle size as determined by the optical measurements is consistent with the effect of fire retardants upon the mass median diameters as determined by direct particulate sampling. The opposite trends obtained from the optical and sampling measurements for the flexible polyurethane foam can not be adequately explained in terms of differences in the two measurement techniques.

Except for the rigid trimer foam, the addition of fire retardants has little effect upon mean particle diameters obtained under flaming combustion of these polymers. For the flaming tests of the flexible polyurethane foam (Figure 24) somewhat smaller smoke particles are produced when fire retardants are present, while slightly larger particles are produced when fire retardants are added to the rigid polyurethane foam (Figure 25). The characteristic values of D_{32} shown in Table 6 also indicate these same trends in the effects of fire retardants upon smoke particle size for these two materials. For the rigid trimer foam in flaming combustion (Figure 26), much smaller particles are produced by the fire retarded sample, especially during the first half of the

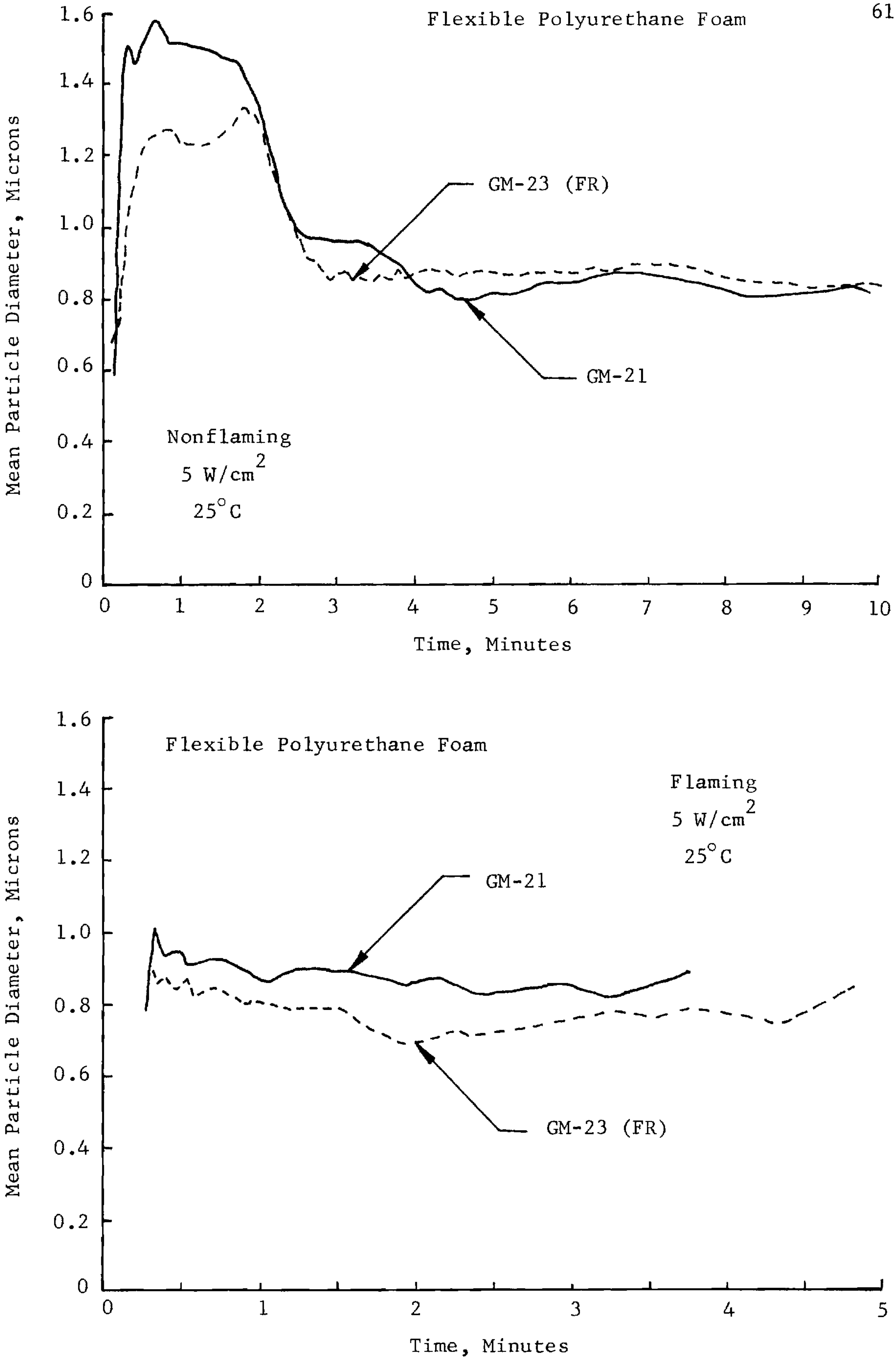
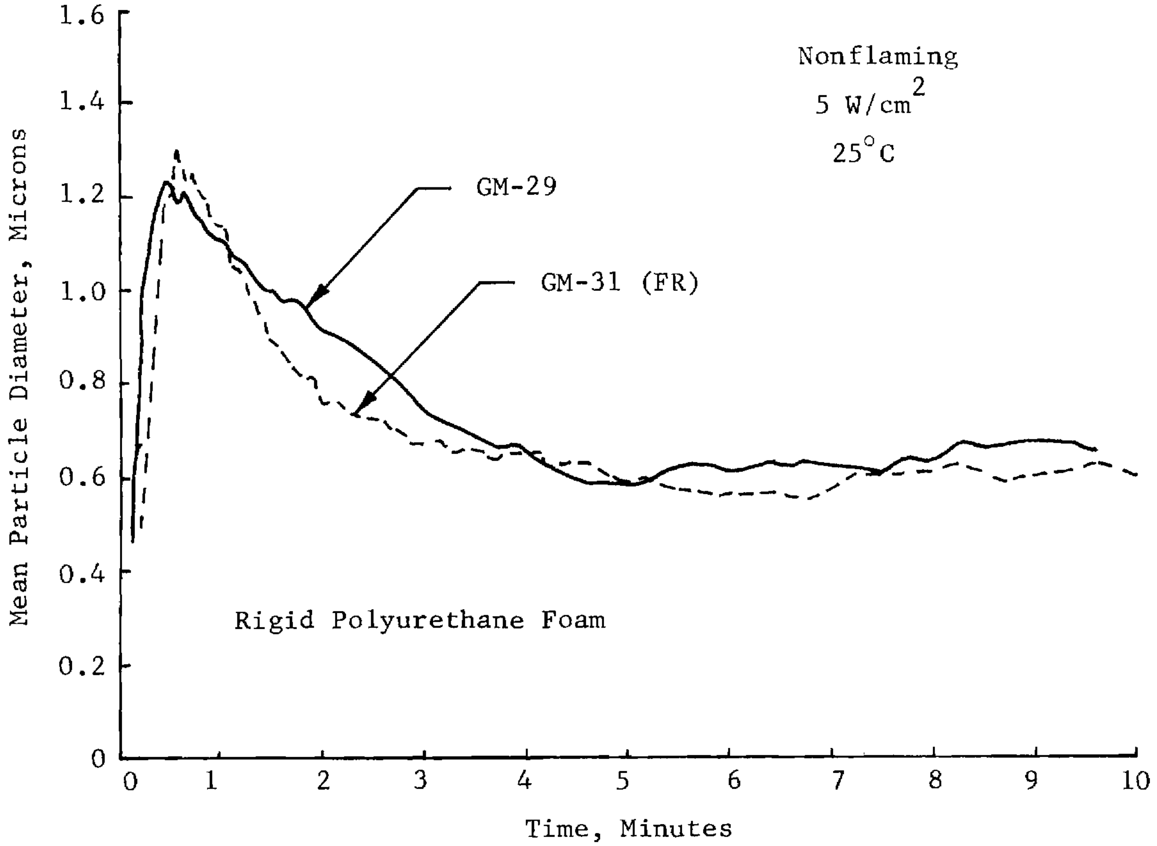


Figure 24. Effect of Fire Retardant Upon Smoke Particle Size for Flexible Polyurethane Foam Burning in Room Temperature Air.



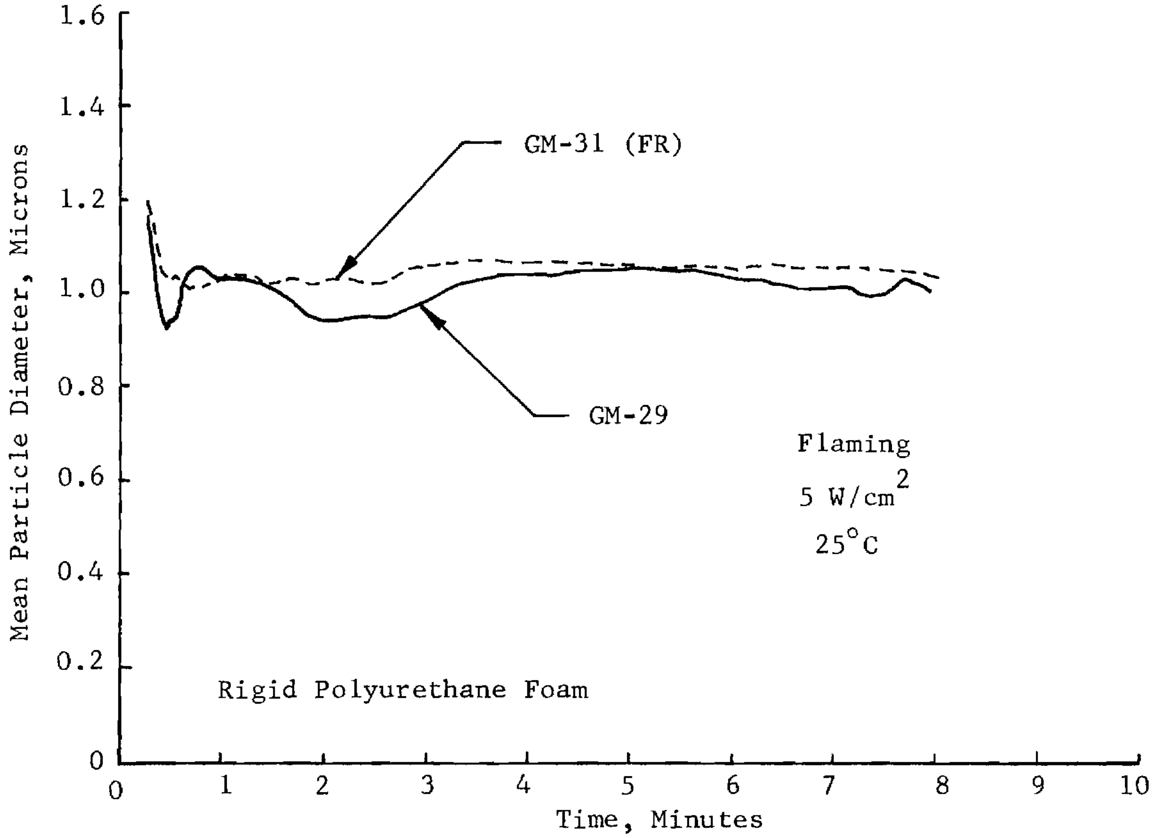
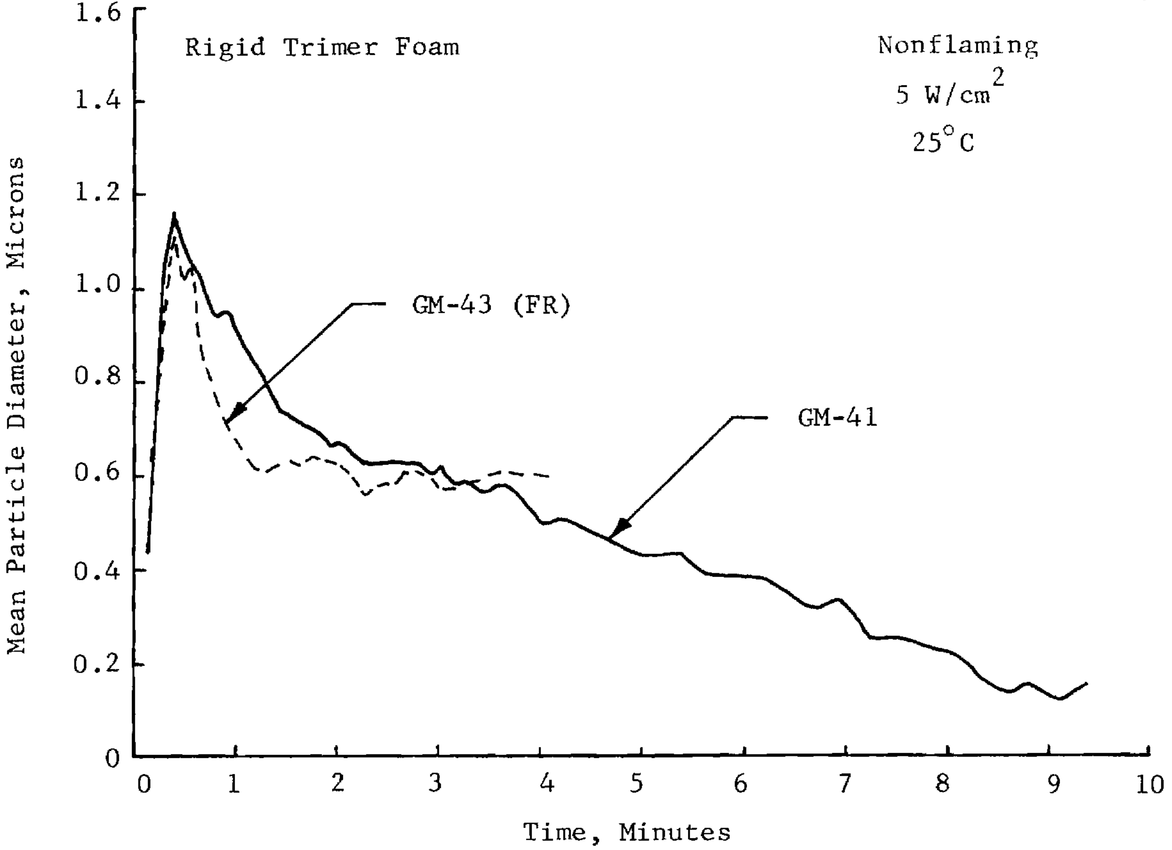


Figure 25. Effect of Fire Retardant Upon Smoke Particle Size for Rigid Polyurethane Foam Burning in Room Temperature Air.



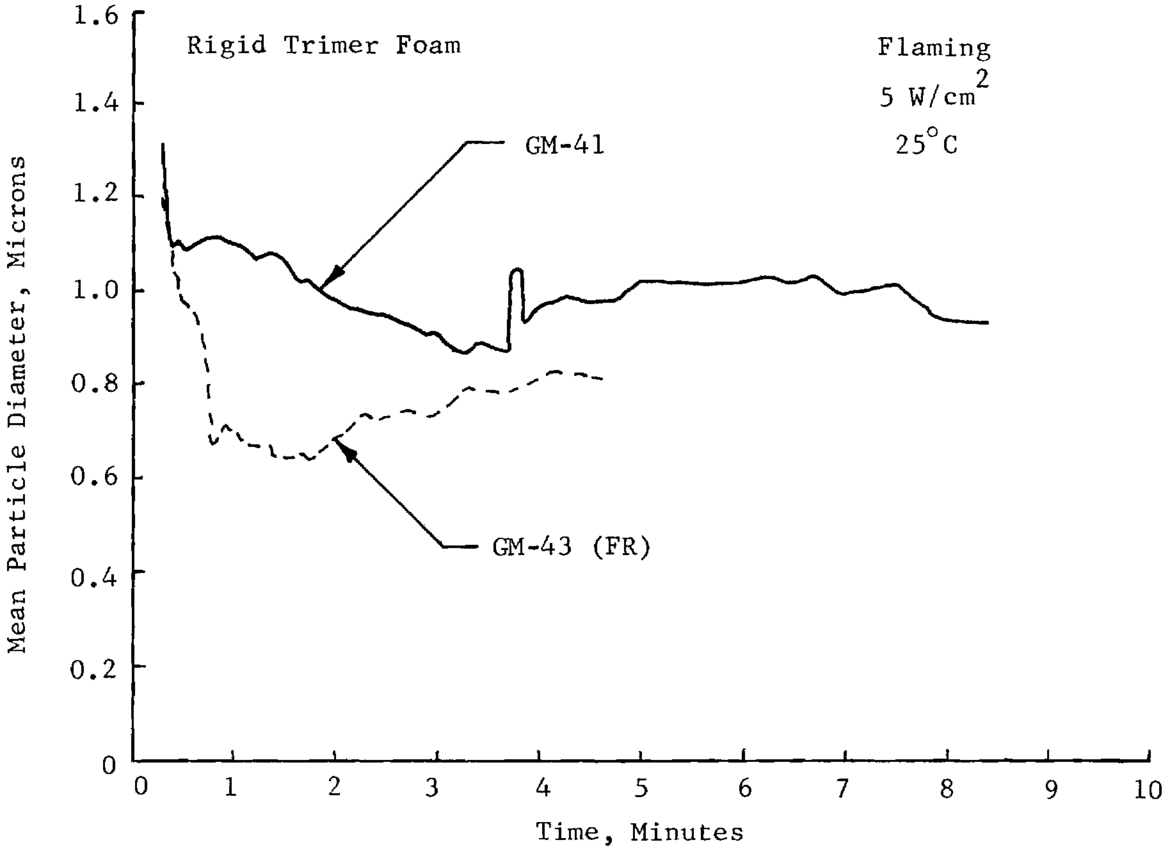


Figure 26. Effect of Fire Retardant Upon Smoke Particle Size for Rigid Trimer Foam Burning in Room Temperature Air.

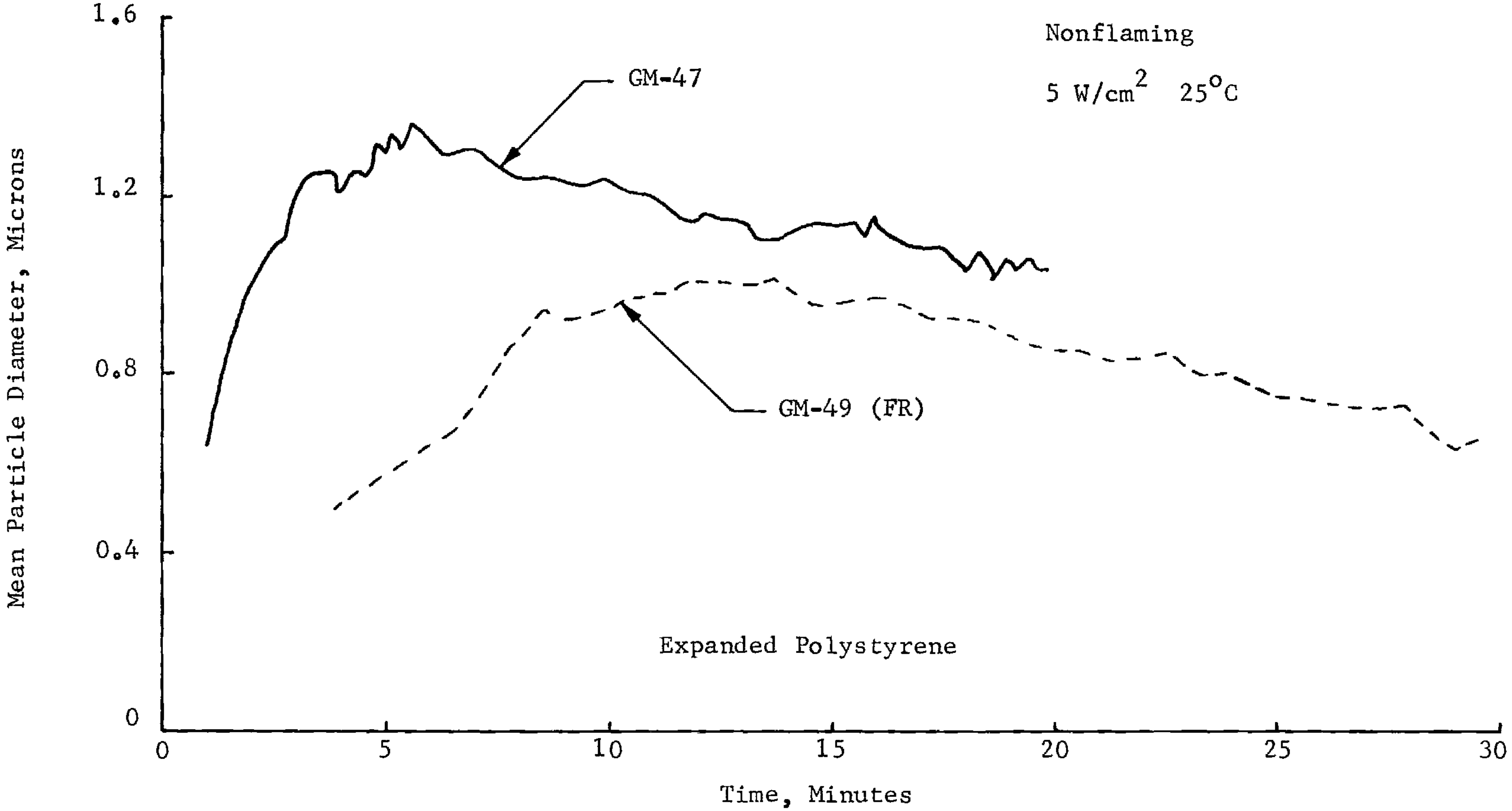


Figure 27. Effect of Fire Retardant Upon Smoke Particle Size for Expanded Polystyrene Burning Under Nonflaming Conditions in Room Temperature Air.

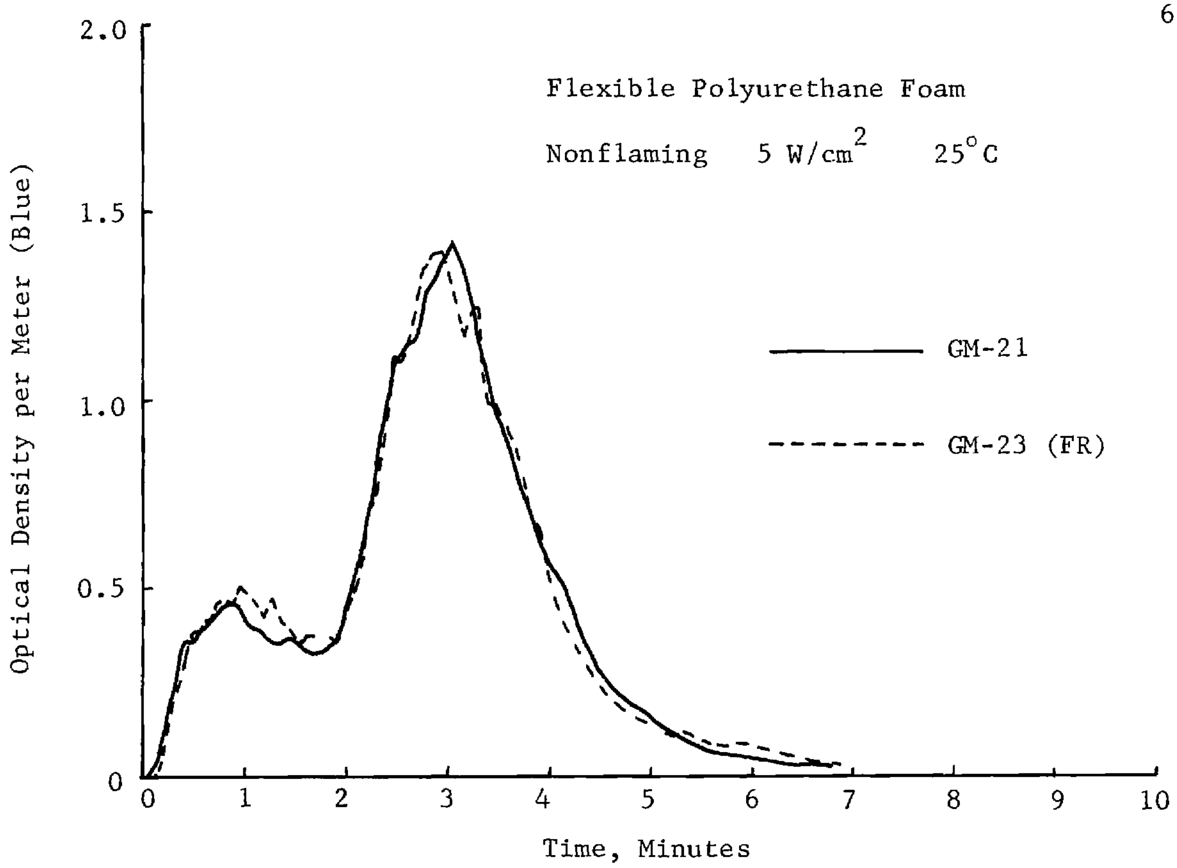
test. The similarity between the D_{32} versus time curves for flaming and nonflaming combustion of the GM-43 trimer foam (Figure 26) suggests that the fire retarded sample did not actually ignite in the room temperature tests. However samples of black sooty particulates collected during the flaming test of GM-43 indicate that flaming combustion did indeed occur. No comparison is shown for the flaming test of the fire-retarded expanded polystyrene foam (GM-49) which would not ignite by the pilot flame in the room temperature atmosphere under 5 W/cm^2 radiant flux.

The optical density variations for the fire-retarded and non-fire retarded materials are compared in Figures 28 through 30 for both flaming and nonflaming combustion. Values of OD_{max} for these materials are compared in Tables 5 and 6.

For nonflaming tests of the flexible polyurethane foam (Figure 28), the OD versus time curves are virtually identical for the fire-retarded and non-fire-retarded materials. In contrast, the addition of fire retardant to the rigid polyurethane foam (Figure 29) reduces the peak optical density obtained under nonflaming conditions to about half of the value obtained for the basic substrate polymer. Fire retardants have the opposite effect upon optical density for nonflaming combustion of the rigid trimer foam (Figure 30). Here the fire retarded sample produces about twice as much light obscuration as the non-fire-retarded sample, and the peak optical density occurs earlier in the test when fire retardants are present. Fire retardants have little effect upon the optical density of the smoke produced by nonflaming combustion of the expanded polystyrene foam, for which OD_{max} is less than 0.1 per meter.

In flaming tests of the flexible polyurethane foam (Figure 28), the fire retarded material yields a peak optical density over twice as great as that produced by the basic substrate polymer. This result is in contrast to the slight effect of fire retardants upon the optical density observed under nonflaming conditions. Adding fire retardant also increases the optical density of the smoke produced by flaming combustion of the rigid polyurethane foam (Figure 29), although the effect is not as great as for the flexible foam. On the other hand, the addition of fire retardant to the rigid trimer foam (Figure 30) results in a drastic reduction in optical density under flaming conditions. For each of these materials, fire retardants do not affect the time required to reach peak optical density. No flaming data is available for the fire retarded expanded polystyrene foam (GM-49) due to its failure to ignite under the imposed test conditions.

The effect of fire retardant upon the fraction of sample weight loss converted to smoke particulates (Γ) can be seen from the data presented in Tables 5 and 6. For nonflaming tests of the flexible polyurethane foam, the expanded polystyrene foam and the rigid polyurethane foam, addition of fire retardant yields large, moderate, and slight increases in Γ respectively (Table 5). In contrast, the Γ value obtained for the fire-retarded rigid trimer foam under nonflaming conditions is about half of that produced by the non-fire-retarded material. Table 6 shows that for both the flexible and rigid polyurethane foams as well as the rigid trimer foam, the relative effect of fire retardants upon Γ is the same for flaming combustion as for nonflaming combustion.



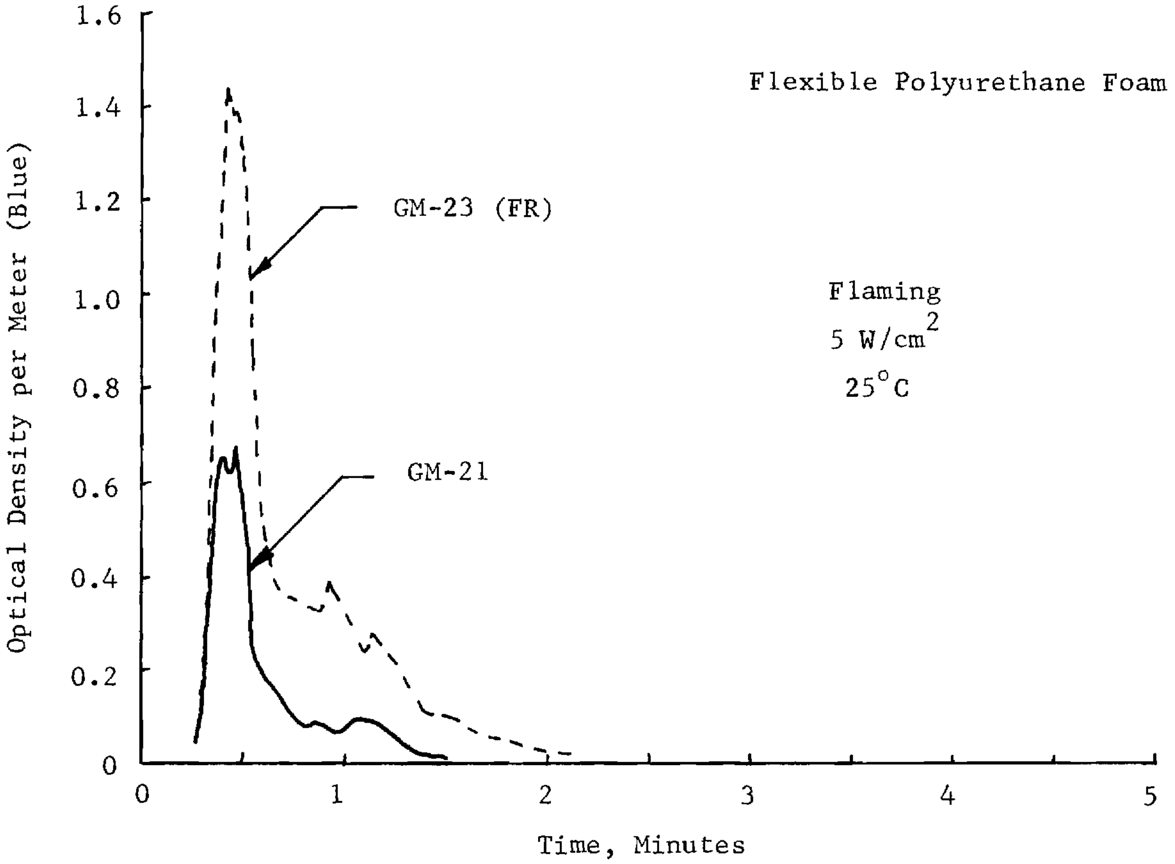
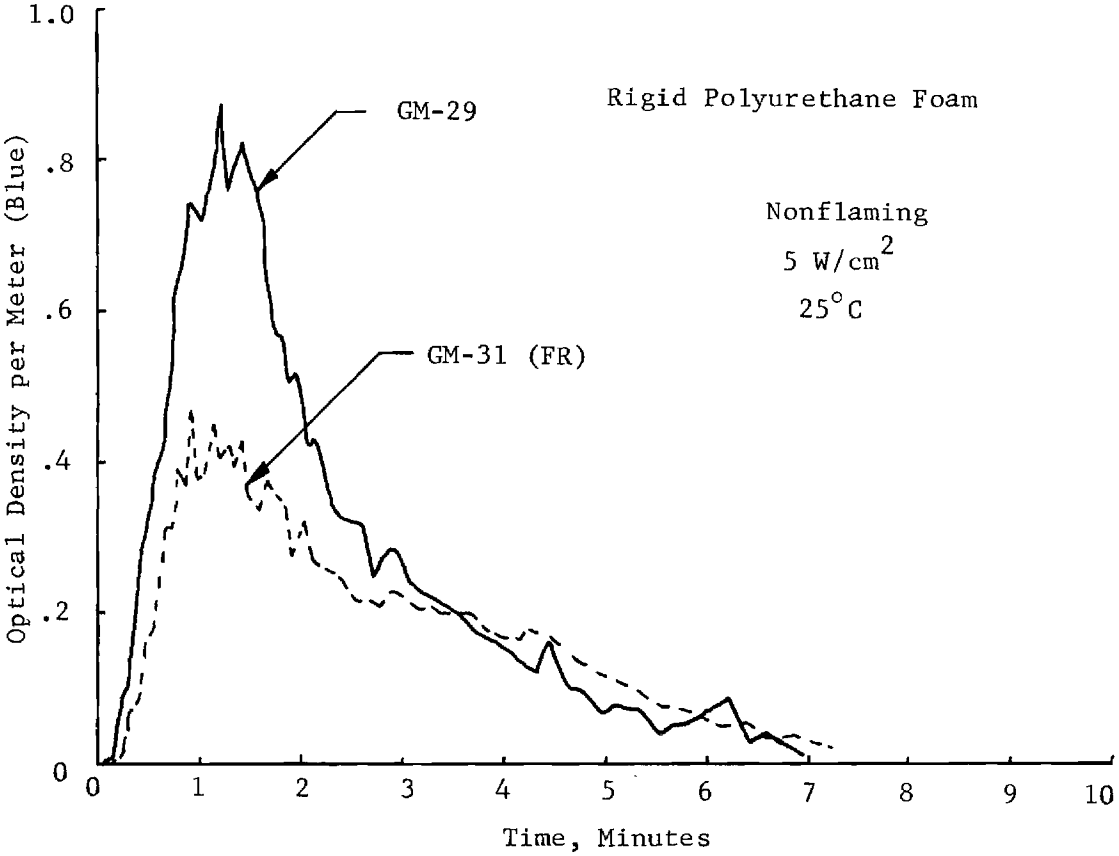


Figure 28. Effect of Fire Retardant Upon Smoke Optical Density for Flexible Polyurethane Foam Burning in Room Temperature Air.



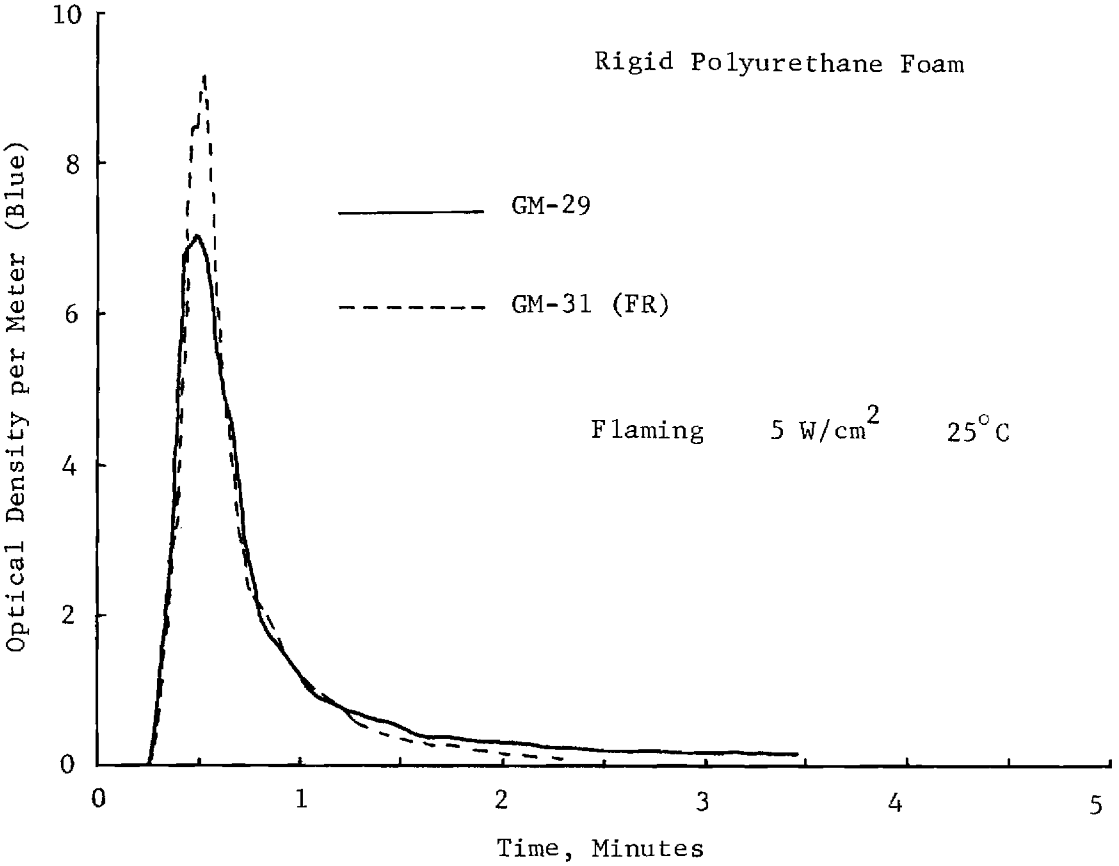
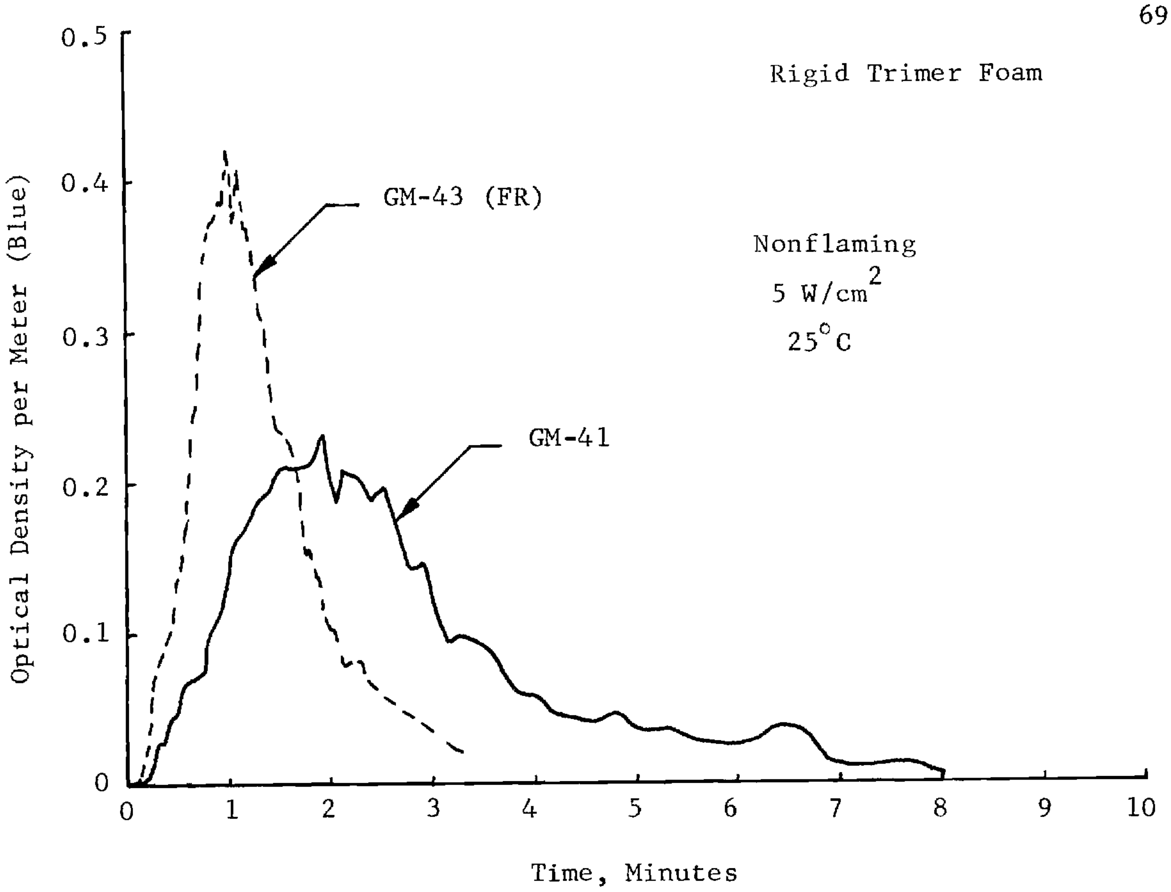


Figure 29. Effect of Fire Retardant Upon Smoke Optical Density for Rigid Polyurethane Foam Burning in Room Temperature Air.



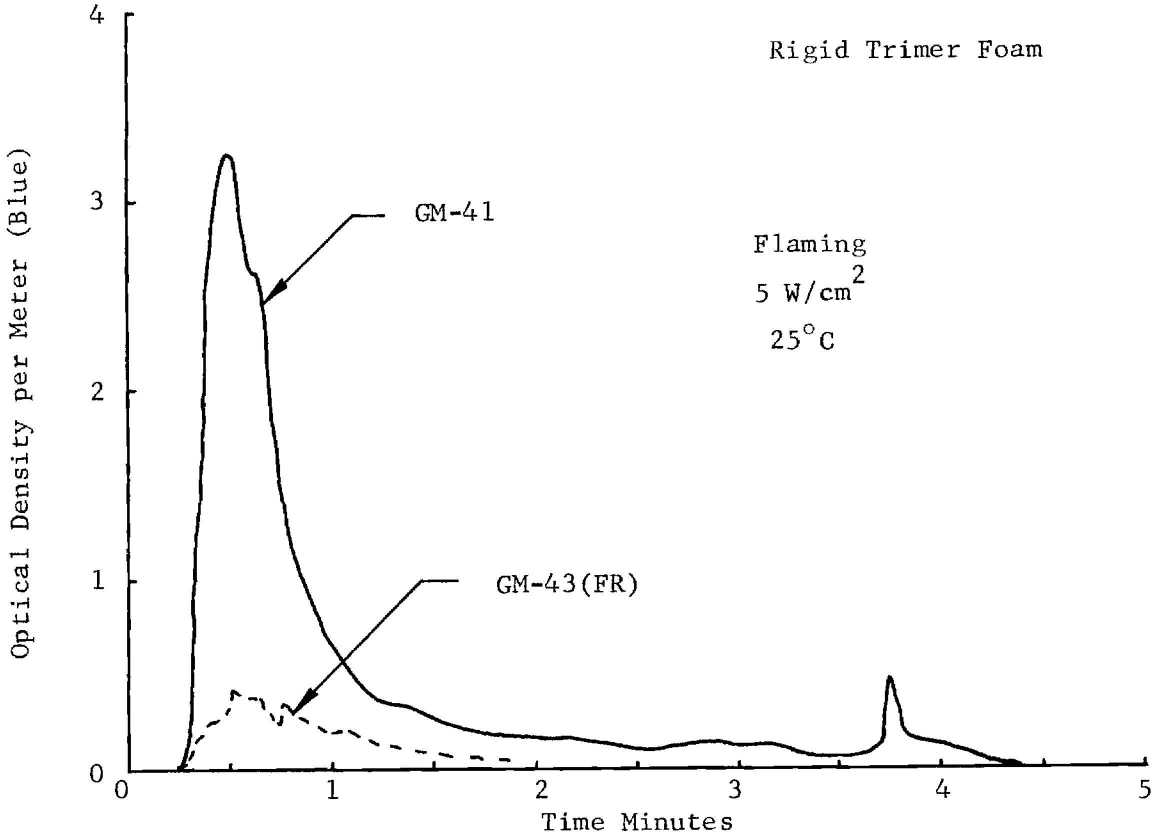


Figure 30. Effect of Fire Retardant Upon Smoke Optical Density for Rigid Trimer Foam Burning in Room Temperature Air.

Table 5. Effect of Fire Retardant Additives Upon Smoke Characteristics Nonflaming Conditions - 5 W/cm^2 - 25°C

Material*	Γ	D_{MMD} (μm)	σ (μm)	OD_{max} Blue	OD_{max} Red	D_{32} (μm)	Time to Peak OD (min.)	Char Residue % Initial Weight
GM-23	.137	1.60	2.22	1.39	1.15	0.87	2.9	13.4
GM-21	.064	1.23	2.56	1.42	1.17	0.96	3.0	T
GM-31	.077	0.80	3.58	0.47	0.46	1.08	1.0	44.6
GM-29	.070	0.82	4.21	0.87	0.87	1.05	1.2	39.0
GM-43	.023	0.59	2.98	0.42	0.31	0.68	1.0	63.5
GM-41	.047	0.26	3.09	0.23	0.19	0.68	1.9	62.0
GM-49	.147	1.15	2.08	-	0.07	0.94	14	25.5
GM-47	.114	1.84	2.17	0.09	0.06	1.17	11.7	T

* Higher-numbered sample contains fire retardant additive.

Γ = Fraction of sample weight loss converted to smoke particulates.

D_{MMD} = Mass median diameter.

σ = Geometric standard deviation.

OD_{max} = Maximum optical density in blue (.458 μm) and red (.633 μm) light at a volumetric flow rate of 283 liters/minute.

D_{32} = Volume-surface mean particle diameter at maximum optical density.

T = Trace quantity.

Table 6

Effect of Fire Retardant Additives Upon Smoke Characteristics

Flaming Conditions - 5 W/cm^2 - 25°C

Material*	Γ	OD_{max} Blue	Red	D_{32} (μm)	Time to Peak OD (min)	Char Residue % Initial Weight
GM-23	.019	1.44	1.03	0.85	0.4	7.2
GM-21	<.01	0.68	0.52	0.94	0.5	T
GM-31	.087	9.16	6.64	1.02	0.5	14.1
GM-29	.085	7.03	4.98	0.93	0.5	15.1
GM-43	.029	0.42	0.25	0.96	0.5	61.2
GM-41	.060	3.23	2.44	1.09	0.5	37.4

* Higher-numbered sample contains fire retardant additive.

Γ = Fraction of sample weight loss converted to smoke particulates.

OD_{max} = Maximum optical density in blue (.458 μm) and red (.633 μm) light at a volumetric flow rate of 283 liters/minute.

D_{32} = Volume-surface mean particle diameter at maximum optical density.

T = Trace quantity.

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

Sample weight loss data for the 200°C tests under flaming and nonflaming conditions are shown in Figure 31 for the rigid polyurethane foam and in Figure 32 for the expanded polystyrene foam. As in the room temperature tests, at 200°C the addition of fire retardant to the rigid polyurethane foam gives a moderate increase in the amount of char residue produced under nonflaming conditions and a small decrease in the amount of char remaining in the flaming tests (Figure 31). For the expanded polystyrene foam, Figure 32 shows that the fire-retarded material exhibits generally slower mass loss rates than the basic polymer under nonflaming conditions in the heated ventilation gas. Under flaming conditions at 200°C the principal effect of adding fire retardant to the expanded polystyrene foam is to delay ignition by a few minutes without appreciably affecting the rate of mass loss during flaming combustion.

The effect of fire retardant on the volume-surface mean diameter D_{32} for the four cellular polymers burning in air at 200°C is shown in Figures 33 through 36. In each figure D_{32} versus time curves are shown for both nonflaming and flaming conditions.

The D_{32} versus time curves for both the fire-retarded and non-fire-retarded materials are similar in shape for nonflaming 200°C tests of the flexible and rigid polyurethane foams (Figures 33 and 34) and the rigid trimer foam (Figure 35). For each material the formulation containing the fire retardant exhibits a more rapid decline in D_{32} from its initial peak value. For the flexible polyurethane foam

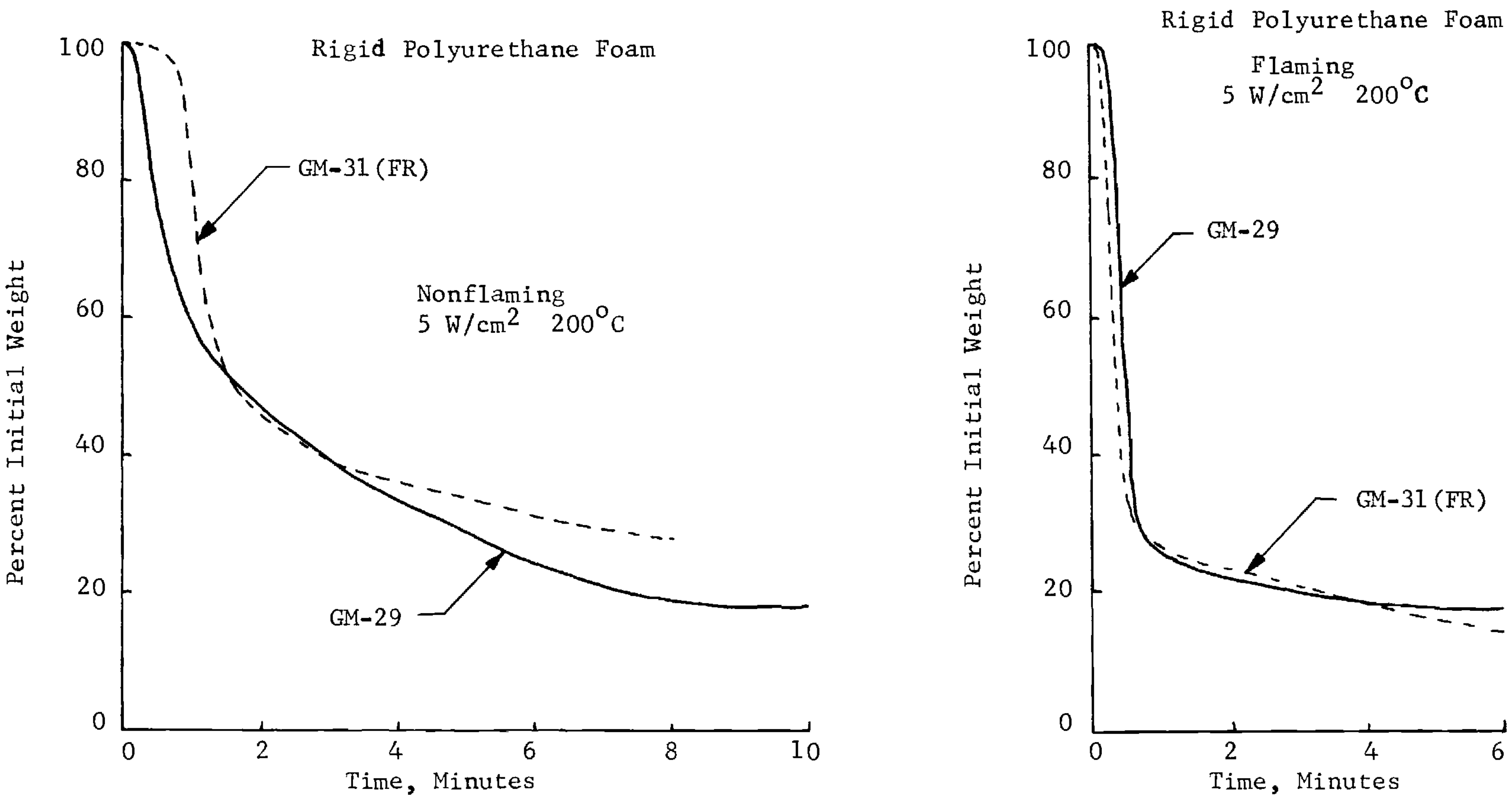


Figure 31. Effect of Fire Retardant Upon Sample Weight Loss for Rigid Polyurethane Foam Burning in Air at 200°C.

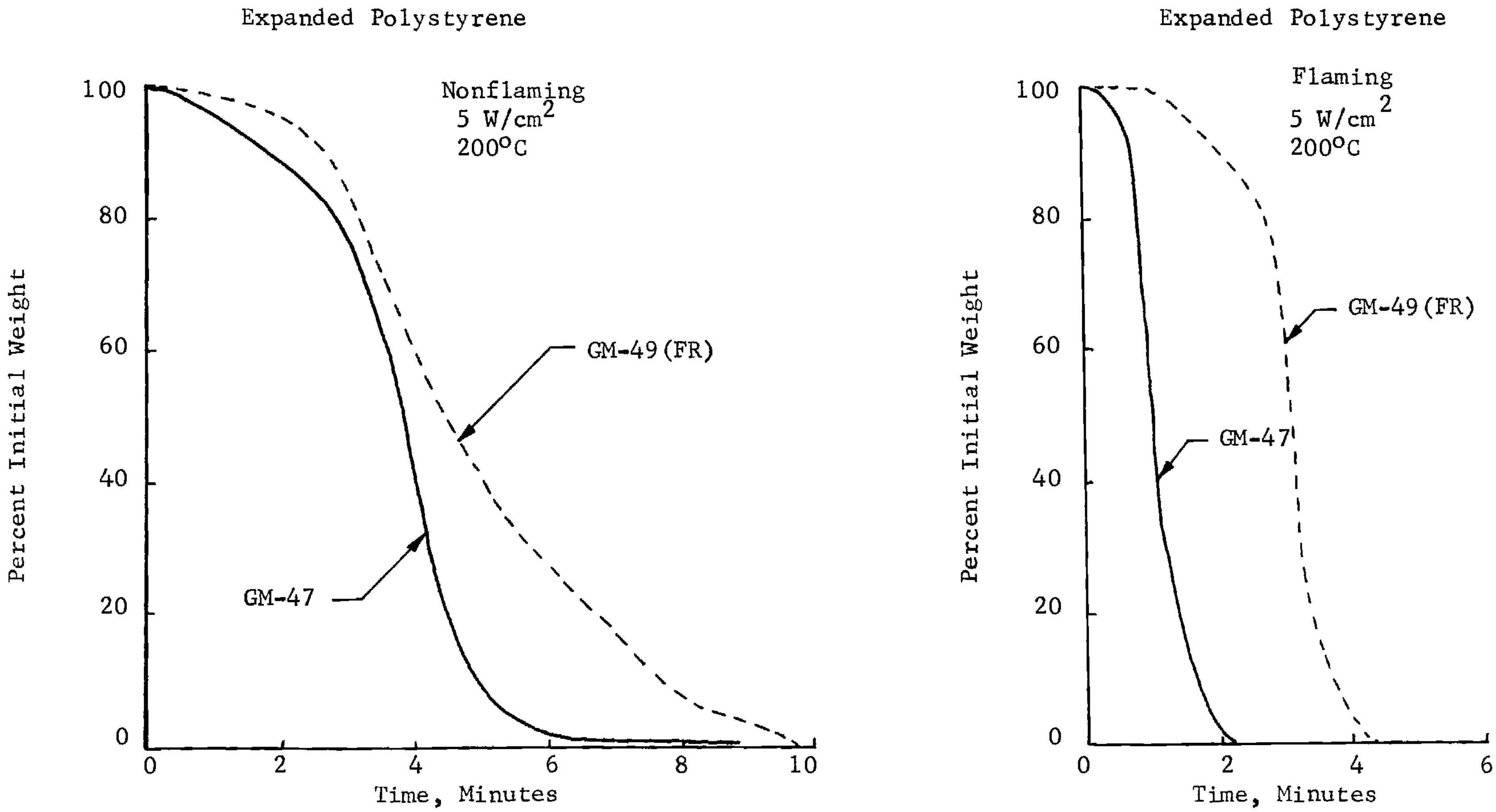


Figure 32. Effect of Fire Retardant Upon Sample Weight Loss for Expanded Polystyrene Burning in Air at 200°C.

(Figure 33), both formulations ignited spontaneously after about 1.4 minutes of exposure to the 5 W/cm^2 radiant flux in the 200°C atmosphere. In high temperature nonflaming tests of the expanded polystyrene foam (Figure 36), the addition of fire retardant yields a small reduction in the peak value of D_{32} obtained. Characteristic mean particle diameters corresponding to peak optical density are given in Table 7 for high temperature nonflaming tests of the four cellular polymers studied. For each material the addition of fire retardant results in small to moderate reduction in the characteristic mean particle diameter obtained under nonflaming conditions at 200°C.

For high temperature flaming tests of these same materials, addition of fire retardant to the substrate polymer yields small reductions in D_{32} for the flexible polyurethane foam (Figure 33) and the rigid trimer foam (Figure 35) and has little or no effect on D_{32} for the rigid polyurethane foam (Figure 34) and the expanded polystyrene foam (Figure 36). The characteristic mean particle diameters shown in Table 8 are also in agreement with the above results.

The effect of fire retardant additives on the optical density of the smoke produced in high temperature tests of the four polymers is shown in Figures 37 through 40. Peak optical densities in red and blue light are also given in Table 7 for nonflaming conditions and in Table 8 for flaming combustion. For the flexible polyurethane foam (Figure 37) and the rigid polyurethane foam (Figure 38), the fire retarded materials yield larger peak optical densities than the corresponding non-fire-retarded materials for both flaming and nonflaming combustion. For the

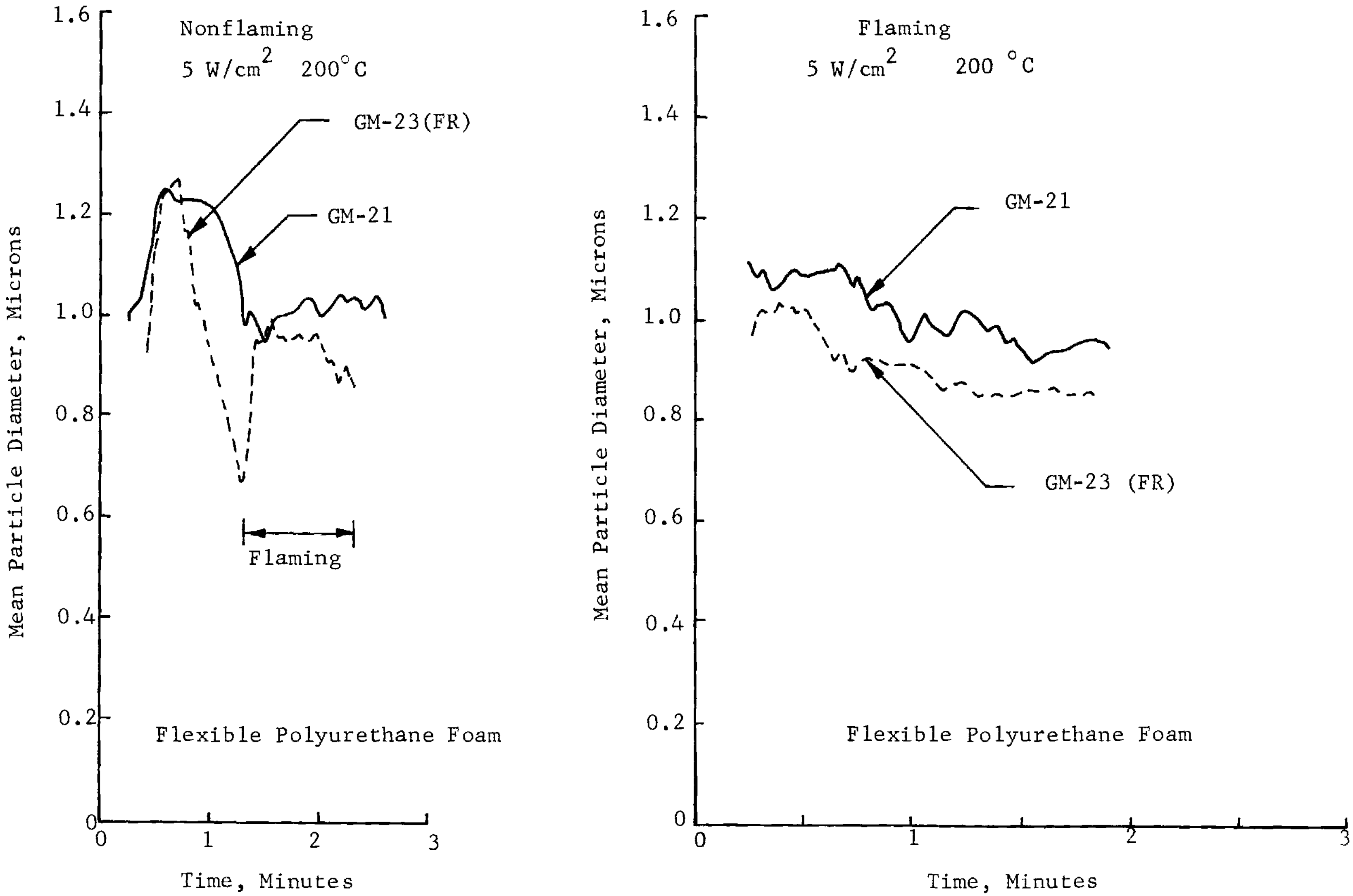


Figure 33. Effect of Fire Retardant Upon Smoke Particle Size for Flexible Polyurethane Foam Burning in Air at 200°C.

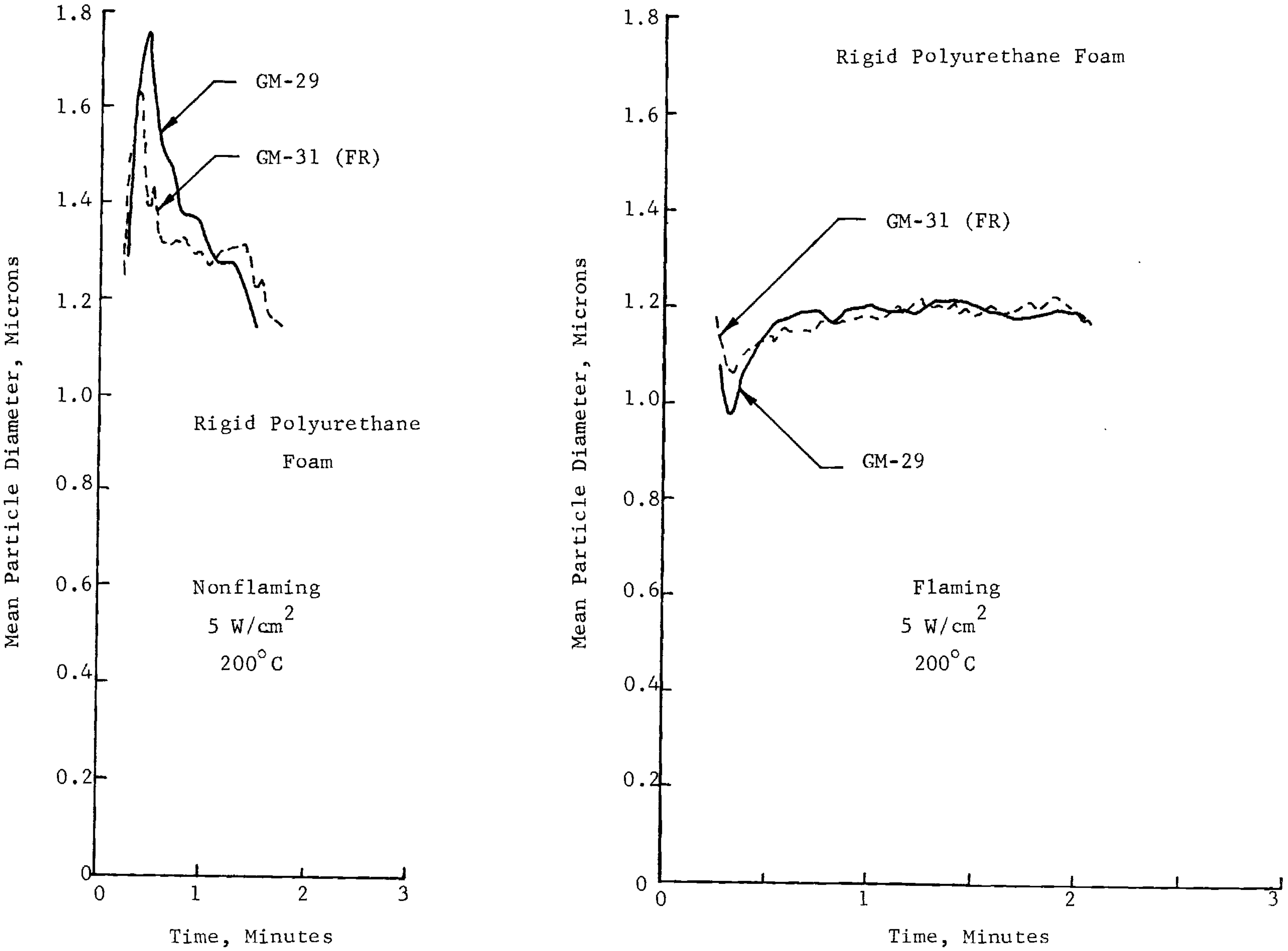


Figure 34. Effect of Fire Retardant Upon Smoke Particle Size for Rigid Polyurethane Foam Burning in Air at 200 °C.

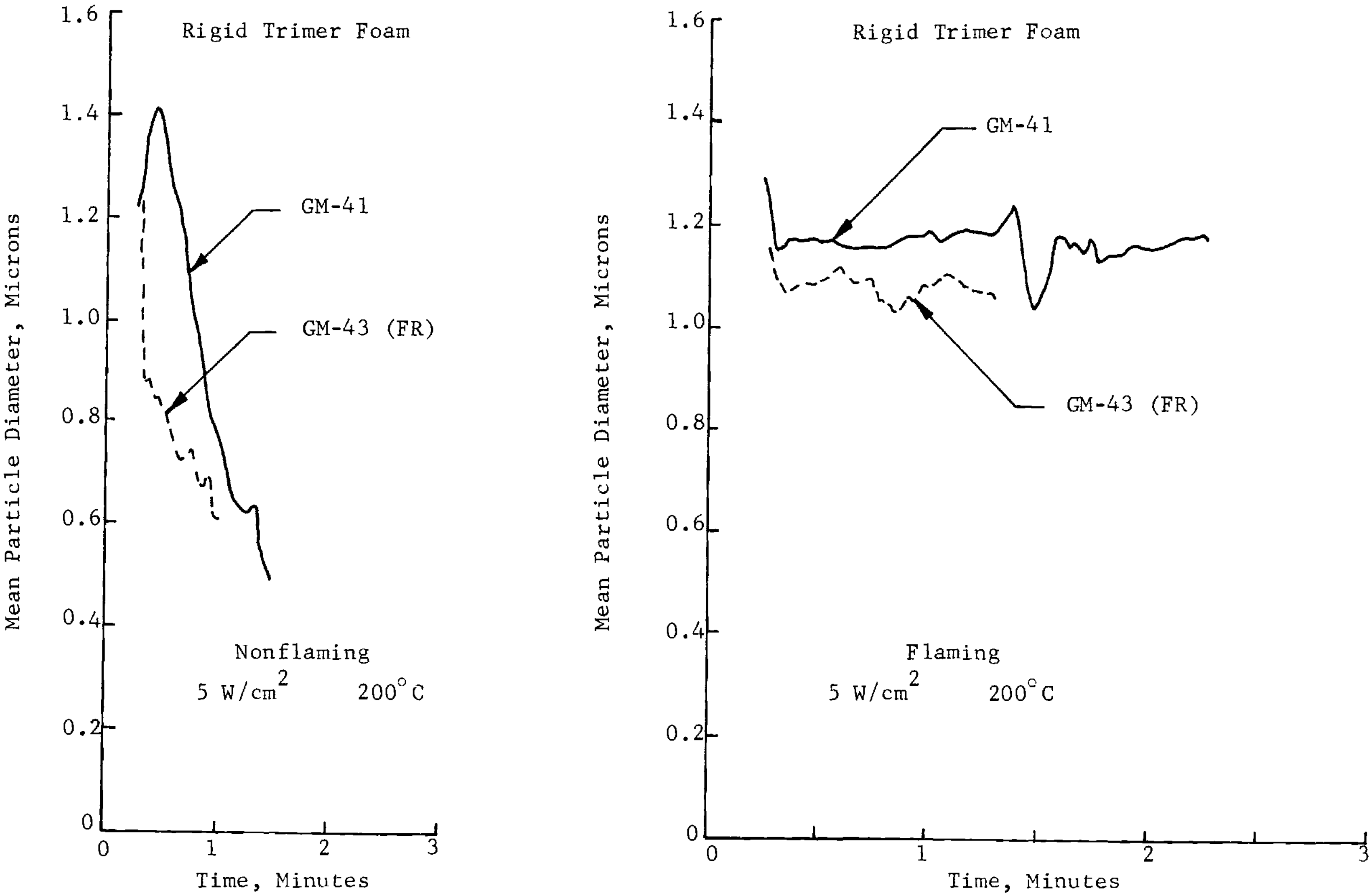
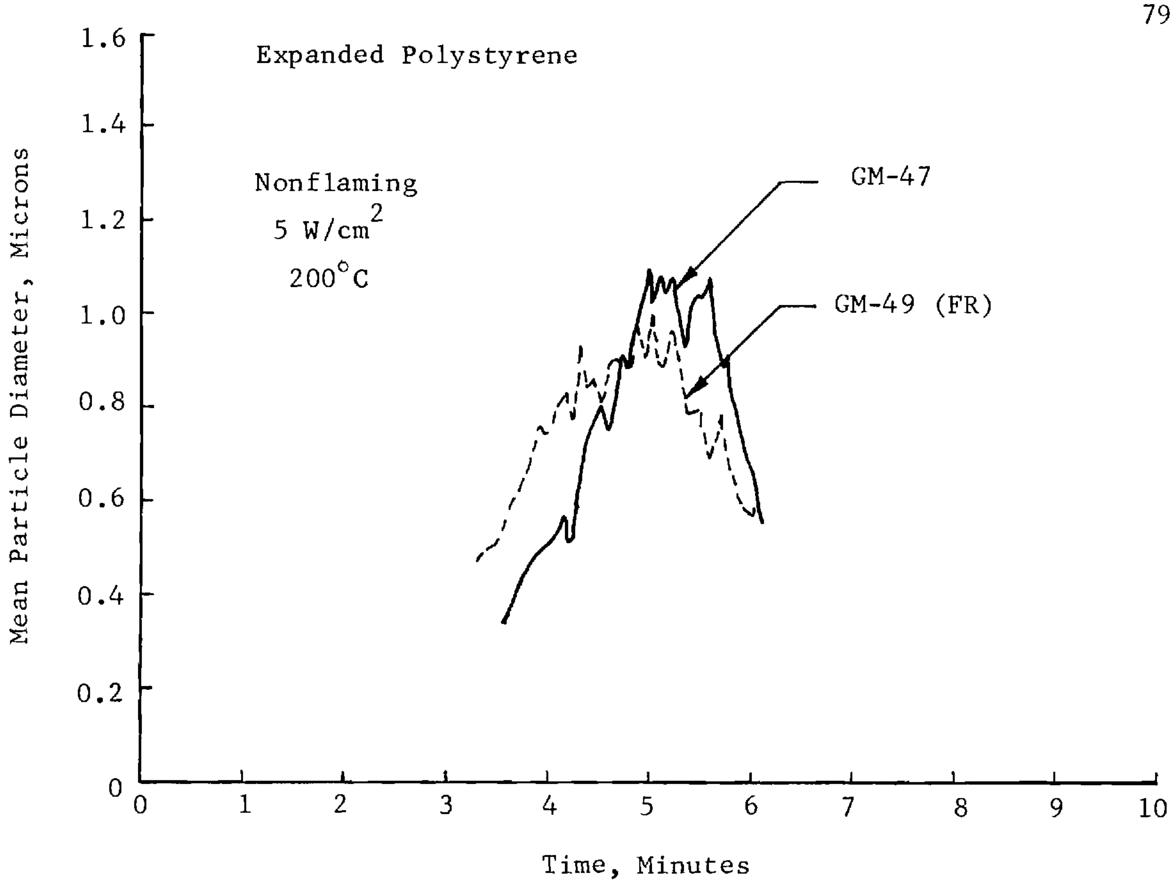


Figure 35. Effect of Fire Retardant Upon Smoke Particle Size for Rigid Trimer Foam Burning in Air at 200°C.



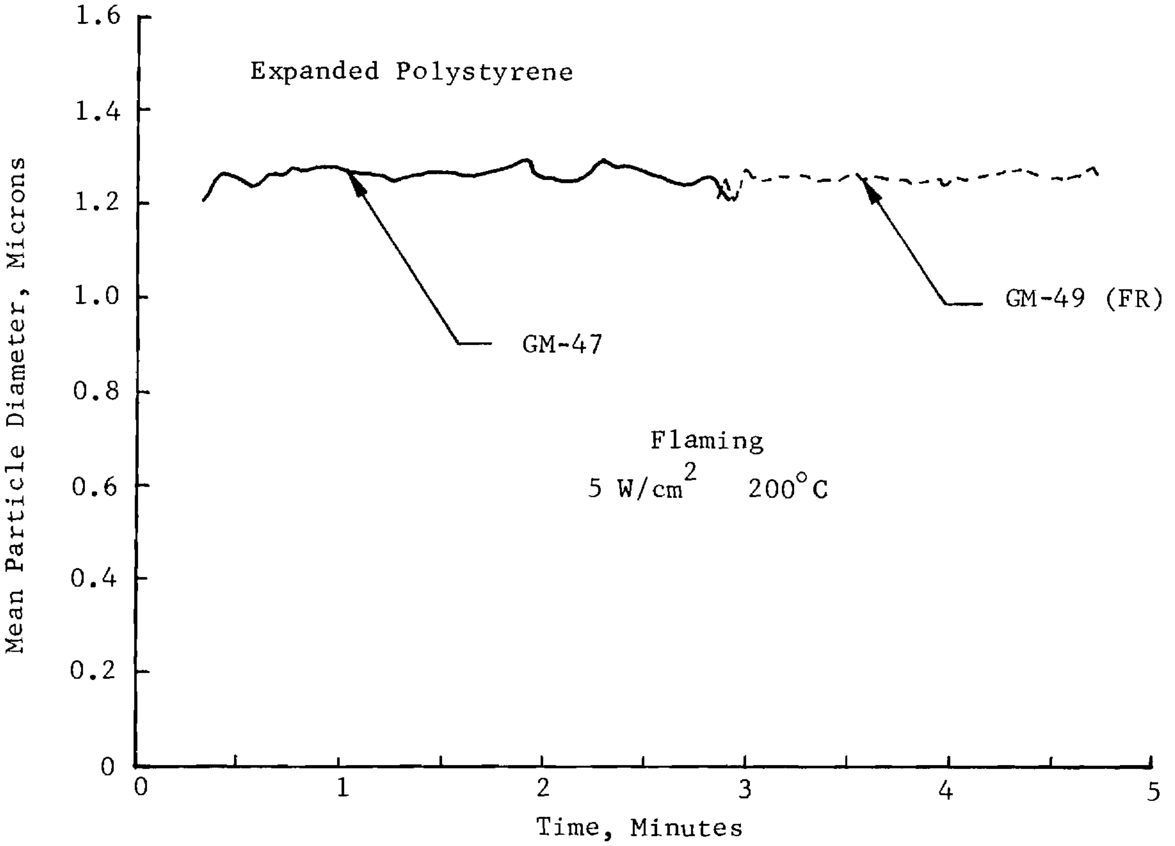


Figure 36. Effect of Fire Retardant Upon Smoke Particle Size for Expanded Polystyrene Burning in Air at 200°C.

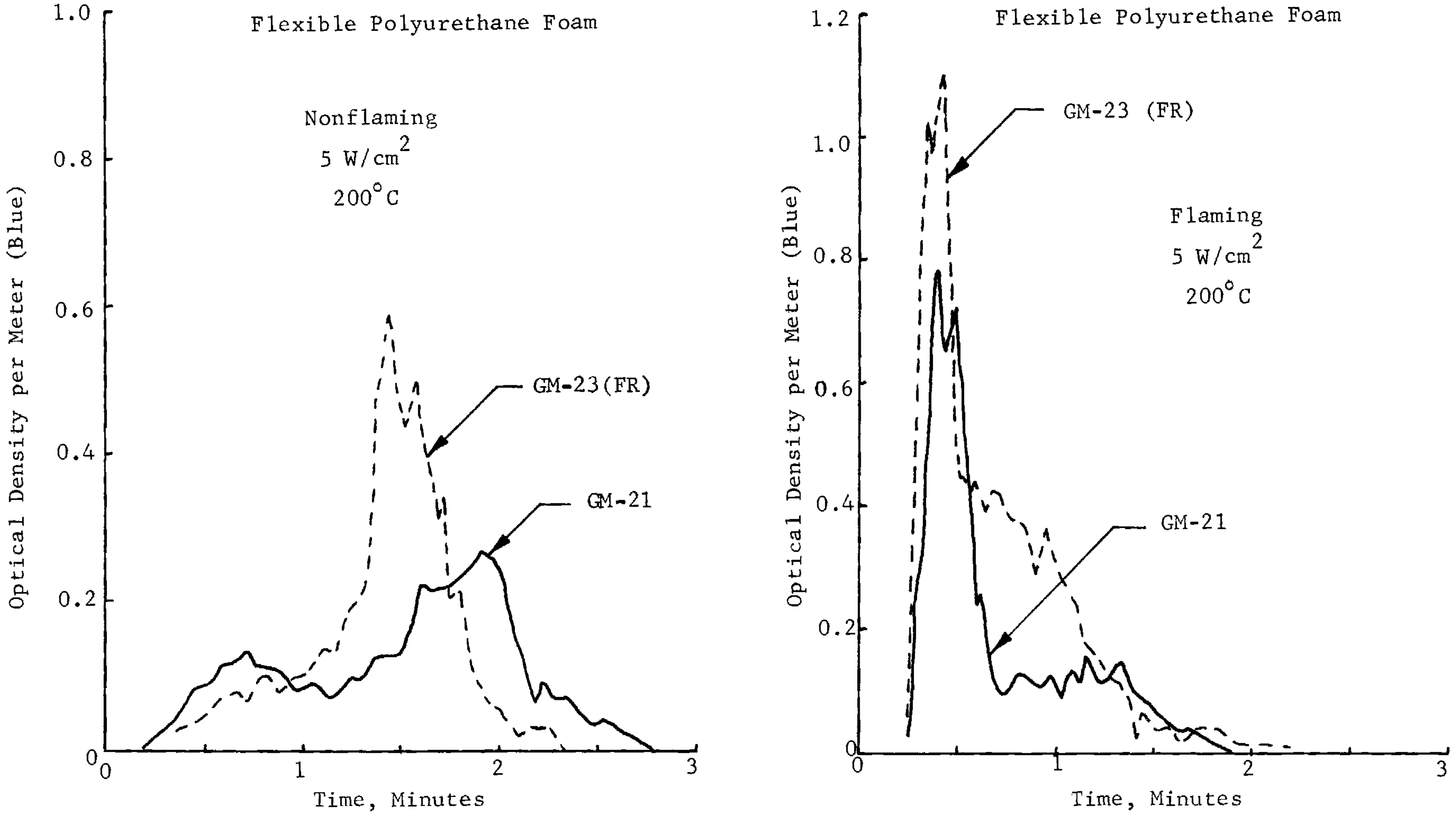


Figure 37. Effect of Fire Retardant Upon Smoke Optical Density for Flexible Polyurethane Foam Burning in Air at 200°C.

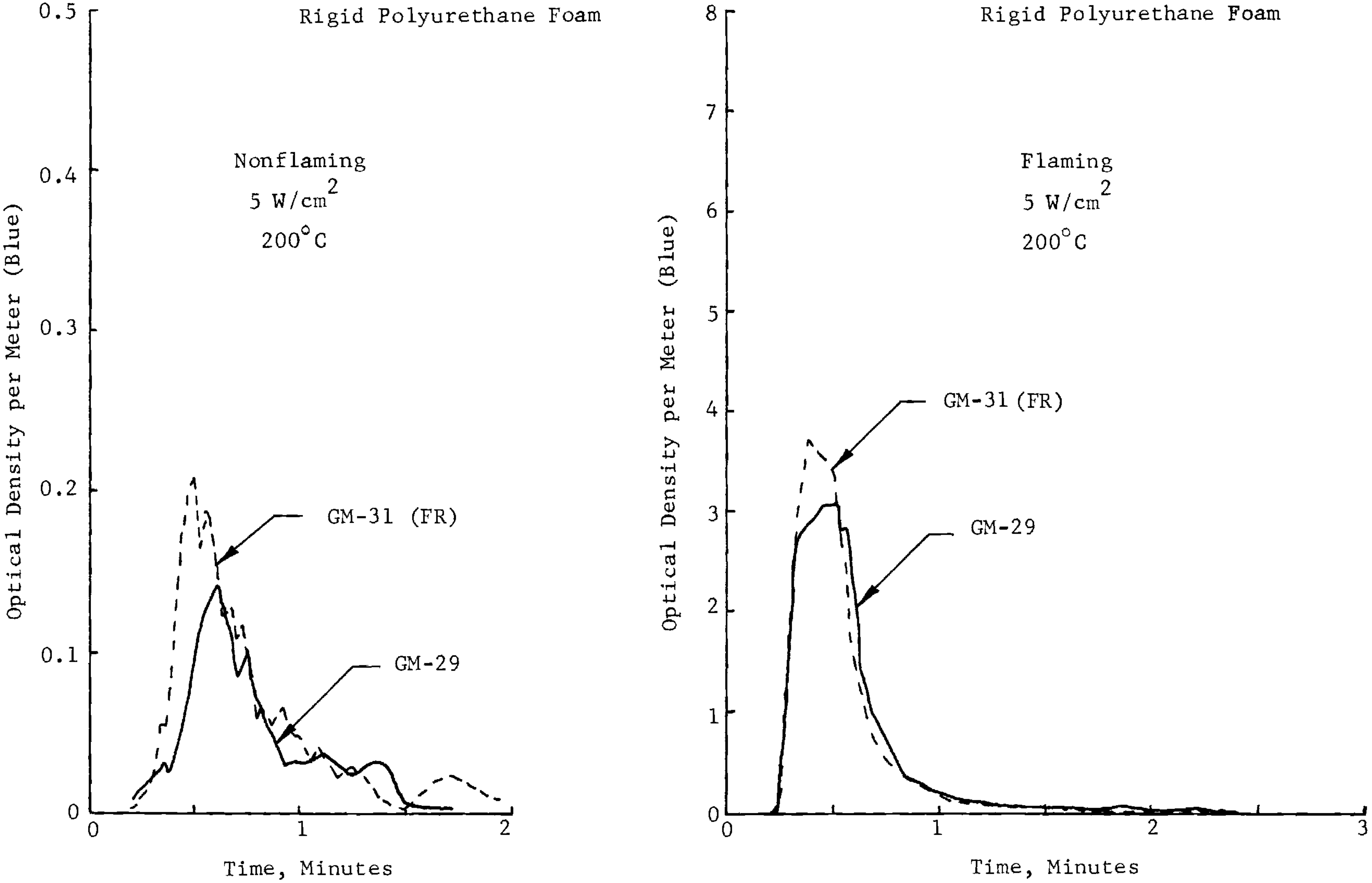


Figure 38. Effect of Fire Retardant Upon Smoke Optical Density for Rigid Polyurethane Foam Burning in Air at 200°C.

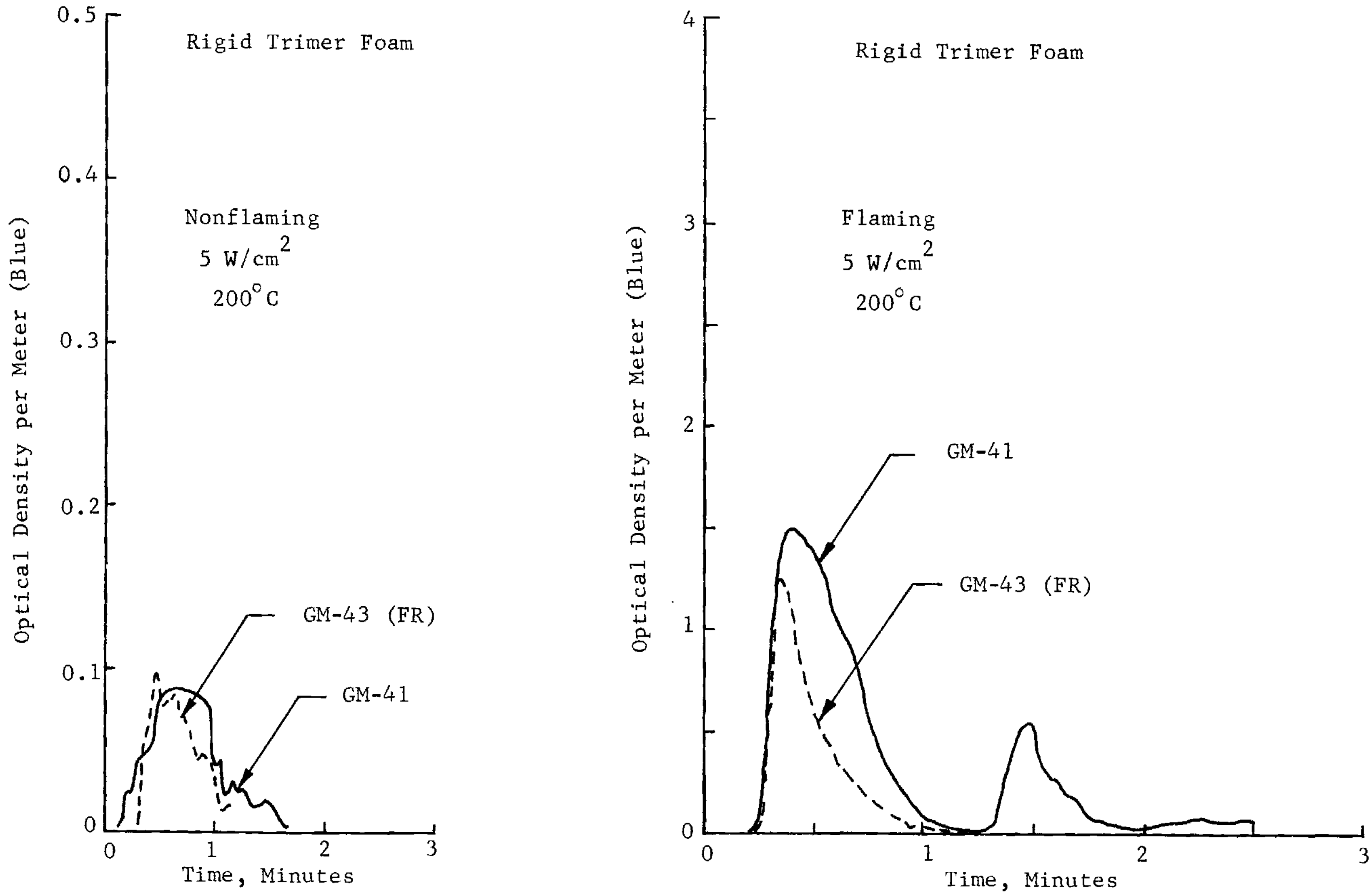


Figure 39. Effect of Fire Retardant Upon Smoke Optical Density for Rigid Trimer Foam Burning in Air at 200° C.

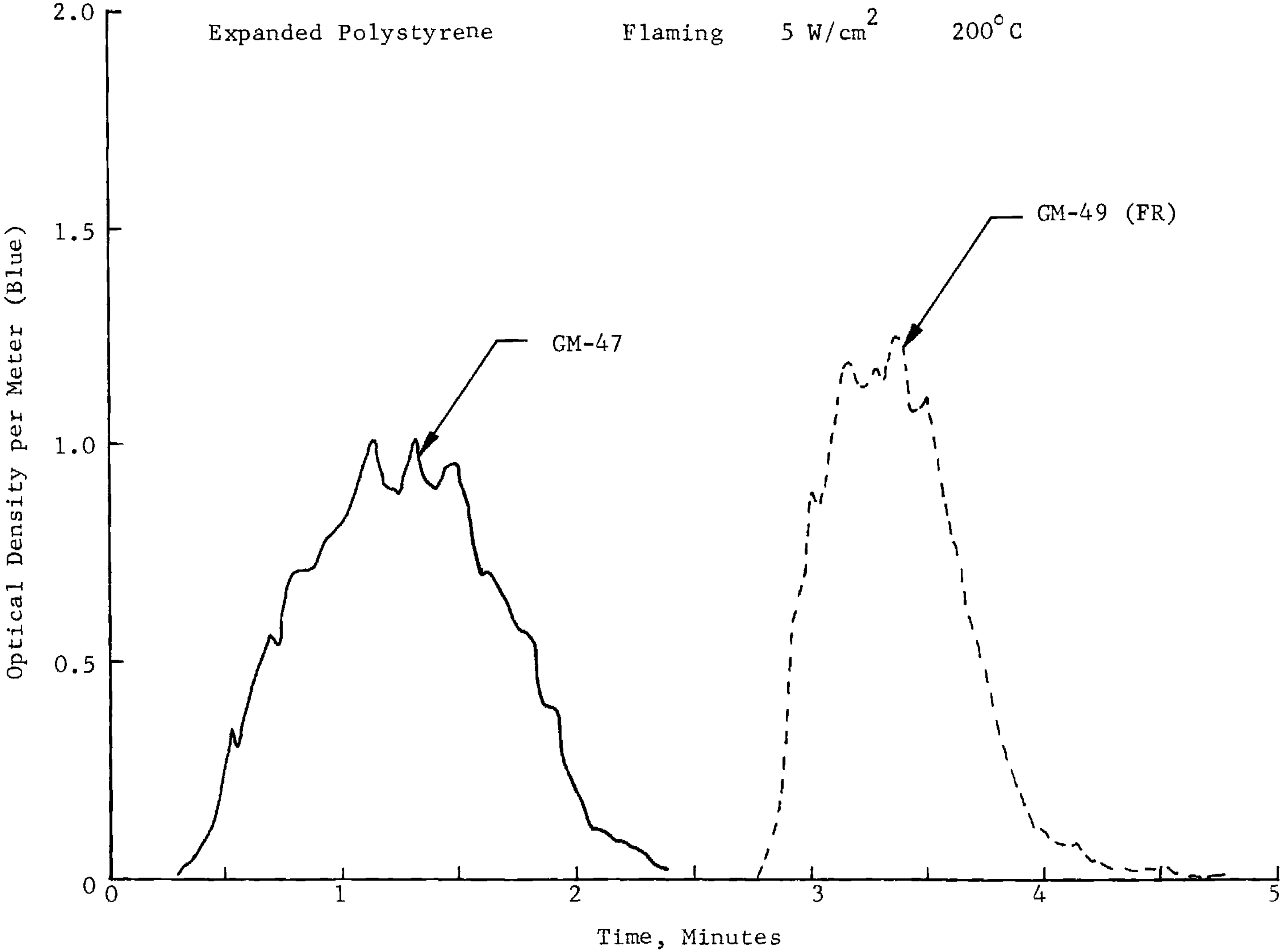


Figure 40. Effect of Fire Retardant Upon Smoke Optical Density for Expanded Polystyrene Burning Under Flaming Conditions in Air at 200°C.

Table 7

Effect of Fire Retardant Additives Upon Smoke Characteristics

Nonflaming Conditions - 5 W/cm^2 - 200°C

Material*	OD_{max} Blue	OD_{max} Red	D_{32} (μm)	Time to Peak OD (min)	Char Residue % Initial Weight
GM-23**	0.16	0.06	1.16	0.8	5.1
GM-21**	0.21	0.11	1.23	0.7	1.2
GM-31	0.33	0.19	1.36	0.5	27.8
GM-29	0.22	0.11	1.52	0.6	17.7
GM-43	0.16	0.06	0.80	0.5	38.3
GM-41	0.15	0.06	1.06	0.7	41.3
GM-49	0.07	0.05	0.90	4.0	T
GM-47	0.12	0.06	1.04	4.7	T

* Higher-numbered sample contains fire retardant additive.

** Measured during nonflaming phase, spontaneous ignition occurred at about t = 1.4 minutes.

OD_{max} = Maximum optical density in blue (.458 μm) and red (.633 μm) light at a volumetric flow rate of 283 liters/minute.

D_{32} = Volume-surface mean particle diameter at maximum optical density.

T = Trace quantity.

Table 8

Effect of Fire Retardant Additives Upon Smoke Characteristics

Flaming Conditions - 5 W/cm^2 - 200°C

Material*	OD_{max} Blue	OD_{max} Red	D_{32} (μm)	Time to Peak OD (min)	Char Residue % Initial Weight
GM-23	1.75	1.30	1.03	0.4	0.5
GM-21	1.24	0.95	1.08	0.4	T
GM-31	5.92	4.52	1.11	0.4	13.7
GM-29	4.86	3.87	1.11	0.5	17.5
GM-43	1.96	1.59	1.07	0.4	41.4
GM-41	2.39	1.89	1.17	0.4	27.2
GM-49	1.98	1.60	1.26	3.4	T
GM-47	1.61	1.33	1.26	1.3	T

* Higher-numbered sample contains fire retardant additive.

OD_{max} = Maximum optical density in blue (.458 μm) and red (.633 μm) light at a volumetric flow rate of 283 liters/minute.

D_{32} = Volume-surface mean particle diameter at maximum optical density.

T = Trace quantity.

rigid trimer foam (Figure 39), the addition of fire retardant has little effect on optical density for nonflaming combustion and yields a reduction in optical density for flaming combustion. For flaming combustion of the expanded polystyrene foam (Figure 40), the fire retarded formulation yields a moderately higher peak optical density which occurs about two minutes later than the corresponding peak for the non-fire-retarded material. For the same material under nonflaming conditions, the addition of fire retardant reduces the peak optical density (Table 7).

C. Summary

The effects of fire retardants upon the quantity and physical characteristics of the smoke produced by combustion of the four cellular polymers studied will now be summarized. The physical quantities which will be considered here are: (1) the fraction of sample weight loss converted to smoke particulates Γ, (2) the percentage of initial sample weight remaining as char, (3) the volume-surface mean diameter D_{32} corresponding to the maximum optical density, and (4) the peak optical density OD_{max}.

For room temperature tests of all materials except the rigid trimer foam, the addition of fire retardant increases the fraction of sample weight loss converted to smoke particulates (Γ) for both flaming and nonflaming combustion. Fire retardants produce the greatest increase in Γ for the flexible polyurethane foam, while addition of fire retardant to the rigid trimer foam results in about a 50% reduction of Γ. Thus fire retardant additives increase the smoking tendencies of the flexible and rigid polyurethane foams and the expanded polystyrene foam and decrease the smoking tendency of the rigid trimer foam.

For each set of test conditions, most of the fire-retarded cellular polymers tested left more char residue than the equivalent non-fire-retarded polymers. The two exceptions are small decreases in the amount of char residue due to the presence of fire retardant for: (1) flaming rigid polyurethane foam in both 25°C and 200°C atmospheres and (2) nonflaming rigid trimer foam at 200°C.

Under both flaming and nonflaming conditions in room temperature air, the fire-retarded polymers produced slightly smaller smoke particles than the basic substrate polymers for all materials except the rigid polyurethane foam. For samples burning in the 200°C environment, fire retardants reduce the mean particle size by varying amounts (0-25%) for each of the four cellular polymers tested.

For a given material, the effect of fire retardant on the optical density of the smoke produced is dependent on the test conditions. For both room temperature and 200°C tests of the flexible polyurethane foam, fire retardants reduce the optical density of the smoke produced by nonflaming combustion and increase the smoke optical density for flaming combustion. The opposite effect of fire retardants upon OD_{max} is observed for the rigid trimer foam, although the magnitude of the effect is smaller at 200°C than at room temperature. Under most of the test conditions, OD_{max} is increased by the addition of fire retardant to the rigid polyurethane foam and the expanded polystyrene foam.

The results of Task B show that the addition of a chlorinated phosphonate ester fire retardant to the four cellular polymers studied usually results in: (1) an increase in the smoking tendency of the material based on Γ, (2) an increase in the amount of char residue, and (3) a small decrease in the mean particle diameter corresponding to maximum light obscuration. The effect of this fire retardant upon the maximum smoke optical density is strongly dependent upon the substrate polymer composition, the mode of combustion (flaming or nonflaming), and the environmental temperature.

VI. CHEMICAL ANALYSIS OF POLYURETHANE SMOKE PARTICULATES

During the period covered by this report, the methodology for the analysis of polyurethane particulates has been developed and refined considerably compared to the techniques described in our last annual report. In particular, a detailed and effective separations scheme has been devised which allows the separation of complex mixtures into distinct chemical classes, according to physical and chemical properties of the compounds. The basis of the separations scheme for non-volatile compounds is illustrated in Figure 41. The non-volatile compounds of major interest to this project are the basic compounds, as combusted products of nitrogen containing polymers would be anticipated to contain a high proportion of compounds with a basic-NH_2 group. The other major area of identification has been the volatile components adsorbed onto the particulates. An apparatus designed specifically to allow the collection and release of the volatiles has been devised and this is illustrated in Figure 42. This allows the separate identification of gas phase combustion products and volatile compounds adsorbed onto the smoke particulates.

The principle of operation is described in the following steps:
1. The polyurethane sample is burned in the glass chamber (non-flaming mode of combustion). This takes place with the ventillation (air) and temperature carefully controlled externally. 2. The combustion products (both gas phase and particulate) are carried in the air stream through PTFE-lined stainless steel tubing to a Gelman glass fiber filter.
3. The particulates are collected on the filter, while the gas phase products pass to a cooled (-70°C) trap filled with Porapak-R solid adsorbent This has been found to be extremely effective for trapping the volatile products of polyurethane combustion. 4. When combustion of the

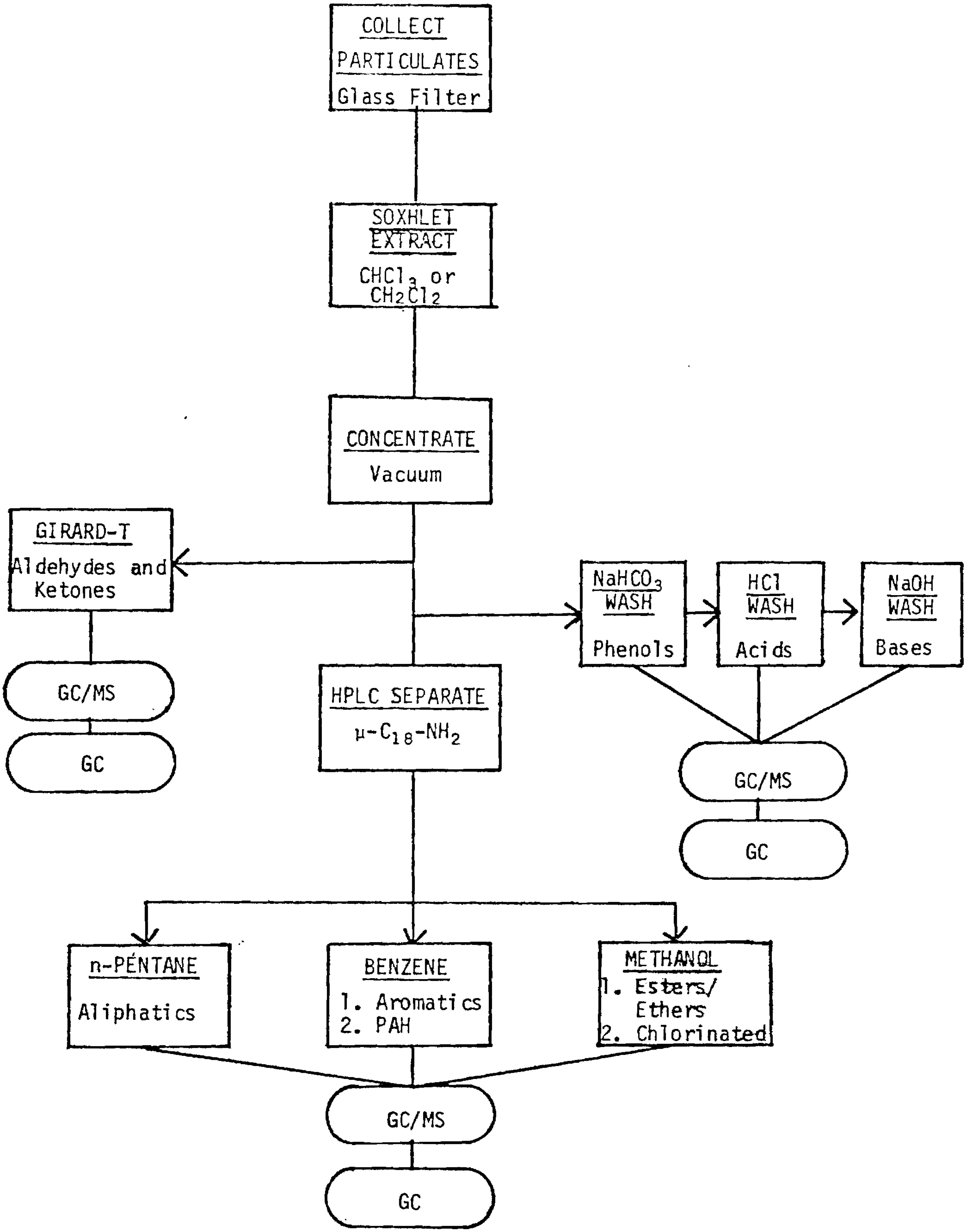


Figure 41. Separations Scheme for Identification of Polyurethane Smoke Particulates

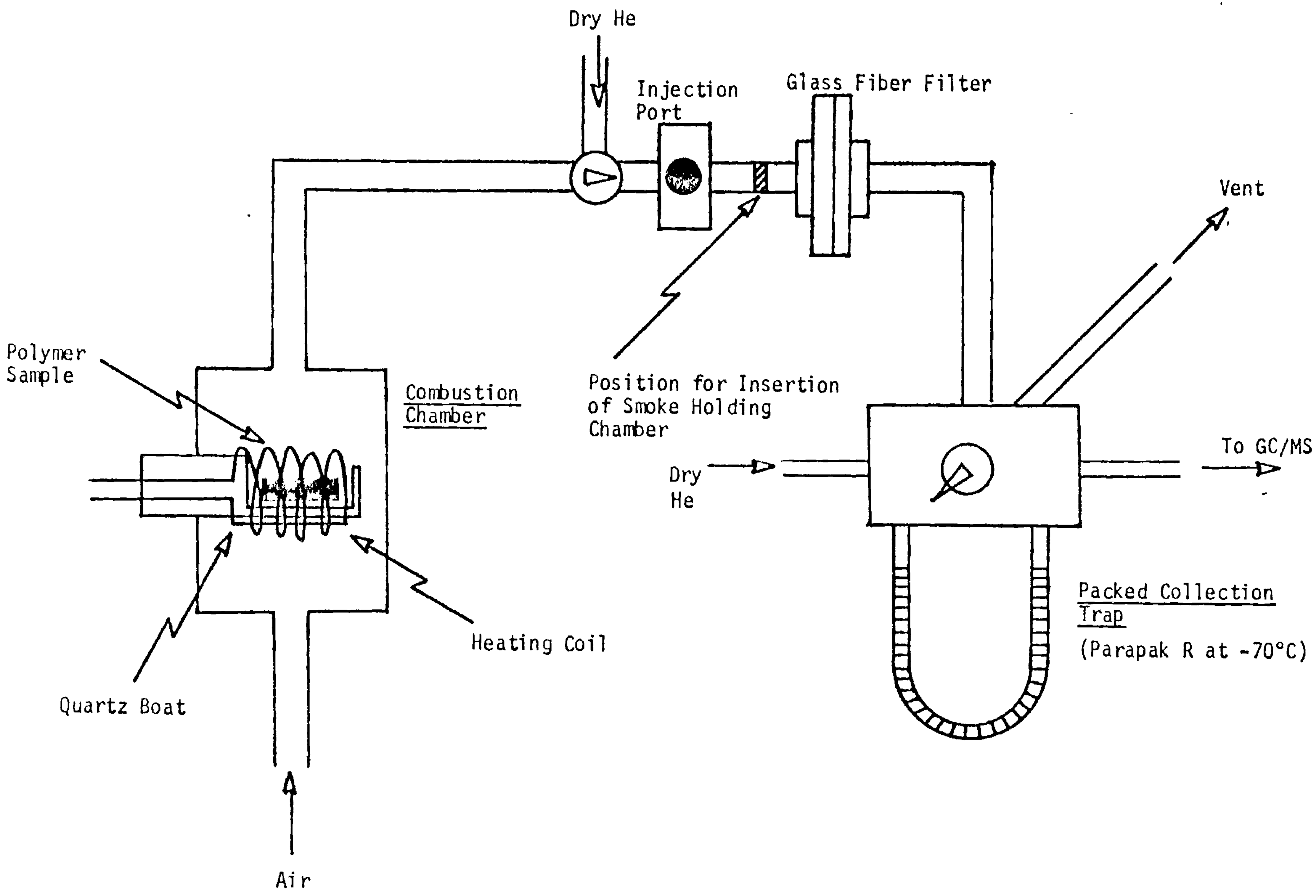


Figure 42. Collection Apparatus for Volatiles Adsorbed on Smoke Particulates

polyurethane sample is complete, air is removed from the system by flushing with He. 5. The solid adsorbent trap is flash heated to 150°C to remove volatile compounds adsorbed onto its surface. 6. The gases released pass down heated transfer lines to the gas chromatograph or gc/mass spectrometer system. Identification is by a combination of retention time and mass spectra. 7. The volatiles adsorbed onto the collected smoke particulates are now released by flash heating the filter to 150°C and these are passed onto the now empty cooled solid adsorbent trap. This acts to preconcentrate these compounds, which may be released over 5-10 minutes from the filter. 8. After collection of this second fraction, the trap is again flash heated and the volatiles pass onto the front of the gas chromatographic column for subsequent identification and ultimately quantitative determination.

The ion chromatograph of polyurethane sample GM-21 gas phase combustion products is shown in Figure 43. The ion chromatograph of the volatiles released from the particulate is not shown here, as it was found to be nearly identical with the gas phase chromatogram in terms of the compounds identified. Concentrations were considerably lower which made identification more difficult. Therefore, once it had been established that the major peaks were indeed due to the same compounds, detailed identification proceeded on the gas phase products initially.

Identification was by a combination of comparison of gc retention time with standard compounds, wherever possible, and by comparison of mass spectra with standard mass spectra. A tabular identification of major peaks shown in Figure 43 is given in Table 9. Single ion chromatograms of the smoke sample from GM-21 are also shown in Figures 44-47.

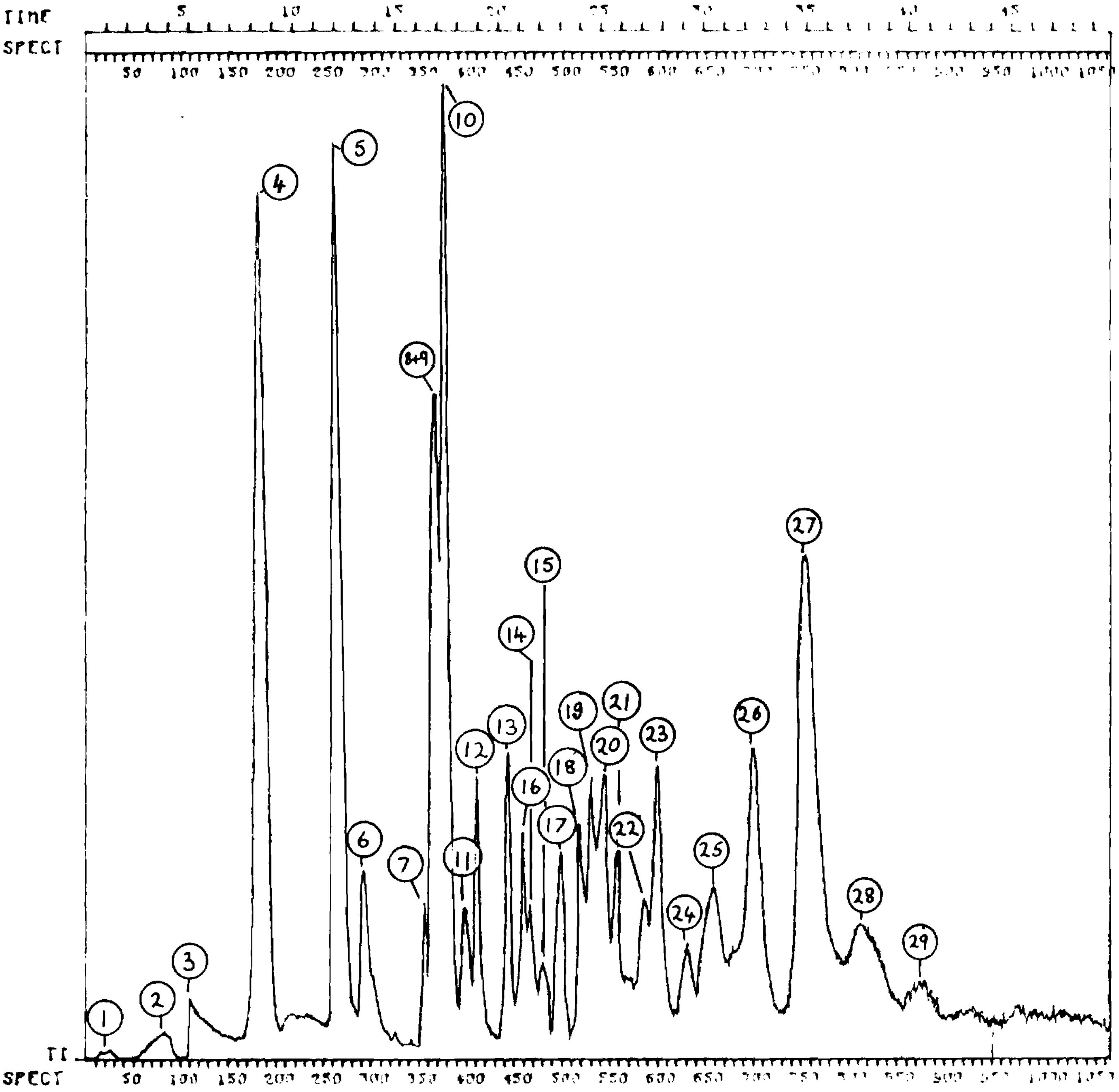


Figure 43. Ion Chromatogram of Smoke from Polyurethane Sample No. GM-21

Peak No.	Molecular Weight	Formula	Name
1			Air
2	44	CO_2	Carbon dioxide
3	42	C_3H_6	Propene
4	44	C_2H_4O	Entanol
5	32	CH_4O	Methanol
6	60	C_3H_8O	Ethyl methyl ether
7	58	C_3H_6O	Methyl vinyl ether
8		?	
9		?	
10	58	C_3H_6O	Acetone
11	74	$C_6H_6O_2$	Methyl acetate
12	60	C_3H_8O	Propan-2-01
13		?	
14	88	$C_5H_{12}O$	2-Pentanol
15	72	C_4H_8O	Methyl ethyl ketone
16	88	$C_5H_{12}O$	3-Pentanol
17		?	
18	60	$C_2H_4O_2$	Acetic acid
19		?	
20	117	$C_6H_{11}O_2$	3-d-butyl acetate
21	102	$C_5H_{10}O_2$	N-propyl acetate
22	84	C_6H_{12}	4-Methyl-pent-2-ene
23	116	$C_6H_{12}O_2$	2,2,4-trimethyl-1,3-dioxalane
24		?	
25	102	$C_5H_{10}O_2$	2-Methyl-1,3-dioxane
26	102	$C_6H_{14}O$	Di-iso-propyl ether
27	132	$C_7H_{16}O_2$	Di-propoxy methane
28	116	$C_5H_8O_3$	Acetoxy acetone
29		?	

Table 9. Identification of Major Peaks of Smoke from Polyurethane GM-21

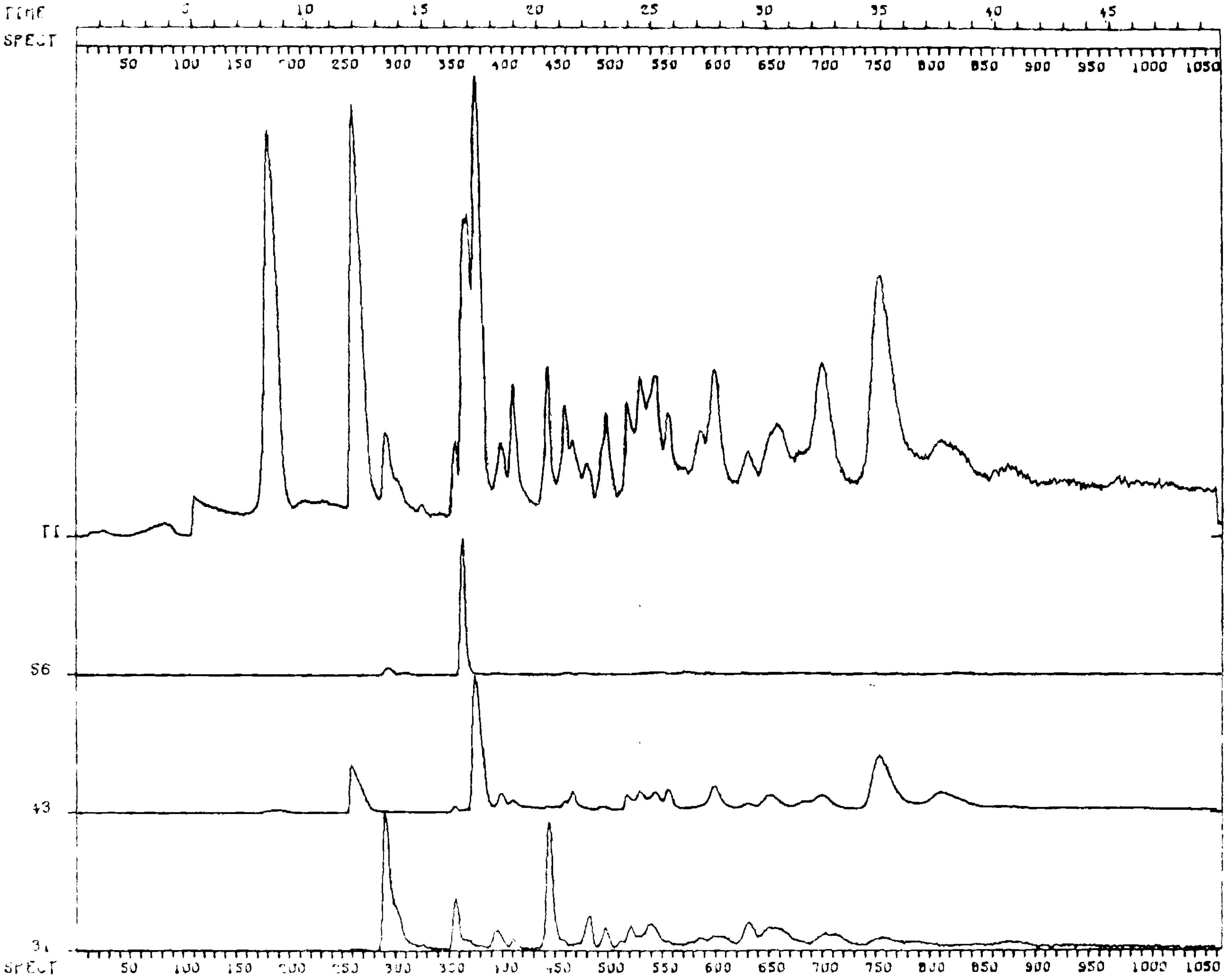


Figure 44. Total and Single Ion Chromatograms of Smoke from Polyurethane Sample No. GM-21

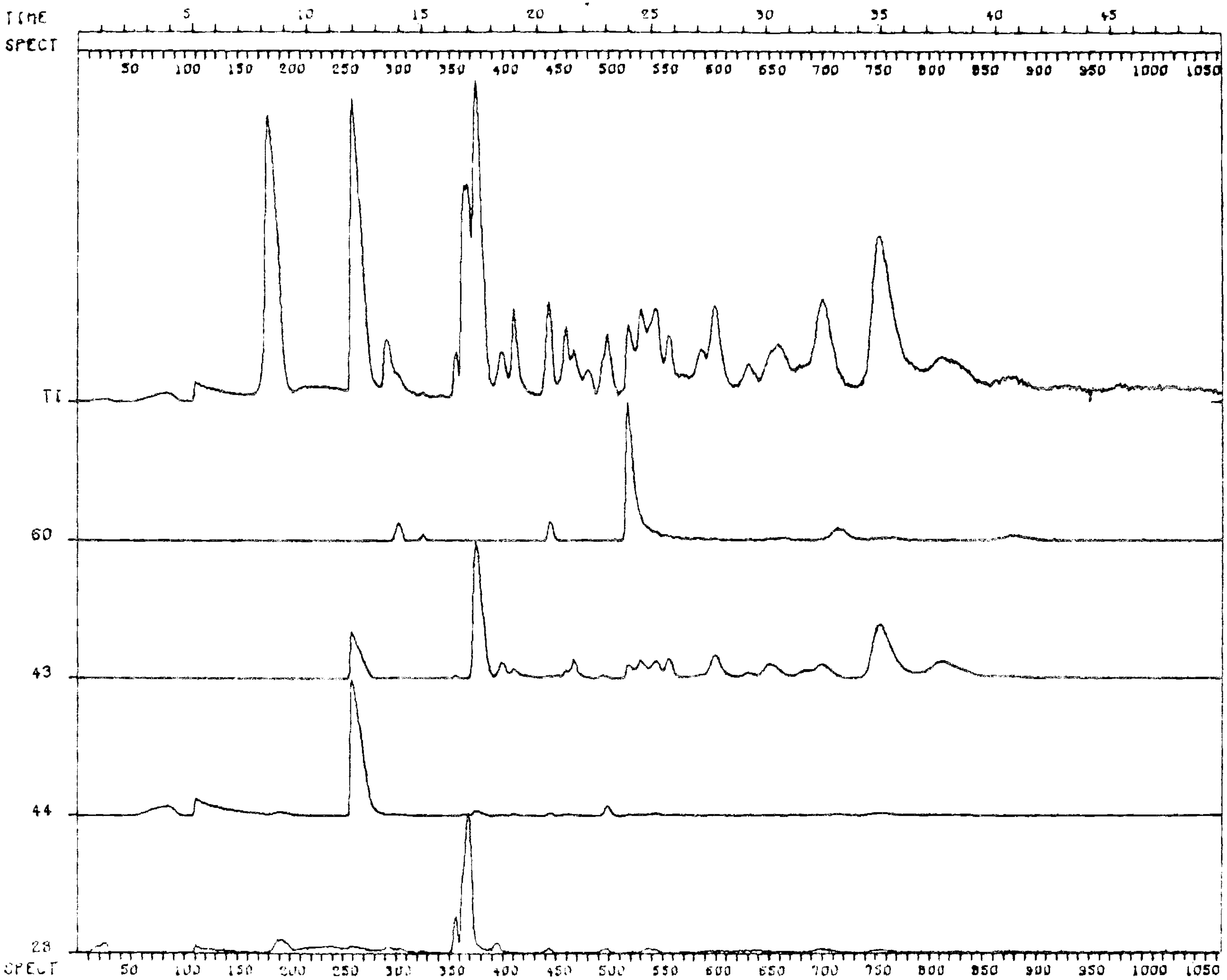


Figure 45. Total and Single Ion Chromatograms of Smoke from Polyurethane Sample No. GM-21

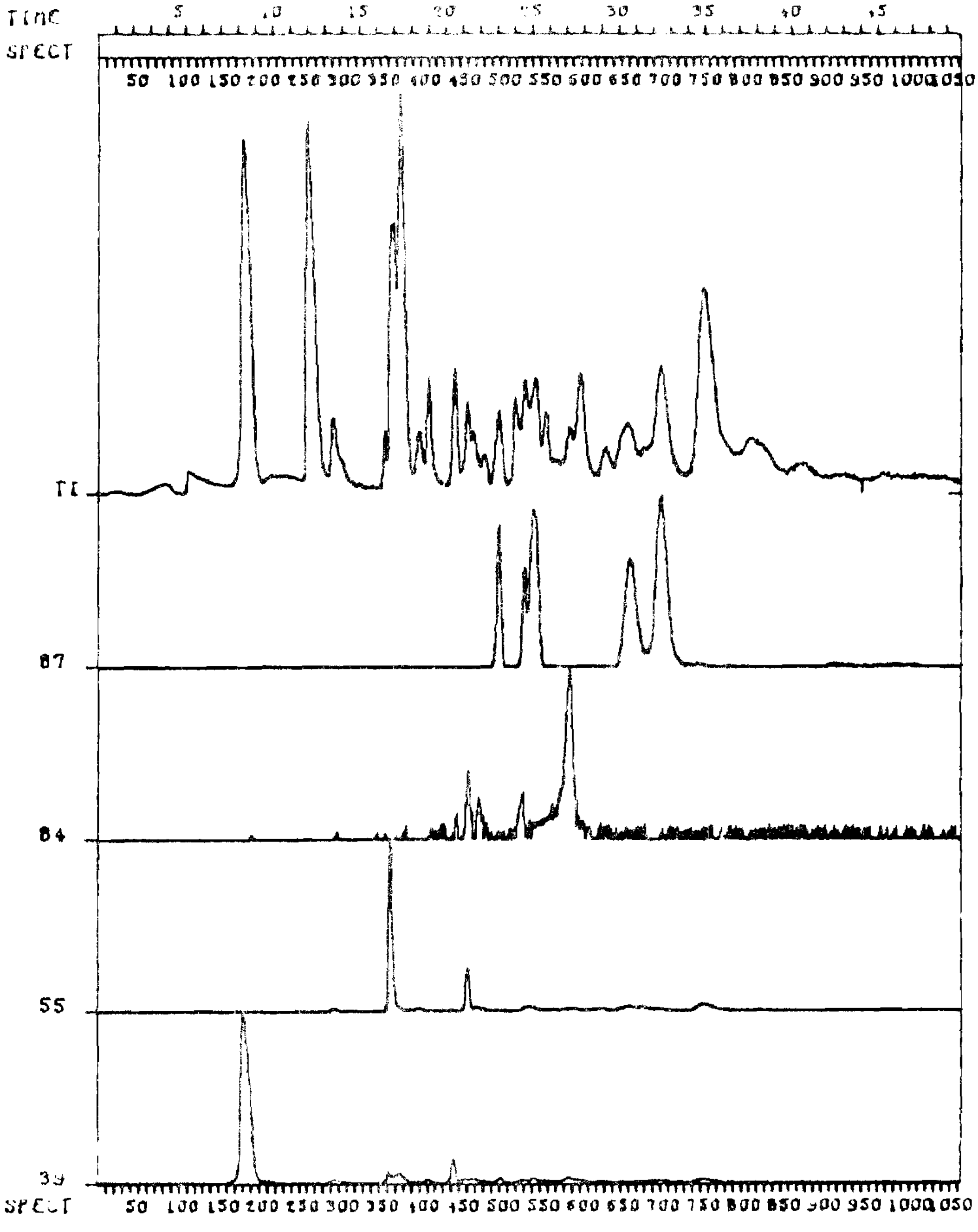


Figure 46. Total and Single Ion Chromatograms of Smoke from Polyurethane Sample No. GM-21

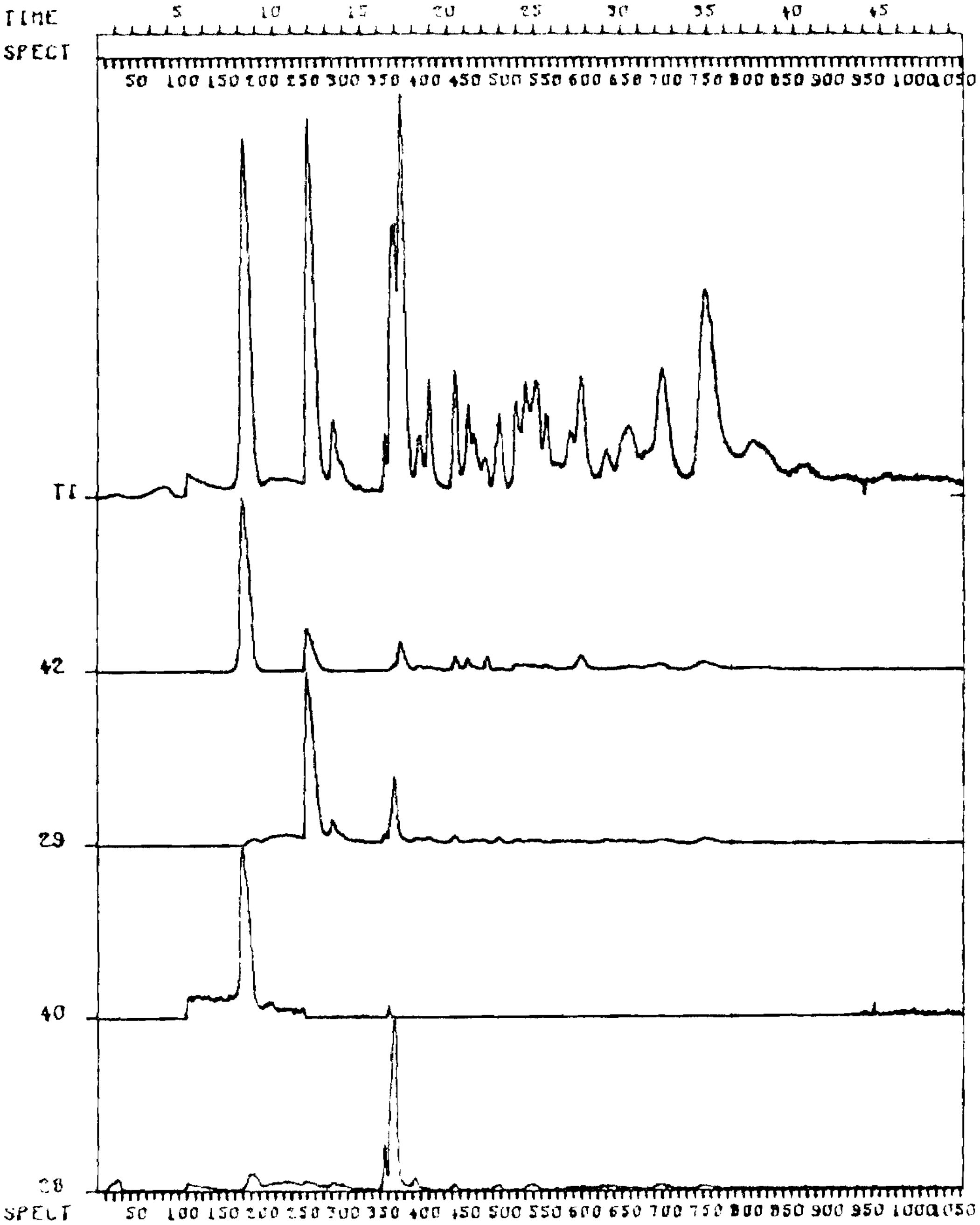


Figure 47. Total and Single Ion Chromatograms of

Smoke from Polyurethane Sample No. GM-21

As can be seen, oxygenated compounds predominate in the lower molecular weight volatile species. The major compound types to be seen are: (i) alcohols, (ii) ethers, (iii) esters, (iv) ketones. This is in marked contrast to the volatiles produced from PVC, which consist to a large degree of alkenes, plus benzene and toluene (the higher molecular weight compounds contain large amounts of polynuclear aromatic hydrocarbons, continuing the trend toward unsaturated cyclic compounds in the PVC products). It is interesting that no basic compounds are found in the volatile polyurethane smoke components. The identification of the non-volatile smoke particulate components is continuing, using chemical ionization mass spectrometry as a means to identify products. Electron impact ionization produces extremely equivocal mass spectra, with no possibility of positive identification, but the preliminary chemical ionization data looks to be much more promising and should yield much valuable data.

VII. REFERENCES

1. C. P. Bankston, R. A. Cassanova, E. A. Powell and B. T. Zinn, "Initial Data on the Physical Properties of Smoke Produced by Burning Materials Under Different Conditions," J. Fire and Flammability, 7, (1976).

2. B. T. Zinn, E. A. Powell, R. A. Cassanova and C. P. Bankston, "Investigation of Smoke Particulates Generated During the Thermal Degradation of Natural and Synthetic Materials," Fire Research, 1, 23 (1977).

3. E. A. Powell, R. A. Cassanova, C. P. Bankston and B. T. Zinn, "Combustion-Generated Smoke Diagnostics by Means of Optical Measurement Techniques," in Experimental Diagnostics in Gas Phase Combustion Systems (Progress in Astronautics and Aeronautics, Vol. 53), edited by Ben T. Zinn, American Institute of Aeronautics and Astronautics, New York, NY (1977), p. 449.

4. Zinn, B. T., Cassanova, R. A., Bankston, C. P., Browner, R. F., Powell, E. A., Rhee, J. U., and Kailasanath, K., "Investigation of the Properties of the Combustion Products Generated by Building Fires," Final Report of National Bureau of Standards Grant Number G7-9001, November 1977.

5. Cadle, R. D., Particle Size, Reinhold Publishing Corporation, New York (1965).

6. Zinn, B. T., et al, "Investigation of the Properties of the Combustion Products Generated by Building Fires," Final Report of National Bureau of Standards Grant No. G8-9003, November 1978.

7. C. J. Hilado, "The Effect of Chemical and Physical Factors on Smoke Evolution from Polymers," J. Fire & Flammability, Vol. 1, p. 217, July 1970.