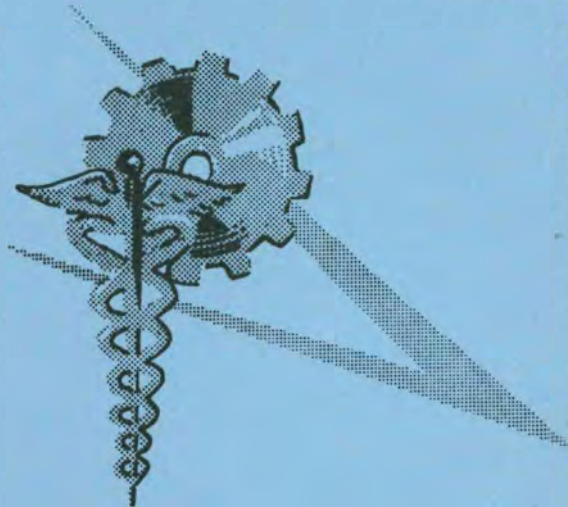


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POLYFLUOROETHYLENE PYROLYSIS STUDIES



TR-47

OCTOBER 1967

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
Public Health Service  
National Center for Urban and Industrial Health

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POLYFLUOROETHYLENE PYROLYSIS STUDIES

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## FOREWORD

This study of the toxicology of fluorocarbon polymer pyrolysis products originated from an inquiry concerning black box fires in aircraft posed to the Toxicology Laboratory, Occupational Health Program, by the Federal Aviation Agency in 1961. After a survey of the literature and discussions with industrial representatives, a cooperative study by industry and the Occupational Health Program was started in 1962.

In the planning and conduct of the study, the cooperation and contributions of Dr. L. Thomas Bunn, David B. Allen, Dr. Norman West, and Dr. John Zapp of the E. I. DuPont de Nemours and Company are very much appreciated.

In supplying selected samples for testing and in participating in the discussions of data that led to this report, the cooperation of Mr. W. A. Knapp, Allied Chemical Corp., Mr. Leonard Barber, Thiokol Chemical Co., Dr. J. C. Gage and Mr. John Davis, Imperial Chemical Industries, Ltd., and Mr. Herman Birnbaum, Minnesota Mining and Manufacturing Company, is also appreciated.

The development of the ideas and mechanisms included in this report, although given under the listed limited authorship in each paper, are in reality, the product of repeated discussions during the accumulation of the data presented. We, the authors, have not only found it stimulating, but rewarding to have had the pleasure of engaging in a free exchange of ideas with these company representatives.

## ACKNOWLEDGMENT

In addition to the authors efforts in compiling this report the editor would like to acknowledge the patient and detailed assistance of Mr. August A. Lauman, Illustrator for the Occupational Health Program, in compiling this report.

# POLYFLUOROETHYLENE PYROLYSIS STUDIES

## SUMMARY

Products generated from the pyrolysis of polytetrafluoroethylene (PTFE) in air were detected, identified, and measured. Both qualitative and quantitative data were collected.

The fast reaction time associated with time-of-flight mass spectrometry made possible the initial qualitative identification of fragments formed from PTFE breakdown products. Gas chromatography with dual flame ionization detectors offered another means of detecting and qualitatively identifying pyrolysis fumes. Infrared spectrophotometric analyses were used to confirm the mass spectrometer findings.

Quantitative amounts of toxic products at a low limit were determined in atmospheric samples from the animal exposure chamber with a 10-meter gas cell. The quantitative determination of toxic products (principally, carbonyl fluoride ( $\text{COF}_2$ ) from the animal exposure chamber) was done by means of a modified version of the Bellack and Schouboe method for rapid detection of fluoride in water. A fluoride electrode was also employed to detect hydrolyzable fluoride. Both methods proved equally accurate. The electrode method, however, required less time for an analysis and had a lower limit of detection. These methods were especially suitable for our purposes since weighed amounts of fluoride salts could be used for calibration curves.

From the mass spectra and infrared spectra of PTFE pyrolysis gases, the principal decomposition product of oxidation pyrolysis was identified as  $\text{COF}_2$ . PTFE pyrolyzed in the presence of silica ( $\text{SiO}_2$ ) formed silicon tetrafluoride ( $\text{SiF}_4$ ), which was detected and identified by the same techniques. Positive identification was made by comparing the mass spectra and infrared spectra of the pyrolysis gases with those of pure  $\text{COF}_2$  and  $\text{SiF}_4$ . Mass spectrometric data obtained from numerous exposures and experiments made possible the formulation of mechanisms showing the oxidation reactions of PTFE pyrolysis gases in air with and without the presence of silica. Infrared analysis of samples of chamber air revealed no evidence of chamber saturated or unsaturated fluorocarbons which would significantly enhance the toxicity of  $\text{COF}_2$ .

The toxic action of the various pyrolysis products from PTFE indicated that the toxicity resulted from the fluoride ion produced when  $\text{COF}_2$  and other

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

hydrolyzable products were absorbed into the tissue. The toxicity of  $\text{SiF}_4$  and the pathology in animals exposed to PTFE pyrolysis products,  $\text{COF}_2$  and  $\text{SiF}_4$  are discussed.

Although severe injury due to fluoride poisoning was inflicted on the experimental rats, it was demonstrated that the metabolic inhibition observed was completely reversible and that with the exception of a small amount of emphysematous changes, the pathologic changes in the lungs and liver were reversible within 18 days after exposure. The evidence indicated that the daily inhalation of pyrolysis products of PTFE produced a toxic syndrome compatible with the description of fluoride poisoning.

Besides the gaseous products generated from PTFE pyrolysis, a particulate residue resulted that is considered by many toxicologists as a likely cause of polymer fume fever. The mass spectrometric data obtained during these studies furnished evidence for thermal rupture of C-C linkages, oxidative rupture of C-C linkages, and terminal depolymerization by fluorocarbene oxidation. Functional groups have been established in an attempt to identify the pyrolyzed material since elemental, infrared, mass spectrometric, and gas chromatographic analyses definitely indicated the particulate residue to be different from PTFE.

### EXPERIMENTAL METHODS FOR EVALUATING FLUOROCARBON PLASTIC DECOMPOSITION BY HEAT

Richard E. Kupel and Lester D. Scheel, Ph. D.

In designing the experiments on the pyrolysis of plastics, the equipment and methodology chosen were those best suited to the collection of both qualitative and quantitative data. A pyrolysis furnace was devised in which the components of the furnace did not react with the products generated and the temperature and environment could be controlled and reproduced at any time. In the following discussion two types of generators and the methodology used in evaluating the pyrolysis of the fluorocarbon plastics are described in detail.

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

Among the analytical methods chosen for their qualitative or semiquantitative capabilities and rapidity in particular applications, the time-of-flight mass spectrometer proved to be one of the more versatile tools and fulfilled the criteria for speed of analysis. For quantitative estimation the methods were evolved in response to the need for definition of the pyrolysis products formed, and both physical and chemical analytical methods were used in the measurement of those products that could be shown to correlate with the toxic effect resulting from the animal exposures.

### PYROLYSIS FURNACES AND EXPOSURE EQUIPMENT

The small pyrolysis furnace attached to the mass spectrometer, although similar to the unit described by Kupel et al.<sup>1</sup>, differs from the earlier one in two important respects: 1. The inner wall of the Monel tube was nickel plated and then swage-surfaced with a four-mil platinum lining; 2. The installation of a stainless steel-shielded thermocouple inside the tube eliminated the ceramic insulators from the hot zone of the pyrolysis chamber. See Figures 1 and 2. The gas flow rates to the furnace were metered to any desired value between 20 ml/min. and 100 ml/min. The hot zone of the pyrolysis unit was 30 cm long, and by calculation the gases generated during the pyrolysis would remain in the hot zone of the furnace for minimums between 1 minute at 100 ml/min. and 5 minutes at 20 ml/min. depending on the gas flow rate. Thus, time was allowed for products to interact in the hot zone to an equilibrium mixture before flowing into the mass spectrometer. To prevent condensation reactions in the decomposition products before they entered the mass spectrometer, the stainless steel tube leading from the pyrolysis furnace to the mass spectrometer was maintained at 140°C.

The pyrolysis apparatus for animal exposures consisted of a 1 1/2 inch diameter Monel tube passing through an electric furnace. The assembled unit was pitched at a 30-degree angle so that the plastic rod fed into the upper end would, after melting, run down the length of the Monel tube wall to insure complete pyrolysis. A variable transformer was used to control the furnace temperature. A diagram of the unit consisting of the animal exposure chamber and the pyrolysis furnace is shown in Figure 3.

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The temperature of the Monel tube was measured by a thermocouple mounted in the asbestos insulation on the outside surface of the tube and inside the electric furnace. This eliminated the need for insulators inside the pyrolysis chamber.

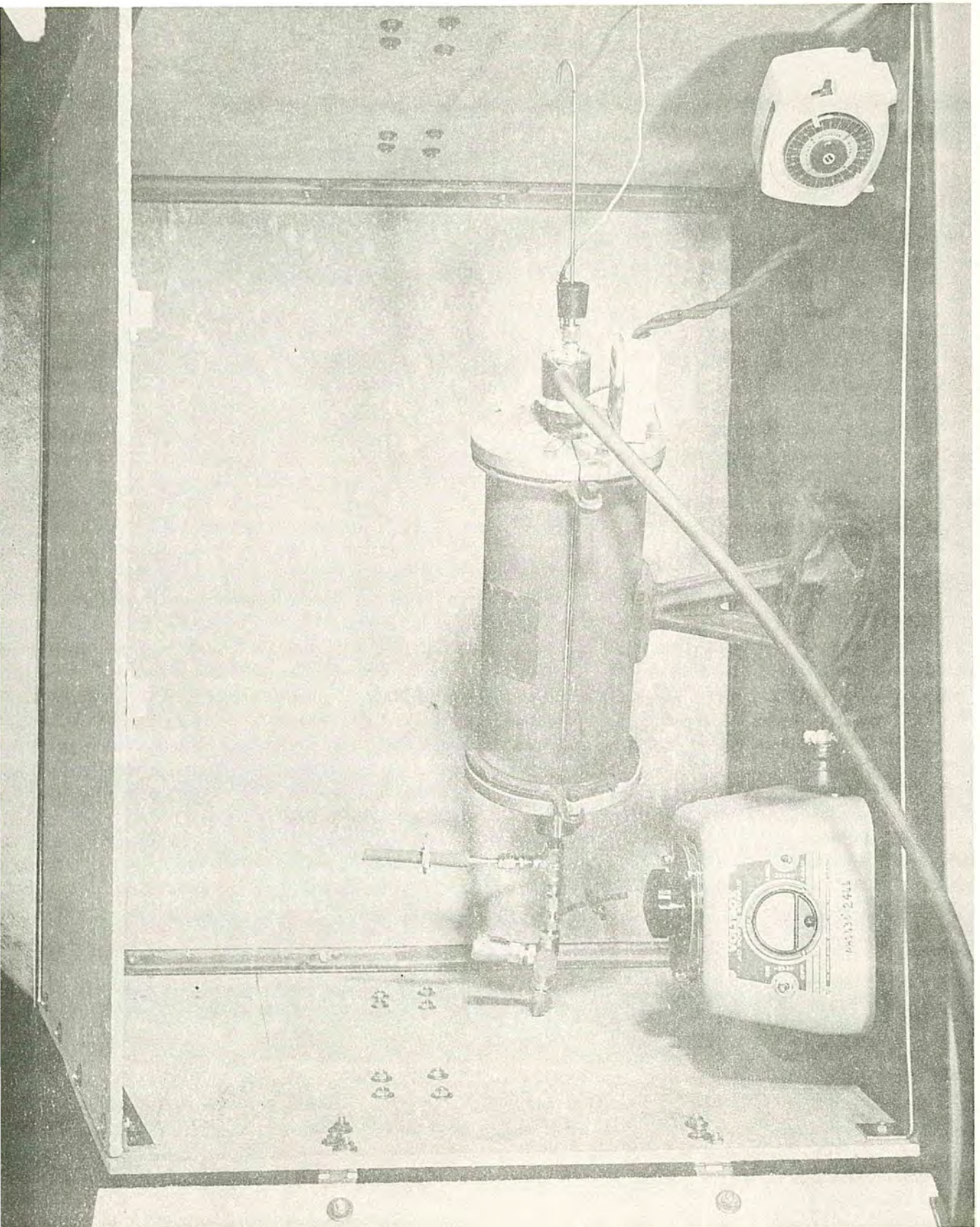
Continuous pyrolysis of the plastic material was provided by feeding rod stock through a feed port at the upper end of the tube with a constant speed, motor-driven pinion gear. The feed rate was controlled by controlling the motor speed.

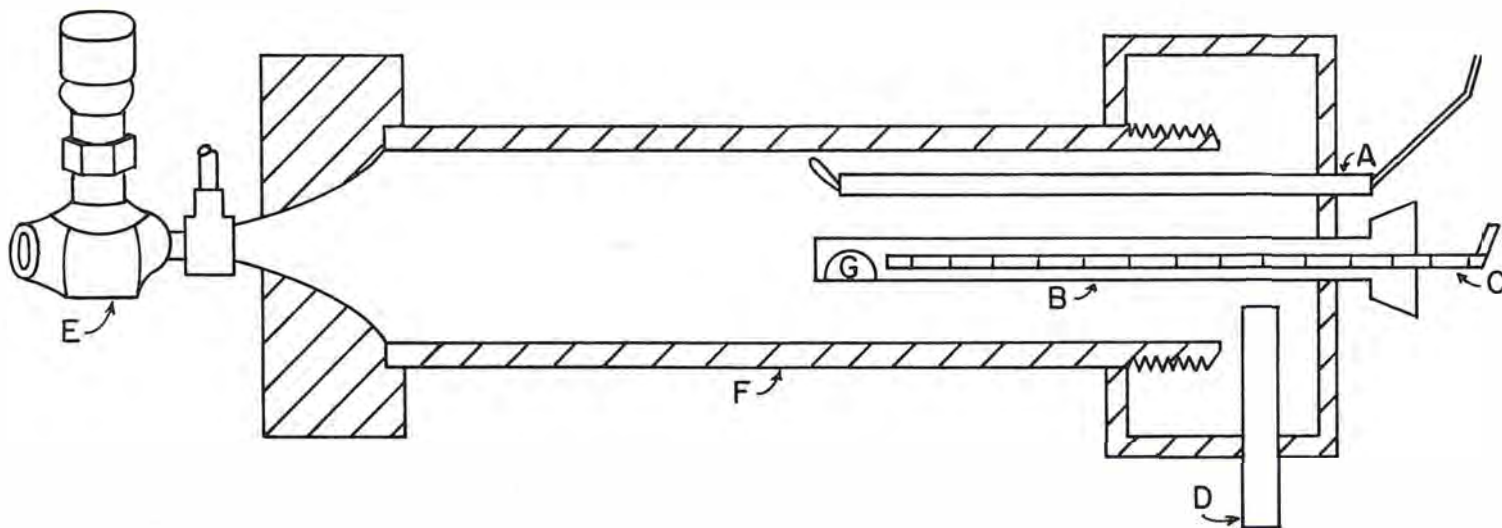
The exit end of the pyrolysis furnace was mounted in a stainless steel cross at a right angle to the dilution air line to the animal exposure chamber. The dilution air was fed into the chamber through a one-inch central delivery tube which passed through the inch-and-a-half cross and discharged the dilution air three inches downstream from the cross.

On the outer end of the cross was mounted a 1/4-inch tube, which ran into the Monel tube three inches, where it ended in a 1.25-inch flare. This tube constituted a sample port through which samples could be drawn directly out of the pyrolysis furnace at a point where the pyrolysis gases were just leaving the furnace. To prevent a back flow of air from the dilution air stream, the sampling rate from the furnace port was regulated so that it never exceeded half the rate at which air was fed into the furnace.

Leakage of air around the rod stock being fed into the furnace was prevented by a doughnut shaped, urethane foam plug with a center hole small enough so that it fitted snugly around the rod. Thus, as the rod was fed into the hole in the feed plate mount, the urethane foam was pressed snugly against the plate, thereby providing a seal around the rod. For an air feed of 4 liters/minute into the furnace, the flow rate was 5.08 cm/sec. The hot zone of the furnace was 32 cm long; thus, the pyrolysis gases were in the hot zone of the furnace for about 6.3 seconds. A temperature profile of the furnace is shown in Figure 4.

The diluted pyrolysis gases entered the chamber through a diffusor and were regulated at any desired rate of flow from 71 to 142 liters/min. by a sharp edge orifice and gate-valve arrangement in the inlet line to the chamber. The volume of flow through the chamber was determined by the adjustment of the valve on the chamber exhaust line. While the unit was in operation, the





- |                                  |  |
|----------------------------------|--|
| A - THERMOCOUPLE TUBE            | E - MICROMETER VALVE                       |
| B - SAMPLE INTRODUCTORY TUBE     | F - MONEL FURNACE TUBE ,<br>PLATINUM LINED |
| C - SAMPLE INJECTION ROD         | G - SAMPLE                                 |
| D - ATMOSPHERE INTRODUCTORY PORT |  |

FIGURE 2. SCHEMATIC DIAGRAM OF DECOMPOSITION CHAMBER .

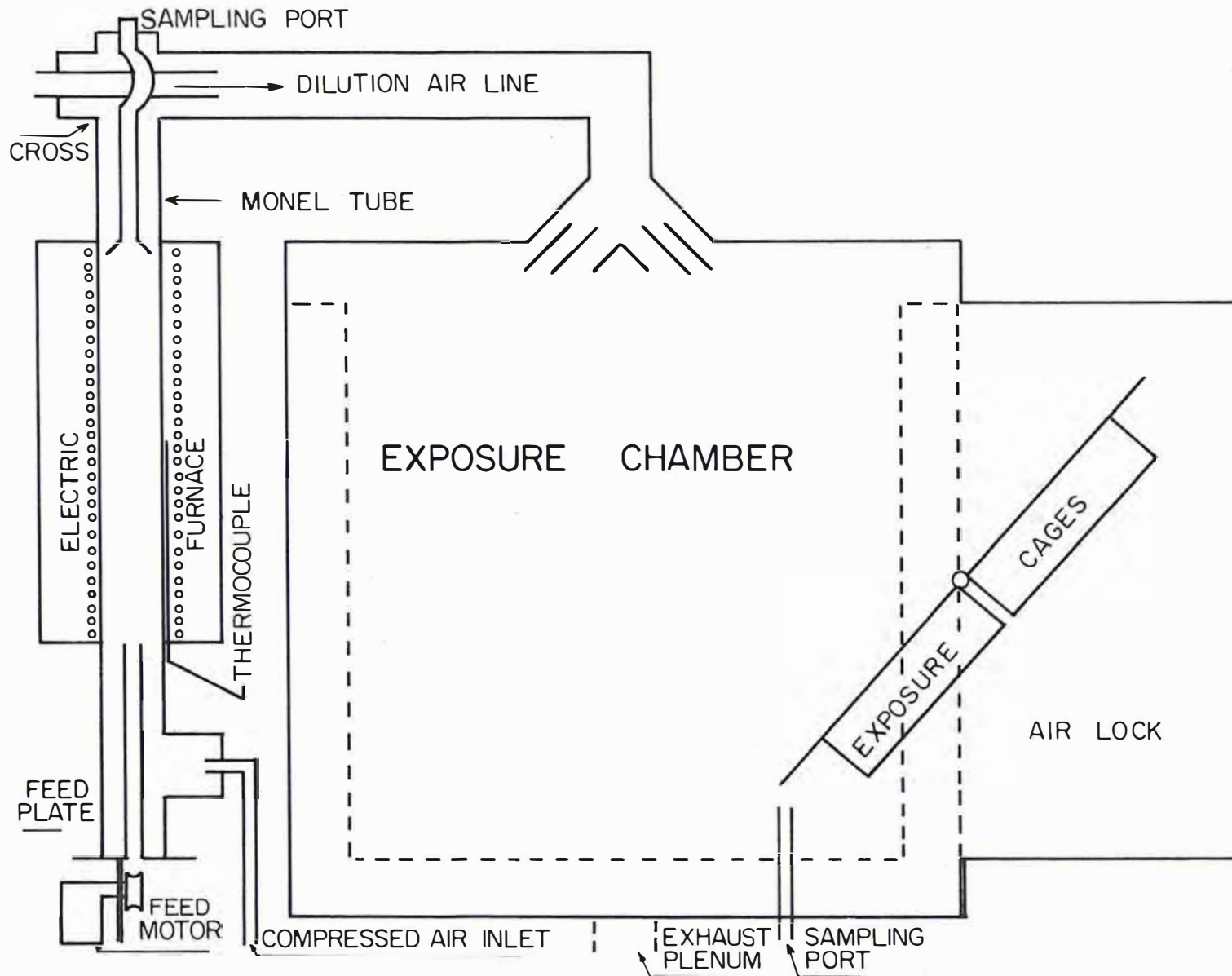


FIGURE 3. PLASTIC PYROLYSIS EXPOSURE UNIT

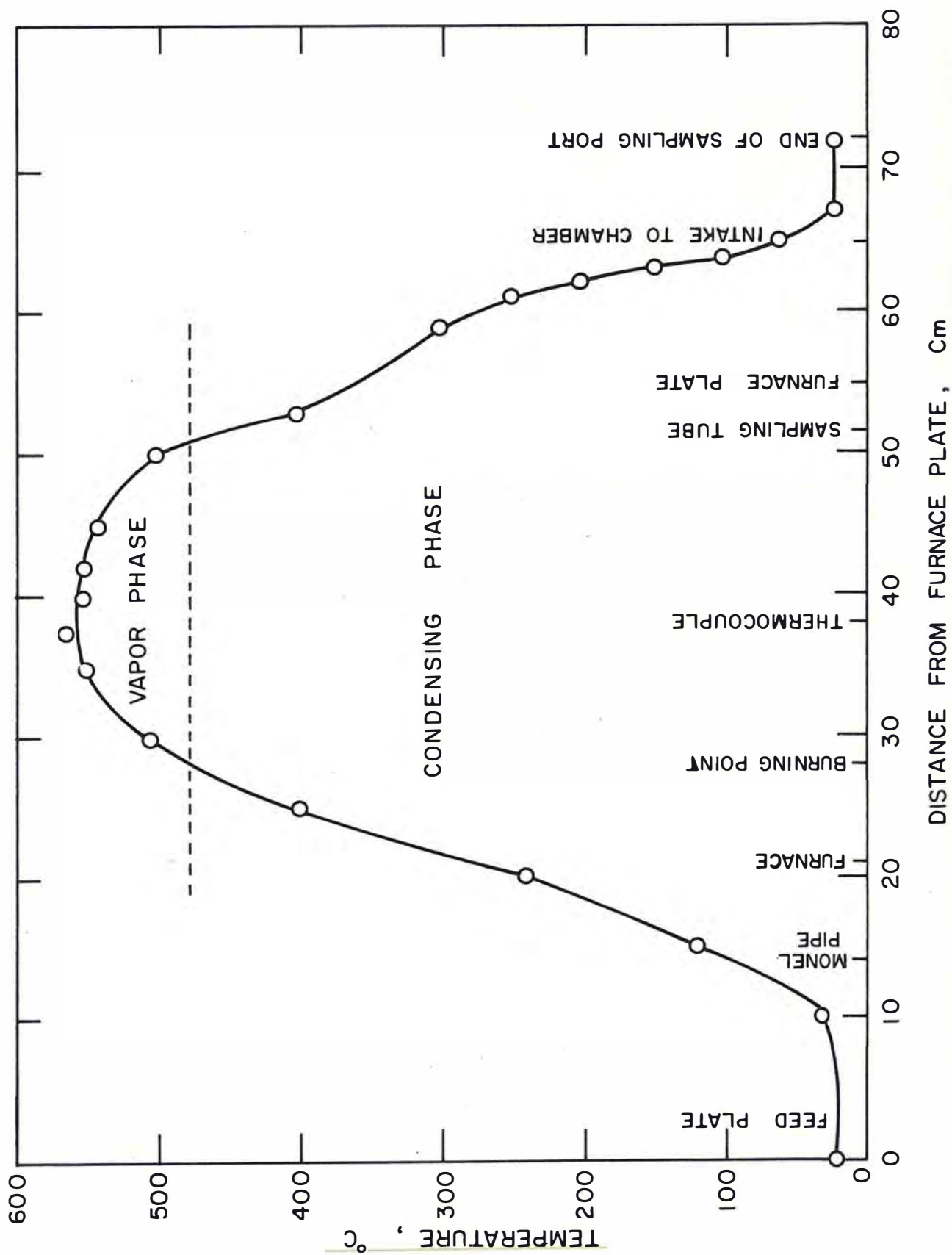


FIGURE 4 . TEMPERATURE PROFILE OF PYROLYSIS FURNACE .

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ambient pressure inside the chamber was maintained negative (0.1 inch of water) to the outside pressure in the room in order to provide proper positive control over the gas flow conditions and to prevent contamination of the exposure room with toxic materials.

The chamber was a welded aluminum cube of 1245-liter capacity equipped with an airlock door on which the animals were mounted in cages. The door could be pivoted to transfer the animals from the air lock into the chamber for exposure. At the end of the desired exposure time the animals could be removed from the chamber and then removed from the air lock. The sampling port for evaluating the chamber atmosphere was a 1/4-inch tube of stainless steel passing through a rubber stopper in a hole in the Plexiglas window of the chamber.

Since fluorocarbons do not oxidize easily and would require added energy to support combustion, potential industrial exposures would probably be short and would probably occur during electrical fires. Therefore, a short exposure time of one hour was chosen for most of the acute toxicity studies.

## PYROLYSIS PRODUCT SCREENING METHODS

The mass spectrometer was selected as the instrument to be used in a screening method of analysis because it is unique in being able to identify simultaneously all of the unit sizes of the molecular fragments in the gaseous pyrolysis products while presenting evidence of their equilibrium with the pyrolysis atmosphere. Under certain specific calibration conditions semi-quantitative calculations of observed concentrations could be made.

Once a compound has been identified, its concentration in an air sample can be determined provided that some of the pure compound is available as a reference standard. Usually, calibration conditions are established using the peak (shown by the cracking pattern), of the major fragment ion of the pure gas under analysis. For example, in carbonyl fluoride ( $\text{COF}_2$ ) analysis, the calibration was accomplished using the mass 47 peak ( $\text{COF}^+$ ). The electron beam energy must be greater than the appearance potential of the ions in order to assure reproducibility. In this study 65 electron volts were used.

The reference gas sample, usually at a pressure of 50 Torr (mm Hg) as measured on a manometer, was allowed to expand into a constant-temperature

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5-liter stainless steel expansion sphere to equilibration and then was permitted to bleed into the mass spectrometer at a constant rate through a gold molecular leak.

The recorder chart peak heights produced during the molecular fragmentation in pyrolysis were directly proportional to the sample pressure. Peak heights of designated mass units were measured in arbitrary scale divisions on chart paper. Once the sample pressure and the peak heights of a standard gas were known, it was possible to calculate the sensitivity factor for the gas and also the concentration of that same gas in a mixture of gases.

Quantitation of  $\text{COF}_2$  was fairly easy since no other ionic fragment in the pyrolysis gases could contribute to mass 47.

Consider a 50-Torr sample of pure  $\text{COF}_2$  that produces a 47 peak height of 5000 scale divisions. From these data, a sensitivity factor for  $\text{COF}_2$  can be obtained:

$$(a) \frac{5000 \text{ Sc. Div.}}{50 \text{ Torr}} = 100 \text{ Sc. Div./Torr}$$

$$(b) \text{ sensitivity factor} = \text{Torr/Sc. Div.}$$

$$(c) \therefore, \text{ sensitivity factor} = \frac{1}{100} = 0.01$$

That is, each scale unit for the characteristic peak represents 0.01 mm pressure of  $\text{COF}_2$ .

Assume that a 50-Torr sample of pyrolysis gases produces for mass 47 a peak of 100 scale divisions. Then,

$$(d) \frac{\text{Torr}}{\text{Sc. Div.}} \times \text{Sc. Div.} = \text{Torr (Partial pressure of } \text{COF}_2 \text{ in mixture)}$$

$$\text{or, (e) sensitivity factor of } \text{COF}_2 \times \text{Sc. Div. (Sample)} = \text{Torr}$$

$$(f) 0.01 \times 100 = 1 \text{ Torr (partial pressure exerted by } \text{COF}_2)$$

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$$(g) \frac{\text{Partial pressure of COF}_2 \text{ in mix.} \times 100}{\text{Total pressure of gas sample}} = \% \text{ COF}_2$$

$$(h) \therefore \% \text{ COF}_2 \text{ in mixture} = \frac{1 \text{ mm}}{50 \text{ mm}} \times 100 = 2\%$$

The conditions for pyrolyzing the samples had been previously determined with a small pyrolysis furnace attached to the mass spectrometer under operating conditions that were the same as above, described by Kupel et al.<sup>1</sup>. The data obtained by pyrolyzing various fluorocarbon materials in atmospheres of air, nitrogen, and oxygen at various temperatures from 350° to 875° C provided the first evidence that oxygen was taking part in the pyrolysis reaction. The large pyrolysis furnace for the chamber exposures was set to produce similar conditions and a 1/4-inch plastic rod was fed into the furnace for the duration of the exposures. During this time samples were collected from the furnace and from the chamber in stainless steel gas sampling tubes (500 ml), and these samples were analyzed with the mass spectrometer.

Additional characterization of the gaseous products formed in both furnaces during pyrolysis was obtained by analyzing samples with a one-meter and a ten-meter infrared gas cell. These cells, suitably calibrated, were also used to obtain quantitative data on the concentrations of various components in the pyrolysis gases. The simplicity of the infrared spectra obtained was an advantage in identifying COF<sub>2</sub> as a dominant pyrolysis product. With the ten-meter cell, it was possible to detect approximately 5 ppm of CO<sub>2</sub> and COF<sub>2</sub> in the chamber air.

In addition to the substantial semiquantitative data obtained by the above methods, product separation, identification, and quantitation were obtained by means of gas chromatographic techniques. A 60-foot, 1/8-inch, stainless steel column, containing 10% dibutyl maleate on 60/80 mesh Chromosorb W, separated tetrafluoroethylene, hexafluoroethane, carbon tetrafluoride, hexafluoropropene, perfluorocyclobutane, and perfluoroisobutylene. All of these gases have nearly the same sensitivity, and amounts as low as 0.05 mg were easily detected. However, neither COF<sub>2</sub> nor SiF<sub>4</sub> were detectable with either the above column or the flame ionization detector.

Another 60-foot column of 1/4-inch copper tubing, containing a 10-foot section of FS-5 and a 50-foot section of 22 B, 20% Fluorolube on 60/80 mesh Chromosorb P, was used to separate COF<sub>2</sub> from other pyrolysis products.

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The latter column was very effective in separating carbonyl fluoride, tetrafluoroethylene, hexafluoroethane, carbon tetrafluoride, hexafluoropropene, and perfluorocyclobutane, but not perfluoroisobutylene. Perfluoroisobutylene appeared to react with the column, and two peaks were recorded. Silicon tetrafluoride could not be detected using this column. Although this column did separate  $\text{COF}_2$ , the extremely low sensitivity made it impossible to measure small quantities of  $\text{COF}_2$ .

The sensitivity of the dibutyl maleate column for all gases separated except  $\text{COF}_2$  was about the same as that of the Fluorolube column; however, the retention times were about twice as long.

Realizing the inadequacy of the two columns for separating  $\text{COF}_2$  and  $\text{SiF}_4$ , we made a quantitative determination of hydrolyzable fluoride from the exposure chamber atmosphere by the Bellack and Schouboe method<sup>2</sup>.

## QUANTITATIVE EVALUATION OF THE BREAKDOWN OF THE FLUOROCARBON POLYMERS

As indicated above, the instruments were calibrated so that semiquantitative and quantitative analyses could be accomplished. However, after evidence had been accumulated that  $\text{COF}_2$  was the predominant reaction product, a quantitative monitoring method based on the following reaction was chosen.



When air containing  $\text{COF}_2$  (1000 ppm) was bubbled into 0.5N NaOH in two or more midjet impingers in series, 99% of the collected fluoride was found in the first impinger. The analysis of the collected sample was accomplished by the zirconium color inhibition method of Bellack and Schouboe<sup>2</sup>, or by the fluoride electrode method of Orion Research and reading the conductivity in millivolts on an expanded-scale pH meter. In the electrode method, the sample was collected in 0.5N NaOH as above, but the pH of the solution was adjusted to 6.5 with 1N HCl before measuring the conductivity.

The limit of detection using the zirconium chemical method was 0.016 microgram per ml of final solution. The working range of the standard curve was from 0 to 0.8 micrograms per ml of solution. With the fluoride electrode the linear response of the fluoride ion electrode covered a range of 0.19 to 1900  $\mu\text{g}/\text{ml}$ .

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The hydrolyzable fluoride positively correlated with the toxicity of the pyrolysis products following the exposures. In addition, the deaths of exposed animals were found to be caused by fluoride and, therefore, all calculations of the results of hydrolyzable fluoride determinations have been made and expressed as ppm of  $\text{COF}_2$ .

The pyrolysis material included not only gaseous products but also particulate matter. These particles were collected on Millipore filters from both the furnace effluent and from the exposure chamber atmosphere. The particles from the chamber were sized by electron microscopy, analyzed for elemental composition, and examined by repyrolyzing the particles in the small furnace, analyzing these breakdown products with the mass spectrometer, and examining by infrared techniques. In addition, differential scanning calorimetry was used to examine the decomposition of the particles. The results obtained with these techniques are presented and discussed in "THE PARTICLES RESULTING FROM POLYTETRAFLUOROETHYLENE (PTFE) PYROLYSIS IN AIR" of this series.

### SUMMARY

The instrumentation, analytical methods, and toxicologic exposure techniques that were useful in the conduct of the fluorocarbon plastic pyrolysis experiments are described. The biochemical techniques and the metabolic methods were not included in this discussion since they are not general techniques useful to the study of the pyrolysis products, but are special techniques concerned with the nature of the particular metabolic problem associated with fluoride exposure. These methods will be discussed in "BIOCHEMICAL CHANGES ASSOCIATED WITH TOXIC EXPOSURES TO POLYTETRAFLUOROETHYLENE PYROLYSIS PRODUCTS" of this series along with the pertinent experiments.

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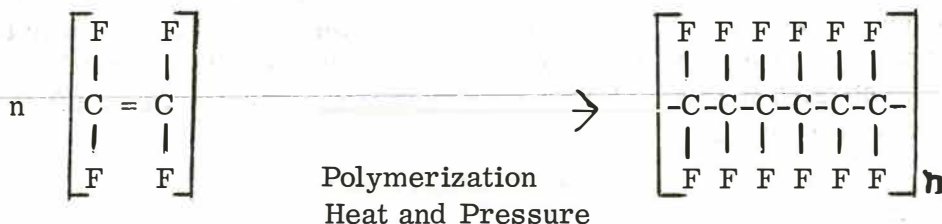
POLYFLUOROETHYLENE PYROLYSIS STUDIES

THE IDENTIFICATION OF TOXIC COMPOUNDS IN THE  
PYROLYSIS PRODUCTS OF POLYTETRAFLUOROETHYLENE (PTFE)

W. Emile Coleman, Lester D. Scheel, Ph. D.  
Richard E. Kupel, and Robert L. Larkin

Polytetrafluoroethylene (PTFE), a ram extruded commercial product, is a linear fluorocarbon polymer of very high molecular weight and very unusual properties.

Gaseous tetrafluoroethylene is polymerized under heat and pressure to yield the PTFE resin.



The basic building block of the resin molecule is  $\begin{array}{c} \text{F} \quad \text{F} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{F} \quad \text{F} \end{array}$ . The

average number of these units per molecule ranges from approximately 10,000 to 100,000. Because of the extremely long chain of CF<sub>2</sub> groups and the strong binding forces between them (the forces binding carbon to fluorine constitute one of the strongest known chemical linkages) PTFE exhibits these properties: extreme chemical inertness, high thermal stability, strength at high temperatures, electrical insulating qualities, insolubility, low friction coefficients, and an antistick nature.

The toxic products from PTFE pyrolysis in air at 500° to 600°C (932° to 1112° F) were identified by mass spectrometric, gas chromatographic, and infrared techniques. Under the conditions set up for the experiments<sup>1</sup>, the principal toxic agent produced was an oxidation product, carbonyl fluoride (COF<sub>2</sub>). A reaction product, silicon tetrafluoride (SiF<sub>4</sub>), was also identified by means of the above techniques. Samples of polytetrafluoroethylene (PTFE) obtained from four major manufacturers were investigated under similar conditions. No major differences in toxic decomposition products were observed.

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### EXPERIMENTAL RESULTS

Table I shows that under the conditions listed, using the relative intensities of the mass fragments, most of the ions produced from the pyrolysis products were attributable to masses 44, 47, 66, and 69. These masses indicated that at the prescribed temperature and furnace air flow, PTFE decomposition products consisted primarily of  $\text{COF}_2$ ,  $\text{CO}_2$  and  $\text{CF}_4$  (carbon tetrafluoride). The major fragment ions respectively are  $\text{COF}^+$  (47);  $\text{CO}_2^+$  (44). The high yield of the mass fragment ions mentioned above confirmed Errede's<sup>2</sup>, hypothesis that the depolymerization of PTFE resulted via elimination of  $\text{CF}_2$  fragments.

The formation of  $\text{COF}_2$  was the dominant reaction during pyrolysis in air in the temperature range of  $490^\circ$  to  $650^\circ$  C ( $914$  to  $1202^\circ$  F). At  $650^\circ$  C and above,  $\text{CF}_4$  and  $\text{CO}_2$  were the major constituents. The fact that the 66/47 ratio of pure  $\text{COF}_2$  (.625) was almost the same as that found in the pyrolysis gases (.614) confirmed the presence of  $\text{COF}_2$  in the pyrolysis gases. The presence of other CF fragments, namely, masses 31, 50, 81, 100, 119, and 131 indicated the formation of trace amounts of other fluorocarbons. Since all appeared together, it was difficult to differentiate between the gases solely with the mass spectrometer. However, in addition to the products already discussed, gas chromatography with flame ionization revealed the presence of tetrafluoroethylene ( $\text{C}_2\text{F}_4$ ), hexafluoropropene ( $\text{C}_3\text{F}_6$ ), perfluorocyclobutane ( $\text{C}_4\text{F}_8$ ), and possibly hexafluoroethane ( $\text{C}_2\text{F}_6$ ). The major fragment ions of these gases are  $\text{CF}^+$ (31) and  $\text{C}_2\text{F}_3^+$ (81),  $\text{CF}_3^+$ (69) and  $\text{C}_3\text{F}_5^+$ (131), and  $\text{CF}_3^+$ (69) and  $\text{C}_2\text{F}_5^+$ (119), respectively.

We used Errede's hypothesis on the depolymerization of PTFE via  $\text{CF}_2$ : fragment elimination and the mass spectrometer data obtained from actual pyrolysis runs to formulate the following mechanisms:



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form CO<sub>2</sub> and CF<sub>4</sub>. Therefore, at 700° C the evidence indicates that equation (2) must be the first step before equation (3).

Table I

Typical Mass Spectrum of PTFE Pyrolysis in Air

Mass No.	Ion (+)	Scale Divisions	Relative Abundance (N <sub>2</sub> =100)
12	C	11.0	0.10
14	N	608.0	5.26
16	O	201.0	1.74
19	F	2.0	0.02
20	HF	19.0	0.16
23.5	COF	1.2	0.01
<u>28</u>	<u>N<sub>2</sub></u>	<u>11,540.0</u>	<u>100.00</u>
31	CF	20.0	0.17
32	O <sub>2</sub>	3116.0	27.18
40	A	276.0	2.40
44	CO <sub>2</sub>	199.0	1.72
47	COF	218.0	1.90
50	CF <sub>2</sub>	13.0	0.11
66	COF <sub>2</sub>	134.0	1.16
69	CF <sub>3</sub>	72.0	0.62
81	C <sub>2</sub> F <sub>3</sub>	0.4	0.003
85	SiF <sub>3</sub>	0.0	0.00
100	C <sub>2</sub> F <sub>4</sub>	14.0	0.12
119	C <sub>2</sub> F <sub>5</sub>	7.0	0.06
131	C <sub>3</sub> F <sub>5</sub>	12.0	0.10

Furnace Temp. : 550° C (1022 °F)  
 Furnace Air Flow: 4 L/min.  
 Chamber Dilution Air: 5 CFM  
 Wgt. of PTFE pyrolyzed: 22.5 g/hr.

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Table II

PTFE Pyrolysis in Air at 550° and 700°C

Date of Run	Pyrolysis Temperature	Mass Spec. Peak Heights				Ratio 44/69	Ratio 44/47
		CO <sub>2</sub> (44)	COF <sub>2</sub> (47)	CF <sub>4</sub> (69)	SiF <sub>4</sub> (85)		
1) 6-1-66	550°C	199	218	72	0	2.8	0.91
2) 10-14-66	550°C	150	152	51	0	2.9	0.99
3) 7-29-65	700°C	315	58	18	30	6.5*	5.4
4) 7-22-65	700°C	464	112	46	20	6.3*	4.2

\* Peak heights of masses 69 and 85 added to calculate 44/69 ratio.

At 700°C the results of the 44/69 ratio were obtained by adding together the peak heights of masses 69 (CF<sub>3</sub><sup>+</sup>) and 85 (SiF<sub>3</sub><sup>+</sup>). This is rational since silicon and carbon attract the same number of fluoride ions. When silica (SiO<sub>2</sub>) is not present in the system, only mass 69 (CF<sub>3</sub><sup>+</sup>) exists in the mass spectra. Equation (4a) shows the general reaction at 700°C in the absence of SiO<sub>2</sub>.

As shown in Table II the 44/69 ratio at 700°C is approximately double the 44/69 ratio at 550°C. This could be possible only if SiO<sub>2</sub> is present. Equation (4) and Table II data demonstrate that the 44/69 ratio is constant at 6.5 at 700°C as compared to 3 at 550°C. Therefore, since equation (4a) in which one-half the CO<sub>2</sub> in equation (4) is formed, is considered to be the general reaction in the absence of silica, the 44/69 ratio should in the absence of silica be constant at 3 at 700°C also.

The basis for the foregoing reactions are found not only in mass spectra data, but also in infrared analyses of chamber gases during PTFE pyrolysis at temperatures of 550° and 700°C. At 550°C infrared analysis showed a very intense band at 1928 cm<sup>-1</sup> due to COF<sub>2</sub> absorption and a weak band at 1280 cm<sup>-1</sup> due to CF<sub>4</sub>. At 700°C an intense band in the region of 1280 cm<sup>-1</sup> was attributed to CF<sub>4</sub><sup>3</sup>. Only trace amounts of COF<sub>2</sub> were observed.

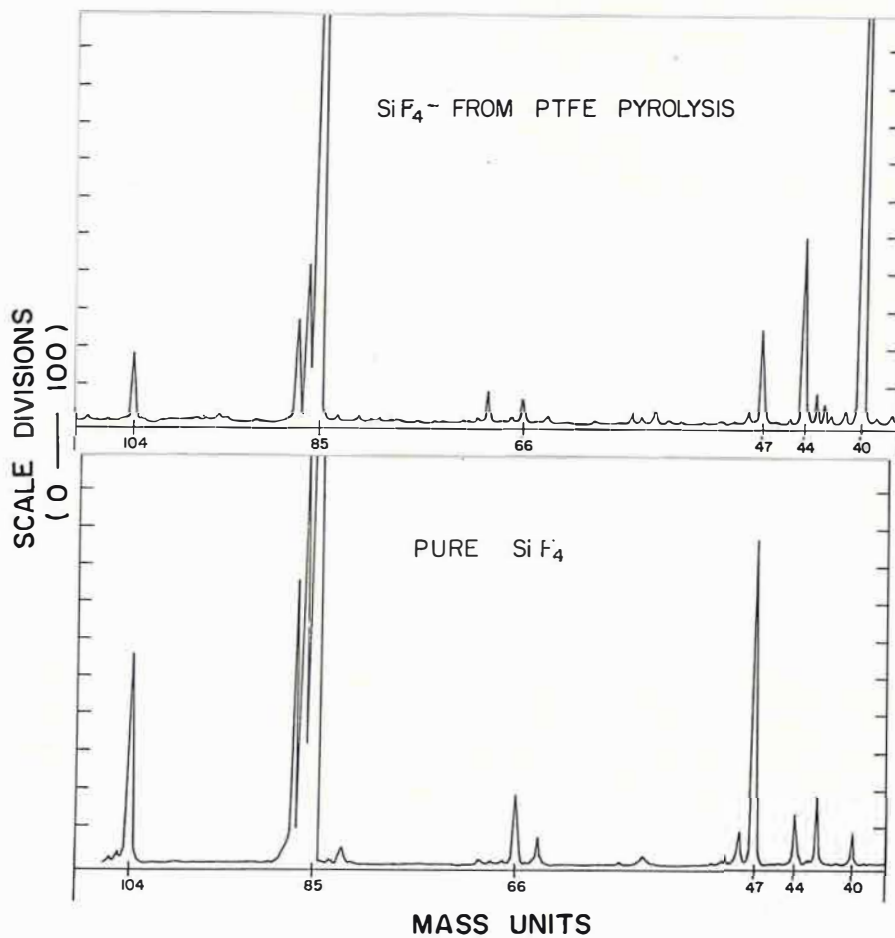


Figure 1. Mass spectra: SiF<sub>4</sub> from PTFE pyrolysis versus pure SiF<sub>4</sub>

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

In addition to the presence of CF groups and  $\text{COF}_2$ , another mass fragment, 85, always appeared in the mass spectra of pyrolysis gases during the early experiments. This peak was initially reported as  $\text{COF}_3^+$  <sup>4</sup>, since the pyrolysis occurred in air. Mass 85 was subsequently shown to be  $\text{SiF}_3^+$ , the major fragment ion of  $\text{SiF}_4$ . The first evidence of a silicon compound was obtained from an infrared analysis of pyrolysis gases showing a very strong band at approximately  $1025 \text{ cm}^{-1}$  <sup>5</sup>. This evidence was supplemented by mass spectra shown in Figure 1. Peaks at masses 85, 86, and 87 suggested isotopes of silicon ( $\text{Si}(28)\text{F}_3^+$ ,  $\text{Si}(29)\text{F}_3^+$  and  $\text{Si}(30)\text{F}_3^+$ ). These items of evidence pointed to  $\text{SiF}_4$ .

The results of mass spectrometric analysis of pure  $\text{SiF}_4$  are presented in Table III. All three isotopes of silicon are shown with their respective fluoride fragments. Comparison of the relative intensities of the mass fragment ions of pure  $\text{SiF}_4$  with the same fragment ions of the chamber sample left little doubt that the chamber sample contained  $\text{SiF}_4$ .  $\text{SiF}_4$  formation in the early experiments resulted from the reaction of fluorocarbon gases on the thermocouple ceramic insulators located inside the pyrolysis furnace.  $\text{COF}_2$  in the presence of a trace of moisture also reacts readily with silica to form  $\text{SiF}_4$ . The reactions involving solid PTFE and  $\text{COF}_2$  with silica are explained by Light et al. <sup>6</sup> in their work with silica-filled PTFE.

POLYFLUOROETHYLENE PYROLYSIS STUDIES

Table III

Mass Spectrometric Data: Comparison of Intensities of Ion Species Arising from Interaction of PTFE Pyrolysis Products and Silica with Those Produced by Pure SiF<sub>4</sub>

m/e	Ion +	Pure SiF <sub>4</sub>		Chamber Sample during PTFE Exposure	
		Scale Divs.	Rel. Int.	Scale Divs.	Rel. Int.
19	F+	104	1.13	8.4	1.08
47	Si(28)F+	324	3.52	26.5	3.41
48	Si(29)F+	39	0.42	4.0	0.52
49	Si(30)F+	15	0.16	1.0	0.13
66	Si(28)F2+	76	0.83	6.0	0.77
67	Si(29)F2+	2.0	0.02	0.6	0.08
68	Si(30)F2+	2.8	0.03	0.6	0.08
85	Si(28)F3+	9194	100.0	775	100.0
86	Si(29)F3+	410	4.46	35	4.51
87	Si(30)F3+	305	3.32	26	3.35
104 (P)	Si(28)F4+	232	2.52	20	2.58
105	Si(29)F4+	1.0	0.01	-	-
106	Si(30)F4+	6.5	0.07	-	-

The finding of SiF<sub>4</sub> in the chamber atmosphere, along with the decomposition products of PTFE led to the suspicion that the toxicity of PTFE pyrolyzed in the presence of silica would be greatly enhanced. Measures were taken to remove all sources of silica from the complete system. Stainless steel (316) was substituted for glass, wherever it occurred in the system, and the thermo-couple with its insulators was moved to the outside of the pyrolysis chamber.

The data obtained from mass spectrometric analysis of pyrolysis products of PTFE indicated that a large percentage of PTFE resin was oxidized to form COF<sub>2</sub>. Since most of the saturated fluorocarbon gases were known to be mildly toxic, COF<sub>2</sub> appeared to be the most toxic product of decomposition.

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

Many 1-hour exposures (Table IV) were conducted to evaluate the toxicity of  $\text{COF}_2$  generated in the pyrolysis gases.  $\text{COF}_2$  yield was measured semi-quantitatively with the mass spectrometer by monitoring the mass 47 peak ( $\text{COF}^+$ ) and quantitatively by determining the hydrolyzable fluoride concentration in the animal exposure chamber. Mass 85 ( $\text{SiF}_3^+$ ) was also monitored to check the formation of  $\text{SiF}_4$  in the pyrolysis furnace. Animal mortality decreased greatly as the 85 peak diminished. The data in the latter half of the experiments also showed that the  $\text{COF}_2$  concentration needed for lethality greatly increased as the  $\text{SiF}_4$  disappeared from the exposures. In order to increase the yield of  $\text{COF}_2$ , the temperature of the pyrolysis furnace was reduced from  $700^\circ$  to  $600^\circ$  C. Infrared samples were taken from the chamber and from the furnace to make certain the pyrolysis products were the same in both areas.

The infrared spectrum of  $\text{COF}_2$ <sup>7,8</sup> versus that of the PTFE pyrolysis products as shown in Figure 2 was a definite "fingerprint" in identifying the toxic products of PTFE decomposition in air. The intensities of bands at  $1928\text{ cm}^{-1}$ ,  $1249\text{ cm}^{-1}$ ,  $965\text{ cm}^{-1}$ , and  $774\text{ cm}^{-1}$  strongly suggest a high degree of oxidation of the PTFE resin to carbonyl fluoride. Bands at  $2350\text{ cm}^{-1}$  and  $1275\text{ cm}^{-1}$  indicate the presence of  $\text{CO}_2$  and  $\text{CF}_4$ , respectively. The carbonyl band ( $\text{C}=\text{O}$ ) appearing at  $1928\text{ cm}^{-1}$  was used in estimating the concentration of  $\text{COF}_2$  in the animal chamber. The absence of unsaturated fluorocarbons in the pyrolysis products is confirmed by a missing olefinic band ( $-\text{C}=\text{C}-$ ) which absorbs in the region of  $1640\text{ cm}^{-1}$  to  $1820\text{ cm}^{-1}$ .

Weighed samples of PTFE were pyrolyzed, and the decomposition gases collected in 0.5N sodium hydroxide for one-half hour at each set temperature. The yield of  $\text{COF}_2$  was calculated using the Bellack and Schouboe Method<sup>9</sup> to determine the hydrolyzable fluoride concentration. The  $\text{COF}_2$  temperature profile presented in Figure 3 shows that the oxidation of PTFE to  $\text{COF}_2$  started at approximately  $490^\circ$  C and rapidly peaked at  $600^\circ$  C. At  $600^\circ$  C the yield of  $\text{COF}_2$  was approximately 63% of the PTFE pyrolyzed. Approximately 60% of the PTFE resin was converted to  $\text{COF}_2$  at the temperature ( $550^\circ$  C) used for the animal exposures. Other workers<sup>10</sup> have reported a 20% yield of  $\text{COF}_2$ .

POLYFLUOROETHYLENE PYROLYSIS STUDIES

Table IV

PTFE 1-Hour Exposures: Effect of Presence of Silica on Lethality of PTFE Pyrolysis Products

Exposure Date	PTFE Pyrolyzed (gm)	Mortality per 10 rats	COF <sub>2</sub> in Pyrolysis Unit-Mass 47 (Avg) %	Scale Divisions of Mass 85 (SiF <sub>4</sub> )	Concentration of Hydrolyzable Fluoride in Exposure Chamber (ppm COF <sub>2</sub> )
7/1/65	3.72	0	0.32	14	21.1*
7/2/65	5.15	0	0.30	27	45.0*
7/7/65am	3.70	6	0.17	15	34.0
7/7/65pm	5.50	5	1.0	26	82.0
7/9/65am	3.76	4	0.16	19	22.
7/9/65pm	3.90	5	0.24	15	40.
7/26/65	5.10	6	0.43	31	48.
7/27/65am	5.7	7	0.61	43	47
-----					
8/10/65	9.8	0	1.1	8	119
8/17/65	15.7	2	2.1	5	150
8/19/65	17.0	0	2.3	2	169
8/23/65	18.0	0	2.4	neg.	187
8/25/67	27.5	2	2.8	2	248
8/26/65	31.0	10	3.1	2	297
9/1/65	28.5	7	-	1	357 $\Delta$

Exposure Dates 7/1/65 thru 7/27/65:

700°C (1292°F) - Furnace Air Flow 1 Liter/min.

142 Liter/min. Chamber Air Flow

\* 282 Liter/min. Chamber Air Flow

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Exposure Dates 8/10/65 thru 9/1/65

600°C (1112°F) - Furnace Air Flow 3 Liter/min.

$\Delta$  4 Liter/min.

142 Liter/min. Chamber Air Flow

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

The positive identification of  $\text{COF}_2$  from the pyrolysis furnace and in the animal exposure chamber, the high yield of  $\text{COF}_2$  from PTFE pyrolysis, and the absence of unsaturated fluorocarbons are evidence that  $\text{COF}_2$  was the most toxic agent in the oxidation pyrolysis of PTFE.

To correlate the PTFE toxicity, many exposures (listed in Table V) were conducted using pure  $\text{COF}_2$ . Ten rats were placed in cages on a rotating chamber door inside an airlock. Pure  $\text{COF}_2$  was fed through a plastic rotameter at a predetermined rate into the chamber dilution air line. The chamber was allowed to equilibrate at this level for one-half hour. The rats were rotated into the chamber, exposed for one hour and then removed.

Several air samples for mass spectrometric and infrared analyses and six air samples for the determination of the hydrolyzable fluoride concentration were taken from the chamber during the exposure hour.

On exposure dates 3/4/66 to 3/9/66 only one of the six-month-old rats died when exposed to a range of 206 to 413 ppm  $\text{COF}_2$  for one hour. On exposure dates 3/10/66 and 3/11/66 there were three and nine deaths, respectively, at average concentrations of 412 and 530 ppm. However, on exposure dates 3/24/66, 4/14/66, and 4/15/66 there were six, nine, and six deaths, respectively, of two-month old rats at average concentrations of 357, 436, and 378 ppm. These results indicated that the  $\text{LC}_{50}$  in rats for  $\text{COF}_2$ , considering all variables including age and weight, was 350 to 450 ppm.

Both the oxidation pyrolysis of PTFE at  $550^\circ\text{C}$  and the  $\text{COF}_2$  exposures previously discussed produced similar animal lethality. The exposures listed in Table VI were conducted in a silica-free system that utilized the airlock door. The method used to expose the animals to PTFE pyrolysis products was much the same as described for the  $\text{COF}_2$  exposures. One-quarter-inch rods of PTFE were fed by a motor-driven positive-feed mechanism into a hot tube furnace at a predetermined and controlled rate along with a 4-liter per minute stream of air. The decomposition products from the furnace were mixed with the chamber dilution air. The resulting mixture of gases and air was allowed to equilibrate in the chamber for one-half hour before the animals on the chamber door in the airlock were rotated into the toxic atmosphere. The animals were exposed for one hour and then removed from the chamber. The PTFE feed system was stopped and the remaining rod was weighed to determine the amount of PTFE pyrolyzed per hour.

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Four to six air samples for hydrolyzable fluoride infrared, and mass spectrometer analyses were taken during the hour exposure. The mass 85 peak representing  $\text{SiF}_4$  was monitored during each exposure. There was no evidence of its formation. The mass spectra (Table I and infrared, Figure 2) data presented earlier are typical of all exposures.

Table V

Pure  $\text{COF}_2$  Exposures\*: Lethality of  $\text{COF}_2$  for Rats

Exposure Date	Exposure Time (hr)	Concentration of $\text{COF}_2$ in Chamber (ppm)		Mortality/10 Rats (5 male, 5 female)
		Avg.	Range	
3/4/66	1	263	206-294	1
3/7/66	1	258	235-294	1
3/8/66	1	307	266-346	1
3/9/66	1	381	322-413	1
3/10/66	1	412	330-490	3
3/11/66	1	530	392-588	9
3/18/66	1	430	361-454	3
3/22/66	4	251	193-273	10
3/23/66	4	172	134-201	10
**3/24/66	1	357	315-371	6
4/12/66	1	438	393-472	3
**4/14/66	1	436	378-472	9
**4/15/66	1	378	353-388	6

\* Chamber dilution air, 5 CFM. Volume, 2500 cc/sample analyzed for  $\text{F}^-$ .

\*\* Rats less than 2 months old. All others at least 6 months old.

Six hydrolyzable  $\text{F}^-$  samples taken during 1-hour run; eight hydrolyzable  $\text{F}^-$  samples taken during 4-hour run.

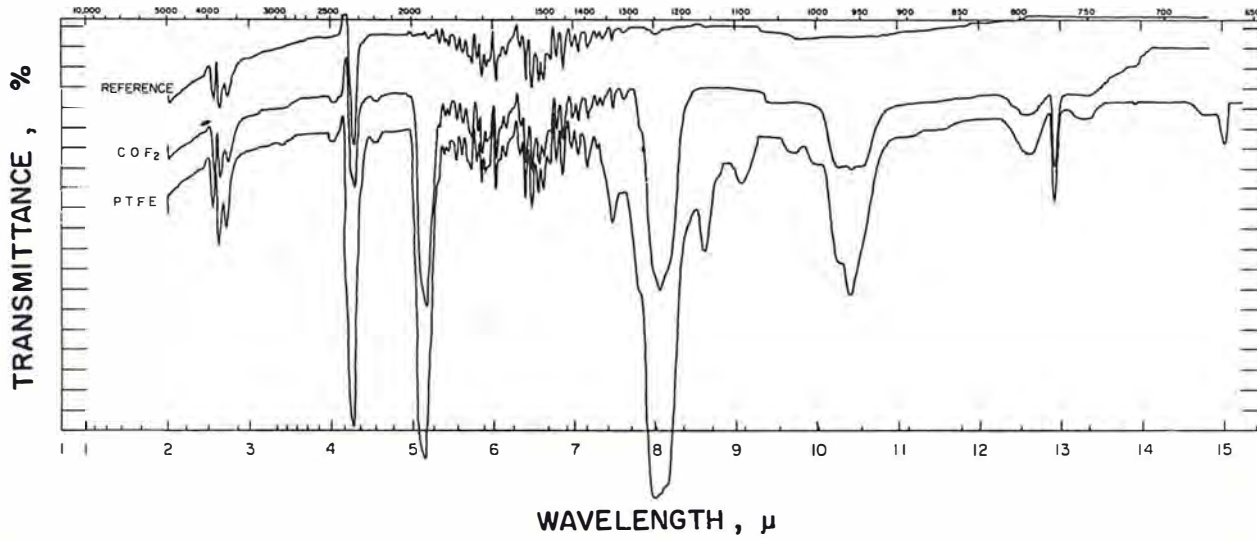


Figure 2. Infrared spectra: pure  $\text{COF}_2$  vs chamber sample of PTFE pyrolysis products.

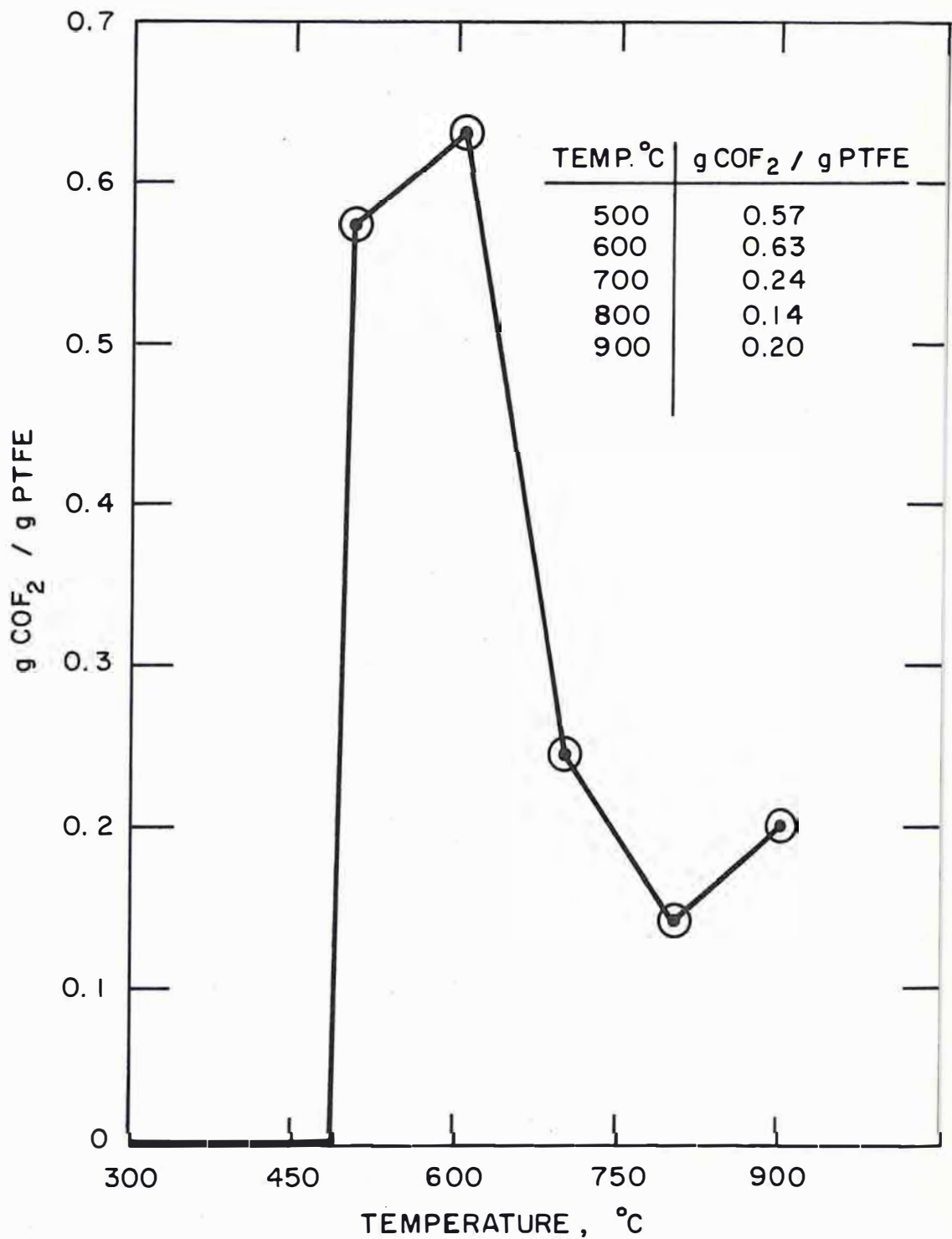


FIGURE 3. RELATION OF COF<sub>2</sub> PRODUCTION TO PYROLYSIS TEMPERATURE OF PTFE BELLACK & SCHOUBOE METHOD.

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Table VI

Lethality of Pyrolyzed PTFE for Rats

Exposure Date	PTFE Pyrolyzed (gm)	Concentration of COF <sub>2</sub> in Chamber (ppm)		Mortality Died/Exposed
		Avg.	Range	
5/13/66	25.5	514	493-525	7/10
5/18/66	23.0	298	258-351	Pathology
6/1/66	22.5	368	286-424	6/18
6/9/66	22.4	317	300-336	0/10
6/16/66	21.5	374	235-420	1/10
6/17/66	23.7	491	438-540	4/10

Exposure Time            1 hour  
 Furnace Temperature    550°C  
 Furnace Air Flow        4 Liter/min.  
 Chamber Dilution Air   5 CFM

The data presented in Table V discloses that an average concentration of 412 ppm COF<sub>2</sub>, killed one-third of the animals. On exposure dates 6/16/66, 6/17/66, and 5/13/66 (Table VI) one, four, and seven rats, respectively, of the ten exposed to PTFE pyrolysis products died at COF<sub>2</sub> concentrations of 374, 491, and 514 ppm. This increase of mortality as COF<sub>2</sub> concentration increased indicates that the toxicity of products of PTFE pyrolyzed in air is due to the presence of COF<sub>2</sub>.

SUMMARY AND CONCLUSIONS

When PTFE was pyrolyzed in an air stream at 490° to 700°C, the mass spectra and infrared spectra of the PTFE pyrolysis gases showed that the principal decomposition product was COF<sub>2</sub>.

PTFE pyrolyzed in the presence of SiO<sub>2</sub> also formed SiF<sub>4</sub>. The SiF<sub>4</sub> was detected and identified in the pyrolysis furnace and in the animal exposure chamber. The reactions involving silica in PTFE pyrolysis led to removal of silica from the pyrolysis unit by substituting stainless steel for glass and placing the ceramic thermocouples outside the furnace.

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A group of mechanisms was formulated to show the oxidation reactions of PTFE pyrolysis gases in air with and without the presence of silica. Results of mass spectra data in accordance with Errede's hypothesis on the depolymerization of PTFE via  $\text{CF}_2$ : elimination showed that the  $\text{CF}_2$ : radical attacked oxygen directly to form  $\text{COF}_2$ , both at  $550^\circ\text{C}$  and at  $700^\circ\text{C}$ . At  $550^\circ\text{C}$ ,  $\text{COF}_2$  formation was the dominant product of pyrolysis in air. Evidence indicated that the  $\text{COF}_2$  at  $700^\circ\text{C}$  could be rearranged to form  $\text{CO}_2$  and  $\text{CF}_4$ . In both cases  $\text{COF}_2$  formation was the preferential reaction.

Results of further experiments showed that the yield of  $\text{COF}_2$  from PTFE at temperatures of  $550^\circ$  to  $600^\circ\text{C}$  and air flow of four liters/minute was as high as 63%.

Experimental exposures of rats also showed  $\text{COF}_2$  to be the most toxic component of the pyrolysis gases. Comparison exposures using pure  $\text{COF}_2$  were made and the toxicity correlated with the toxicity of pyrolyzed PTFE. The toxicity was due to the presence of  $\text{COF}_2$ . Infrared spectra and mass spectra data, from numerous pyrolysis runs and animal exposures, complement each other with respect to the chemical nature and toxicologic properties of the products. The analytical techniques revealed no evidence of saturated or unsaturated fluorocarbons which would enhance the toxicity of  $\text{COF}_2$ .

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### THE TOXICITY OF POLYTETRAFLUOROETHYLENE PYROLYSIS PRODUCTS - INCLUDING CARBONYL FLUORIDE AND A REACTION PRODUCT, SILICON TETRAFLUORIDE

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The development of polymerized tetrafluoroethylene provided a highly thermostable resin which has found acceptance in a large variety of applications despite certain toxic effects that accompanied its use<sup>1,2,3</sup>. Our study of the toxic effects of the pyrolysis products of polytetrafluoroethylene (PTFE) was started in 1962, and this paper presents an evaluation of the acute toxicity

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data collected and describes the pathologic changes found in animals after inhalation exposure.

### MATERIALS AND METHODS

PTFE was pyrolyzed inside an electric furnace at 550 °C in an air stream flowing through the furnace at 4 liters per minute. The fumes entered a 44-cubic foot exposure chamber constructed of aluminum and Plexiglass through a diffusor. The temperature in the chamber during the exposures was in the range of 74° to 82° F. The dynamic flow of the air-fume mixture was maintained throughout the exposure period, and the chamber was continuously ventilated with the fumes.

For the evaluation of toxic effects, Greenacres Controlled Flora rats were selected as the test animal because these rats are free from respiratory diseases and are uniformly healthy. Each test exposure group consisted of 10 rats, 12 weeks old, 5 male and 5 female, which were placed in the airlock to the chamber 10 minutes before the start of the exposure.

A special exposure for evaluation of pathologic changes was conducted using dogs, rabbits, guinea pigs, rats, and mice. Four dogs, six rabbits and in the case of guinea pigs, rats, and mice the group consisted of 20 animals each which were sacrificed over the period of 3 weeks following the exposure.

A one-hour exposure time was chosen for all animals, and a 14-day observation time after the exposures was used to determine the LC<sub>50</sub> values for all samples of PTFE tested. The data were analyzed by the probit method of Miller and Tainter<sup>4</sup> in which the hydrolyzable fluoride analysis of the chamber air is expressed as ppm carbonyl fluoride (COF<sub>2</sub>) plotted against the probit of the mortality at 14 days. As shown in Figure 1 this plot yields a straight line and therefore can be used to provide information about the toxic effect of the material over the whole range of the toxic stress.

### RESULTS

In the plot (Figure 1) the intercept on the ordinate indicates the approximate minimum lethal dose of COF<sub>2</sub> for rats and the point at probit 6.96 represents the approximate LC<sub>100</sub>. Therefore, the slope of the line gives the mortality-dose rate for the toxicant under the particular test conditions. The LC<sub>50</sub>

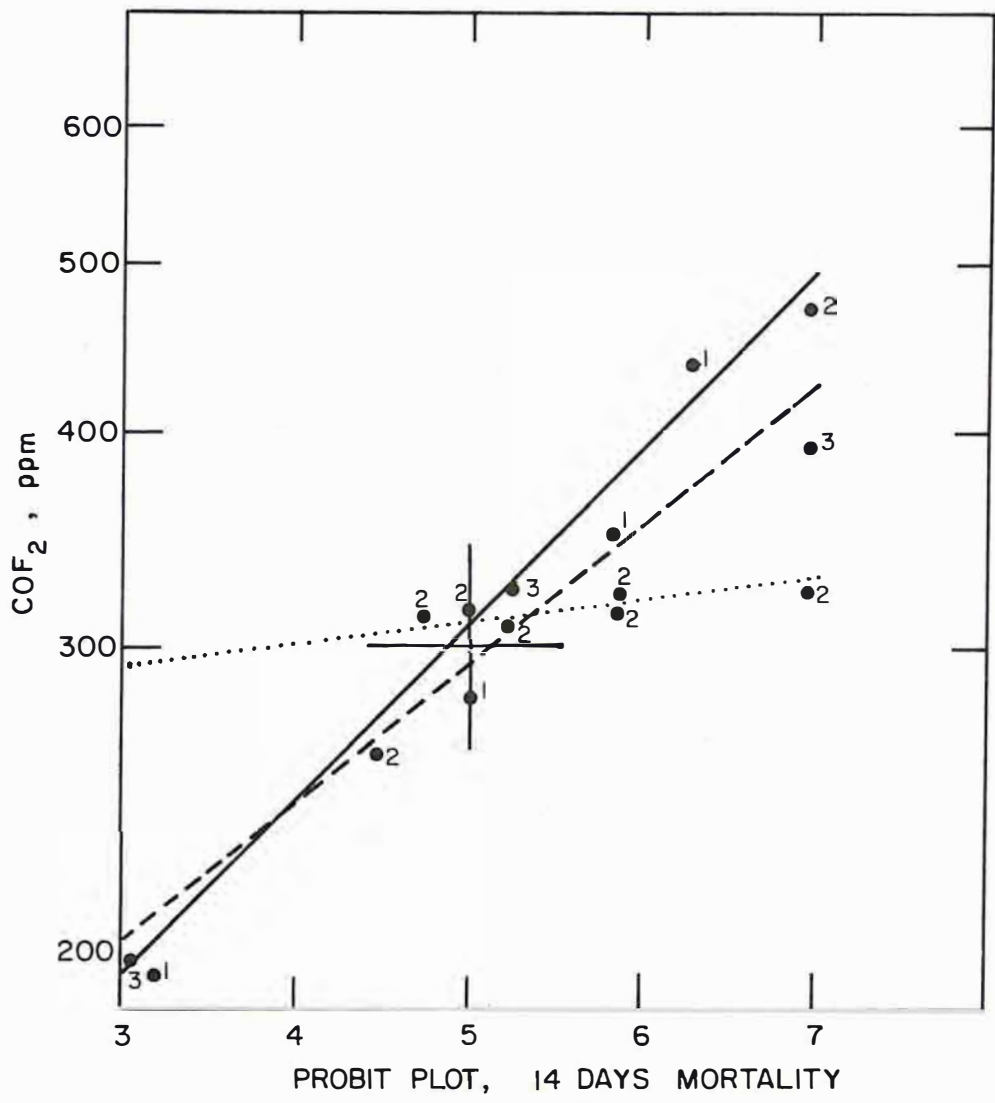


FIGURE 1. LC<sub>50</sub> EXPOSURES FOR PTFE .

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

represented by mortality probit 5 is shown in Figure 1. These data constitute the mortality for rats produced by a single one-hour exposure to both gaseous and particulate pyrolysis products of PTFE.

The identification of carbonyl fluoride as the principal toxic component of the pyrolysis gases led to the work which developed the  $LC_{50}$  for this gas<sup>5</sup>. The effects of age and time exposed at this  $LC_{50}$  were also determined as follows: The  $COF_2$  was metered into the dilution air stream through a Kel-F rotameter, and its concentration was measured in the chamber by the hydrolyzable fluoride method<sup>6</sup>. The results of these studies (Figure 2) indicate that young rats are more susceptible than older rats to the toxic action of  $COF_2$ . However, when the exposure concentration is reduced and the exposure time is increased, a mortality equal to the total mortality is obtained in the same 1-hour exposure at the  $LC_{50}$  concentration as shown in Figure 2. Thus, for carbonyl fluoride there is definitely a concentration-x-time to dosage correlation for a single-dose exposure. This effect does not hold true for the multiple-dose exposure<sup>7</sup>.

The  $LC_{50}$  for  $COF_2$  (Figure 2) is slightly higher than the value obtained for the PTFE pyrolysis products. This is principally due to the fact that with  $COF_2$  exposure, the deaths produced usually occur in 24 hours, whereas the PTFE pyrolysis products usually produce both acute (24-hour) deaths and latent (7-10 day) deaths. For instance the 24-hour  $LC_{50}$  for PTFE using 12-week old rats is 370 ppm  $COF_2$ , which is very good agreement with the 360 ppm shown for the 8-week old rats exposed to  $COF_2$ . These data led to the postulation that the 24-hour mortality caused by the PTFE pyrolysis products is principally due to the  $COF_2$  produced during the breakdown of the resin structure, and the latent deaths are produced by the slow cumulative toxic effect of the inhaled particulate material. There is some support for this hypothesis<sup>7,8</sup>.

As mentioned previously<sup>5</sup>, one of the products whose concentration appeared to correlate with the toxicity of the PTFE pyrolysis products was identified by mass spectrometry and infrared analysis as silicon tetrafluoride ( $SiF_4$ ). When the source of the  $SiF_4$  was eliminated, the pyrolysis products of PTFE became less toxic, an indication that there might be some relationship between the presence of  $SiF_4$  and the toxic properties of the pyrolysis products.

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The LC<sub>50</sub> exposure data for SiF<sub>4</sub> (Figure 3) cannot explain the early results observed on the toxicity of SiF<sub>4</sub> in the presence of the porcelain insulators<sup>8</sup>. To study the effect of SiF<sub>4</sub> on the pyrolysis of the PTFE, the gas was run into the feed end of the pyrolysis furnace while the 1/4 inch PTFE rod was being pyrolyzed. The results of these tests indicated only an additive type of toxic effect, and not a synergistic effect. The data given in Figure 3 indicate that SiF<sub>4</sub> does produce a latent mortality since the LC<sub>50</sub> for the 14-day mortality is about 1/2 the concentration necessary for a similar 24-hour mortality. The effect of silica on the level of COF<sub>2</sub> generated was discussed in the preceding pages, but this effect does not explain the toxicity observed when the pyrolysis takes place in the presence of the insulating material. Additional studies need to be conducted to determine the nature of this observed synergistic toxic effect.

As mentioned previously it has been the policy during these studies to use groups of rats composed of equal numbers of males and females in each exposure. During the period 11-2-65 to 1-10-67 there were 25 exposures which produced more than 10% mortality, but less than 90% mortality. The following calculations confirm that there is no significant difference in mortality based on sex.

$$\frac{\text{Males killed}}{\text{Males exposed}} = \frac{79}{131} = 60\%$$

$$\frac{\text{Females killed}}{\text{Females exposed}} = \frac{72}{130} = 56\%$$

Since the pathologic changes produced in the respiratory tract and in the lives of the exposed animals are similar for all the species they will be discussed for all the species used although the illustrations of specimens presented will all be taken from the rats. In general the photomicrographs were prepared from H&E stained sections and are presented in the following order: normal, exposed to pyrolyzed PTFE, and exposed to carbonyl fluoride.

### PATHOLOGY

In Figures 4 and 5 are shown a 50x and a 150x photomicrograph of the lungs from a control rat which was housed, handled, and fed the same as the exposed animals. The absence of peribronchial lymphatic tissue and the uniform, continuous thin-walled alveolar architecture are evidence of freedom from respiratory disease in these animals.

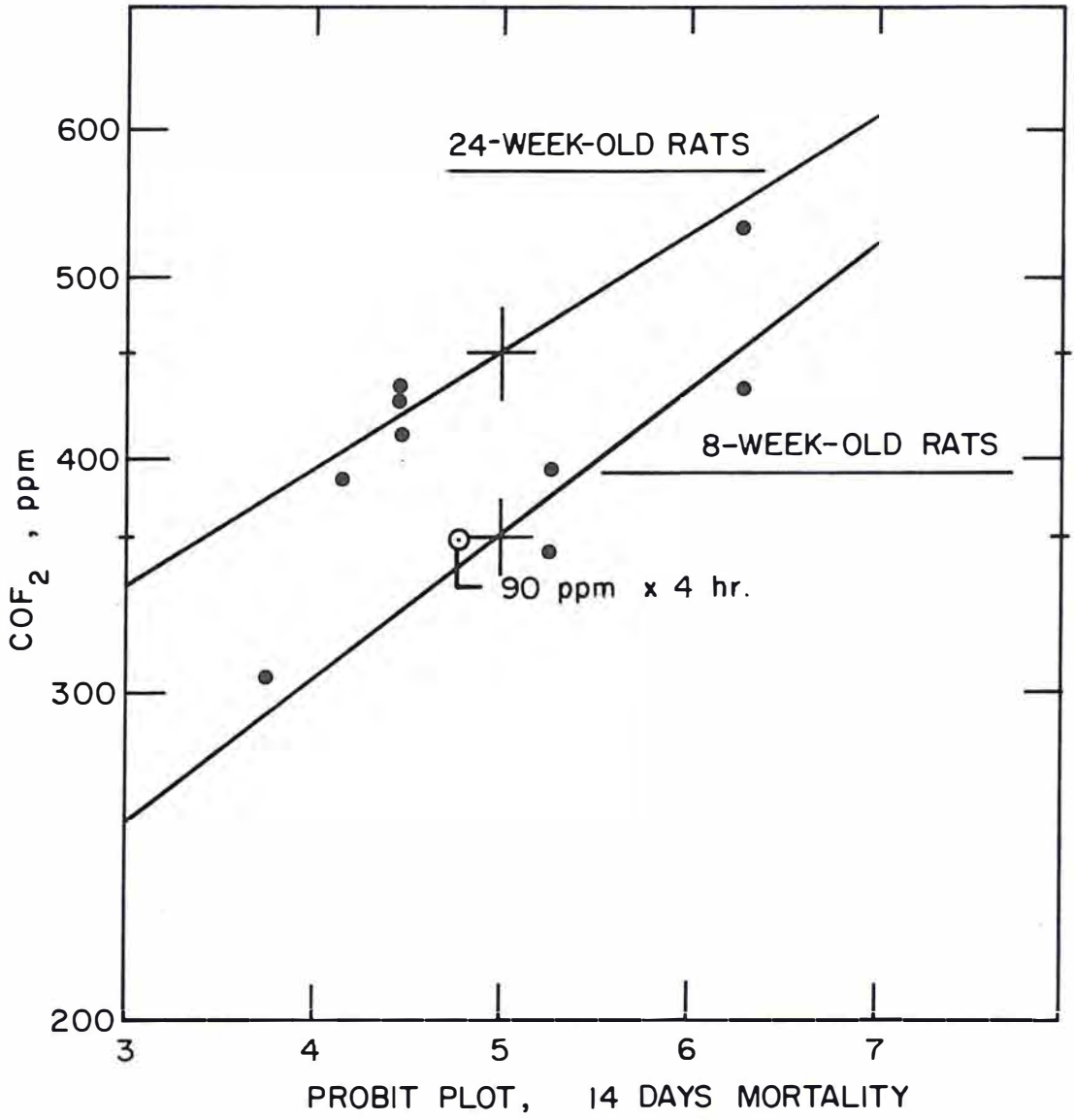


FIGURE 2. LC<sub>50</sub> EXPOSURES TO COF<sub>2</sub>.

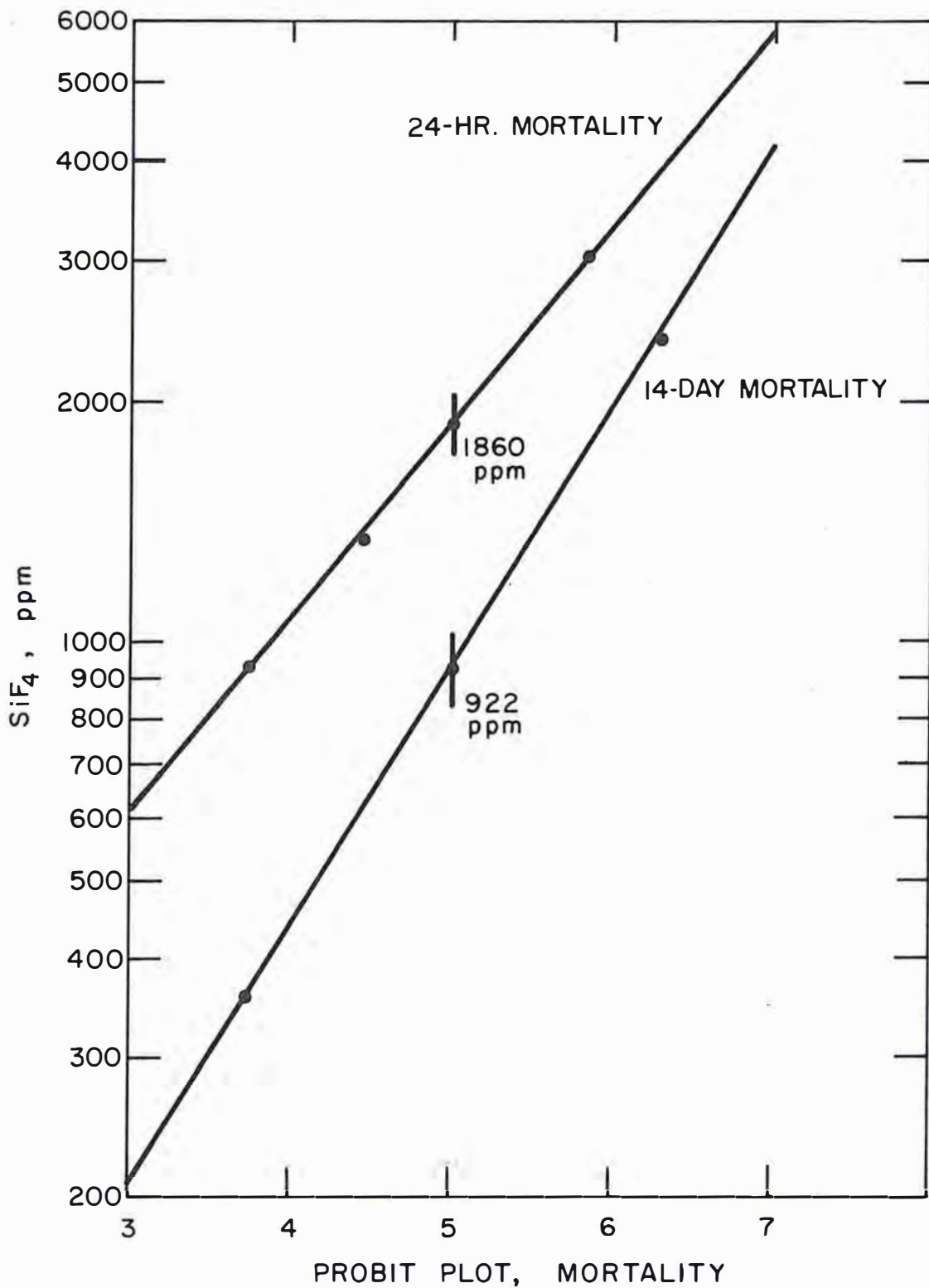


FIGURE 3. LC<sub>50</sub> EXPOSURES TO SiF<sub>4</sub>.

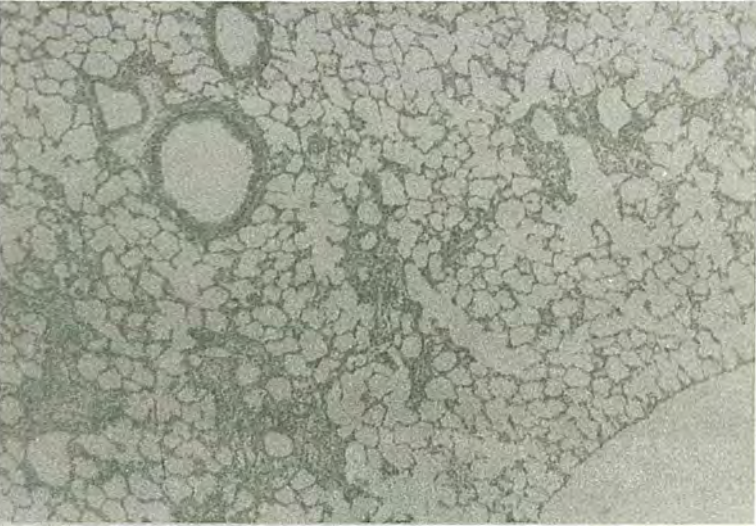


Figure 4. Normal lung 50X.

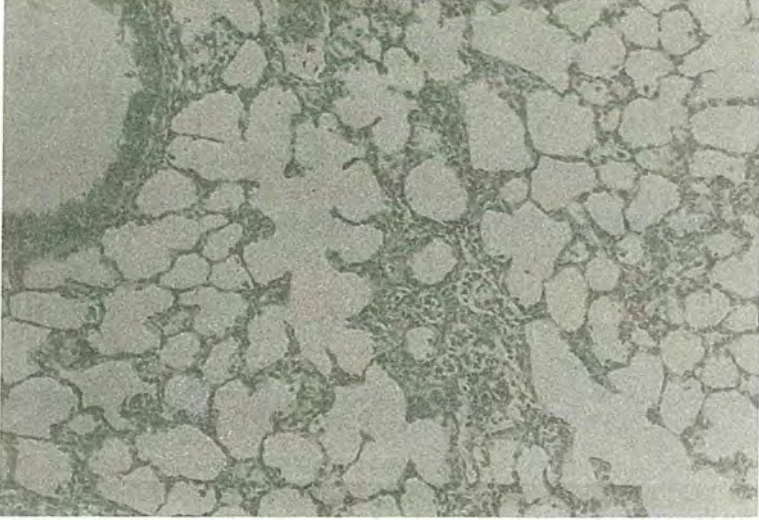


Figure 5. Normal lung 150X.

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

Figure 6 shows the alveolar pigment and exudative reaction found in the lungs after three daily 1-hour exposures to 50 ppm of  $\text{COF}_2$  generated during the pyrolysis of PTFE. A yellow-brown pigment was seen in most of the alveoli, and atrophy of the alveolar lining cells was present. Little or no edema was seen at this time.

Figure 7 illustrates the accumulation of particulate material in the alveoli located near the pleura of the lung and the mononuclear and macrophage reaction around this material after the fifth daily 1-hour exposure to less than 30 ppm of  $\text{COF}_2$  generated from PTFE pyrolysis.

In Figure 8 the organization of the reaction to this type of deep lung irritation is illustrated. The macrophage response around the pigment with the periarteriolar inflammatory cells and the focal emphysema, which began to develop three days after the fifth exposure, would classify this material as a deep lung irritant.

Fatty liver degeneration was observed five days after the fifth exposure as shown in Figure 9. When frozen sections were stained for fat, the vacuoles in the cytoplasm of the cells were shown to be filled with fat. Also present at this time in the liver were enlarged nuclei as shown in Figure 10. For comparison Figure 11 shows a photomicrograph of a normal liver at the same magnification.

The above description of the pathologic changes following exposure to PTFE pyrolysis products was taken from the experiment to be described under the heading "Biochemical Changes Associated with Toxic Exposures to Polytetrafluoroethylene Pyrolysis Products" of this report. Although the low dosage eliminated the acute edema reaction, it did not change the other manifestations found with these toxic exposures.

As mentioned earlier the  $\text{COF}_2$  exposures caused acute reactions leading to death in 24 to 48 hours with very few latent deaths. The pathologic changes which are described here for  $\text{COF}_2$  exposures can also be found in the PTFE pyrolysis exposures when the  $\text{COF}_2$  concentration in the pyrolysis products approaches 310 ppm.

Figures 12 and 13 are photomicrographs of the lungs of a rat sacrificed 24 hours after a 1-hour exposure to 310 ppm of  $\text{COF}_2$ . The focal hemorrhage and

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

pulmonary edema shown are typical of the acute toxic effect seen following exposure to this gas in all species used. The guinea pigs appeared to be slightly more susceptible to this type of toxic response, and this effect could be the result of the presence of pulmonary disease in the guinea pigs used.

The 48-hour post exposure lesions seen in Figures 14 and 15 show the rapid organization and the clearing of the edema from the lung. This rapid clearing action is not seen in exposures to PTFE pyrolysis products (see Figures 12 and 13). The authors interpret this as being due to the presence of particulate material in the pyrolysis products. In the rapid clearing of the edematous response due to  $\text{COF}_2$  exposure the alveolar damage done does not resolve as readily. In general extravasation of red cells from damaged capillaries proceeds for 3 to 4 days, but usually stops before 7 days. Some residual focal emphysema is left as the final irreversible lesion with only a little mild interstitial fibrosis as seen in the 7-days lesions in Figures 16 and 17.

The pathology of silicon tetrafluoride is not appreciably different from that of carbonyl fluoride and therefore will not be discussed further here.

### SUMMARY

The pyrolysis products from PTFE are toxic; the principal toxic effects are due to the hydrolyzable fluoride produced when  $\text{COF}_2$  and other hydrolyzable products are absorbed into the tissue. The lesions associated with the particulate material observed in the lungs of exposed animals prove that the particulate is irritating for at least 7 to 10 days following inhalation. Although the hemorrhage and edema from a single acute insult to the lung tissue do not produce extensive permanent damage to the lung tissue, the residual focal emphysema and interstitial fibrosis remaining after the acute lesions have cleared constitute the irreversible portion of the injury.

This work extends and confirms the earlier work of Treon et al.<sup>9</sup> and Zapp<sup>10</sup>.

Based on the results of this work the PTFE products tested would be classified "moderately toxic" according to the Hine and Jacobsen toxicity scale<sup>11</sup>. This classification arises from both the calculation of the hydrolyzable fluoride as  $\text{COF}_2$  and the establishment of 20 to 25 grams of PTFE as the dose necessary to kill half the animals exposed for 1-hour. It is pertinent to point out here

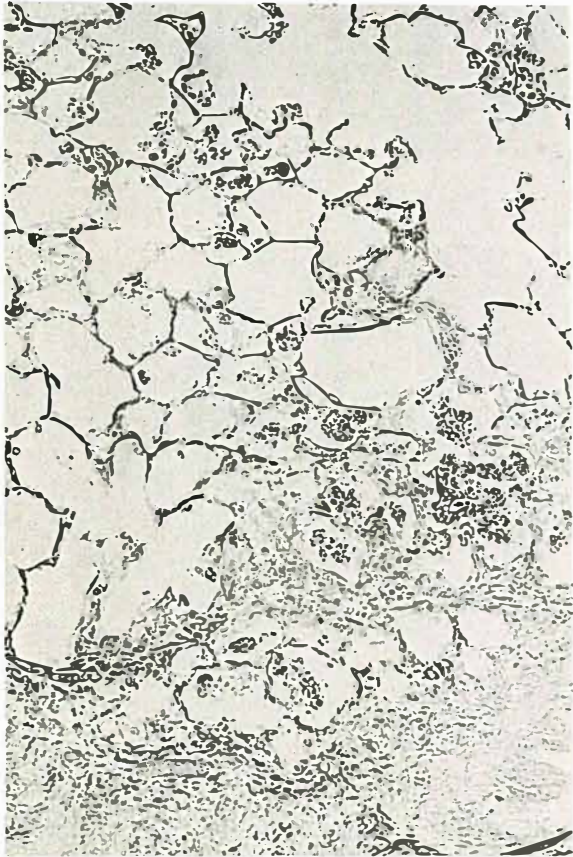


Figure 6. Diffuse pigment after three 1-hour exposures to PTFE pyrolysis products with cumulative doses of 120 ppm-hours as  $\text{COF}_2$  and sacrifice after 3rd exposure. Pigment is present in most air sacs. Some atrophy of the alveolar lining cells is observed. No edema is seen.



Figure 7. Sub-pleural pigment after five 1-hour exposures to PTFE pyrolysis products with cumulative dose of 185 ppm hours as  $\text{COF}_2$  and sacrifice after 5th exposure. Note focal accumulation of pigment around the bronchiole; adjacent to this is an area of mononuclear accumulation and condensation of parenchyma.

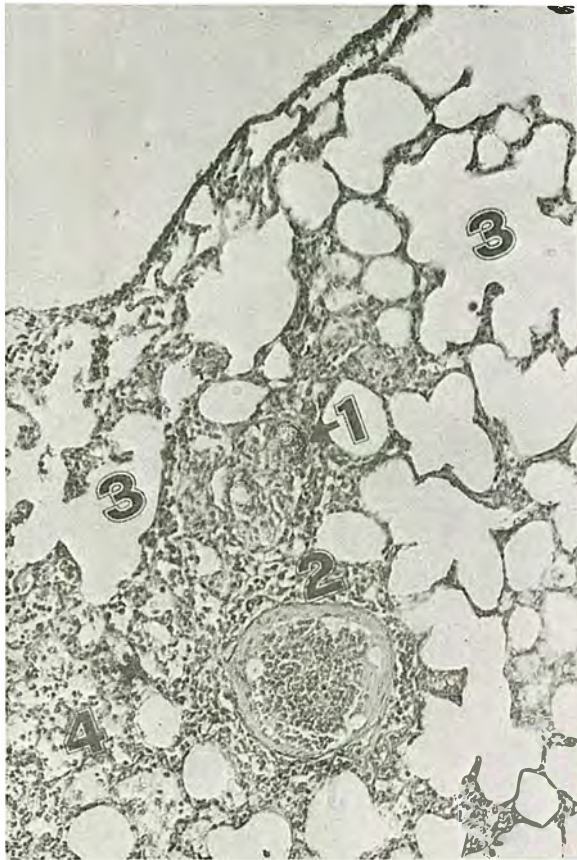


Figure 8. Lesions at three days post-exposure after five 1-hour exposures to PTFE pyrolysis products with cumulative dose of 185 ppm hours as COF<sub>2</sub>. The lesions of note are (1) sub-pleural pigment, (2) peri-arteriolar inflammatory cells, (3) focal emphysema, and (4) macrophage response about pigment.

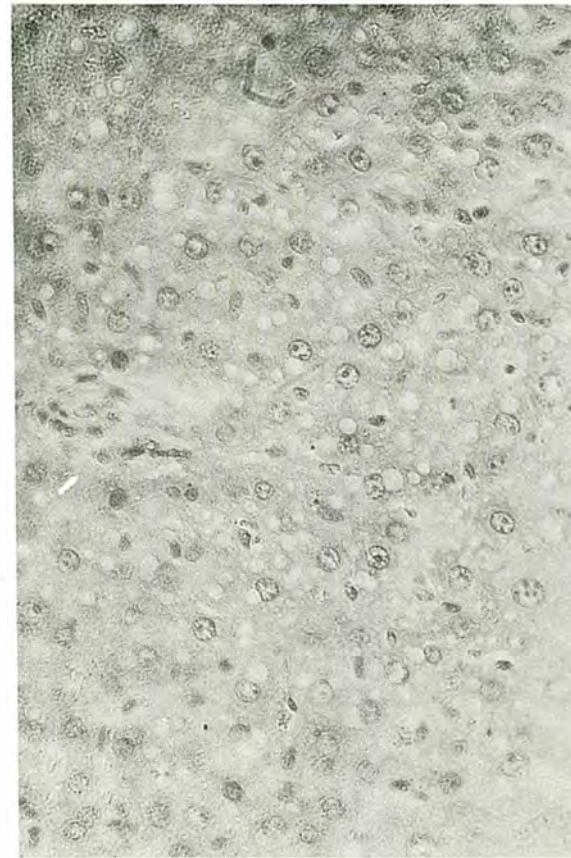


Figure 9. Fatty liver at five days post-exposure after five 1-hour exposures to PTFE pyrolysis products with cumulative dose of 185 ppm-hours as COF<sub>2</sub>. Note extensive vacuolization of cytoplasm. These areas were positive for fat with frozen sections.

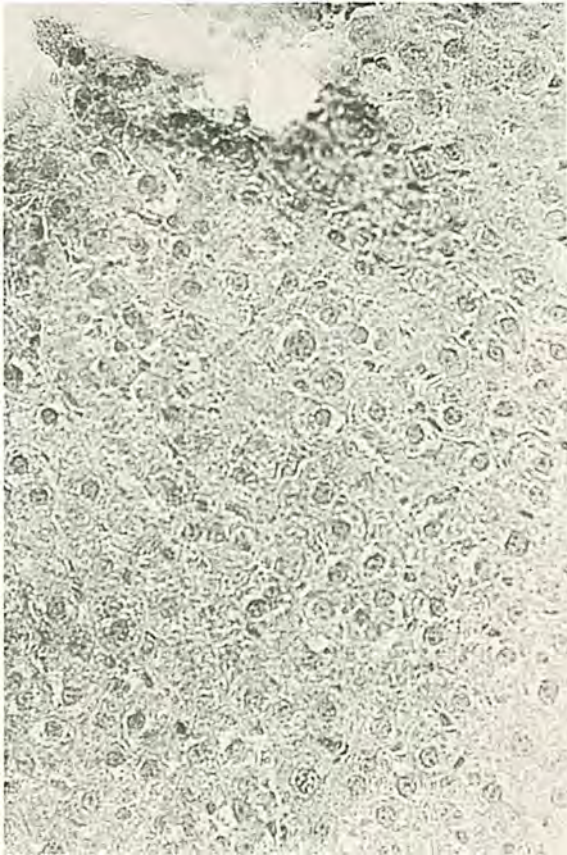


Figure 10. Hepatic nuclei enlargement at five days post-exposure with some conditions as Figure 9. Note the absolute increased mass of the nucleus as compared to the cytoplasmic border in several of these cells.

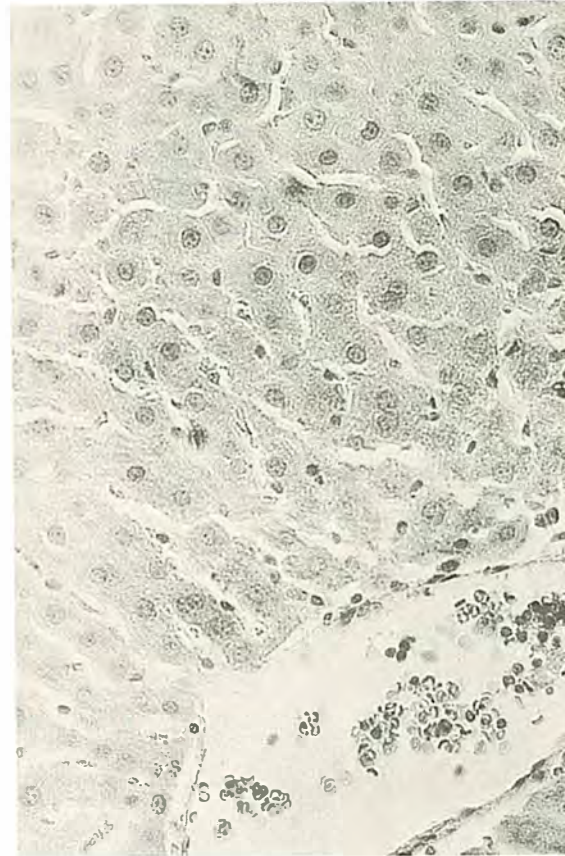


Figure 11. Normal liver. Observe relative size of nucleus as compared to cytoplasmic border; also observe absence of vacuoles.

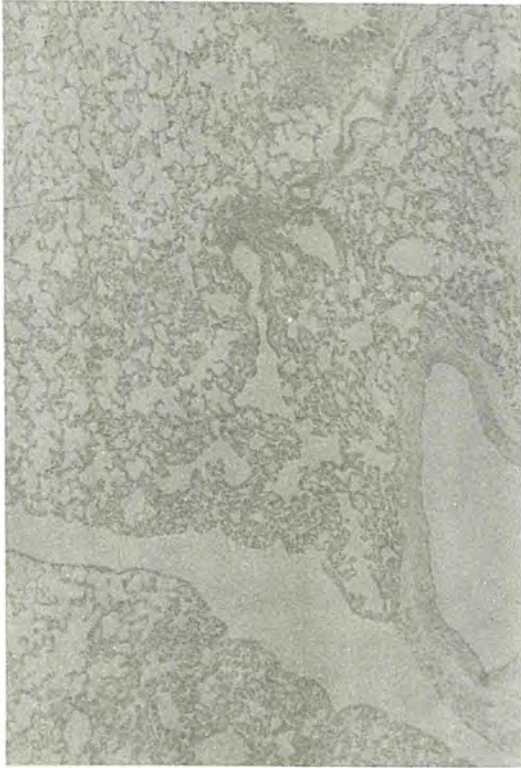


Figure 12. Focal hemorrhage and peribronchial and perivascular lymphatic distention at 24 hours after 1-hour exposure to 310 ppm  $\text{COF}_2$ . 50X.



Figure 13. Same specimen as Figure 12. Deep lung injury showing focal hemorrhage in the area of the alveolar duct. 150X.

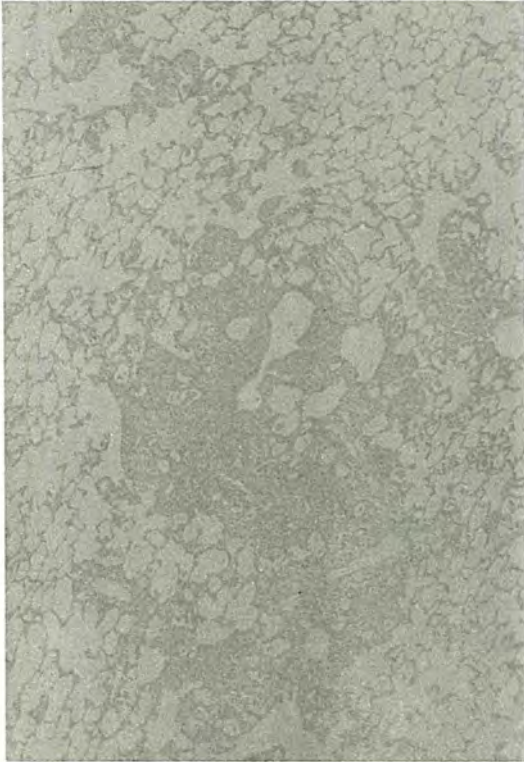


Figure 14. Organization of the peribronchial chemical pneumonitis and clearing of the edema from the alveolar area at 48 hours after 1-hour exposure to 310 ppm  $\text{COF}_2$ .

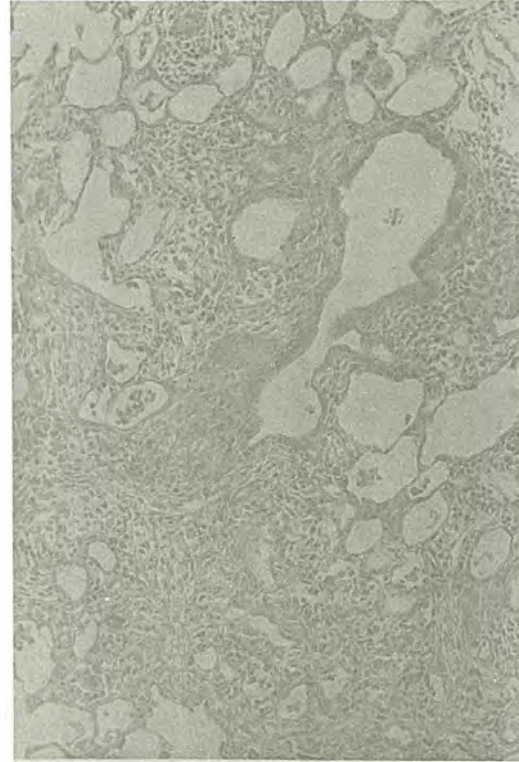


Figure 15. Same specimen as Figure 14. Peribronchial macrophage infiltration and fibrinous coagulation pneumonitis. 150X.

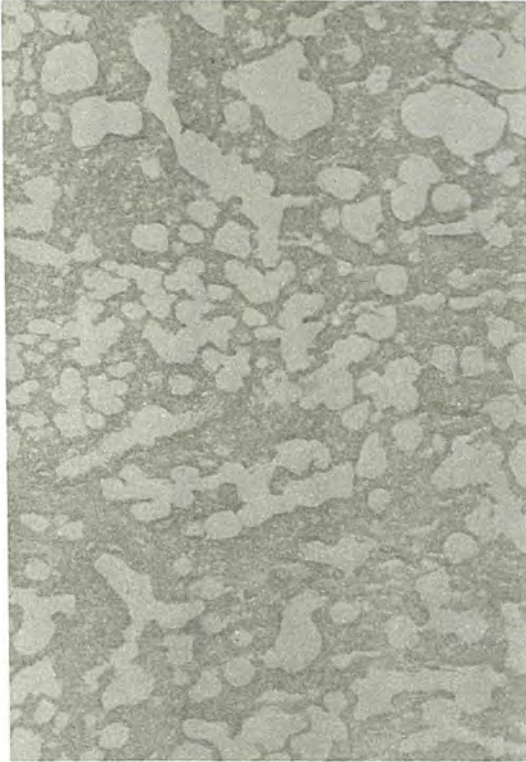


Figure 16. Alveolar wall thickening and focal emphysema, residual from the coagulation pneumonitis, 7 days after 1-hour exposure to 310 ppm COF<sub>2</sub>. 50X.

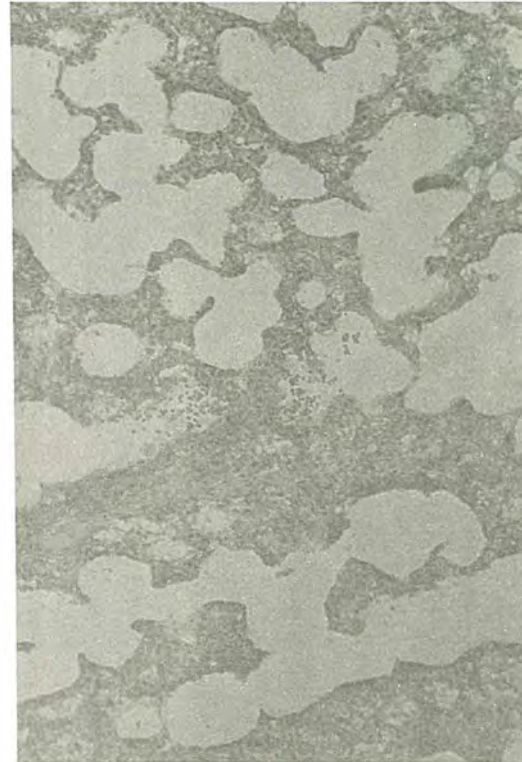


Figure 17. Same specimen as Figure 16. Rupture of capillary in the alveolar wall with extravasation of blood into alveoli. 150X.

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

that polytetrafluoroethylene is a most unusual plastic material since it has been repeatedly demonstrated that it does not decompose at an appreciable rate below 450°C (842 °F).

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## BIOCHEMICAL CHANGES ASSOCIATED WITH TOXIC EXPOSURES TO POLYTETRAFLUOROETHYLENE PYROLYSIS PRODUCTS

Lester D. Scheel, Ph.D. , Lofton McMillan,  
and Frederick C. Phipps

Polymers formed from tetrafluoroethylene are straight-chain saturated compounds of high molecular weight ( $10^6$ ) that contain only carbon and fluorine. Toxicologic studies of this material were undertaken to evaluate the nature of the products formed during its pyrolysis and to determine the toxic action following inhalation of these products. The major pyrolysis reaction from the rapid destruction of the plastic material at temperatures just above  $500^{\circ}\text{C}$  ( $932^{\circ}\text{F}$ ) produced  $\text{COF}_2$  (carbonyl fluoride) as the principal toxic product<sup>1,2</sup>. All other products identified were saturated fluorocarbon fragments or carbon dioxide.

The acute toxic actions in rats of both  $\text{COF}_2$  and the hydrolyzable fluoride ( $\text{F}^-$ ) from pyrolyzed polytetrafluoroethylene (PTFE) are nearly identical; therefore, the following experiment based on the  $\text{F}^-$  type of toxic action was designed to identify the mechanism by which the pyrolyzed products affect the animal body. When  $\text{COF}_2$  comes in contact with water, it rapidly hydrolyzes to form  $\text{CO}_2$ , and 2 moles of hydrogen fluoride (HF). An experiment was planned to demonstrate that this is what produces the toxic action in exposed animals.

As a result of the work of Machle et al.<sup>3,4,5</sup> and Stokinger<sup>6</sup>, the inhalation toxicity of HF is known. The acute, single, 1-hour exposure  $\text{LC}_{50}$  for HF given in the data of Machle is 1.5 to 2.0 mg/liter (1835 to 2446 ppm). The cumulative toxicity from repeated daily exposures indicated that HF became

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

lethal for some of the animals above 30 ppm. Therefore, if the PTFE pyrolysis products are toxic because of fluoride generation, then it should be possible to show increasing fluoride excretion after repeated sublethal exposures<sup>3,4</sup>, inhibition of succinic dehydrogenase in the kidney<sup>7,8</sup>, deaths due to cumulative dosage<sup>6</sup>, and liver and/or kidney injury in intoxicated animals<sup>5</sup>.

### METHODS AND RESULTS

In the experiment, 20 male and 20 female rats of the Greenacres Controlled Flora stock were exposed to PTFE pyrolysis products containing hydrolyzable fluoride equal to 50 ppm of  $\text{COF}_2$  for 1 hour each day until maximum toxicity compatible with life was obtained. The data in Figure 1 indicate the cumulative nature of the exposures, which caused nine deaths during and shortly after the five 1-hour exposures. These data show that 158 ppm-hours of inhaled gases plus 18 mg of inhaled particles produced a 22% mortality. This total dose is less than 1/2 the  $\text{LC}_{50}$  from single acute exposures. The deaths, which occurred before January 20, the last day of exposure, took place in the exposure chamber. The signs of toxicity preceding death indicated extreme malaise and weakness in the rats.

After the first exposure, 10 exposed and 10 control rats were placed in metabolism cages, and 24-hour urine specimens were collected for fluoride determination. This procedure was repeated on the dates shown in Figure 2. Even 18 days after the last exposure, January 20, the amount of fluoride in the urine of exposed rats was four times that of the controls.

In Figure 3 the 30% weight loss by the animals after exposure to PTFE pyrolysis products is strong evidence that metabolism is inhibited. The significant increase in the urinary fluoride coincident with the weight loss period and the weight recovery period coincident with the elimination of the fluoride are evidence for the cause and effect relationship between fluoride toxicity and the body metabolism.

Before, during, and after exposure, total white cell counts and differential white cell counts were done to determine if only fluoride irritation was present in the animals or if infection was also present, especially during the recovery phase. The data in Figure 4 on the lymphocyte-neutrophil changes, in the presence of a stable total white cell count, are strong evidence that only chemical irritation was present in the animal body during the entire

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

time of this experiment. The proof for this statement is the prompt recovery of an approximately normal lymphocyte-neutrophil ratio within 7 days (January 28) after the last exposure (January 20).

Botelli and Stern<sup>7</sup>, observed fluoride inhibition of succinic dehydrogenase in 1910; and Slater and Bonner<sup>8</sup>, in a detailed study of the kinetics of this system, showed the specific nature of fluoride inhibition on this enzyme system. Therefore, if the toxic action of the PTFE pyrolysis products is caused by the fluoride ion in the body fluids, it should be possible to show the inhibition of succinic dehydrogenase in the rat kidney. The method of Shelton and Rice<sup>9</sup>, was used to measure this enzyme activity in tissue hemogenates. In Figure 5 the succinic dehydrogenase activity in the rat lung and kidney tissues is shown. The data for January 16 were obtained on animals sacrificed 4 hours after the first exposure to PTFE pyrolysis products. It is obvious from these data that the lung, which is the target organ for exposure, reacted by the fifth exposure (January 20) to produce increased amounts of enzyme to compensate for the fluoride inhibition effect. In the kidney, however, inhibition of the succinic dehydrogenase activity increased with increasing exposures. After the exposures were terminated, normal activity in both the lung and kidney tissues was attained by the 18th day after the last exposure (February 7).

The positive correlation of the change in succinic dehydrogenase activity *in vivo* with the degree of exposure to PTFE pyrolysis products is evidence for a cause and effect relationship in this enzyme system. Data confirming such a relationship are presented in Figure 6. The excellent correlation between the concentration of urinary fluoride and the degree of succinic dehydrogenase inhibition in the kidney tissue represents proof of the cause and effect relationship between the concentration of urinary fluoride and the inhibition of the enzyme.

Urine specimens which were collected from the 10 exposed and 10 control rats after the first exposure (January 16), the fifth exposure (January 20), the second post-exposure day (January 23), the seventh post-exposure day (January 26), and the eighteenth post-exposure day (February 7) were checked for glucose, protein, ketones, occult blood, and specific gravity by Labstix methods and by microscopic examination. After the first exposure (January 16), protein was detected in the urine of the exposed rats, but the other factors were negative. After the fifth exposure (January 20) the exposed rats showed positive glucose, protein, and ketones. On the second

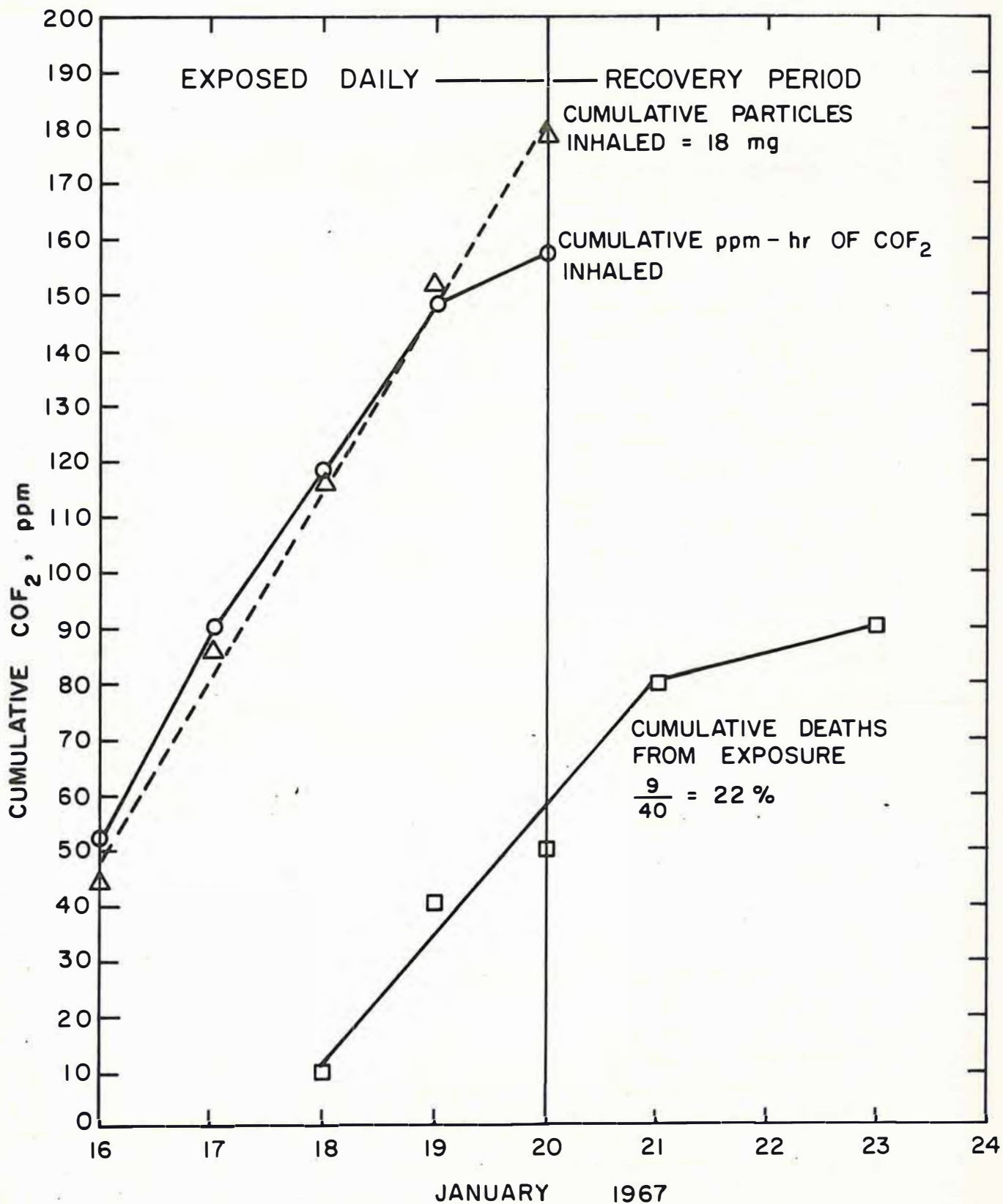


FIGURE 1. CUMULATIVE DATA FOR 40 RATS EXPOSED TO PTFE PYROLYSIS PRODUCTS DURING 5 DAILY ONE-HOUR EXPOSURES.

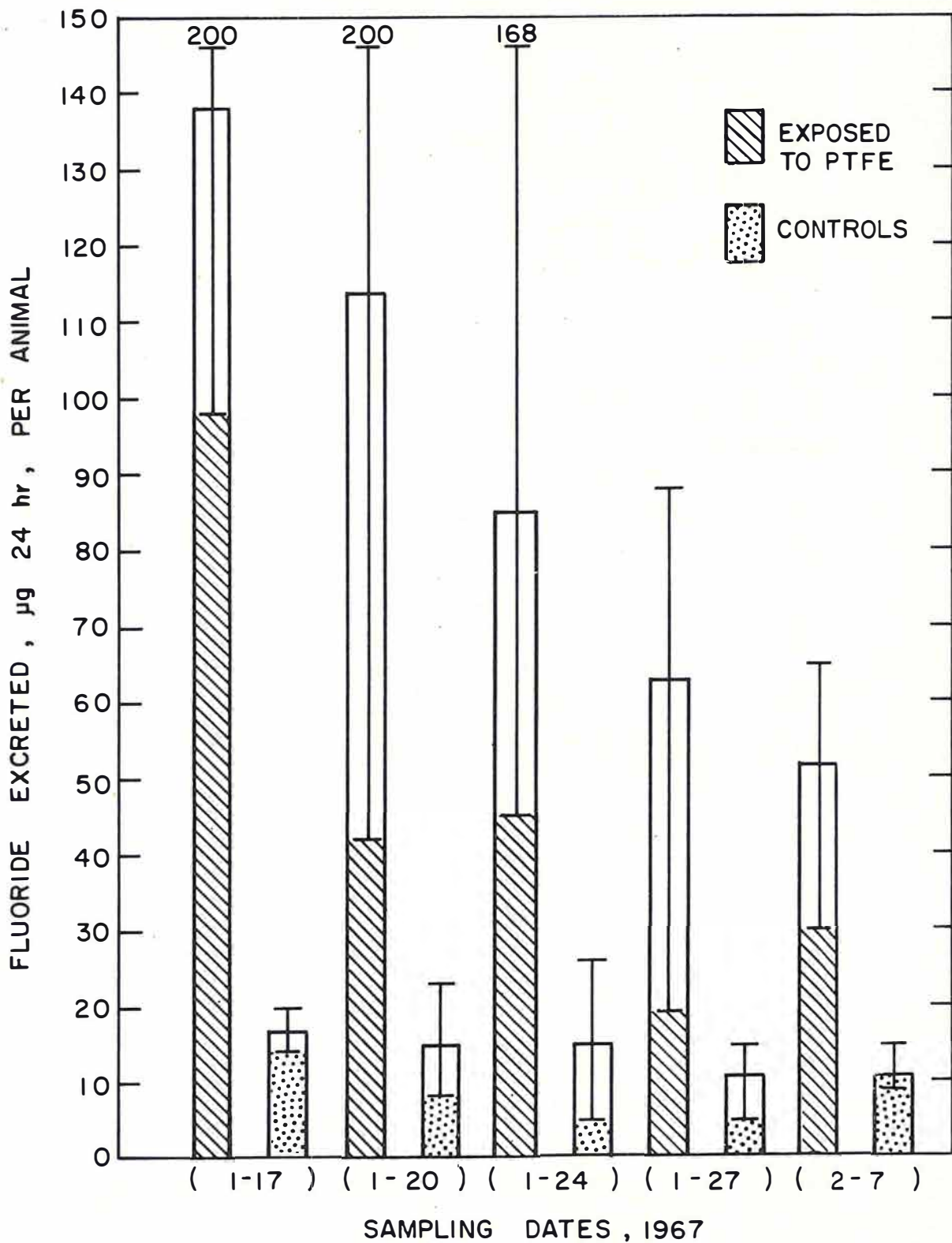


FIGURE 2. TOTAL FLUORIDE EXCRETION FOR THE 24-HOUR COLLECTION FROM 10 RATS EXPOSED TO PTFE PYROLYSIS PRODUCTS AND FROM 10 RATS NOT EXPOSED.

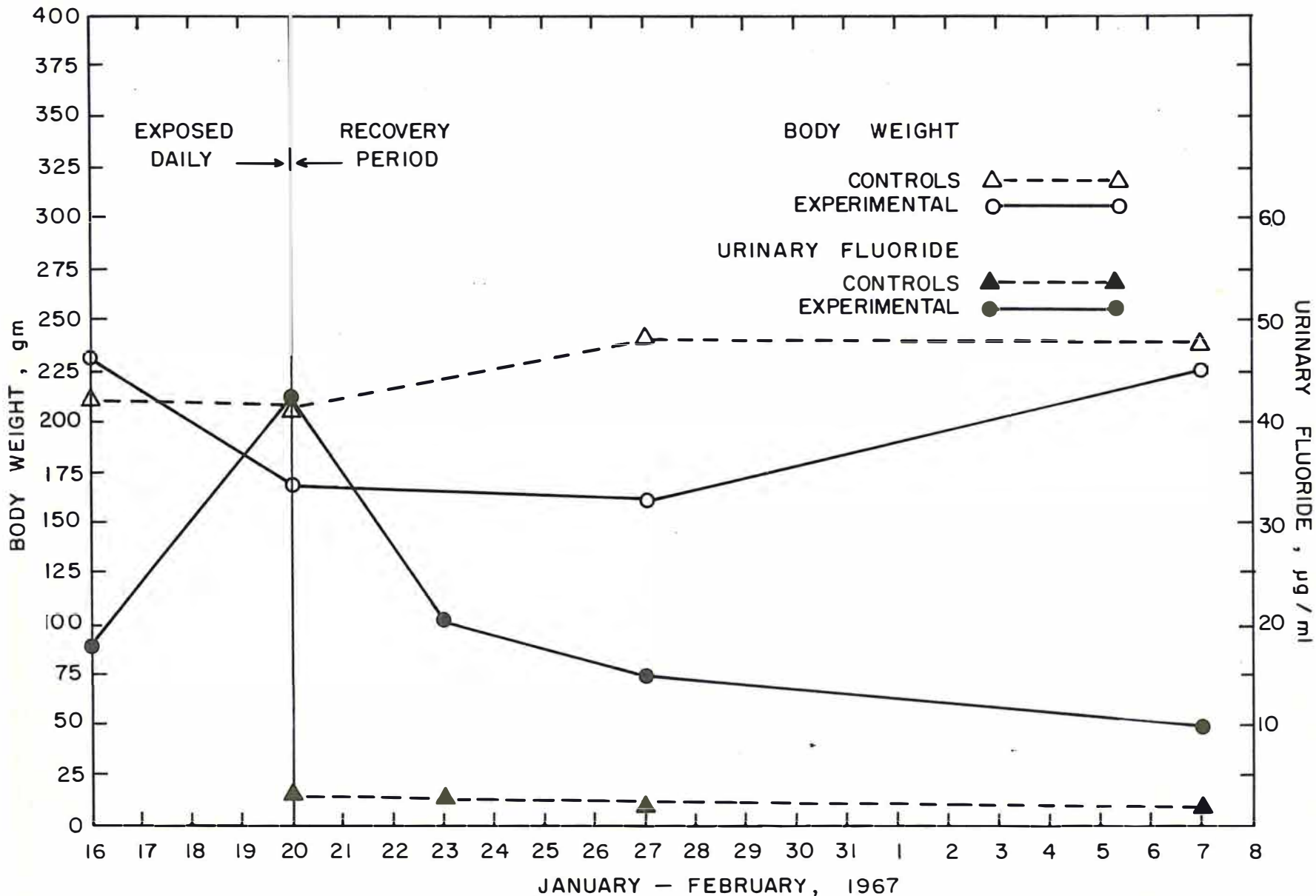


FIGURE 3. WEIGHT LOSS IN RATS EXPOSED TO PTFE PYROLYSIS PRODUCTS SHOWING CORRELATION WITH THE LENGTH OF EXPOSURE AND THE INCREASE IN CONCENTRATION OF URINARY FLUORIDE.

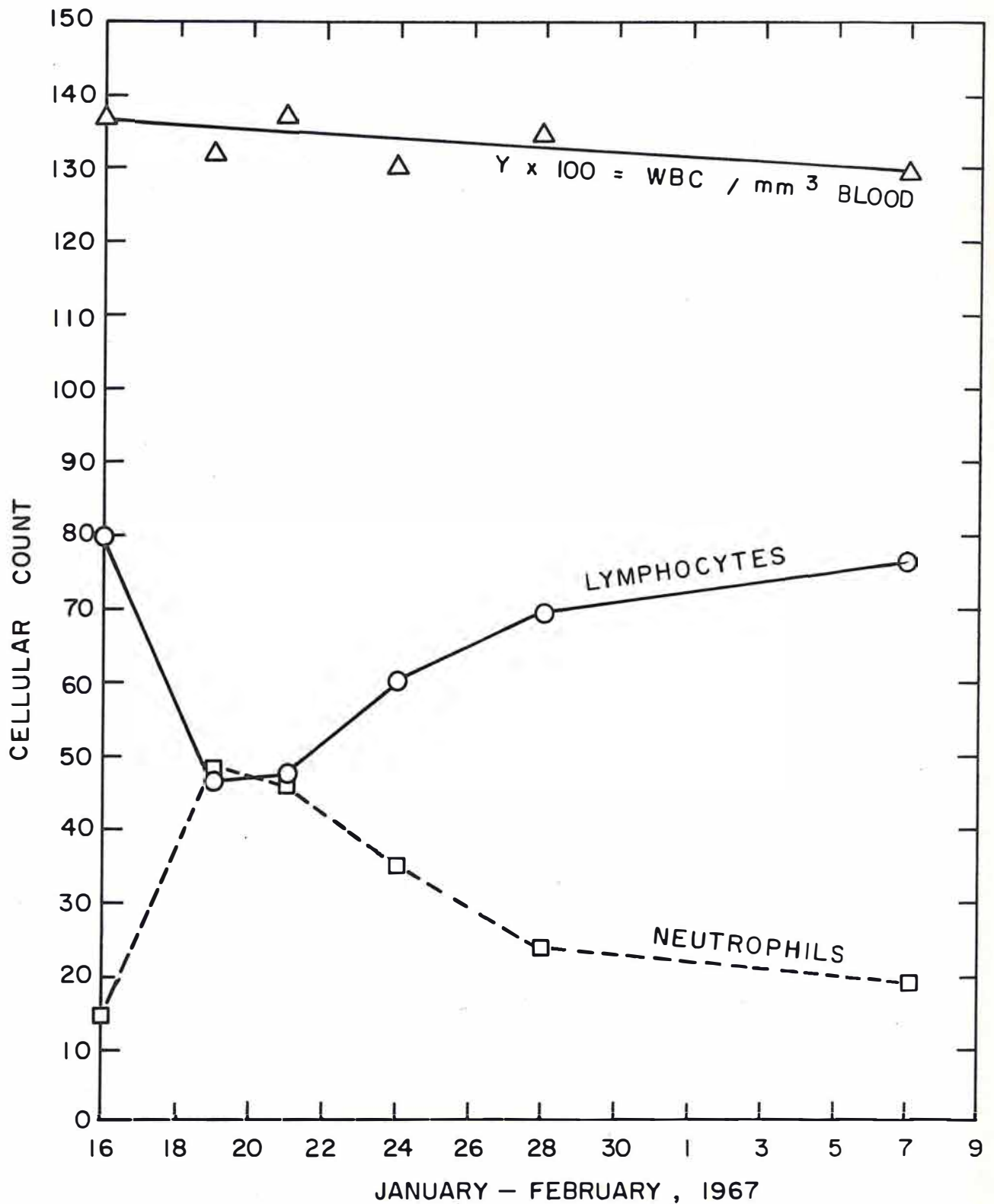


FIGURE 4. THE INCREASE IN THE NEUTROPHILIC GRANULOCYTES WITH AN APPARENT DECREASE IN THE NUMBER OF LYMPHOCYTES WITHOUT APPRECIABLE CHANGE IN THE TOTAL WHITE CELL POPULATION INDICATED AN ACUTE, NONINFECTIOUS INFLAMMATORY RESPONSE.

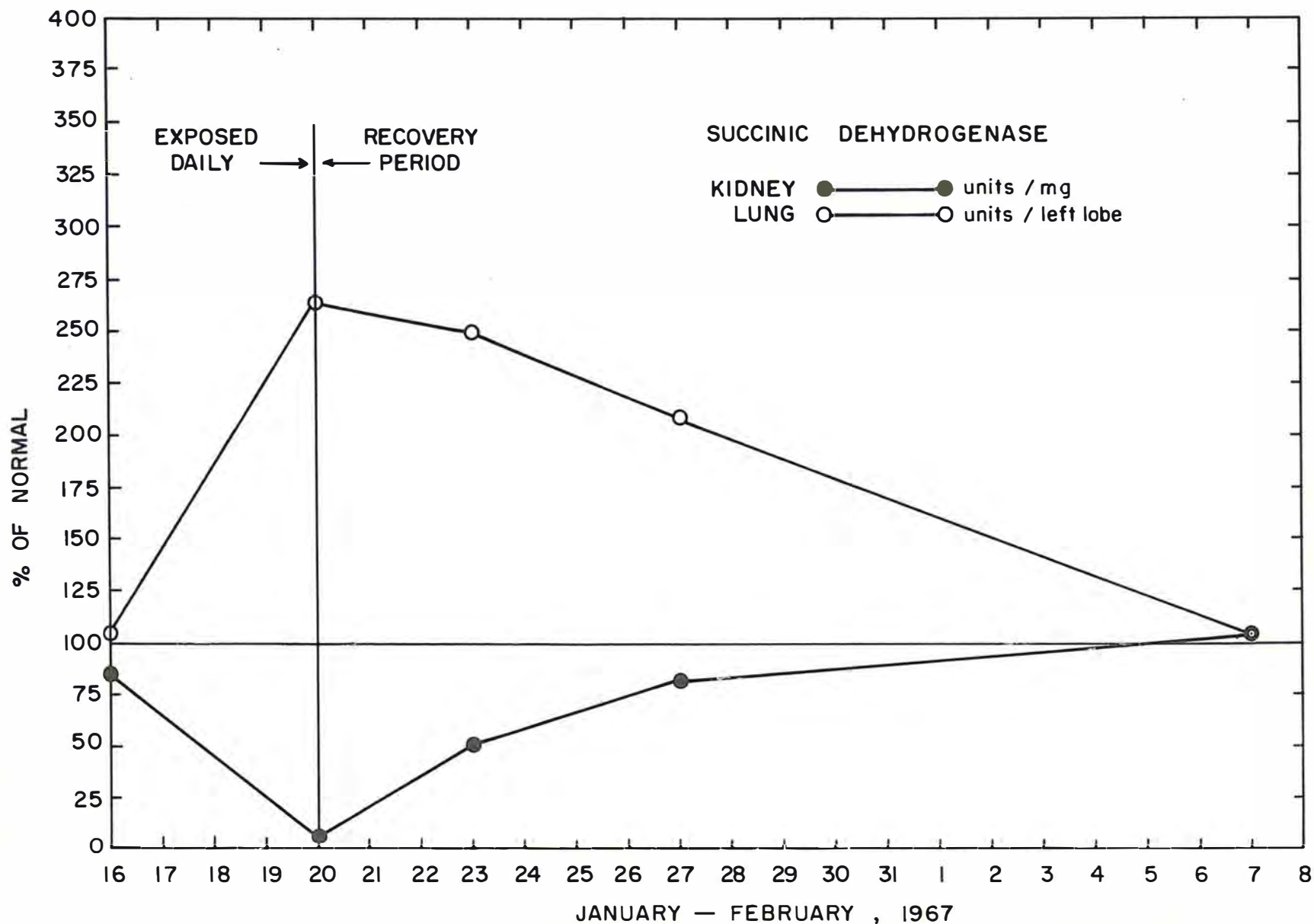


FIGURE 5 . CHANGES IN SUCCINIC DEHYDROGENASE ACTIVITY DURING THE PERIOD THE RATS WERE EXPOSED TO PTFE PYROLYSIS PRODUCTS AND DURING THE POST-EXPOSURE RECOVERY PERIOD .

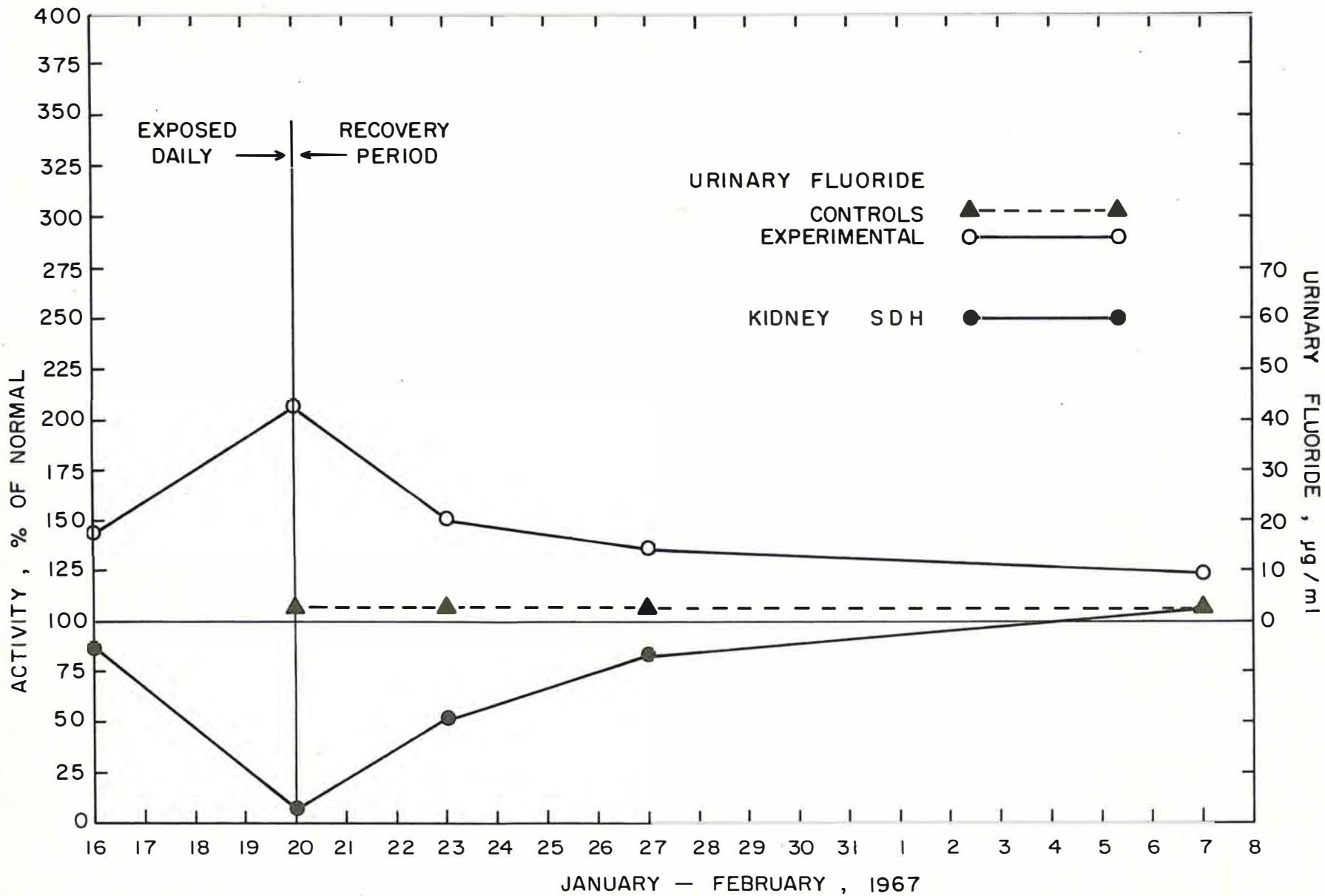


FIGURE 6. THE INVERSE CORRELATION OF URINARY FLUORIDE CONCENTRATION WITH THE SUCCINIC DEHYDROGENASE ACTIVITY OF THE KIDNEY.

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

post-exposure day (January 23) the glucose was negative and protein, ketones, and occult blood were positive. On the seventh post-exposure day (January 26) the glucose, protein, and occult blood were negative and only the ketones were positive. The only abnormal finding in the urine on the 18th post-exposure day (February 7) was a high fluoride excretion. These data indicate kidney injury that is reversible. Nuclear changes in the liver cells were discussed under the heading "The Toxicity of Polytetrafluoroethylene Pyrolysis Products - Including Carbonyl Fluoride and a Reaction Product, Silicon Tetrafluoride."

### DISCUSSION

These data and the pathology described previously, as well as the fluoride excretion data (Figure 6), indicate the reversible nature of this severe fluoride injury. The total exposure dose in these animals was less than 1/2 the acute lethal dose, indicating that the cumulative effect from repeated exposures is much more damaging to the metabolic system than a higher concentration administered in a single exposure. This evidence supports the works of Machle and Scott<sup>5</sup> and Stokinger<sup>6</sup>, which show that the cumulative effects of daily exposures to hydrogen fluoride are much more toxic to exposed animals than is a single exposure of an equal concentration-x-time value.

### SUMMARY

The cumulative sublethal daily exposures to PTFE pyrolysis products used in this experiment increased the fluoride in the urine from 3 µg/ml to 42 µg/ml in 5 days. The presence of this fluoride in the body fluids of exposed rats caused an increase in the succinic dehydrogenase activity in the lung tissue (severe pathologic change), but inhibited this enzyme to less than 5% of normal activity in the kidney tissue (no pathologic change). The liver tissue of exposed rats showed enlarged nuclei and fatty infiltration of the cells. Five sublethal daily exposures to PTFE pyrolysis products of 52, 43, 29, 25, and 9 ppm-hours as COF<sub>2</sub> produced marked body weight loss and changes in the blood leucocyte composition (but not in the total count), caused protein, glucose, ketones and occult blood to appear in the urine, and caused 22% mortality in the exposed rats.

Our data show that the COF<sub>2</sub> generated during the pyrolysis of PTFE hydrolyzed in the body fluids and produced fluoride toxicity in the exposed rats.

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Although severe injury due to fluoride poisoning was inflicted on the rats, the metabolic inhibition observed was completely reversible, and with the exception of a small amount of emphysematous changes, the pathologic changes in the lungs and liver were reversible within 18 days following exposure.

Based on the evidence presented, we believe that the daily inhalation of the pyrolysis products of PTFE produces a toxic syndrome compatible with the description of fluoride poisoning.

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## THE PARTICLES RESULTING FROM POLYTETRAFLUOROETHYLENE (PTFE) PYROLYSIS IN AIR

W. Emile Coleman, Lester D. Scheel, Ph. D.,  
and Charles H. Gorski

Particulate matter resulting from pyrolyzed PTFE is the subject of new interest among toxicologists, first because the symptoms of polymer fume fever<sup>1,2,3</sup>, produced in humans by the particulate have not been reproduced in animals and second, because little is known of the particulate chemical structure. These particles were first thought to be unpyrolyzed or recondensed PTFE.

In the experiments conducted at this Facility, large quantities of particles were collected during the PTFE pyrolysis at 550° C (1022° F). Particle size was determined by electron microscopy. Infrared, mass spectrometric, gas chromatographic, and other instrumental techniques were used in an attempt to determine the chemical structure.

This report presents evidence indicating that the particulate residue resulting from PTFE pyrolysis in air is distinctly different from PTFE, and it reports analytical results which might aid in the identification of the particulate residue.

### PROCEDURES AND RESULTS

Samples of the particulate pyrolysis products from the exposure chamber were obtained on membrane filters for periods of approximately five minutes each when the pyrolysis rate was 20 to 30 grams of PTFE per hour. Samples

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

were prepared for electron microscopy by mounting portions of the filter medium on Formvar-coated copper grids. The filter medium was dissolved in acetone leaving the dust particles adhering to the coated grids. The specimens were examined with the electron microscope at a total magnification of approximately 5000X. Particle sizes were determined from the electron micrograph by means of a Zeiss TGZ-3 particle sizer which estimated the diameter of a projected area of the particle. A typical electron micrograph is shown in Figure 1. Figure 2 shows a particle-size distribution curve. All particles are in the respirable range of three microns with 96% of them below one micron in diameter.

A commercial laboratory reported (Table I) that the elemental analyses of PTFE pyrolysis particles were distinctly different from those of raw powdered PTFE. The results of the analyses of the pyrolysis particulate residue indicated the following percentage compositions: 24.8 for C, 63.8 for F, 1.8 for H, and trace for N.

Since oxygen could not be determined in the presence of fluorine by the commercial laboratory, we assumed that the missing 9.6% composition was oxygen inasmuch as the pyrolysis occurred in air. An empirical formula using the reported percentages of C, F, H, and an assumed percentage of O could not be devised. It was, therefore, necessary to use instrumental techniques to determine the presence of functional groups that would be indicative of hydrogen, oxygen, and hydrolyzable fluoride.

The first approach to this problem began with an infrared analysis of the particulate residue. Preparation of the sample for analysis was extremely difficult. The submicron particle size and the high electrostatic charge exhibited by the particles made it difficult to prepare films of the residue. When used in a KBr die and pelletized, the powder would often squeeze out and leave only the KBr. Due to this fact, the spectra obtained were not very well defined. A new infrared spectrophotometer was obtained and by using the scale expansion better spectra and more accurate frequency band designation were obtained.

The spectra presented in Figures 3 and 4 were obtained from the pyrolysis particulate residue and powdered PTFE which had been pelletized into a thin film in the KBr die. Spectrum 1 in Figure 3 is that of a thin film of pure PTFE. Spectrum 2 is that of PTFE and the particulate residue pressed



Figure 1. PTFE PYROLYSIS PARTICLES - MEAN DIAM  $0.50 \mu$   
5000 X

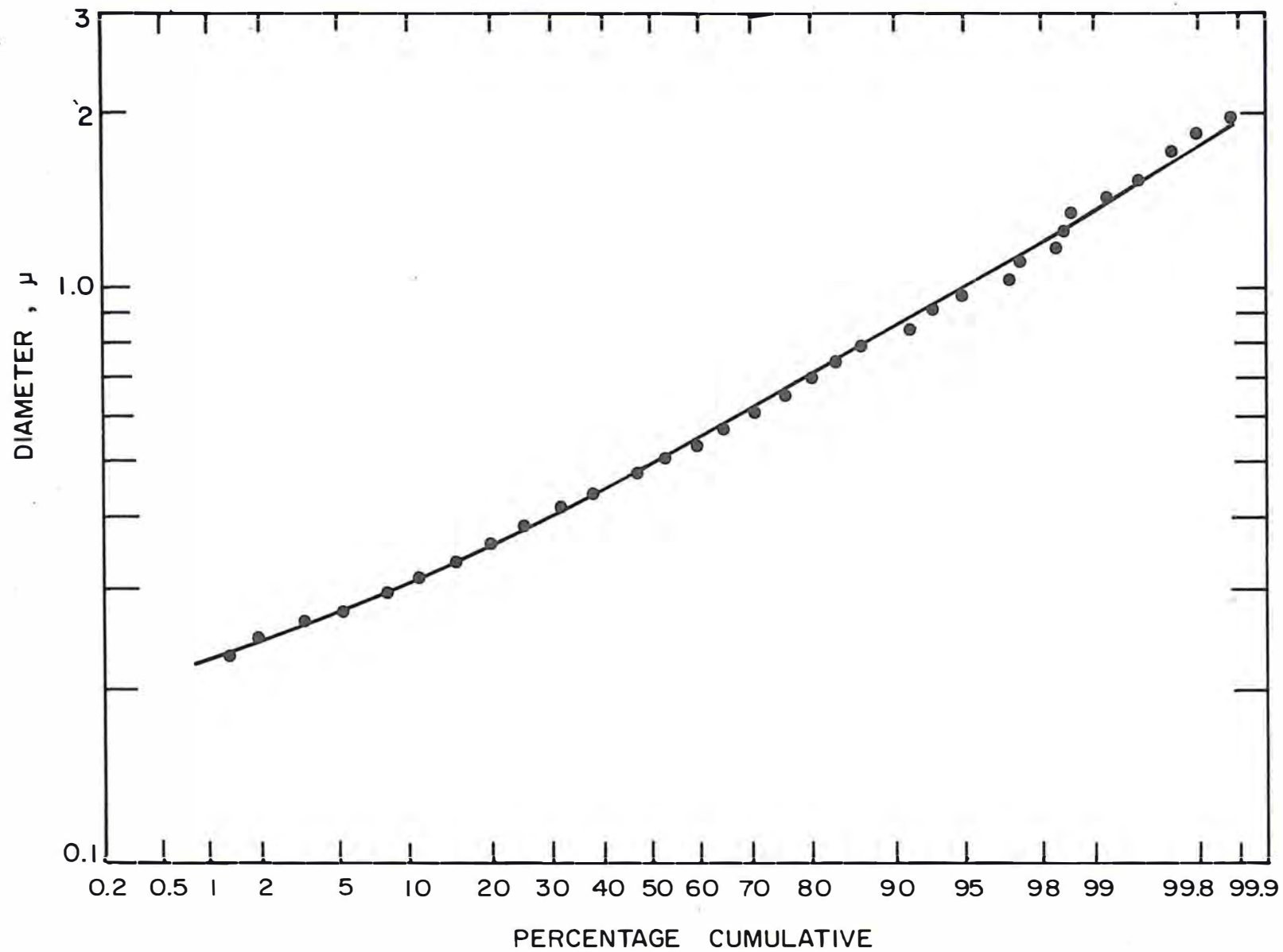


FIGURE 2. PARTICLE SIZE DISTRIBUTION CURVE .

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into a thin film. Spectrum 3 is that of PTFE and the residue pressed into a thin film with a thin film of pure PTFE in the reference beam. Spectra 1 and 2 did not have anything in the reference beam. Spectrum 3, therefore, shows bands of frequencies distinct from pure PTFE.

Table I

Commercial Laboratory Report of Particulate Analysis

Element	Pyrolyzed PTFE, %		Raw PTFE, %	
	1	2	1	2
C	24.74	24.89	23.49	24.14
H	1.89	1.73	Trace	Trace
N	Trace	Trace	ND	ND
F	63.99	63.67	76.40	76.25
O*				
Total	90.62	90.29	99.89	100.39
Average	90.45		100.14	

\* Cannot be determined in the presence of F unless special methods are used.

The latter spectrum is further expanded in Figure 4 so that accurate frequency designations can be made. The region between  $3600\text{ cm}^{-1}$  and  $3000\text{ cm}^{-1}$  displays very broad absorption. This could be due to the bonded O-H stretching absorption, which is common to acids. Ten spectra of fluorine-containing acids presented by Simons<sup>4</sup>, showed absorption in this region.

The three bands of frequencies in the region of  $1800\text{ cm}^{-1}$  to  $1700\text{ cm}^{-1}$ , namely  $1709\text{ cm}^{-1}$ ,  $1757\text{ cm}^{-1}$ , and  $1772\text{ cm}^{-1}$  are commonly attributed to carbonyl (C=O) absorption in halogen substituted compounds<sup>5</sup>. This region might also include olefinic<sup>6,7</sup>, absorption with bands at  $1350\text{ cm}^{-1}$  and  $1375\text{ cm}^{-1}$ . Two other bands at  $1095\text{ cm}^{-1}$  and  $987\text{ cm}^{-1}$  appear to be distinct from PTFE absorption bands. The very broad band of frequencies centered at  $1200\text{ cm}^{-1}$  establishes the residue as a fully fluorinated compound composed mainly of  $\text{CF}_2$  units. At this writing we are not prepared to make accurate band designations as to functional groups, but the evidence thus far does indicate the possibility of an unsaturated acid or an olefin and an acid. The possibility

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

of carbonyl (C=O) absorption and bonded O-H absorption strengthened the commercial laboratory report of the presence of hydrogen and our assumption of the presence of oxygen. However, the omission of a C-H vibration normally occurring in the region of  $3000\text{ cm}^{-1}$  to  $2840\text{ cm}^{-1}$  led us to believe that the H composition given may be somewhat high.

To substantiate the presence of oxygen and hydrogen in the particulate residue, the gas chromatograph in conjunction with the mass spectrometer were employed to identify the pertinent fragments. Samples of the pyrolyzed particulate residue were pyrolyzed in a platinum tube furnace<sup>8</sup>, in a stream of helium flowing 50 to 70 cc/minute. The furnace exhaust gases were fed simultaneously into a chromatograph with a silica gel column and into the mass spectrometer. At approximately  $280^{\circ}\text{C}$  the formation of  $\text{CO}_2$  as observed with the mass spectrometer was verified by a peak eluted from the gas chromatograph. The retention time of this peak matched that of pure  $\text{CO}_2$  as shown in Figure 5. Incidentally, a sample of the pyrolyzed particulate residue examined with a differential scanning calorimeter showed an endothermic reaction in which a broad melt peaking at  $292^{\circ}\text{C}$  took place followed by decomposition above  $317^{\circ}\text{C}$ .

A mass spectrum of the gases from repyrolysis of PTFE pyrolysis particulate residue (Table II) was obtained at  $525^{\circ}\text{C}$ . The only indications of the presence of oxygen and hydrogen were masses 44 ( $\text{CO}_2^+$ ) and 51 ( $\text{CHF}_2^+$ ) respectively. Mass 51 has been reported by Stacey et al.<sup>9</sup>, as a common rearrangement ion in the mass spectra of perfluoro acids. The high yield of  $\text{CO}_2$  revealed in the mass spectrum of pyrolysis gases and the absence of other oxygenated fragments indicate the decarboxylation of an acid. After decarboxylation produces the  $\text{CO}_2$ , breakdown of the residue in an inert atmosphere is almost similar to the breakdown of PTFE resin in an inert atmosphere. It is proposed that if decarboxylation takes place, only a long chain  $\text{CF}_2$  compound remains, thereby giving similar breakdown products in a helium atmosphere. Other workers<sup>10</sup>, have reported the decomposition products of PTFE in inert atmospheres as consisting of mainly tetrafluoroethylene ( $\text{C}_2\text{F}_4$ ), hexafluoropropene ( $\text{C}_3\text{F}_6$ ), and octafluorocyclobutane ( $\text{C}_4\text{F}_8$ ). The results shown in Table II indicate the presence of these gaseous products in the thermal breakdown fumes from the particulate residue.

The particles that had accumulated in the line leading to the mass spectrometer from the exit of the pyrolysis furnace were jumped out directly into the electron beam, and a mass spectrum (Figure 6) was obtained.

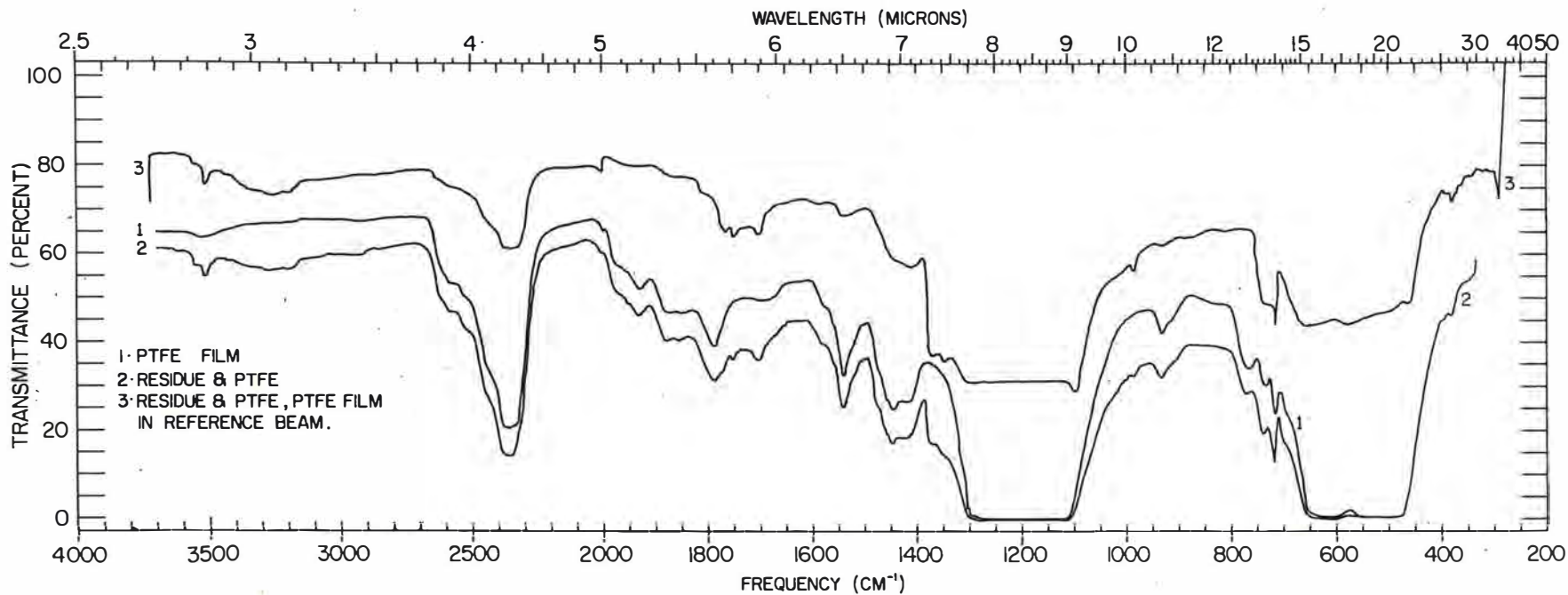


Figure 3. Infrared spectra of pure PTFE versus PTFE particulate residue.

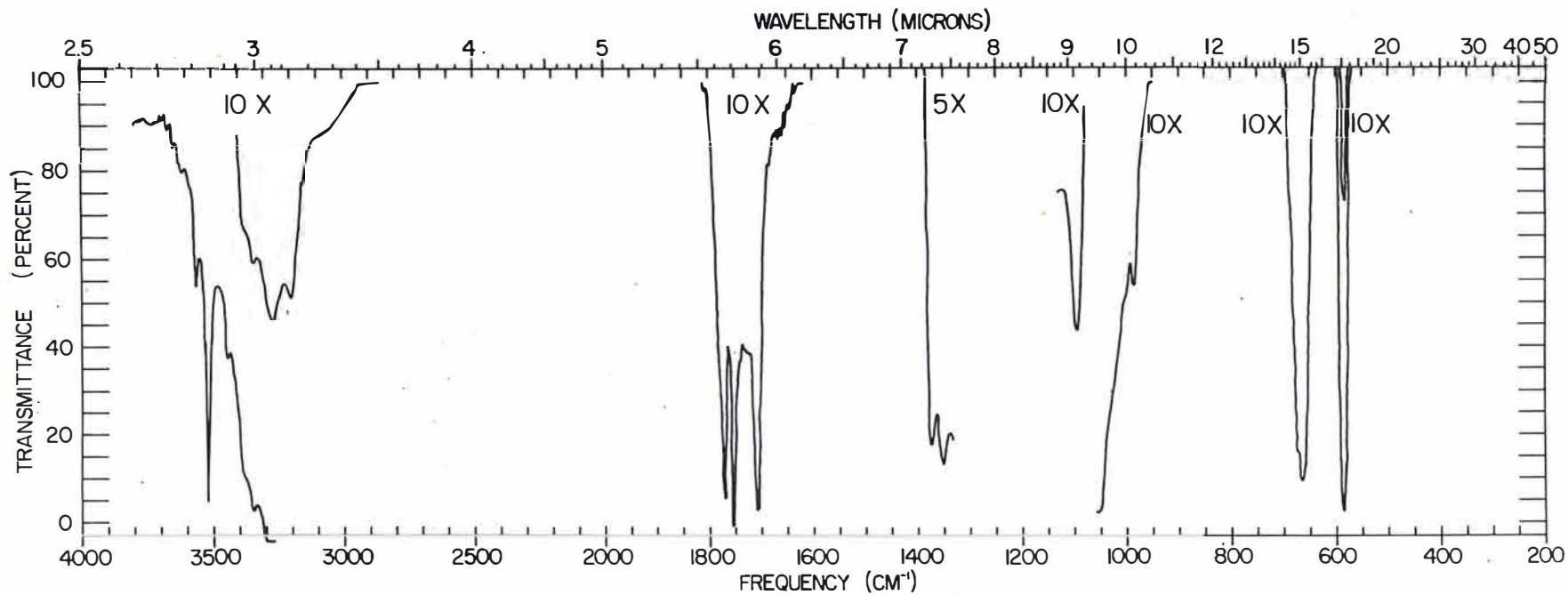


Figure 4. Ordinate expansion of spectrum 3 (Figure 3).

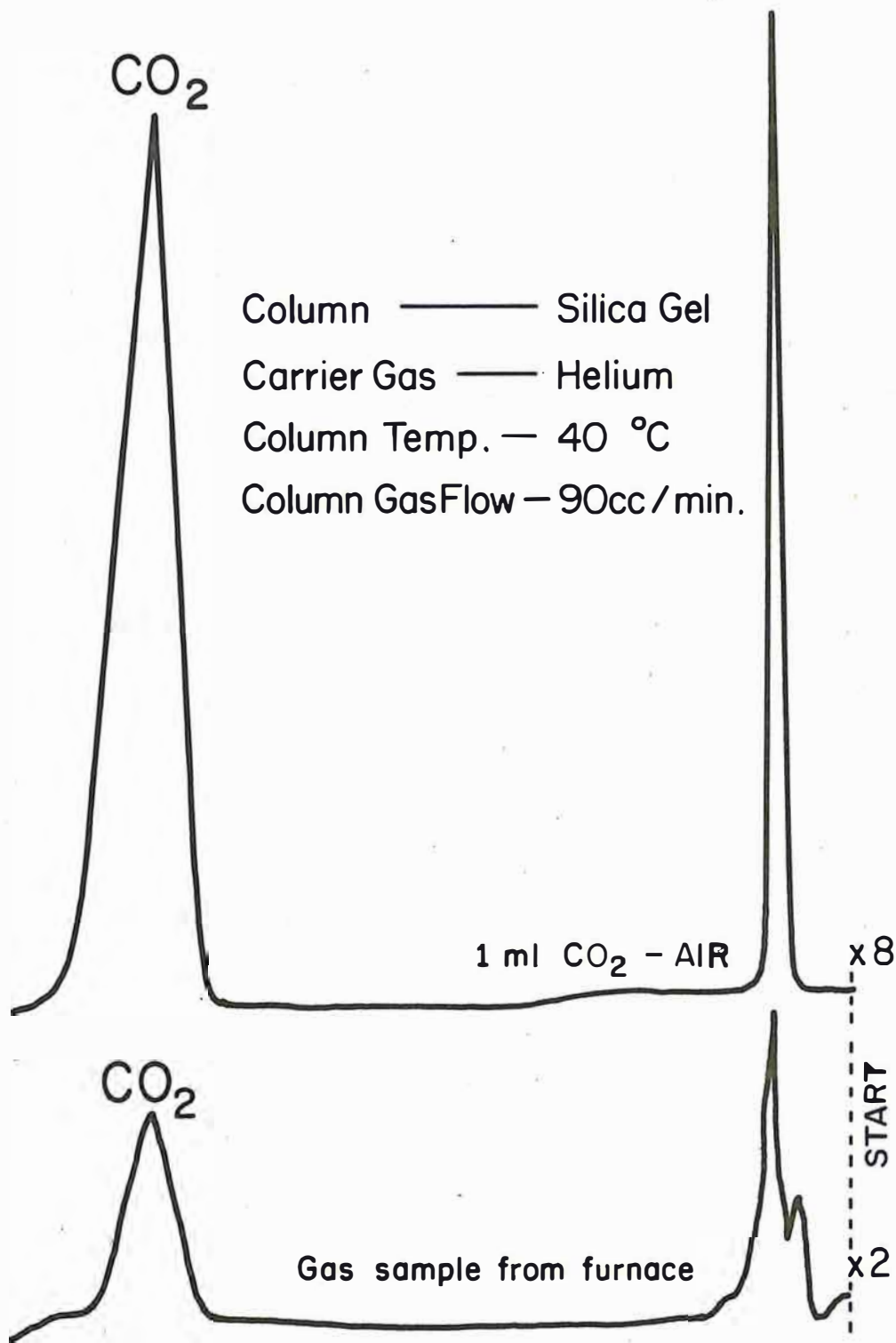


Figure 5. Gas Chromatographic Analysis of PTFE Pyrolysis Residue Gases in Helium at Approximately 300 °C.

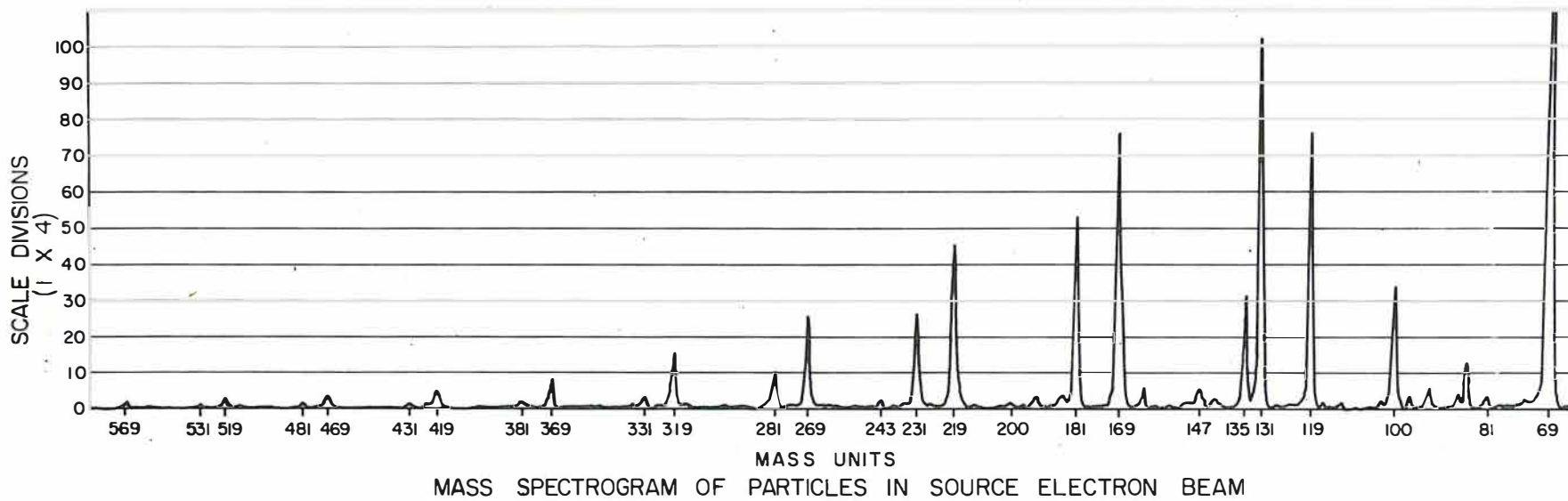


Figure 6. Mass spectrogram obtained with inlet tube residue particles.

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Table III shows the possibility of several oxygenated fragments, namely masses 47, 97, 135, and 147. However, there is no evidence of the presence of hydrogen. The air used in the small experimental furnace was from a pressurized tank and therefore dry. In addition, the inlet line to the mass spectrometer was continually evacuated and heated to approximately 150°C. Therefore, it is likely that water was not a contributing factor in the formation of this particular residue. An analysis of the results in Table IV discloses two groups of mass units, separated by 50 mass units (CF<sub>2</sub>). The following example illustrates a proposed mechanism which would explain the mass units observed in the pyrolysis products from the spectrometer inlet line.

Table II

Mass Spectrum of Gases from PTFE Pyrolysis  
Particulate Repyrolyzed in a Helium Atmosphere

Mass-Charge Ratio m/e	Ions (+)	Scale Divisions	*Relative Intensities
31	CF	518	<u>100.0</u>
44	CO <sub>2</sub>	300	57.9
50	CF <sub>2</sub>	218	42.1
51	CHF <sub>2</sub>	40	7.7
69	CF <sub>3</sub>	208	40.1
81	C <sub>2</sub> F <sub>3</sub>	490	94.5
100	C <sub>2</sub> F <sub>4</sub>	380	73.5
131	C <sub>3</sub> F <sub>5</sub>	209	40.3
150	C <sub>3</sub> F <sub>6</sub>	90	7.7
169	C <sub>3</sub> F <sub>7</sub>	10	1.9
181	C <sub>4</sub> F <sub>7</sub>	20	3.9
200	C <sub>4</sub> F <sub>8</sub>	Trace	-

\* Ionizing Voltage—65 Volts

Table III

## Mass Spectrum of Particles in Source Electron Beam (No Heat)

Mass-Charge Ratio m/e	Ion(+)	Scale Divisions	*Relative Intensities	Mass-Charge Ratio m/e	Ions(+)	Scale Divisions	*Relative Intensities
12	C	nil	-	219	C <sub>4</sub> F <sub>9</sub>	172	15.70
19	F	1	0.10	231	C <sub>5</sub> F <sub>9</sub>	81	7.40
31	CF	25	2.28	269	C <sub>5</sub> F <sub>11</sub>	102	9.30
50	CF <sub>2</sub>	7	0.64	281	C <sub>6</sub> F <sub>11</sub>	38	3.47
69	CF <sub>3</sub>	1094	100.00	319	C <sub>6</sub> F <sub>13</sub>	55	5.02
81	C <sub>2</sub> F <sub>3</sub>	8	0.73	331	C <sub>7</sub> F <sub>13</sub>	18	1.64
93	C <sub>3</sub> F <sub>3</sub>	19	1.73	369	C <sub>7</sub> F <sub>15</sub>	28	2.58
100	C <sub>2</sub> F <sub>4</sub>	132	12.10	381	C <sub>8</sub> F <sub>15</sub>	8	0.73
112	C <sub>3</sub> F <sub>4</sub>	8	0.73	419	C <sub>8</sub> F <sub>17</sub>	20	1.83
119	C <sub>2</sub> F <sub>5</sub>	282	25.80	431	C <sub>9</sub> F <sub>17</sub>	6	0.55
131	C <sub>3</sub> F <sub>5</sub>	350	32.00	469	C <sub>9</sub> F <sub>19</sub>	14	1.28
143	C <sub>4</sub> F <sub>5</sub>	6	0.55	481	C <sub>10</sub> F <sub>19</sub>	4	0.40
150	C <sub>3</sub> F <sub>6</sub>	8	0.73	519	C <sub>10</sub> F <sub>21</sub>	12	1.10
162	C <sub>4</sub> F <sub>6</sub>	20	1.83	531	C <sub>11</sub> F <sub>21</sub>	3	0.30
169	C <sub>3</sub> F <sub>7</sub>	290	26.50	569	C <sub>11</sub> F <sub>23</sub>	6	0.55
181	C <sub>4</sub> F <sub>7</sub>	201	18.34				
	Oxygenated Fragments						
47	COF	2	0.20				
97	C <sub>2</sub> F <sub>3</sub> O	nil	-				
135	C <sub>2</sub> F <sub>5</sub> O	100	9.15				
147	C <sub>3</sub> F <sub>5</sub> O	nil	-				

\* Ionizing Voltage — 65 Volts ✓

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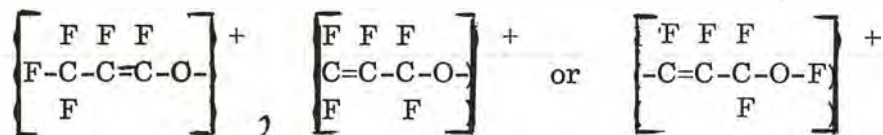
Table IV

Mass Ions From Inlet Tube Residue

Peak Height	Mass Ion	Mass Number
18	( F F F F F F ) (F-C-C-C-C-C-C)+3	331
	( F F F F F F )	(C) -12
55	( F F F F F F ) (F-C-C-C-C-C-C)+1	319
	( F F F F F F )	(2F) -38
38	( F F F F F ) (F-C-C-C-C-C)+3	281
	( F F F F F )	(C) -12
102	( F F F F F ) (F-C-C-C-C-C)+1	269
	( F F F F F )	(2F) -38
81	( F F F F ) (F-C-C-C-C-C)+3	231
	( F F F F )	(C) -12
172	( F F F F ) (F-C-C-C-C)+1	219
	( F F F F )	

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The above action would continue until the molecule was completely fragmented. The high intensity of mass 69 and the many fragment ions composed of a CF<sub>3</sub> group, as seen above, strongly indicated a CF<sub>3</sub> terminal group. The oxygenated fragments indicate that a carbonyl linkage is not present mainly because a structural ion could not be written for mass 135 (C<sub>2</sub>F<sub>5</sub>O) using the C=O group. It is, therefore, proposed that an ion formation such as



could exist. The above ions, designating mass 147, through continuous fragmentation would yield masses 135, 97, and 47. Therefore, the overall spectrum presented in Table III indicates a compound on the order of CF<sub>3</sub>(CF<sub>2</sub>)<sub>x</sub>-O-R or CF<sub>3</sub>(CF<sub>2</sub>)<sub>x</sub>-O-F<sup>11,12,13</sup>. Since the decarboxylation data presented earlier provides evidence for the presence of an acid in the particulate residue from air pyrolysis, it appears possible that hydrolysis could convert such a compound to an acid. Simons<sup>14</sup>, points out that a CF<sub>2</sub> group in the α-position to the oxygen bridge is quite sensitive to hydrolysis.

In Table V can be seen the wide variation in yield of particles collected per weight of PTFE pyrolyzed. Three PTFE samples were compared. The PTFE sample 1 consistently yielded less particles than samples 2 and 3 under the same pyrolysis conditions. The yield of particles on a wet day increased greatly over that obtained on a dry day. The results on 12-23-66 indicate an average particle yield of 65%, whereas on 12-28-66 the average particle yield was 109% of the PTFE input. The latter percentage is rational, since it has been established that the particles are composed of elements other than carbon and fluorine. The fact that humidity plays an important role in the formation of these particles makes it even more difficult to establish an empirical formula. The average carbonyl fluoride (COF<sub>2</sub>) concentration is inversely proportional to the yield of particles. This was expected since some oxygen was shown to be combined in the particulate residue.

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Table V

Yield of Particles Collected from Chamber During PTFE Pyrolysis

Date and Weather	PTFE* Pyrolyzed (gm)	Time (min)	PTFE Burned (mg/min)	Air Flow (L/min)	PTFE Input (mg/L)	Particles Found (mg/L)	Particles (% of Input)	COF <sub>2</sub> (ppm)
12-22-66 Dry	#1 38.32	90	425	142	3.00	1.14	38	532
	#2 36.98	90	410	142	2.90	2.47	85	479
	#3 42.15	90	467	142	3.30	2.20	67	560
12-23-66 Dry	#1 33.41	90	370	142	2.61	1.10	42	531
	#2 28.85	90	320	142	2.25	1.70	75	323
	#3 28.58	90	317	142	2.24	1.74	78	391
12-28-66 Wet	#1 29.18	90	325	142	2.28	2.08	91	438
	#2 28.05	90	313	142	2.20	2.76	126	320
	#3 26.61	90	295	142	2.08	2.27	109	310
12-30-66 Dry	#1 25.60	90	285	142	2.00	0.89	45	348
	#2 25.05	90	278	142	1.96	1.12	57	332
	#3 24.52	90	272	142	1.91	1.08	57	325

\* The numbers 1, 2, 3 represent PTFE from different companies.

Table VI

Effect of Filtration on Hydrolyzable Fluoride Expressed as COF<sub>2</sub>

Sample	Time	Unfiltered Sample	Filtered Sample
1	2:45	410	
2	2:50		380
3	2:56	515	
4	3:02		380
5	3:08	577	
6	3:20	—	425
Avg		501	395

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

Table VI shows the results from an experiment set up to determine the possibility of hydrolyzable fluoride in the particulate residue. Samples were collected with and without membrane filters, and the  $\text{COF}_2$  concentrations calculated from the amount of hydrolyzable fluoride detected. The results in Table VI give evidence that the hydrolyzable fluoride concentration increased an average of 20% when the effluent samples were not filtered, this increase indicating that some of the particulate could be readily hydrolyzed.

## CONCLUSIONS

The data reported shows that pyrolysis of PTFE in air generates particles of respirable size composed of various fluorocarbon compounds. The evidence from chemical analysis, mass spectrography, gas chromatography, infrared spectroscopy, and differential calorimetry all showed that the particulate residue formed during PTFE pyrolysis has a different composition and structure than PTFE. This conclusion is supported by the finding of hydrogen in the particles by elemental analysis, and by the occurrence of oxygen in the particles. The appearance of absorption bands in the infrared spectra of the pyrolysis particles, indicating carbonyl ( $\text{C}=\text{O}$ ) absorption and a bonded OH structure, suggests that the oxygen in the particles is present as a carboxyl group. The presence of a strong absorption band in the  $1700\text{ cm}^{-1}$  to  $1800\text{ cm}^{-1}$  region is interpreted as indicating the presence of olefinic ( $\text{C}=\text{C}$ ) bonds in the particles. The absence of a C-H absorption band, which would normally appear in the  $2840\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$  region of the infrared spectrum, and the absence of oxygenated fragment ions in the mass spectrum, following decarboxylation of the particles repyrolyzed in an atmosphere of helium, support the interpretation that the  $\text{CO}_2$  generated during the repyrolysis is liberated by a thermal decarboxylation. The appearance of a mass 51 fragment ion ( $\text{CF}_2\text{H}^+$ ) following after the decarboxylation reaction in the mass spectrum of the repyrolyzed particles is additional evidence for the decarboxylation reaction.

The evidence presented above supports the interpretation that the particles generated during the pyrolysis of PTFE are composed of a mixture of compounds, some of which may be fluorinated acids and/or fluorinated olefins. Furthermore, since the yield of particles has been shown to be a function of the humidity in the pyrolysis chamber, the composition of the mixture of compounds in the particles may change with changes in the pyrolysis atmosphere.

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As a result of mass spectrometry performed on particles formed in the transfer line from the pyrolysis furnace to the mass spectrometer, clear-cut evidence has been obtained that carbon chain fragments as large as mass 569 (11 carbons) are present in the particles. In fact, the data obtained on this particular material show the occurrence of all the saturated molecular analogs from  $C_{11}F_{23}^+$  to  $CF_3^+$ . In addition, certain oxygenated fragments suggested by the mass spectra could explain a proposed mechanism for generating the olefinic bonds observed by infrared absorption.

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### THE TOXICOLOGY OF THE PYROLYSIS PRODUCTS OF POLYCHLOROTRIFLUOROETHYLENE

H. A. Birnbaum,\* L. D. Scheel, and W. E. Coleman

The polymerization of chlorotrifluoroethylene (CTFE) produced a linear polymer with a density of 2.1-2.2, a tensile strength of 4500 to 6000 psi and heat resistance up to 350° to 390° F (176° to 193° C). It has a useful temperature range for applications of -423° F to 390° F (-253° to 198° C) and can be molded in conventional thermoplastic molding equipment. Its very low water vapor transmission makes it an outstanding gas and liquid barrier. The high melt viscosity of the plastic at temperatures around 500° F to 600° F (350° to 385° C) requires great care to be taken during the molding process to prevent fracture lines and excessive degradation of the melt during molding operations.

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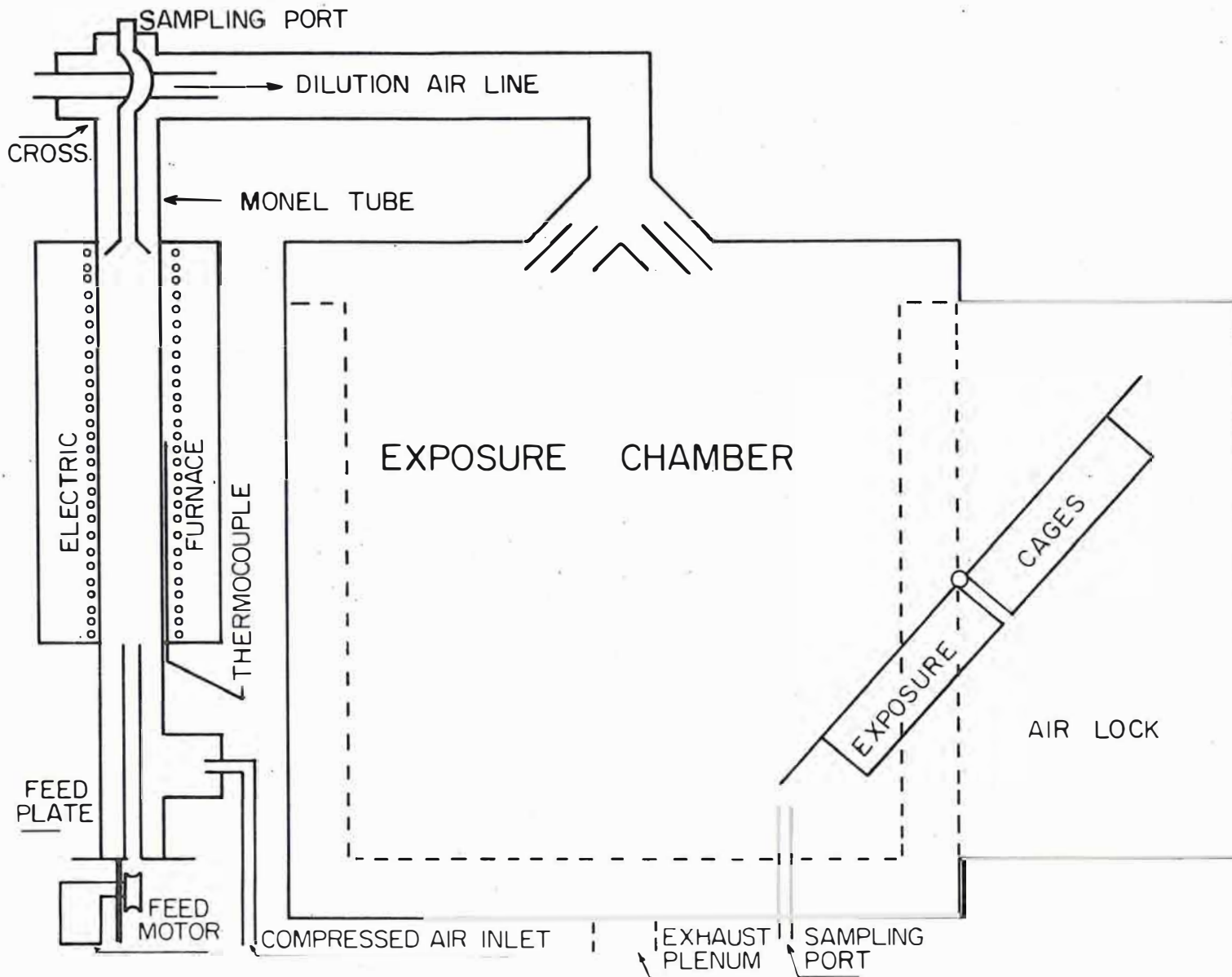
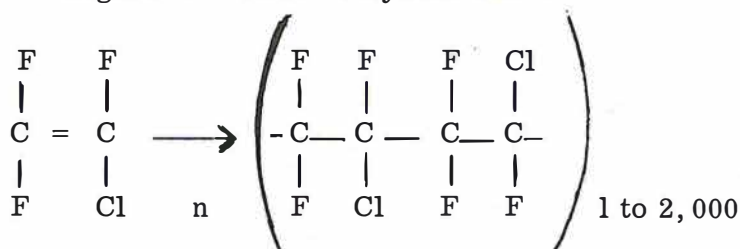


FIGURE 2. PLASTIC PYROLYSIS EXPOSURE UNIT

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

The CTFE polymerization reaction which produces long molecules of up to 2,000 linked CTFE units is shown in Figure 1.

Figure 1. CTFE Polymerization



In earlier studies on the pyrolysis of poly-CTFE by Treon<sup>1</sup>, it was reported that the toxicity of the fumes formed during pyrolysis was highest for cats and guinea pigs, less effective in rats and mice and least toxic to rabbits. The cause of death after exposure, in their studies, was reported as acute pulmonary irritation (chemical pneumonitis) and diffuse degeneration of the brain, liver and kidney cells. Their data indicated, but they did not state, that the toxicity of the pyrolysis fumes increased as the temperature of pyrolysis increased above 392° F (200° C).

### METHODS

Additional studies on the pyrolysis products of poly-CTFE were conducted in cooperation with the Toxicology Section of The Occupational Health Program at the National Center for Urban and Industrial Health in Cincinnati, Ohio.

In these studies 1/4 inch poly-CTFE rod was continuously fed into a 1 1/2 inch monel pipe heated to the desired temperature by an electric furnace. The air flow through the furnace was regulated at 4 liters per minute. This air flow produced a rate of flow around the pyrolyzing rod of 5.075 cm/sec. The hot zone in the furnace was 32 cm long and therefore the pyrolysis gases from the rod were present in the hot zone of the furnace for 6.31 seconds. Thus ample time for gas phase or particle and gas phase interaction was available. The furnace and chamber diagram is shown in Figure 2.

The products of pyrolysis contained in the furnace air stream were then delivered into a dilution air stream of 142 liters per minute in a stainless

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

steel pipe connected to the chamber inlet. The chamber was an aluminum wall with plexiglas window, 1240 liter capacity unit. It was operated as a continuous flow-dynamic system during the exposures.

The exposures were accomplished by placing 10 rats (5 males and 5 females) in the airlock attached to the chamber and after allowing the chamber to come to equilibrium (30 minutes) the animals were rotated into the chamber exposure atmosphere. The animals were then exposed for the desired time and then removed into the airlock and immediately removed to room air from the airlock. The rats used in these studies were Greenacres, Controlled Flora, Wister strain rats, 8-10 weeks old, which are free of endemic respiratory disease. All exposure groups consisted of 10 animals at each exposure concentration and an unexposed group of 10 controls was used for each series of exposures.

During each exposure 4 air samples of 2800cc were collected in 0.5N NaOH for hydrolyzable fluoride determinations. One sample for mass spectrographic evaluation and 1 sample for infrared analysis were also taken from the chamber during each exposure.

Table I

One Hour Exposure to CTFE Pyrolysis  
Products at a Furnace Temperature  
of 375°C

G/Hour CTFE Decomposed	Hydrolyzable Fluoride in Chamber (ppm)	Mortality (14 days)
21.2	0	0/10
27.9	0	0/10
28.8	0	1/10
35.5	4.8	1/10
42.9	0	0/10

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### RESULTS

During the exposure period of one hour at 375 °C (See Table I for the results of this exposure) all of the animals showed minimal discomfort and survived for the total of 14 days, except for one animal lost at the 28.8 g/hr and one at the 35.5 g/hr concentration. During the exposure a heavy fog was formed by the decomposition particles making it difficult to see the animals. No hydrolyzable fluoride was found in the samples taken except during the 35.5 g/hr exposure.

At the end of the 1 hour series a final run at 375°C was carried out. The furnace was run at the maximum rate of pyrolysis for a total of 3 1/4 hours. A total of 185.5 grams was decomposed. During exposure, these animals showed hyperactivity but otherwise appeared to be normal. However, shortly after removal from the chamber the animals showed respiratory difficulties, and within two hours two of the animals had died. At the end of 24 hours, three additional animals had died. All the rest died within 48 hours. These animals showed respiratory difficulty due to pulmonary edema, possibly from the particles inhaled.

In the second series of exposures animals were exposed for 3 hours to quantities pyrolyzed ranging from 27.6 grams to 40.5 g/hr. For the 3 hour period this gave total quantities pyrolyzed during the exposure of 83 to 122 grams. During the exposure period a very heavy fog was produced in the chamber. These animals showed some hyperactivity but otherwise showed no ill effects during the time of exposure. As shown in Table II, at the 27.6 g/hr level, 4 out of 10 animals died in 14 days, while at the 32.8 g/hr level, 7 out of 10 animals died in 14 days, and at the 40.5 g/hr concentration 10 out of 10 died. At the 35.2 g/hr concentration only 1 out of 10 died. The calculated LC<sub>50</sub> for this exposure is 31.5 g/hr or 99 grams for the total exposure to CTFE.

POLYFLUOROETHYLENE PYROLYSIS STUDIES

Table II

Three Hour Exposure to CTFE Pyrolysis Products  
At a Furnace Temperature of 375 °C

<u>G/Hour CTFE</u> <u>Decomposed</u>	<u>Total Grams of</u> <u>CTFE Burned</u>	<u>Hydrolyzable Fluoride</u> <u>in Chamber (ppm)</u>	<u>Mortality</u> <u>(14 days)</u>
27.6	82.8	15	4/10
32.8	98.4	37	7/10
35.2	105.5	13	1/10
40.5	121.5	39	10/10

Upon autopsy of the animals following a 3 1/4 hour exposure to the pyrolysis products from 185.5g of CTFE, all of the lungs exhibited essentially similar findings. The gross appearance of the lungs exhibited hemorrhagic edema. The microscopic examination of these lungs revealed numerous small focal hemorrhages, congestion of alveolar walls, and peribronchiolar edema. In addition, focal emphysema and alveolitis were observed. One animal exhibited focal alveolar cell hyperplasia and fibrin deposition within the alveoli. The livers exhibited prominent sinusoidal congestion. No hepatic necrosis was observed. The spleens of the animals exhibited prominent reticulum cells. The kidneys exhibited severe congestive changes but no foci of necrosis were observed. No particles are seen in the lungs. It would appear that most of the inhaled materials are in the liquid phase (See Figure 3).

Figure 4 shows the particle size distribution obtained by electron microscopy from a "Millipore" Filter sample obtained from the exposure chamber during a 28 g/hr pyrolysis. This figure shows that the mean particle size is 0.5 micron with 85% of the particles being less than 1 micron and 99% of the particles less than 2 microns. Thus the data indicates that all the particles found on the filter are of inhalable size. These results are similar to the size distribution reported in previous papers<sup>2</sup>.

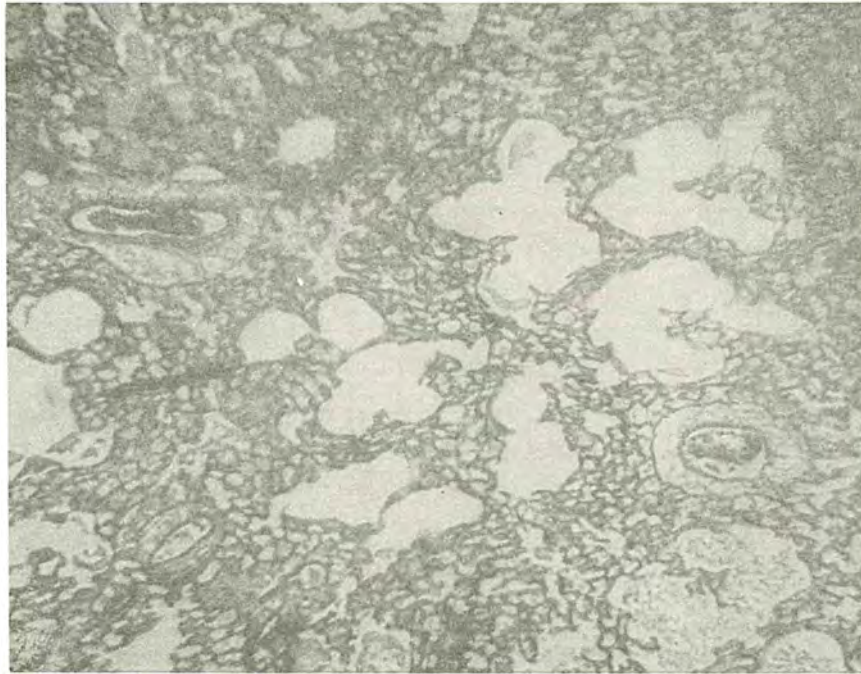


Figure 3. Proteinaceous, exudative, chemical pneumonitis following 3 hr. exposure to CTFE pyrolysis fume.

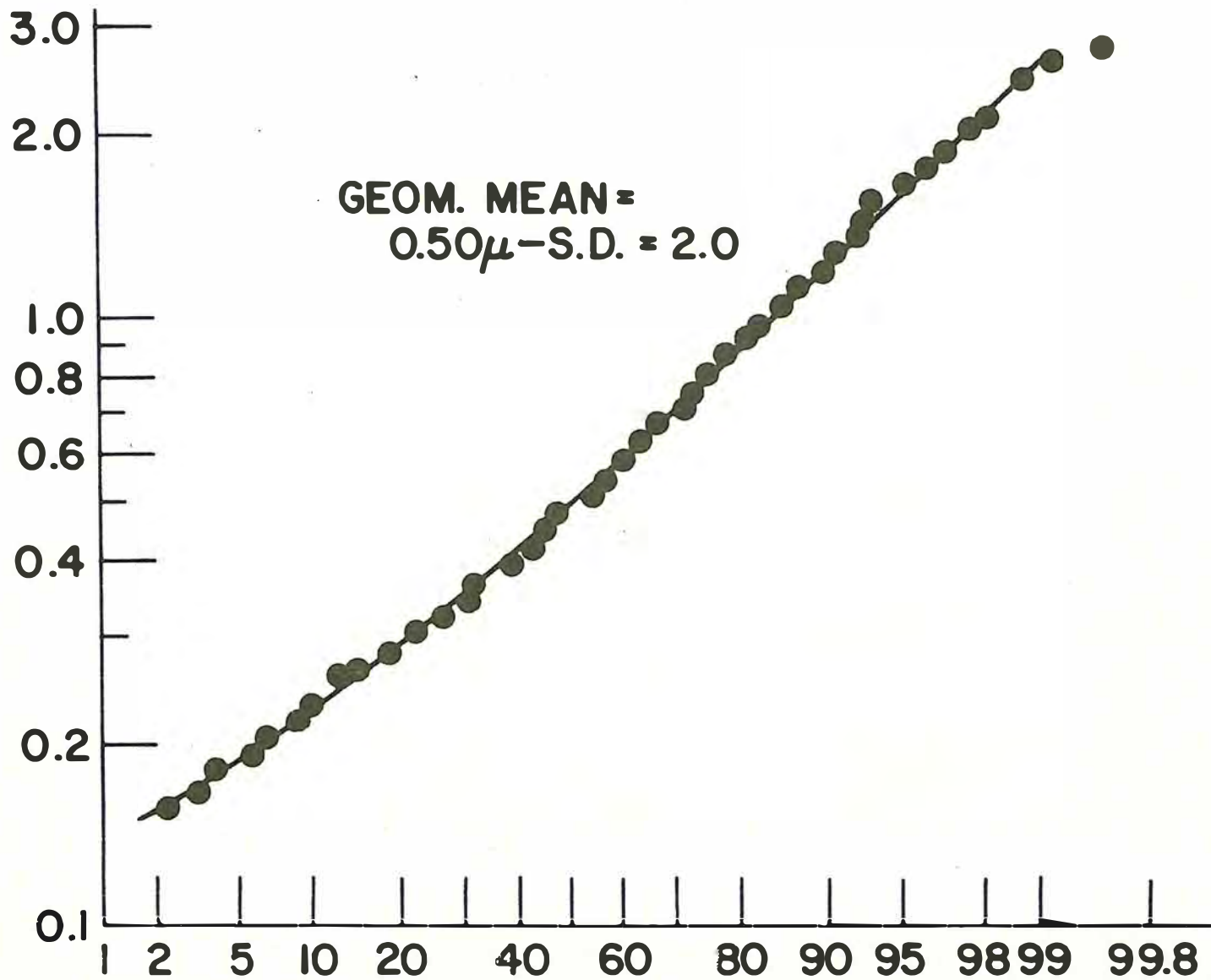


Figure 4 Particle Size Distribution

POLYFLUOROETHYLENE PYROLYSIS STUDIES

Table III

One Hour Exposure to CTFE Pyrolysis Products  
at a Furnace Temperature of 400°C

<u>G/Hour CTFE</u> <u>Decomposed</u>	<u>Hydrolyzable Fluoride</u> <u>in Chamber (ppm)</u>	<u>Mortality</u> <u>(14 days)</u>
16.5	2.2	0/10
21.2	2.6	1/10
22.8	4.7	2/10
26.5	4.7	10/10

Since the previous exposure for 1 hour to 375°C had not produced sufficiently lethal results, it was decided to increase the temperature. A series of exposures was carried out using decomposition products at 400°C, results of which are shown in Table III. An approximate LC<sub>50</sub> value of 23.5 grams of CTFE pyrolyzed per hour was obtained. Mortality at other levels are shown in the table. During this exposure the same fog type conditions existed in the chamber. It appears that the increase in temperature greatly increased the effect of the decomposition products of CTFE. Although there is an increase in the hydrolyzable fluoride correlating with the total grams burned, no extrapolation can be made for the amount of hydrolyzable fluoride giving a midway point, since 4.7 p.p.m. in one case killed 2 out of 10 animals and in another case killed all of the animals.

During exposures, samples were taken for infrared spectra and one spectrum is shown in Figure 5. This particular one was for an exposure carried out at 540°C which was the highest temperature used in our studies. The spectra at lower temperatures were quite similar, except that the intensities at the various peaks such as 5.18, 8, 11, etc. were lower. Examination of the spectra show peaks which may be attributable to COF<sub>2</sub> or CClF and other peaks which may be due to the COCl groups, and COFCl. It is postulated that the COCl absorption may come from CF<sub>2</sub>ClCOCl.

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Table IV

Typical Scan

<u>Mass #</u>	<u>Ion +</u>
47	COF+ or CCl+
50	CF <sub>2</sub> <sup>+</sup>
66	COF <sub>2</sub> <sup>+</sup> or CClF <sup>+</sup>
69	CF <sub>3</sub> <sup>+</sup>
81	C <sub>2</sub> F <sub>3</sub> <sup>+</sup>
85	CF <sub>2</sub> Cl <sup>+</sup>
93	C <sub>3</sub> F <sub>3</sub> <sup>+</sup>
101	CFCl <sub>2</sub> <sup>+</sup>
116	C <sub>2</sub> F <sub>3</sub> Cl <sup>+</sup>
131	C <sub>3</sub> F <sub>5</sub> <sup>+</sup>
147	C <sub>3</sub> F <sub>4</sub> Cl <sup>+</sup>

A typical scan on the mass spectrometer is shown in Table IV. Again, the amount of many of these components increases with the increase in temperature. In all of the analytical work carried out there was no evidence for phosgene. Some other preliminary conclusions appeared to be that the ratio of fluorine to chlorine seems to be similar to that found in the polymer. Presence of many of the ions may be due to the depolymerization of polytrifluorochloroethylene. Additional work is necessary to separate the various components and carry out the identification.

The amount of hydrolyzable fluoride when converted to carbonyl fluoride does not seem to be present in sufficient quantities to account for the toxic effect. No other known compounds were found that could account for the lethal results. The action may be similar to polytetrafluoroethylene in that the "particulate" matter may account for the toxic action of the pyrolysis products<sup>3,4,5</sup>.

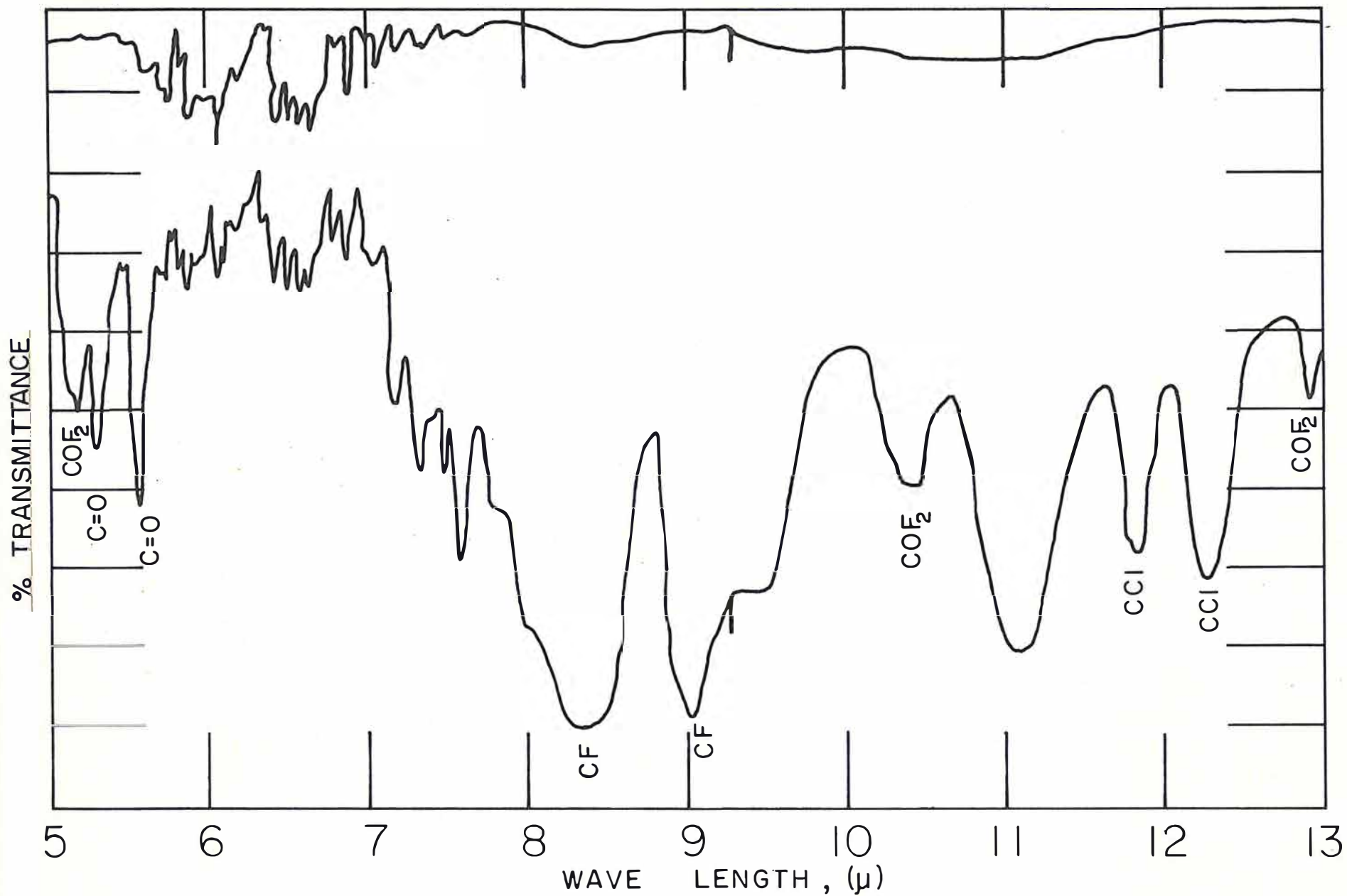


FIGURE 5. INFRARED SPECTRUM OF DECOMPOSITION PRODUCTS AT 540°C

## POLYFLUOROETHYLENE PYROLYSIS STUDIES

### SUMMARY

A series of exposures of rats to the pyrolysis products of polytrifluoro-chloroethylene has been carried out. In an exposure for 1 hour at 375°C as much as 43 grams was pyrolyzed without attaining a lethal concentration. An approximate LC<sub>50</sub> figure of 31 1/2 g/hr or a total of 99 grams in the 3 hours, was obtained for the 3 hour exposure at 375°C. At a higher temperature of 400°C an LC<sub>50</sub> of 23 1/2 g/hr was obtained. During exposure large amounts of particles are formed having a size range of less than 2 microns. Mean particle size was 1/2 micron. Death may be due to inhalation of particles rather than toxic by-products.

Analysis of the breakdown products shows a large number of different components present which may include small amounts of carbonyl fluoride, COFCl and COCl containing groups.

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