

31

AD 668109

# Free Radical Yields in Polytetrafluoroethylene as the Basis for a Radiation Dosimeter

FEBRUARY 1968

Prepared by HENRY S. JUDEIKIS, HERBERT HEDGPETH, and SEYMOUR SIEGEL  
Laboratory Operations  
AEROSPACE CORPORATION

Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION  
AIR FORCE SYSTEMS COMMAND  
LOS ANGELES AIR FORCE STATION  
Los Angeles, California



THIS DOCUMENT HAS BEEN APPROVED FOR PUBLIC  
RELEASE AND SALE: ITS DISTRIBUTION IS UNLIMITED

Reproduced by the  
CLEARINGHOUSE  
for Federal Scientific & Technical  
Information Springfield Va. 22151

UNCLASSIFIED

AD 668 109

FREE RADICAL YIELDS IN POLYTETRAFLUORO-  
ETHYLENE AS THE BASIS FOR A RADIATION DOSIMETER

Henry S. Judeikis, et al

Aerospace Corporation  
El Segundo, California

February 1968

*Processed for . . .*

DEFENSE DOCUMENTATION CENTER  
DEFENSE SUPPLY AGENCY



U. S. DEPARTMENT OF COMMERCE / NATIONAL BUREAU OF STANDARDS / INSTITUTE FOR APPLIED TECHNOLOGY

Air Force Report No.  
SAMSO-TR-68-140

Aerospace Report No.  
TR-0158(3250-20)-6

FREE RADICAL YIELDS IN POLYTETRAFLUOROETHYLENE  
AS THE BASIS FOR A RADIATION DOSIMETER

Prepared by  
Henry S. Judeikis, Herbert Hedgpeth, and Seymour Siegel  
Materials Sciences Laboratory

Laboratory Operations  
AEROSPACE CORPORATION

February 1968

Prepared for  
SPACE AND MISSILE SYSTEMS ORGANIZATION  
AIR FORCE SYSTEMS COMMAND  
LOS ANGELES AIR FORCE STATION  
Los Angeles, California

This document has been approved for public release  
and sale; its distribution is unlimited.

## FOREWORD

This report is published by the Aerospace Corporation, El Segundo, California, under Air Force Contract No. F04695-67-C-0158.

This report, which documents research carried out from June 1965 through September 1967, was submitted on 13 February 1968 to Captain William D. Bryden, Jr., SMTTM, for review and approval.

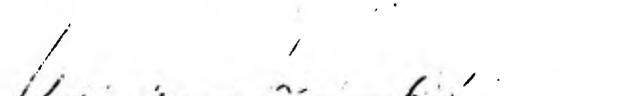
Approved



---

W. C. Riley, Director  
Materials Sciences Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.



---

William D. Bryden, Jr.  
Captain, United States Air Force  
Project Officer

## ABSTRACT

Exposure of polytetrafluoroethylene (PTFE) to ionizing radiation results in chemical degradation of the polymer and formation of long-lived free radicals. This paper describes the use of quantitative measurements of the electron spin resonance (ESR) spectra of the free radical produced in irradiated PTFE to determine radical yields and attempts to correlate these radical yields with the absorbed radiation dose. The experimental results indicate sufficient correlation over the experimental range from  $10^4$  to  $10^8$  rad to permit use of PTFE as a passive radiation dosimeter. Analysis of the data indicates that, with minor modifications, the useful range can be extended to  $< 10^2$  to  $> 10^9$  rad with uncertainties  $\leq 15$  percent. The advantages inherent in the use of the PTFE dosimeter for the measurement of low energy electromagnetic or particulate radiation are also discussed. Energy deposition as a function of depth from the incident surface can be determined by sectioning of the polymer after irradiation. The resulting dose - depth curves can then be used to obtain spectral and profile data from polychromatic sources.

## CONTENTS

FOREWORD . . . . .	ii
ABSTRACT . . . . .	iii
INTRODUCTION . . . . .	1
EXPERIMENTAL PROCEDURE . . . . .	3
Material and Preparation . . . . .	3
Instrumentation and Standardization . . . . .	4
Uncertainties . . . . .	5
RESULTS AND DISCUSSION . . . . .	7
Radical Identification and Stability . . . . .	7
Dosimeter Standardization and Use . . . . .	15
Dose - Depth Curves . . . . .	18
Other Considerations . . . . .	20
SUMMARY OF CONSIDERATIONS FOR USE OF PTFE AS A DOSIMETER . . . . .	25
Batch Control and Standardization . . . . .	25
Other Considerations . . . . .	26
CONCLUSIONS . . . . .	29
FOOTNOTES . . . . .	31
REFERENCES . . . . .	33

## FIGURES

1.	ESR Spectrum from PTFE Slices Irradiated and Observed in Vacuum . . . . .	8
2.	Free Radicals Produced in Irradiated PTFE . . . . .	9
3.	ESR Spectra from PTFE Slices Irradiated and Observed in Air . . . . .	10
4.	Radical Concentration in 1/8-in. Solid Rod as a Function of Time after Irradiation . . . . .	12
5.	Radical Concentration in 40- $\mu$ Slices as a Function of Time after Irradiation . . . . .	13
6.	Radical Concentration in Air-Saturated PTFE as a Function of Total Dose . . . . .	16
7.	Radical Yield in PTFE Rod as a Function of Total Dose . . . . .	17
8.	Radical Concentration as a Function of Distance from the Incident Surface for Electron-Irradiated PTFE . . . . .	19
9.	Radical Concentration as a Function of Slice Thickness for Blocks Irradiated to $10^6$ rad . . . . .	21

## INTRODUCTION

Polymers have been used as passive radiation dosimeters since 1950. These materials possess a number of advantages over other types of dosimeters, such as ease of handling, long shelf life, and absence of need for containment. The latter advantage makes polymer dosimeters particularly useful in detection and measurement of low-energy electromagnetic or particulate radiation (i. e.,  $< 10$  Kev photons or  $< 2$  Mev electrons), since container walls can absorb appreciable fractions of the energy from such radiation. Although a number of physical or mechanical property changes, or both, could be used as the basis for a radiation dosimeter, changes in the optical transmission or molecular weight of the polymer have been the most frequently used (1).

Most of the radiation-induced changes result from chemical degradations occurring within the polymer, such as crosslinking or double bond formation. In many cases, free radical intermediates, that is, molecular fragments produced by irradiation that contain unpaired electrons, have also been observed. In general, the free radical lifetimes in irradiated polymers are too short at ambient temperatures to permit radical yields to be of much use for dosimetry purposes. However, lifetimes of many months are observed for the free radicals produced in irradiated polytetrafluoroethylene (PTFE). This stability is probably related in some manner to the C-F bond energy, which is considerably greater than the C-H bond energy occurring in other types of polymers examined.

The experiments described in this paper examine some of the properties of the long-lived free radicals produced in irradiated PTFE. Quantitative correlations are made between the free radical yield and absorbed radiation dose for the purpose of using PTFE as a radiation dosimeter. ESR spectroscopy is used as the diagnostic tool.<sup>1</sup> The results indicate a range of application from  $<10^2$  to  $>10^9$  rad with uncertainties of  $\leq 15\%$ . The advantages over other types of polymer dosimeters are discussed. Also, the potential use of this dosimeter in obtaining spectral information and profile data for various types of radiation sources is illustrated.

## EXPERIMENTAL PROCEDURE

### Material and Preparation

The PTFE samples were in the form of rods, blocks, or slices. The rods were 11-mm segments cut from 1/8-in.-diam Teflon T.F.E. rod obtained from The Fluorocarbon Company. The blocks were 1 x 1 x 2 cm cut from 1 x 2 x 2 cm pieces of DuPont's Teflon<sup>(R)</sup> 7, a high molecular weight PTFE. The irradiated slices were 40  $\mu$  thick, cut from either the 1 x 1 cm or the 1 x 2 cm side of the block. Slices cut from irradiated blocks were generally 40  $\mu$  x 1 cm x 1 cm.

The slices were cut on an American Optical Co. Model 860 sliding microtome. Blade angle was adjusted so that the slice coiled tightly and resembled a cylinder  $\sim$  1 mm diam x  $\sim$  1 cm long.

For irradiations in air, both slices and rods were mechanically fastened (e.g., no adhesives were used) inside polystyrene boxes ( $\sim$  1 x 1 x 1/2 in.) and oriented so that the radiation was incident perpendicular to the cylindrical axis. These boxes and the blocks were placed on a meter stick, the blocks being covered by larger polystyrene boxes and oriented so that the radiation was incident upon the 1 x 1 cm face.

Most samples were irradiated in the presence of air and were shielded by polystyrene as described; however, some air-saturated and all vacuum-irradiated samples were contained in pyrex or quartz tubes. Samples for irradiation in vacuo were prepared from slices degassed at  $\leq 10^{-5}$  torr from 3 to 14 days at room temperature or 180°C and sealed under vacuum in either 4-mm pyrex or 7-mm quartz tubes. After irradiation, the air-saturated samples were

transferred to unirradiated sample tubes. The degassed samples were inverted and the end of the sample tubes heated with a gas-oxygen torch, care being taken to avoid heating the Teflon samples. After cooling, the sample was reinverted for ESR measurements. The heating procedure is necessary to avoid observation of radical signals produced by the irradiation in the sample tubes themselves.

### Irradiation

Most irradiations were performed at the UCLA Laboratory for Radiation Biology and Nuclear Medicine with a nominal 10,000 Ci  $^{60}\text{Co}$   $\gamma$ -radiation source. The dose rates at the various distances from the source were determined by  $\text{FeSO}_4$  dosimetry.<sup>2</sup> Several sets of runs were made with irradiation times ranging from 6 to 140 hr. Some preliminary runs were also made with  $^{60}\text{Co}$  sources at Atomics International and at the Air Force Cambridge Research Laboratories. In addition, electron irradiations were performed at Physics International.

### Instrumentation and Standardization

The samples were analyzed with a Varian V-4502 X-band ESR spectrometer equipped with 100-Kc field modulation. The magnetic field was controlled and swept by a VFR-2100 Fieldial. The first derivative spectrum was recorded on a Mosely 2D-2 X-Y recorder synchronized with the Fieldial sweep. All spectra were recorded at low microwave powers to avoid saturation effects.

The samples were run in a dual-cavity system consisting of a sample cavity and a reference cavity containing a standard sample (a mixture of activated charcoal and KCl was used). Variations in the detection system

were reflected in variations in the signal intensities from the reference standard, which were then used to normalize sample data. This procedure made it possible to correct for long- and short-term variations in the detection system.

Absolute measurements were made by insertion of a primary standard containing a known amount of free radicals into the sample cavity. Absolute radical concentrations in the PTFE samples were then determined from comparison of the first moments of their ESR derivative spectra to those obtained from the primary standard, taking into account any variations in the reference standard signal intensity. Solutions of 1, 1-diphenyl-2-picrylhydrazyl (DPPH) were used as the primary standard. The DPPH concentration was monitored via optical absorption spectra and using published values for molar extinction coefficients (2).

#### Uncertainties

The  $\text{Co}^{60}$  source at UCLA has a high secondary electron radiation. Studies by Edgerton, Germeshausen, and Grier, Inc. (Santa Barbara)<sup>3</sup> show that unshielded samples receive an average 20% higher dose than shielded samples because of the secondary electron radiation. Therefore, the  $\text{FeSO}_4$  dosimetry of the  $\text{Co}^{60}$  source performed in the present experiments was done in well browned pyrex test tubes to avoid uncertainties arising from the  $\text{Co}^{60}$  source; the uncertainty in the present experiment is  $\leq 5\%$ . Browned glass, i. e., glass exposed to ionizing radiation long enough to become significantly brown in color, is thought not only to be a more effective trap for secondary electrons than is unbrowned glass, but also to have less secondary radiation of its own.

The polystyrene boxes used to contain the PTFE samples were an effective trap for secondary electrons. Some samples, however, were irradiated in unbrowned pyrex or quartz sample tubes. At low doses, the actual dose received by the latter samples could be as much as 30% higher than calculated because of secondary electron radiation. At the higher doses, where discoloration of the glass container was significant, there was less difference,  $\leq 5\%$  above  $10^7$  rad.

The uncertainty in positioning the meter stick (with the samples attached) with respect to the source was about 1 mm. Most samples were more than 10 cm from the source, and the uncertainty was  $< 3\%$ . The uncertainties in positioning test tube samples correspond to dose uncertainties  $\sim 10$  to  $15\%$  in the center of the source and  $\sim 10\%$  at 5 and 8 cm distances. These uncertainties are indicated in the applicable figures.

The relative uncertainties in the integrated EPR signal are  $\sim 5\%$  for short term and could be as high as  $10\%$  over 3 to 4 months. The reproducibility in the absolute DPPH calibration was  $\leq 10\%$ .

Additional uncertainties arose from variations from one sample to another in the radical yield per unit of absorbed energy. For samples obtained from different batches of material from the same or different sources, these variations could be as high as  $\sim 20\%$ . However, within a given batch of material from the same source, variations were  $\sim 5\%$ . In addition, unirradiated samples stored at room temperature for 6 to 12 months prior to irradiation gave virtually the same results as did samples that were used immediately.

## RESULTS AND DISCUSSION

### Radical Identification and Stability

#### Radicals Produced

The ESR spectrum obtained from PTFE slices irradiated and observed in vacuum is indicated in Fig. 1. The radicals giving rise to the spectrum in Fig. 1 have been identified as the chain and propagating fluorocarbon radicals (3); see Fig. 2. Over the range  $10^6$  to  $10^8$  rad, the chain-to-propagating radical ratio is  $\sim 10:1$ ; at lower doses the signal is too weak to allow accurate estimates of the contribution of propagating radicals. If air is subsequently admitted to these samples, the corresponding peroxide radicals are formed in the same ratio (Fig. 2).

If the irradiation and observation are performed in air, the chain and propagating peroxide radicals are observed directly. The spectra obtained for samples irradiated and observed in air are indicated in Fig. 3. The variation in the spectral shape as a function of dose has been attributed to variations in the ratio of chain to propagating peroxide radical yields (3), since the chain peroxide radical is radiolytically converted to the propagating peroxide radical on prolonged exposure to radiation.

In air-saturated PTFE rod the same two radicals are formed, with the chain peroxide radical predominating at doses  $< 10^7$  rad. However, the variable ratio of the peroxides is not as evident with increasing dose, since at doses  $> 10^7$  rad the vacuum spectrum is also present, probably due to the depletion of oxygen in the center of the sample (via peroxide radical formation) and low diffusion of atmospheric oxygen into the sample. When they stand after irradiation ( $\sim 1$  year), the fluorocarbon radicals are gradually converted to the peroxide radicals in solid rod.

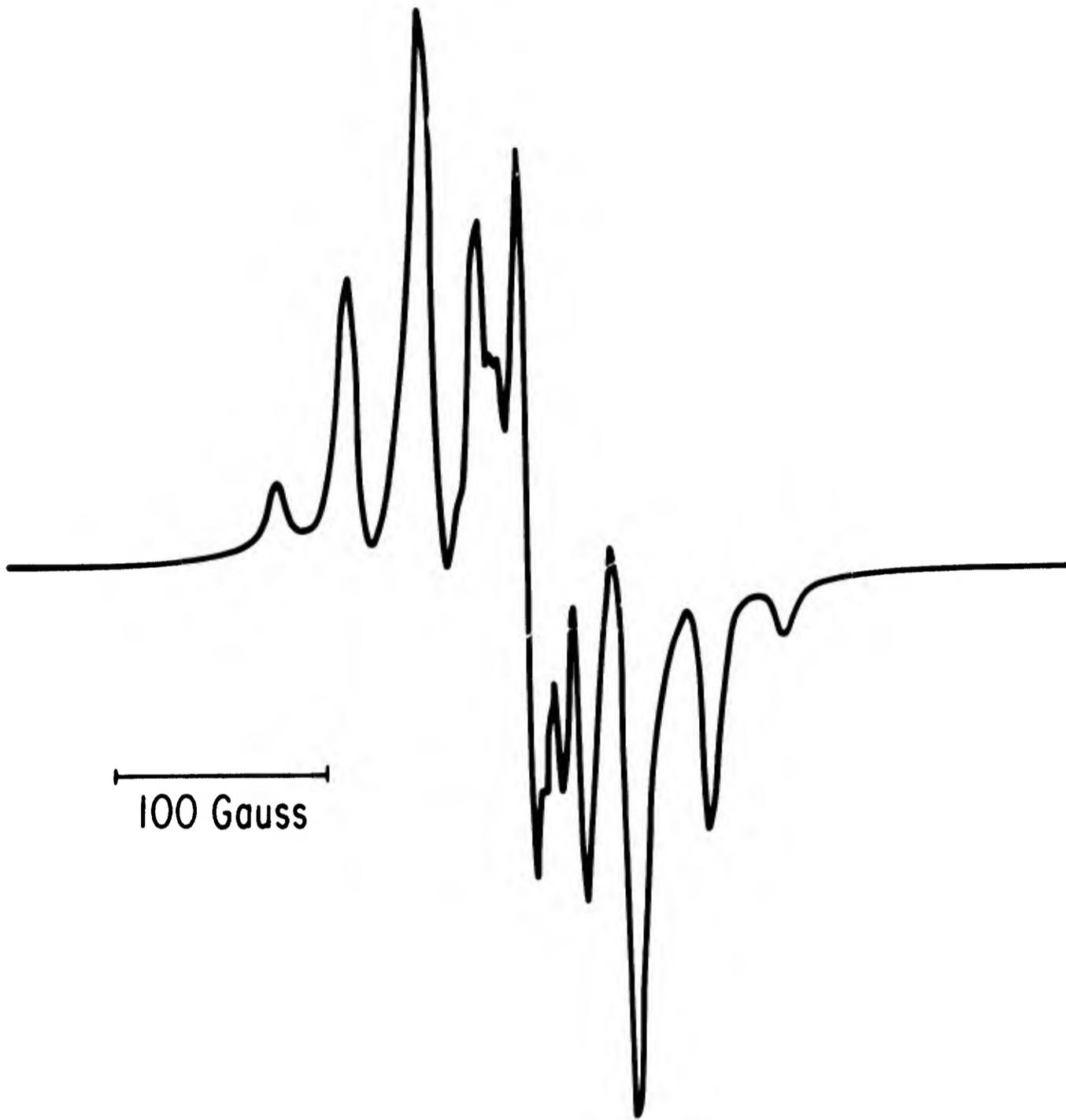
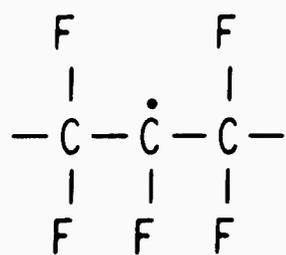


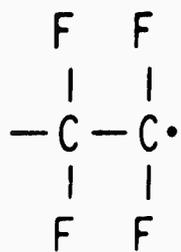
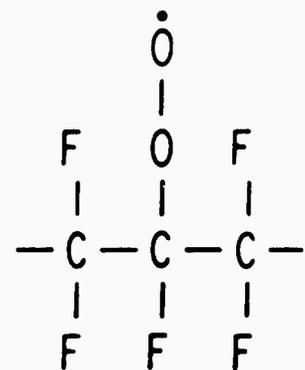
Figure 1. ESR Spectrum from PTFE Slices Irradiated and Observed in Vacuum  
(Spectral presentation is the first derivative of the absorption curve.)

FLUOROCARBON RADICAL

PEROXIDE RADICAL



CHAIN



PROPAGATING

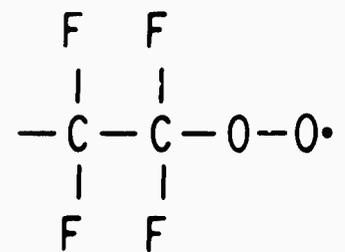


Figure 2. Free Radicals Produced in Irradiated PTFE

(The fluorocarbon radicals are observed when irradiation and observation are performed in vacuum. In the presence of air, the corresponding peroxide radicals are obtained.)

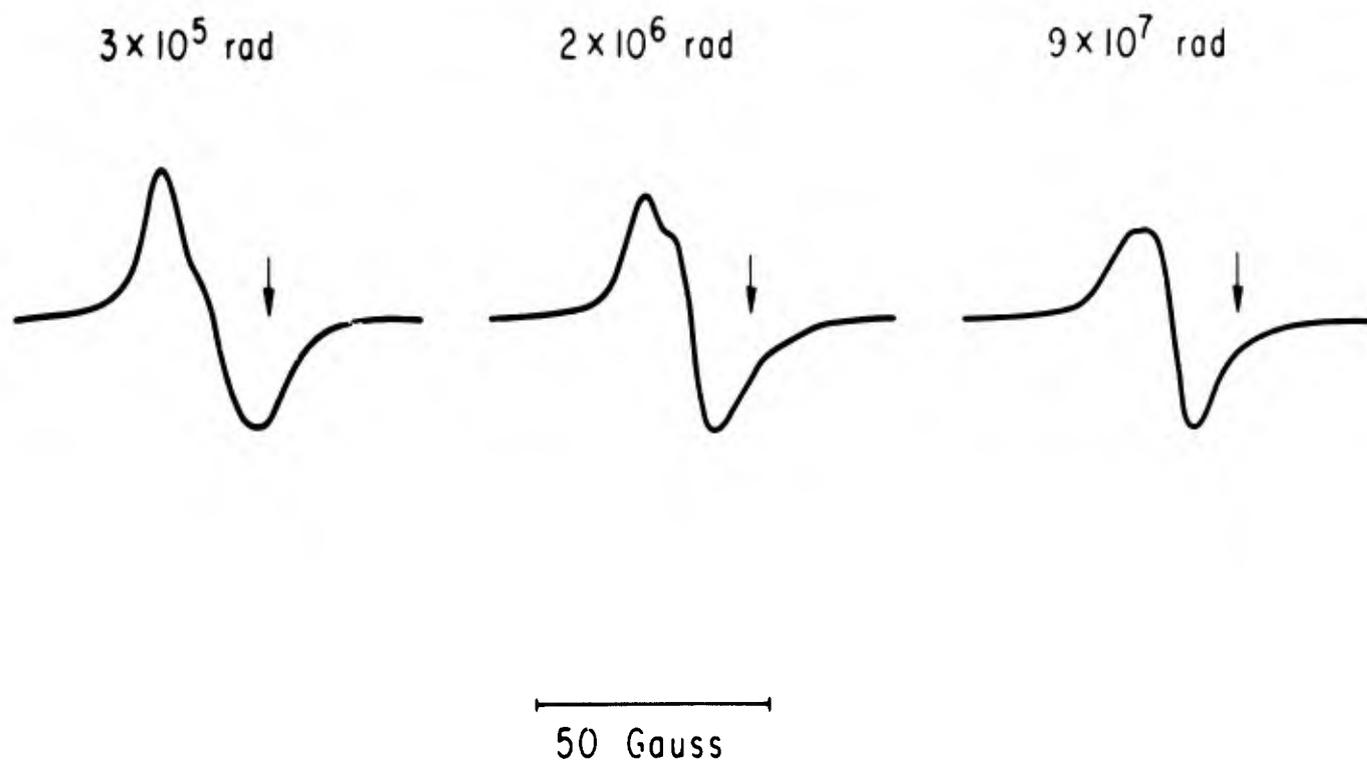


Figure 3. ESR Spectra from PTFE Slices

[Spectral presentations are the first derivative of the absorption curves. The spectral intensities have been arbitrarily adjusted for presentation. Experimentally the intensities increase significantly from left to right. The arrows indicate the g-value of DPPH (2.0036).]

Although the reader is referred to Ref. 3 for detailed analysis and interpretation of the spectra, one comment is worthy of mention here. The spectra of the peroxide radicals are considerably narrower than those of the fluorocarbon radicals. Since the integrated spectral intensity is the same for the same total numbers of free radicals, reduction in spectral line width results in an increase in peak height intensity. This is quite significant in the present case (a factor of  $\sim 10$ ). Consequently, when small radical signals are expected (low doses), it is better to use air-saturated samples, since these will give a better signal-to-noise ratio. Or, if the irradiation is performed in vacuum, samples should be exposed to air ( $O_2$ ) before measurement to convert the fluorocarbon radicals to the corresponding peroxide radicals.

#### Radical Stability

After irradiation the PTFE radicals exhibited a short-term ( $< 20$  days) decay. The rate and extent of the decay were inversely proportional to dosage. Figures 4 and 5 illustrate typical decay curves for air-irradiated PTFE rods and slices. The subsequent decay of the free radical concentration after 20 days, if any, is comparable to the experimental uncertainty (e. g. ,  $\leq 10\%$  after 6 months). The data in Figs. 4 and 5 are for the total radical signal. Detailed analysis of the spectra indicated that the propagating peroxide radical decayed somewhat more than the chain peroxide radical.

Slices of PTFE irradiated and stored in vacuum at doses ranging from  $5 \times 10^5$  to  $10^8$  rad were compared to slices irradiated in air 1 and 2 weeks

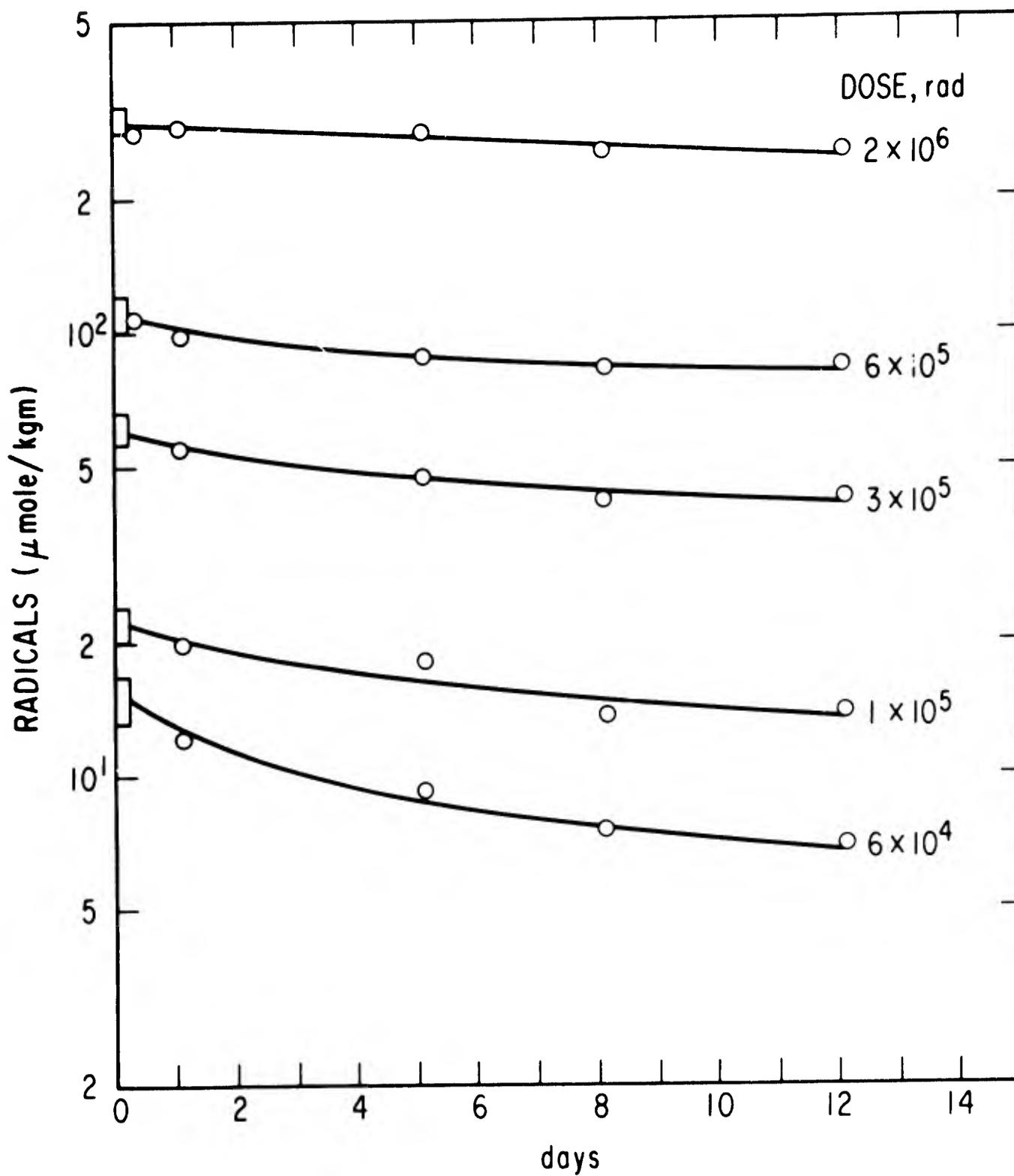


Figure 4. Radical Concentration in 1/8-in. Solid Rod as a Function of Time after Irradiation (Samples were irradiated and observed in air.)

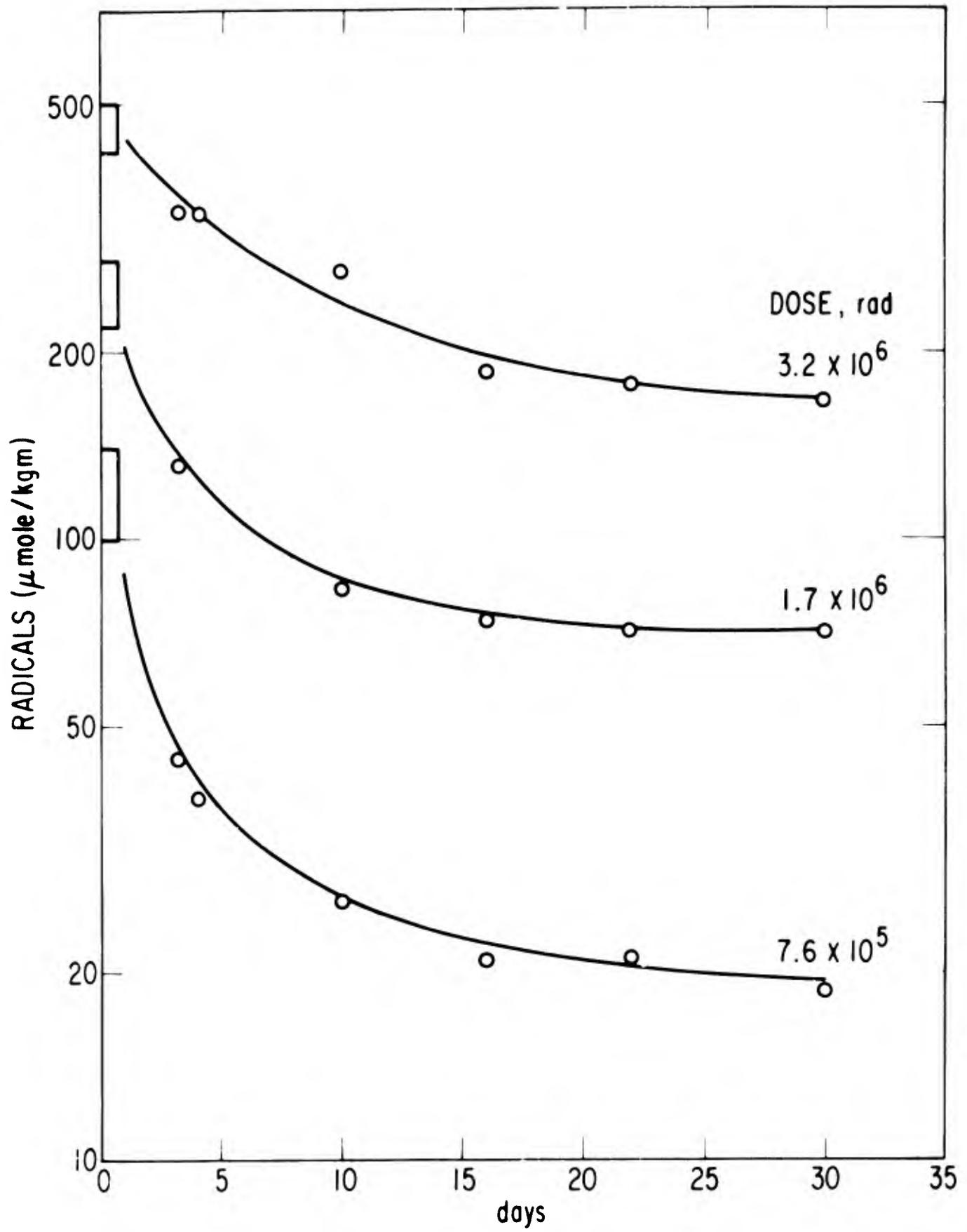


Figure 5. Radical Concentration in  $40\text{-}\mu$  Slices as a Function of Time after Irradiation  
(Samples were irradiated and observed in air.)

after irradiation. The maximum differences in radical concentration were 20 to 25%. Later work showed that during this period the air-irradiated slices decayed by nearly a factor of 4 at  $5 \times 10^5$  rad and perhaps 10% at  $10^8$  rad. In another experiment, over a 1-year period, a  $10^8$  rad vacuum-irradiated sample exhibited little or no decay, while  $10^6$  rad vacuum-irradiated samples decayed by  $\geq$  a factor of ten. It is therefore concluded that the vacuum slices also decayed at the low dosages. Although the decay characteristics for degassed samples were similar to those for aerated samples (e. g. , a short-term decay followed by long-term stability), quantitative correlations indicate that the fluorocarbon radical decay may be somewhat greater ( $\sim$  a factor of two) than the peroxy radical decay. No attempt was made to correlate air-saturated and degassed results for thicker samples because of the difficulty in degassing thick PTFE samples.

Because of the short-term signal decay after irradiation, some care must be taken in analyzing data. Curves such as those in Figs. 4 and 5 could be used to empirically correct for the amount of decay occurring in the time interval between radiation and observation. An alternative procedure might be to anneal samples at  $\sim 50$  to  $100^\circ\text{C}$  after irradiation to expedite the transition indicated in Figs. 4 and 5. In this case, the correction would be independent of the time between irradiation and observation. While the annealing procedure would probably be more desirable and easier from the standpoint of making empirical corrections,<sup>4</sup> experiments have not been conducted to test the feasibility of such a procedure or to define the necessary experimental parameters.

## Dosimeter Standardization and Use

### Radical Yield

The radical concentration produced for air-irradiated samples and for a given radiation dose is indicated in Fig. 6. The data have been corrected for the amount of radical decay occurring between irradiation and observation by use of the curves in Figs. 4 and 5 (e. g., the data in Fig. 6 represent radical concentrations at the termination of the radiation). The linearity of the data in Fig. 6 demonstrates the usefulness of PTFE as a radiation dosimeter. Similar data were obtained for degassed samples.

The major difference between the air-saturated and degassed samples is the slope of the straight line of the log-radical-concentration (R)-vs-log-dose (D) curve. For degassed samples, the slope of the log-log curve was 1.0 to within experimental error, indicating  $R \propto D$ . For aerated samples, however, the slope was .88 and  $R \propto D^{0.88}$ . This difference in slope results from the fact that the G-value (radicals produced per 100 ev of absorbed energy) decreases with increasing dose in air-saturated samples. This is illustrated in Fig. 7, which shows that the G value decreases from  $\sim 0.22$  to  $\sim 0.12$  over the range  $1 \times 10^5$  to  $1 \times 10^7$  rad in air-saturated PTFE. By comparison,  $G \approx 0.22 \pm 0.02$  over a similar dose range for the degassed samples. Thus, while the radiation yields are the same at low doses, they differ by a factor of two at the high doses. The anomaly may be due to an efficiency of  $< 100\%$  for the chain-to-propagating peroxide radical conversion, which occurs upon prolonged irradiation; a small amount of diamagnetic product may be formed in the reaction.

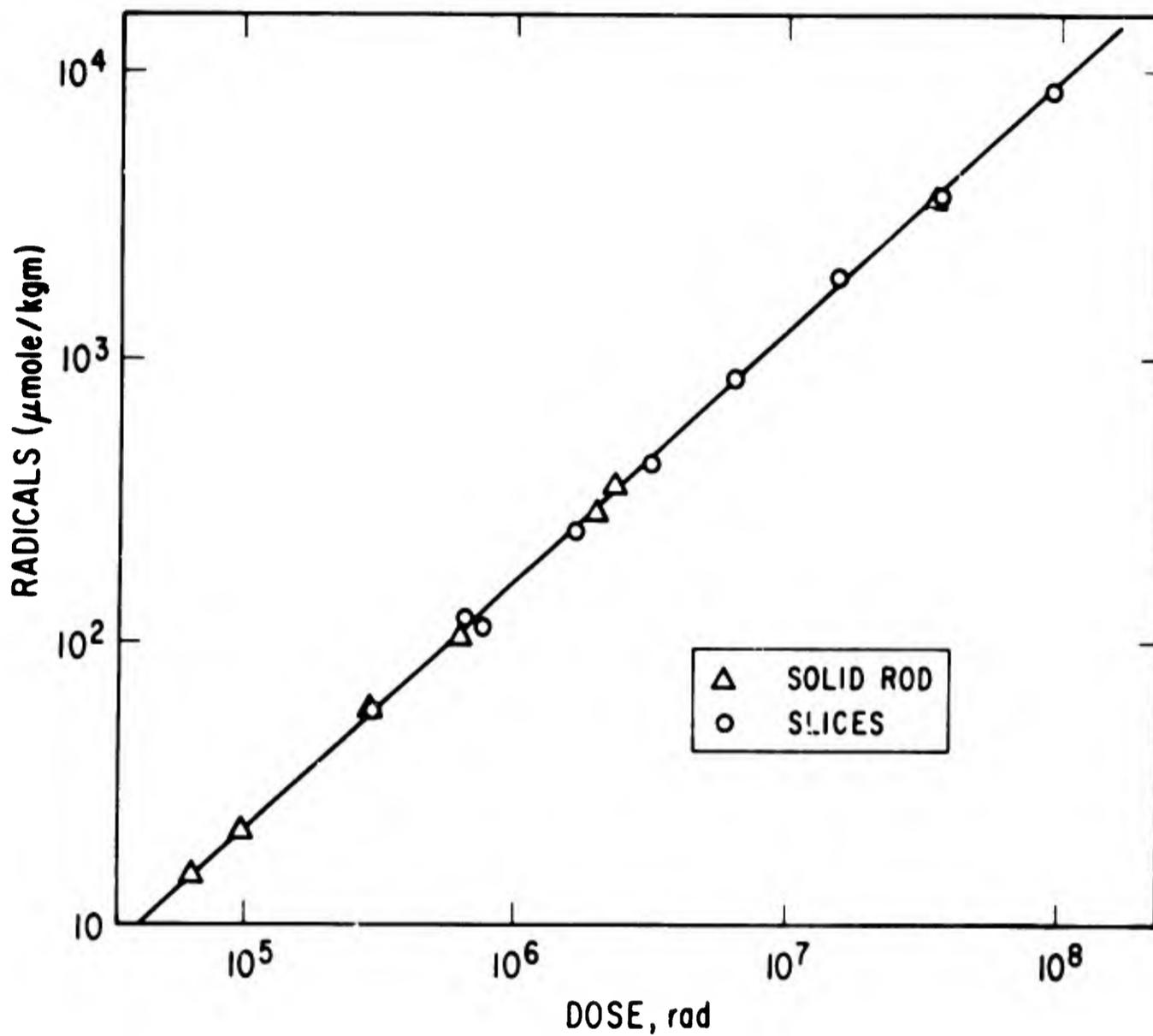


Figure 6. Radical Concentration in Air-Saturated PTFE as a Function of Total Dose

[Data have been corrected for decay loss between radiation and observation (see text). The straight line in the figure represents a plot of the equation  $R = 0.87 \times 10^{-3} (D)^{0.88}$ , where R is the radical concentration ( $\mu$  mole/kgm) and D is the dose (rad).]

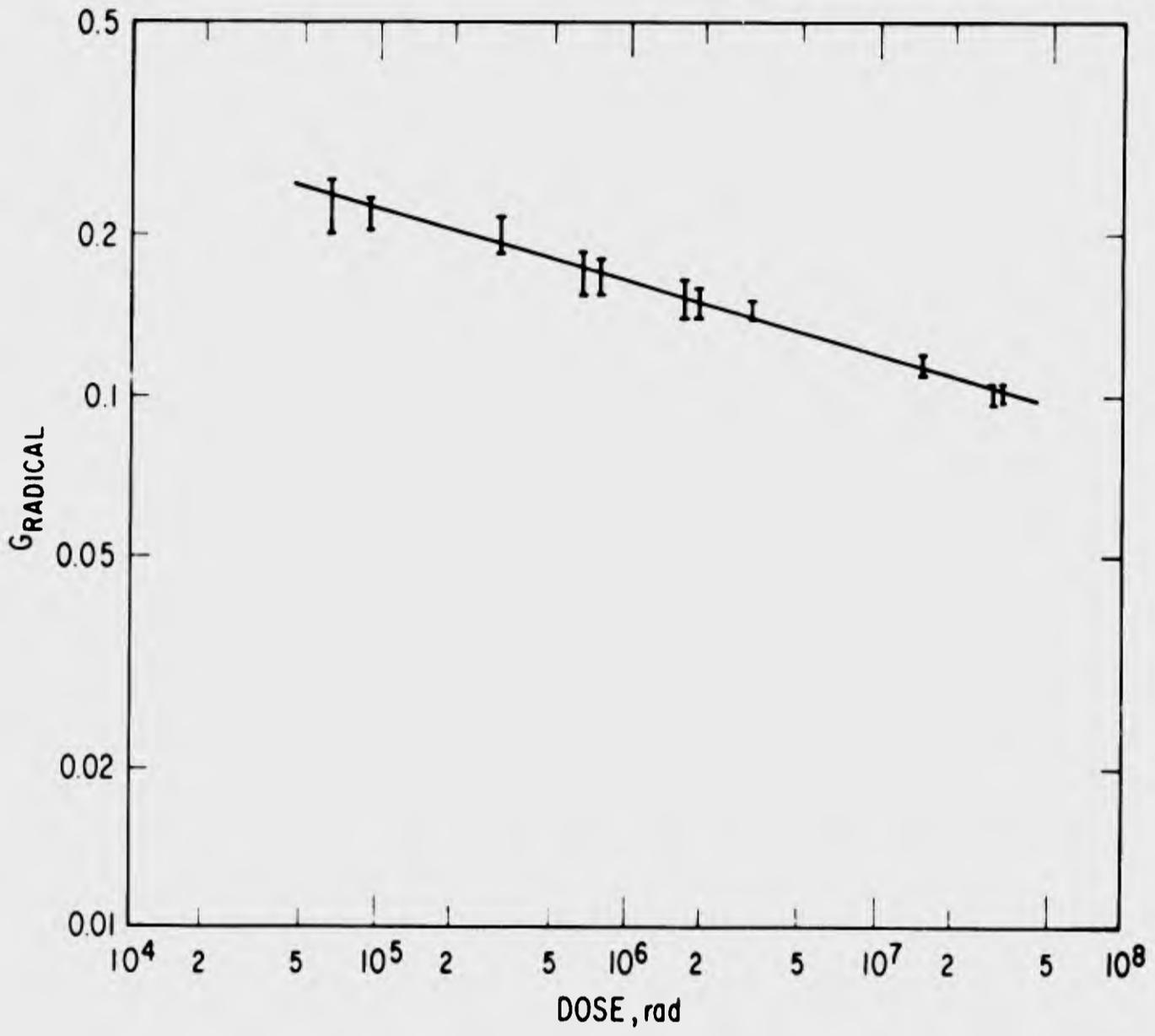


Figure 7. Radical Yield in PTFE Rod as a Function of Total Dose  
 (Samples were irradiated and observed in air.)

The decrease in yield with increasing dose does not limit the usefulness of PTFE as a dosimeter, but necessitates use of the experimentally determined yield-vs-dose curve. Alternatively, an empirical correction to the yield could be made with data similar to those in Fig. 7, in which case the corrected yield would be directly proportional to dose.

#### Dose - Depth Curves

For low-energy photons or particulate radiation, PTFE can be used to determine source spectral information. The only requirement for the analysis is that an appreciable fraction of the incident energy be absorbed by the sample thickness or, more exactly, that a gradient in the energy deposition exists in the sample. Under these conditions, analysis of the radical yield as a function of depth can be used to determine the energy of the incident photons or particles or, in the case of a polychromatic source, the energy distributions.

An example of a dose - depth curve is illustrated in Fig. 8. The sample was irradiated with 5-Mev electrons at Physics International. The solid curve in the figure represents a Monte Carlo calculation of electron energy deposition. The experimental data were obtained by irradiation of a 1-cm-thick PTFE block and sectioning of the sample after irradiation. With microtoning procedures, depth definition of 5  $\mu$  is obtainable at total doses  $> 10^4$  rad. For lower doses, some definition must be sacrificed because of sensitivity limitations (e. g., for  $10^3$  rad, definition is only 50  $\mu$ ).

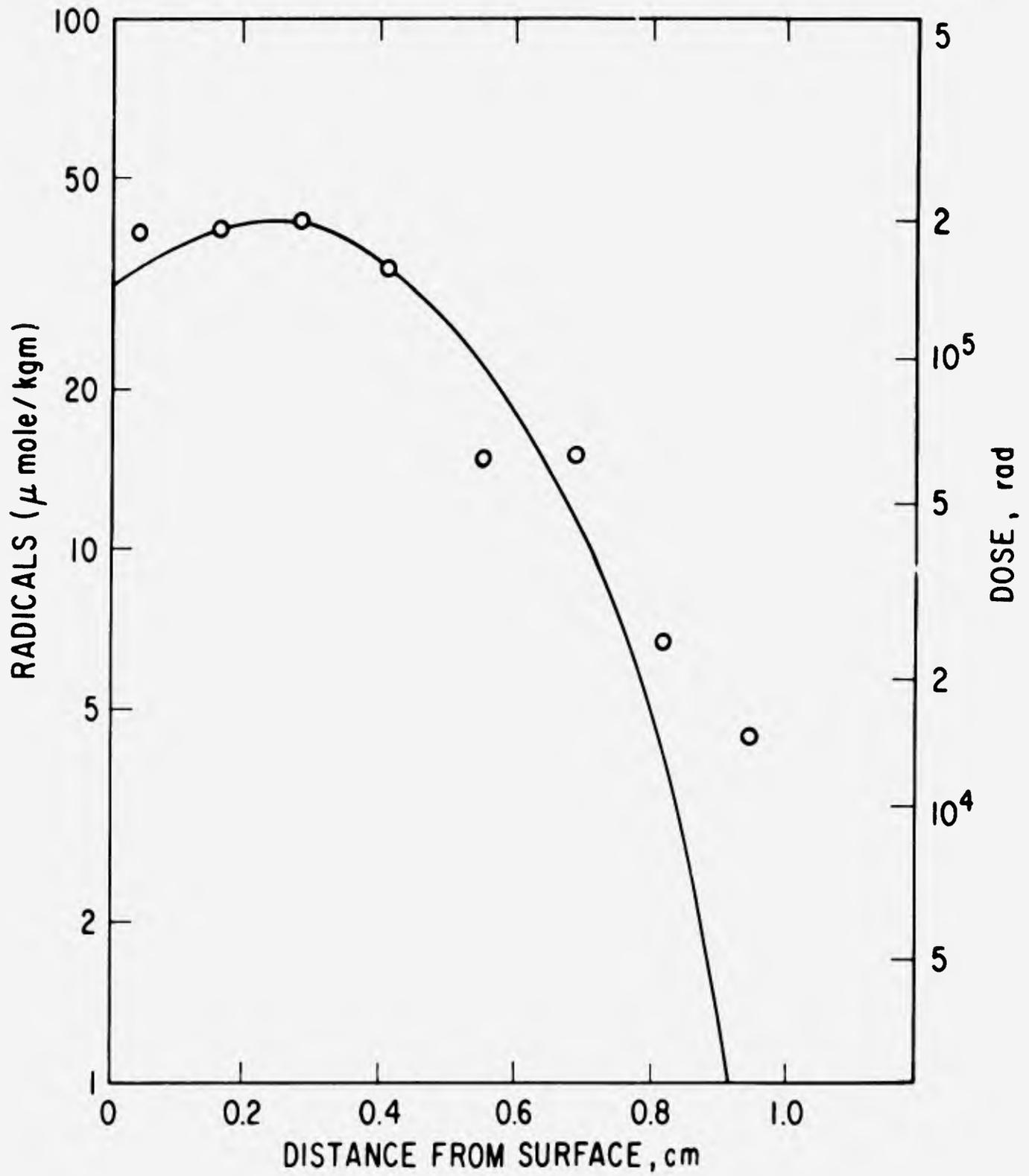


Figure 8. Radical Concentration as a Function of Distance from the Incident Surface for Electron-Irradiated PTFE (Sample was irradiated and observed in air.)

Dose - depth information is of further advantage in cases in which contained samples are irradiated by very penetrating radiations (e. g. , Co<sup>60</sup> rays), but a background of low-energy radiation is also present. Secondary electrons from container walls can be a problem. With dose - depth curves, determined from PTFE, the contribution from this source can be isolated and compensated for.

#### Other Considerations

##### Microtoming

During the experiments in which microtoming procedures were employed, it was found that the microtoming process led to some radical destruction. The fraction of radicals destroyed varied with slice thickness in a fairly reproducible manner, as is shown in Fig. 9. Thus, in experiments in which samples are microtomed to thicknesses  $< 100 \mu$  after irradiation, an empirical correction must be made to obtain the "uncut" radical yield.

The reproducibility indicated in Fig. 9 is, of course, a reflection of experimental procedures used in this laboratory. It is likely that samples processed elsewhere might give results somewhat different than those indicated, depending upon the microtome used and the procedures. The most likely explanation of these results is that the pressure applied to the sample by the knife causes the losses. This could be due to molecular reorientations resulting from the applied pressure, bringing two radicals in close proximity to one another and permitting recombination. In a

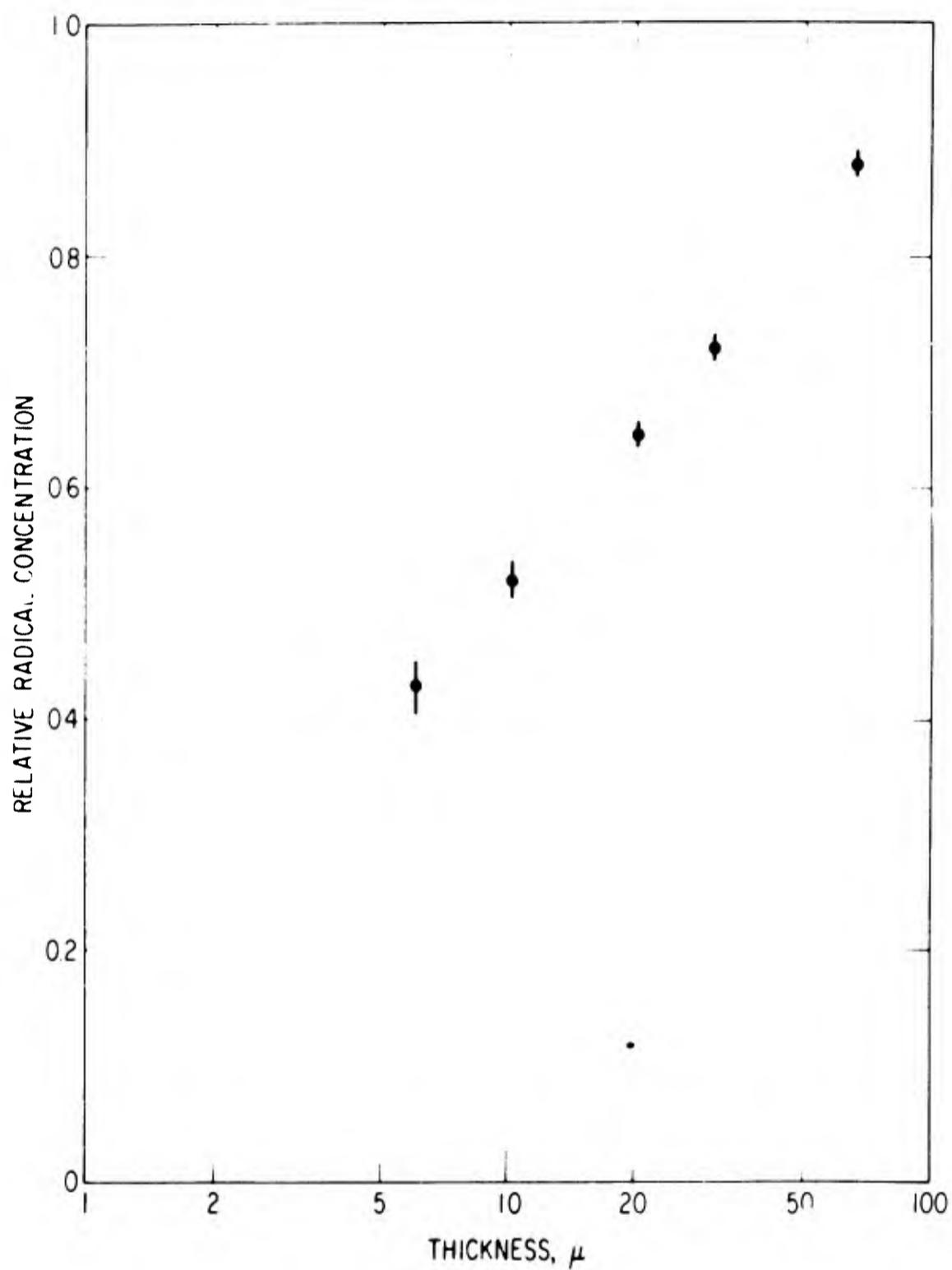


Figure 9. Radical Concentration as a Function of Slice Thickness for Blocks Irradiated to  $10^6$  Rad  
(Radical concentrations for samples microtomed after irradiation are relative to that obtained in the uncut block.)

separate experiment a  $\gamma$ -irradiated PTFE sample was compressed in a high pressure cell to  $\sim 5$  kbar. The radical signal was almost completely destroyed during this compression.

#### Temperature and Dose Rate Effects

In one experiment, air-saturated block samples were irradiated as a function of temperature from 25 to 127°C (these samples were  $\text{Co}^{60}$ ,  $\gamma$ -irradiated to a total dose of  $\sim 10^6$  rad). The result of this experiment indicated a temperature effect resulting in a radical yield that gradually increased with temperature. Thus the G value at  $\sim 120^\circ\text{C}$  was about 50 to 60% higher than that obtained at 25°C. One possible explanation of these results is that at the lower temperatures cage effects are more prevalent and limit radical production. That is, the two radical fragments produced by molecular bond rupture have low mobilities and consequently a high probability for recombining before diffusion away from one another. At higher temperatures (increased mobility) there would be less chance for cage recombination, and the fluorine atom produced could escape, leaving a stabilized radical. Ultimately, of course, a temperature would be reached where mobilities are sufficiently high to permit recombination of neighboring radicals. At this point yields would begin to drop again.

These temperature effects could become important in cases in which irradiations are performed at very high dose rates (e. g., pulsed accelerators). In these cases, the energy deposition rate could result in thermal spikes and corresponding ambiguity in radical yields unless some care is exercised in allowing for thermal considerations.

In addition to the thermal effects indicated above, it is likely that nonthermal dose rate effects may exist for pulsed irradiation of air-saturated PTFE. The radical yield (G-value) in the aerated polymer decreased with increasing dose (Fig. 7). This result was interpreted in terms of reactions associated with the radiation sensitivity of the chain peroxy radical and its radiolytic conversion to the propagating peroxy radical. An efficiency of  $< 100\%$  was assumed for the conversion to explain the lower G-value at higher doses. In the case of pulsed irradiation, where the pulse width is much less than the time required for oxygen diffusion and reaction with the primary fluorocarbon radicals, the radiolytic conversion of chain peroxy to propagating peroxy radical cannot occur. Consequently, the G-value should remain constant over the entire dose range. This effect would be important only at total doses greater than  $\sim 10^6$  rad. However, with the latter type of energy deposition over a short time interval, thermal dose rate effects could also occur and could mask the nonthermal effect.

#### Irradiation in Atmospheres Other Than Air

Great care must be exercised if the irradiations are to be performed in atmospheres other than air. While rare gas atmospheres will probably not affect results, irradiation in a hydrogen atmosphere would yield no radicals detectable by ESR because the fluorocarbon radicals react very readily with hydrogen to form diamagnetic products (3, 4). Gases other than hydrogen (e. g.,  $\text{CH}_4$ ,  $\text{NH}_3$ ) are also reactive to varying degrees (4, 5).

**BLANK PAGE**

## SUMMARY OF CONSIDERATIONS FOR USE OF PTFE AS A DOSIMETER

### Batch Control and Standardization

Because of variations in the radiation yield of radicals from one batch of material to the next, it is desirable to calibrate each new batch of material. This can be done with  $\text{Co}^{60}$   $\gamma$ -radiation.

### Sample Geometry

#### Air-saturated Samples

The first decision regarding the use of the PTFE dosimeter is that of sample geometry. At low doses ( $< 10^5$  rad), it is desirable to use thicknesses  $\geq 1/8$  in. The reasons for this are twofold: 1) With a large thickness the total number of radicals formed and the ESR sensitivity are greater, and 2) the radical decay, which is significant at low doses, is less in thick samples than in thin samples. With increasing dose, these considerations assume less importance, and smaller thicknesses could be used. In fact, it is desirable to use smaller thicknesses ( $\sim 40 \mu$  or less) at high doses. At doses  $> 10^7$  rad, the fluorocarbon radical spectrum begins to appear in solid rod, presumably because of the depletion of oxygen in the center of the sample (via peroxide radical formation) and the low diffusion of atmospheric oxygen into the sample. Since the radiation yields of fluorocarbon and peroxide radicals differ at high doses, some difficulty could be anticipated in determining the dose for thick samples above  $10^7$  rad.

For samples from which dose - depth information is desired, two alternatives are possible. These are: 1) use a solid block and microtome

after irradiation, or 2) premicrotome the sample and irradiate the stack of slices. The arguments presented in the preceding paragraph for using thick or thin samples apply here (e. g. , at lower doses it is preferable to use thick samples because there is less decay). Aside from these considerations, the choice between the two alternatives indicated for dose - depth samples is arbitrary. In 1) the sample is easier to handle, but corrections for microtome losses must be made. The opposite arguments apply for alternative 2).

#### Degassed Samples

Samples to be irradiated in vacuum are limited to thicknesses  $\leq \sim 40 \mu$  because of the slow gas diffusion in PTFE, which would require unreasonable times for the preparation of thicker samples. Degassed samples might be used in cases where the dosimeter is to be immersed in a liquid or in an atmosphere that would be reactive to the PTFE radicals. However, because of the nature of the ESR spectra, the lower limit of dose detection is approximately a factor of ten greater for degassed samples than for air-saturated samples. This limitation can be overcome, on the other hand, by mere exposure of the degassed samples to air ( $O_2$ ) after irradiation, which forms the peroxy radicals. Of course, because of the thin slice limitation, radical decay will also be more of a problem at lower doses.

#### Other Considerations

##### Contained Samples

When samples are to be contained, care must be exercised to avoid problems arising from secondary radiation from container walls. Alternatively, samples could be sectioned after irradiation to isolate contributions

from secondary radiation. There is one additional consideration regarding aerated samples contained in closed systems. It is important that sufficient air ( $O_2$ ) be present in closed systems to permit complete conversion of the fluorocarbon to peroxy radicals. If allowance is made for five times the required amount of oxygen,  $1 \times 10^{-8} \text{ cm}^3$  of  $O_2$  at STP/gm PTFE/rad,  $5 \times 10^{-8} \text{ cm}^3$  of air is required at STP/gm PTFE/rad. For a 1-gm sample irradiated to  $10^{10}$  rad (assuming the radical yield is proportional to dose at  $10^{10}$  rad), 500 cc of air is required. This feature (sufficient oxygen for reaction) is important because of the difference in radical yield for the fluorocarbon and peroxy radicals at high doses.

#### Temperature and Dose Rate

Because of radical yield variations with temperature, it is desirable to conduct irradiations at ambient temperature, although calibrations could be performed at other temperatures. At high dose rate (as in pulsed accelerators), yields may vary according to sample temperatures reached during radiation (thermal dose rate effects). At present, no information is available regarding the existence of nonthermal dose rate effects, although some experiments are planned to answer this question.

#### Measurement and Storage

Because of the short-term (3 weeks) partial decay that occurs immediately after irradiation, some care must be exercised in taking data. For low dose samples where sensitivity limits become a problem, it is desirable to make measurements as soon after irradiation as possible, because the percentage of short-term decay increases with decreasing dose.

Storage at room temperature for 6 to 12 months prior to irradiation had no adverse effects on dosimeter results. Because of photochemical reactions that occur in irradiated PTFE (3), it is desirable to store samples in the dark after irradiation.

## CONCLUSIONS

The use of PTFE as a passive radiation dosimeter has been demonstrated. With existing instrumentation, the applicable dose range has been shown to be  $10^4$  to  $10^8$  rad. The linearity of the results indicated in Fig. 6 suggests that the upper limit of the dosimeter is  $> 10^8$  rad, possibly as high as  $10^9$  or  $10^{10}$  rad. The lower dose limit is the result of sensitivity limitations. This limit could be lowered an order of magnitude by use of fluorocarbon polymers containing some FEP fluorocarbon. In one instance, PTFE containing 5% FEP fluorocarbon was found to exhibit a factor-of-7 increase in radiation sensitivity over 100% PTFE. An additional gain of a factor of 10 or more could be obtained by employing currently available signal averaging devices. Consequently, PTFE dosimetry is probably applicable over the range of  $< 10^2$  to  $> 10^9$  rad with uncertainties of  $\leq 15\%$ .

Polytetrafluoroethylene, used as described in this paper, offers several advantages over other types of polymeric radiation dosimeters. Foremost among these is the simplicity of the sample geometry requirements. The only restriction imposed by the ESR diagnostic technique is that the sample for observation must be capable of fitting into the spectrometer cavity. (If desired, larger samples could be used for irradiation and subsequently reduced to the size required for measurements.) Consequently, samples can be machined to any desired shape to accommodate source geometry requirements. Surfaces that may become scratched or distorted during preparation or use will not affect the measurements, unlike surfaces of

polymer dosimeters where optical transmission techniques are used. In addition, the test method is simple, quick, and nondestructive, so that samples can be reexamined after an extended period.

## FOOTNOTES

1. Free radicals are generally detected and measured with electron spin resonance (ESR) techniques. ESR spectroscopy takes advantage of the Zeeman splitting of magnetic energy levels in an applied magnetic field and measures transitions between the Zeeman levels. The technique is sensitive only to those molecules or fragments possessing unpaired electrons and is capable of detecting  $< 10^{11}$  unpaired electrons/cc. See M. Bersohn and J. C. Baird, An Introduction to Electron Paramagnetic Resonance, W. A. Benjamin, Inc., New York, 1966.
2. Aerated solutions of  $\text{FeSO}_4$  in 0.8N  $\text{H}_2\text{SO}_4$  were used, and  $G(\text{Fe}^{+3})$  was assumed to be 15.6.
3. Dr. L. Meyers, UCLA Laboratory of Nuclear Medicine and Radiation Biology, private communication.
4. For very low doses where sensitivity limits are reached, the short-term decay could be sufficient to reduce signal levels below the minimum detection limit. In these cases, measurements should be made without annealing, immediately after radiation.

## REFERENCES

1. C. Artandi, Nucleonics 17, 57 (1959).
2. H. E. Ungnade, ed., Organic Electronic Spectral Data, Vol. II, 1953 - 1955, p. 548, Interscience Publishers, Inc., New York, 1960.
3. S. Siegel and H. Hedgpeth, J. Chem. Phys. 46, 3904 (1967), and references therein.
4. T. Matsugashita and K. Shinohara, J. Chem. Phys. 35, 1652 (1961).
5. F. Ueda, Z. Kuri, and S. Shida, J. Polymer Sci. A1, 3537 (1963).

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Aerospace Corporation El Segundo, California		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE Free Radical Yields in Polytetrafluoroethylene as the Basis for a Radiation Dosimeter			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
5. AUTHOR(S) (Last name, first name, initial) Judeikis, Henry S., Hedgpeth, Herbert, and Siegel, Seymour			
6. REPORT DATE February 1968		7a. TOTAL NO. OF PAGES 36	7b. NO. OF REFS 5
8a. CONTRACT OR GRANT NO. F04695-67-C-0158		9a. ORIGINATOR'S REPORT NUMBER(S) TR-0158(3250-20)-6	
b. PROJECT NO.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) SAMSO-TR-68-140	
c.			
d.			
10. AVAILABILITY/LIMITATION NOTICES This document has been approved for public release and sale; its distribution is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Space and Missile Systems Organization Air Force Systems Command United States Air Force	
13. ABSTRACT Exposure of polytetrafluoroethylene (PTFE) to ionizing radiation results in chemical degradation of the polymer and formation of long-lived free radicals. This paper describes the use of quantitative measurements of the electron spin resonance (ESR) spectra of the free radical produced in irradiated PTFE to determine radical yields and attempts to correlate these radical yields with the absorbed radiation dose. The experimental results indicate sufficient correlation over the experimental range from 10 <sup>4</sup> to 10 <sup>8</sup> rad to permit use of PTFE as a passive radiation dosimeter. Analysis of the data indicates that, with minor modifications, the useful range can be extended to <10 <sup>2</sup> to >10 <sup>9</sup> rad with uncertainties ≤ 15 percent. The advantages inherent in the use of the PTFE dosimeter for the measurement of low energy electromagnetic or particulate radiation are also discussed. Energy deposition as a function of depth from the incident surface can be determined by sectioning of the polymer after irradiation. The resulting dose - depth curves can then be used to obtain spectral and profile data from polychromatic sources.			

KEY WORDS

Dosimetry  
Irradiated polymers  
Teflon

Abstract (Continued)