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DIVISION OF ISOTOPES DEVELOPMENT

on

RADIOISOTOPE AND RADIATION APPLICATIONS

April 18, 1962

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RADIOISOTOPE AND RADIATION APPLICATIONS

Duane N. Sunderman

This is the Twelfth Quarterly Progress Report on research programs in radioisotope technology and radiation chemistry under the sponsorship of the Division of Isotopes Development of the United States Atomic Energy Commission. The report period is January 1 to March 31, 1962. During this period research continued in the areas of intrinsic radioactive tracers for industrial process control and the influence of structural factors in radiation-induced graft polymerization.

During March, 1962, work was begun on a study of the effect of internal radiation on the physiochemical activity of catalyst materials. Progress in this area will be reported in subsequent quarterly progress reports.

Intrinsic-tracer research is being concentrated upon the use of isotope neutron sources of polonium-beryllium for the production of short-lived isotopes. Data are reported herein on the influence of volume, high-Z scattering media, target-isotope concentration, and macroscopic cross-section on specific and total activation produced with a 10-curie polonium-beryllium source. Future experimentation will investigate the use of a 50-curie polonium-beryllium source in a dynamic system simulating flow under process conditions.

Graft-polymerization research continues to evaluate the effect of structural factors on free-radical site concentrations and grafting efficiency. Present results indicate that the radical formed in a variety of substituted methacrylate polymers is the same in all cases. Attempts to employ radioactive iodine as a radical scavenger have been unsuccessful at low site concentrations but satisfactory at high doses. Dose-rate effects have been observed in radiation-induced free-radical formation in polymethylmethacrylate over the range of 10^4 to 10^6 rads per hr and total doses of 1.7×10^5 to 3.5×10^6 rads. Effects of temperature, crystallinity, structure, and molecular weight will be studied in future work.

I. USE OF INTRINSIC RADIOTRACERS FOR PROCESS CONTROL

James L. McFarling, Peter Gluck, John F. Kircher,
and Duane N. Sunderman

SUMMARY

Exploratory and optimization experiments on the use of in-process isotope neutron sources to produce short-lived intrinsic radiotracers were continued. The variables studied were activation-cell volume, target-isotope concentration, and the effect of a high-Z moderator around the source.

Experimental data relating activation-cell volume and macroscopic absorption cross section of the target solution were obtained. The range of solution cross sections studied varied from 2.22 to 19 x 10^{-2} barns per cm^3. Cell volumes ranged from 40 ml to 11 liters. Surrounding the neutron source with a 1/2-in. lead moderator was shown to give a marginal increase in efficiency in large volumes and an efficiency decrease in small volumes.

INTRODUCTION

Battelle is currently conducting a research program for the Division of Isotopes Development on the use of intrinsic radioactive tracers for industrial process control. The proof of principle for this concept has already been demonstrated on several laboratory-scale processes.

The objective of the present phase of this program is to investigate the feasibility of using in-process isotope neutron sources to produce short-lived intrinsic radiotracers. These tracers might be useful for stream analysis and process control in the same way as longer lived radiotracers. However, use of such short-lived radioisotopes will eliminate most contamination problems which could arise from use of long-lived tracers.

Previous reports have described the construction and operation of a neutron-source storage shield-activation cell assembly containing a 10-curie polonium-beryllium neutron source. The results of neutron-flux mapping in water around the source have also been given. The present report describes experiments aimed at determining optimum conditions for in-process tracer activations.

EXPERIMENTAL WORK

Neutron-Activation Optimization Studies

The effect of changing several variables has been studied as a continuation of the activation-cell optimization program. The following variables are among those considered important in a continuously operating process:

(1) Geometry of the activation cell

(2) Holding time in activation cell

(3) Activation-cell volume

(4) Concentration of target isotope and/or macroscopic absorption cross section

(5) Neutron moderators and shields used.

The first of these variables was found to be less significant than originally thought. For this reason, the majority of the experiments described were performed in simple cylindrical geometry. The second variable, holding time, is very important; but it is so closely related to tracer half-life and process requirements that it will not be studied until later in the program. The third and fourth variables were the parameters studied most intensively during this period, with some attention also being given to the fifth.

Activation as a Function of Volume and Target-Isotope Concentration

Experimental Techniques

The cylindrical activation-cell geometry used for this part of the investigation is shown in Figure I-1. The solution volumes employed ranged from 40 ml to 11 liters. The aqueous solutions studied were:

(1) Manganese sulfate

(2) Manganese sulfate plus cadmium sulfate

(3) Manganese sulfate plus boric acid

(4) Indium nitrate.

Manganese was chosen as the target isotope for the investigation because of its high sensitivity, desirable half-life, 100 per cent gamma emission, and low cost. Cadmium and boron were used because of their high neutron capture cross sections,

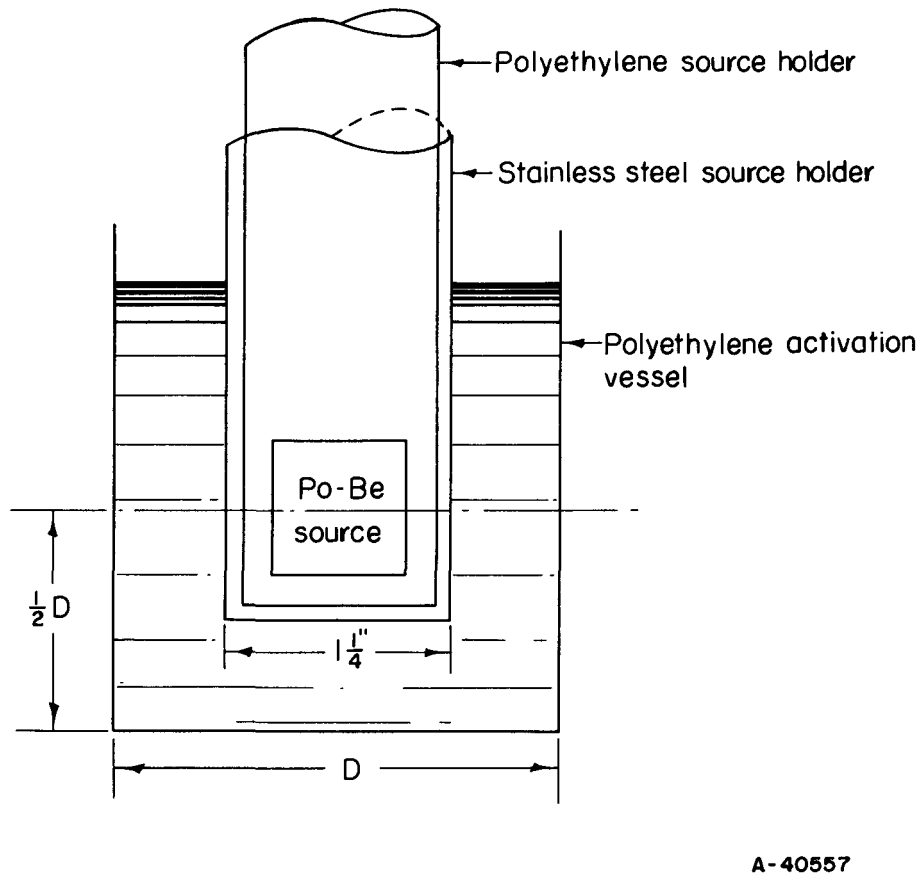

FIGURE I-1. IRRADIATION CELL FOR ACTIVATION EXPERIMENTS

which made it possible to achieve high macroscopic absorption cross sections. Indium was used for a few experiments in order to compare its behavior with that of manganese.

The experiments were carried out by irradiating each solution in the series of cylindrical vessels of different volumes. After irradiation, the activity of the solution from a given vessel was measured with the 750-ml, 2 by 2-in. NaI(Tl) dip counter described previously.[1] For activation-cell volumes of less than 750 ml, an aliquot of the active solution was diluted to a volume suitable for counting.

The measured manganese and indium activities, in counts per minute, were converted to disintegrations per second per milliliter at zero time. These are the maximum activities obtainable at saturation with a 10-curie polonium-beryllium source. In these calculations counting-cell efficiencies of 10.0 ± 0.1 and 7.8 per cent were used for manganese and indium, respectively. The indium calibration is not as accurate as that for manganese since only one determination was made.

Experimental Results

The results of the experiments relating cell volume and solution concentration are shown graphically in Figures I-2, I-3, and I-4.

Figure I-2 shows the relationship between gross activity, solution volume, and target-isotope concentrations. Here, the concentration of solution goes up to a manganese equivalent of 1200 g per liter. This concentration, which is some five or six times the maximum solubility of manganese in water, is achieved by adding cadmium to a solution containing from 10 to 30 g per liter of manganese. The macroscopic absorption cross section of this solution is then the same as it would be if 1200 g per liter of manganese was used. It is obvious from the figure that in solutions of high manganese equivalent there is very little increase in gross activity. This indicates that the neutrons are being absorbed essentially as fast as they are thermalized.

In Figure I-3 the results are plotted somewhat differently, namely, as gross activity versus macroscopic absorption cross section. In this figure the results from the manganese-boron solution activations are also shown. The data indicate that there is very little difference between the absorption characteristics of the boron and cadmium solutions.

The comparison between the results for indium and manganese solutions are shown in Figure I-4. The gross activity is divided by the decay constant for the isotope so that the results may be compared directly. It is evident that there are some differences between the activation characteristics of these solutions, as might be expected from their different neutron-absorption modes. Manganese is approximately a 1/v absorber while indium has significant resonance absorption.

Effect of Surrounding Source With a High-Z Moderator

It is known from the neutron-energy spectrum emitted by a polonium-beryllium source[2] that most of the emitted neutrons have energies greater than 4 Mev. These

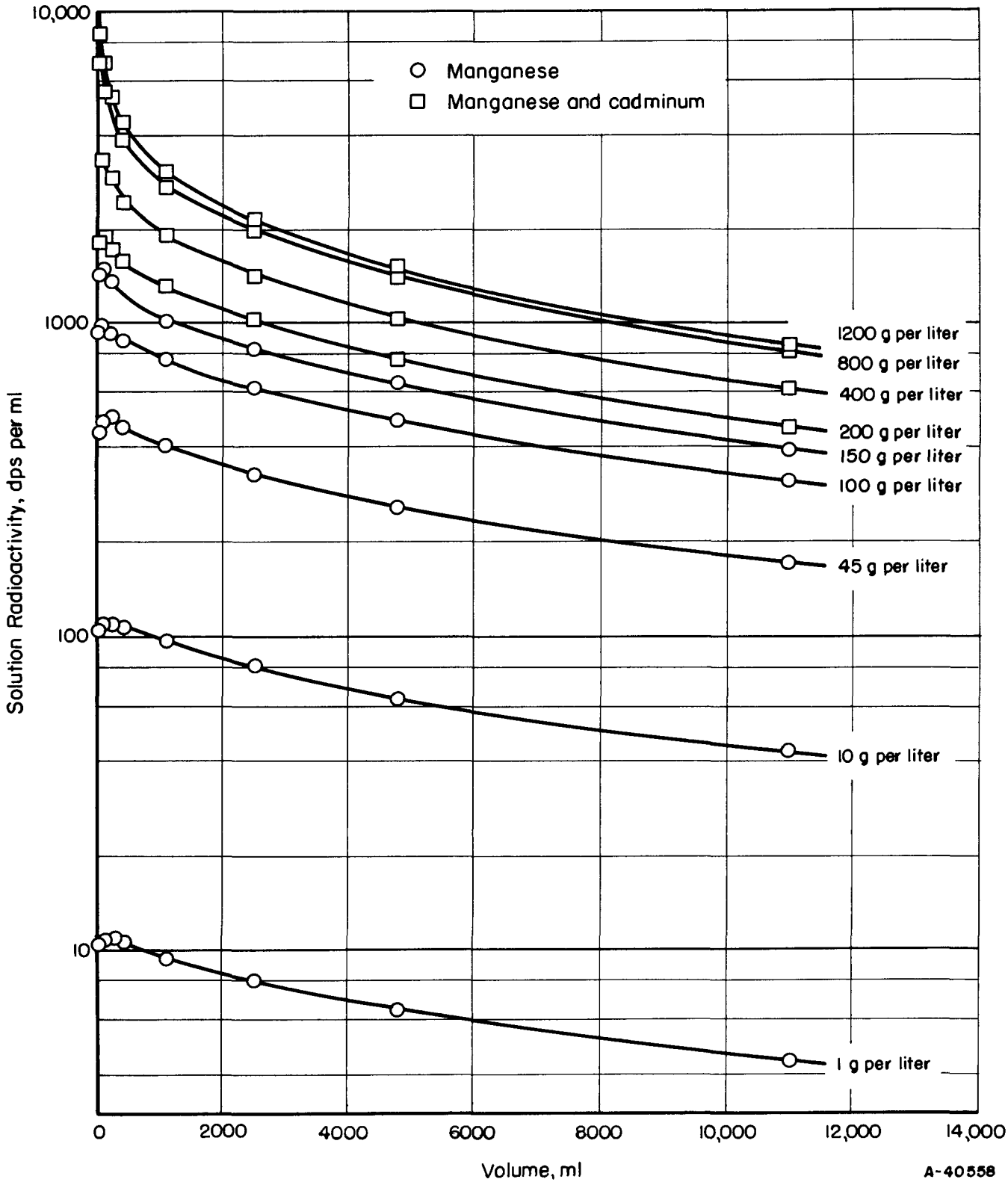

FIGURE I-2. GROSS SOLUTION ACTIVITY IN RELATION TO CELL VOLUME AT DIFFERENT MANGANESE CONCENTRATIONS

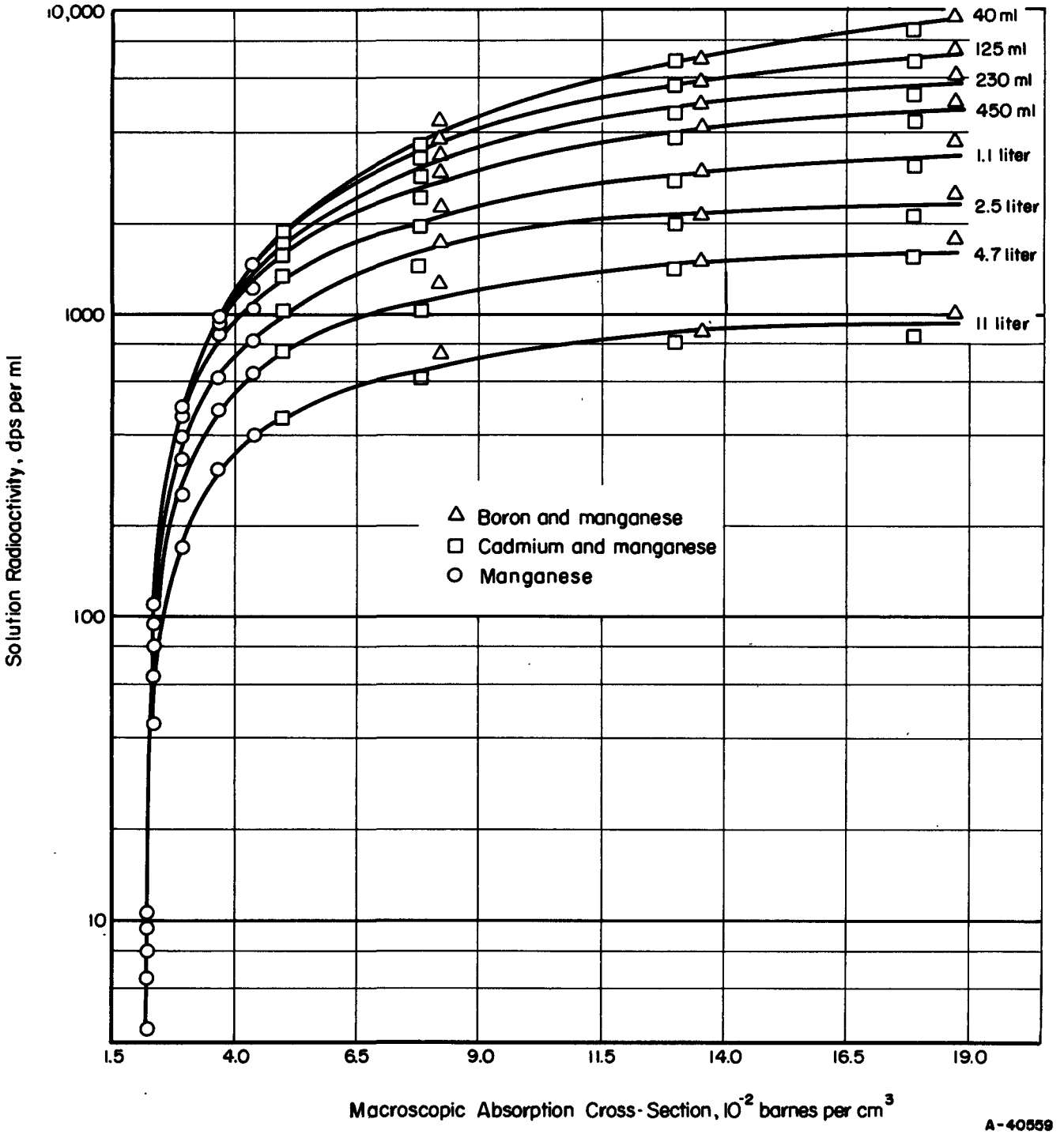

FIGURE I-3. RELATION OF GROSS SOLUTION ACTIVITY TO MACROSCOPIC ABSORPTION CROSS SECTION IN DIFFERENT CELL VOLUMES

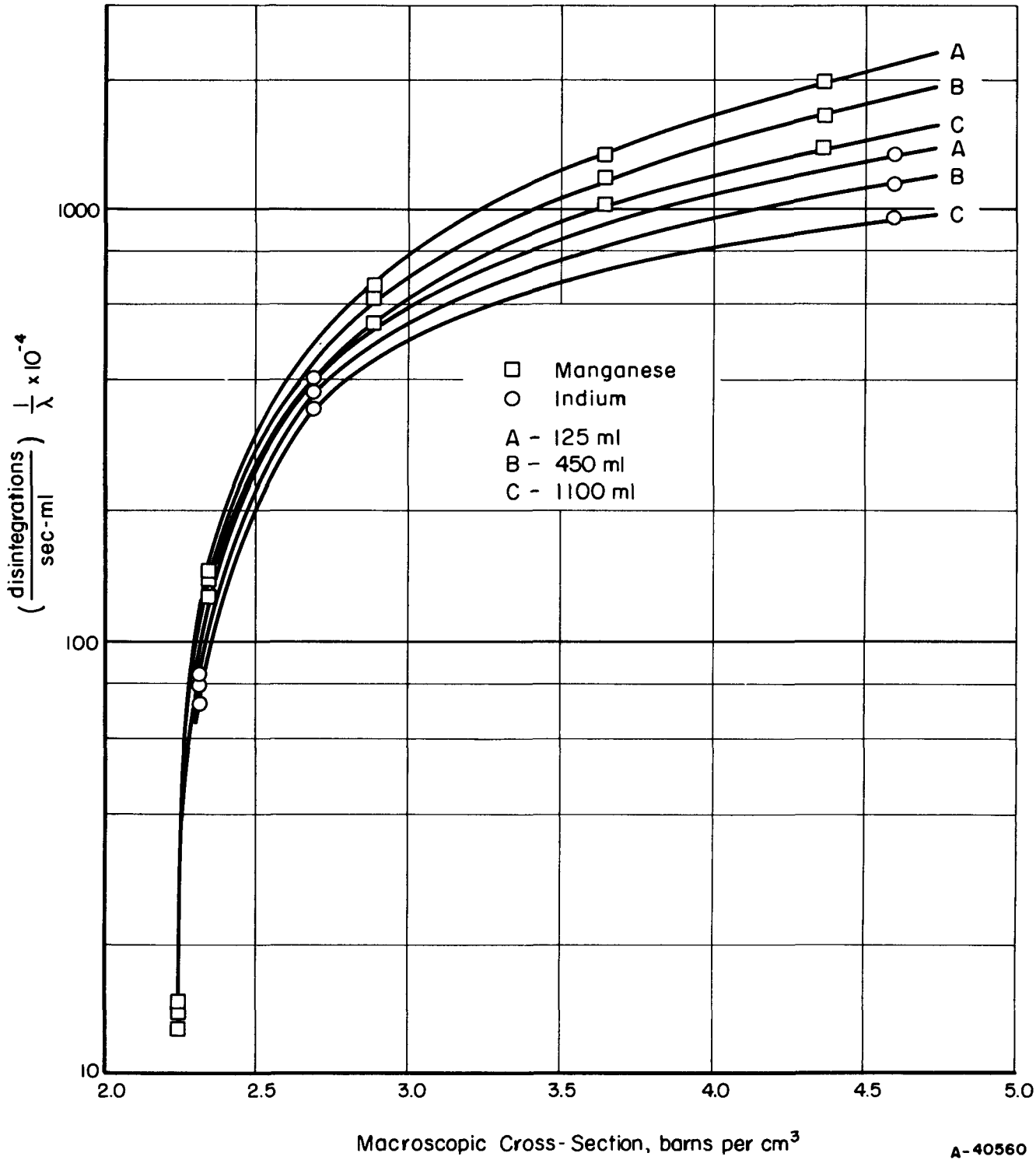

FIGURE I-4. GROSS ACTIVATION OF INDIUM AND MANGANESE AS A FUNCTION OF MACROSCOPIC CROSS SECTION IN THREE CELL VOLUMES

high-energy neutrons are moderated more effectively by high-Z nuclei than by low-Z nuclei[3]. Therefore, it was thought desirable to determine the effect of interposing a high-Z moderator between the neutron source and the solution being activated. Several such experiments at different solution concentrations were carried out using the setup illustrated in Figure I-5, with lead as moderator. A paraffin moderator of the same thickness was substituted in order to provide a water-equivalent material for comparison.

The results of the experiments are shown graphically in Figure I-6. It is apparent from the data that there are significant differences in the activation efficiencies observed with the two moderators; however, the use of the high-Z moderator only gave improved efficiency in large cell volumes.

Neutron-Activation Sensitivities of the Experimental System

Neutron-activation sensitivities are of primary importance in order to put this general method of process control in the proper perspective. Therefore, sensitivity data were obtained on several common elements with the present system.

The sensitivities presented in Table I-1 are those actually found for the designated species with a 10-curie polonium-beryllium source and the laboratory counting system. This system, which has been described previously[1], consists of a 2 by 2-in. NaI(Tl) crystal dip counter holding 750 ml. The activation sensitivities are given as relative counting rates for the saturated activities extrapolated to zero decay time.

TABLE I-1. ACTIVATION EFFICIENCIES OBTAINED WITH 10-CURIE POLONIUM-BERYLLIUM NEUTRON SOURCE

Element	Principal Activity	$t_{1/2}$	Saturated Activity at Zero Decay Time[a], cpm per g per liter
Indium	In^{116m}	54 min	255,000
Vanadium	V^{52}	3.76 min	26,000
Dysprosium	Dy^{165m}	1.25 min	21,000
Manganese	Mn^{56}	2.57 hr	11,000
Iodine	I^{128}	25 min	2,350
Aluminum	Al^{28}	2.3 min	1,200

(a) Solutions were counted with a 2 by 2-in. NaI(Tl) crystal dip counter holding 750 ml.

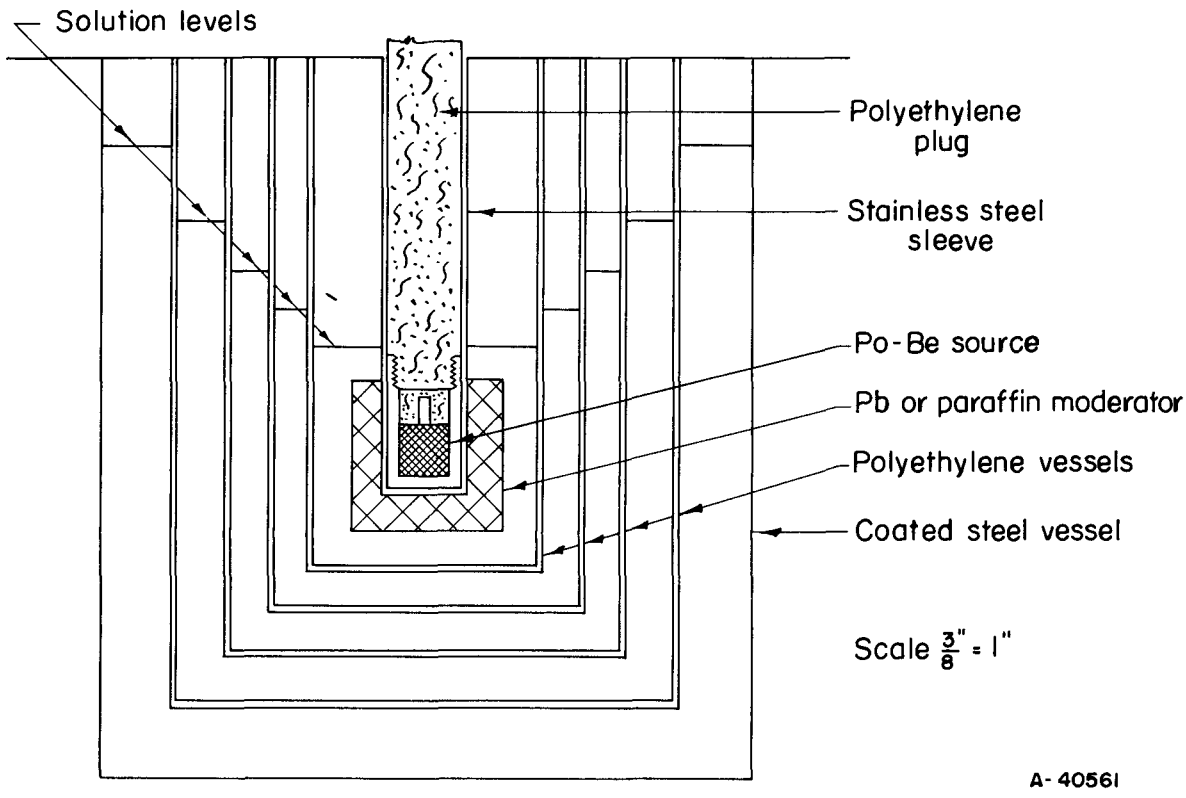

FIGURE I-5. SETUP USED FOR EXPERIMENTS ON EFFECT OF LEAD MODERATOR

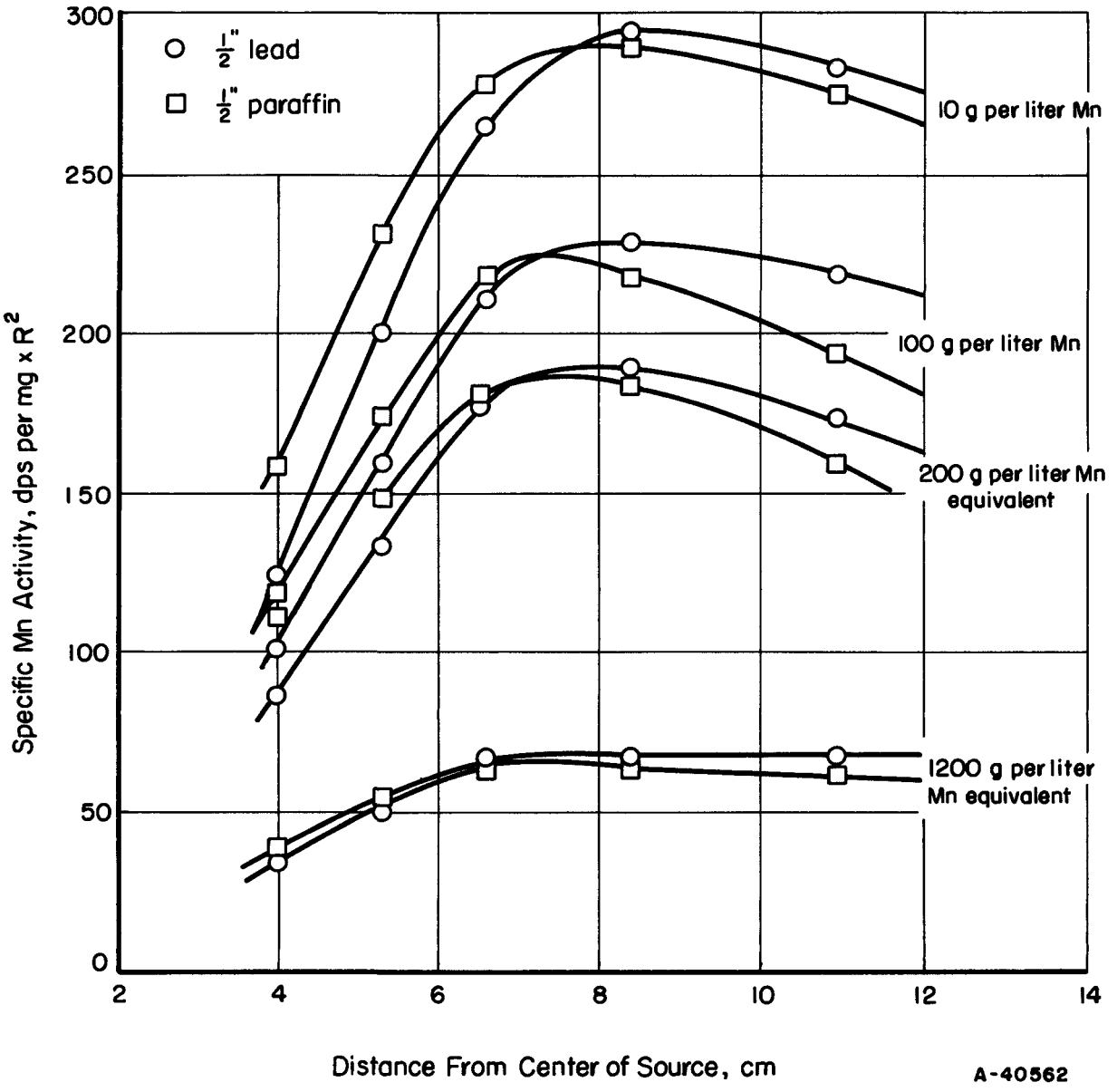

FIGURE I-6. EFFECTIVE NEUTRON ACTIVATION IN MANGANESE-BORON SOLUTIONS WITH LEAD AND PARAFFIN MODERATORS IN GEOMETRY SHOWN IN FIGURE I-5.

DISCUSSION

Experimental study this quarter provided general information useful in stream-activation applications. It is expected that the data presented in the series of plots and the table of activation efficiencies will be of value to an engineer whose knowledge of radioisotopes is meager but who wants to learn whether the use of in situ production of short-lived isotopes affords another or better approach to his process-control problem.

The engineer who knows the flow rate, concentration of salts in solution, available neutron flux, efficiency of production of the isotope to be traced, and cell counting efficiency can combine this knowledge with the information presented in the graphs. He should then be able to decide the applicability and the possible advantages to be gained from radioisotope process control.

The data collected are shown in Figures I-2, I-3, I-4, and I-6. The family of curves in Figure I-2 shows the activity in disintegrations per second per milliliter of solution as a function of activation volume at manganese or manganese equivalent concentrations of 1 to 1200 g per liter. The lower five curves cover the range of $MnSO_4 \cdot H_2O$ solubility and show actual activities. The activities of the manganese equivalent concentrations, from 200 to 1200 g per liter, represent calculated results. These were obtained by multiplying the actual manganese activity by the ratio of the absorption cross sections of the equivalent manganese to actual manganese contained in the solution. Good agreement between activities in the manganese and manganese equivalent solutions was observed in the range of 10 to 150 g per liter, but for reasons of clarity the data were not shown.

An inspection of the curves shows that total activity increases with target-isotope concentration; however, the benefits gained diminish continuously with increasing concentration. This phenomenon is due to the immediate absorption of the neutrons as soon as they are thermalized. The shift in the activation peak toward the source as the target-isotope concentration is increased supports this conclusion.

Figure I-3 contains all of the data shown in Figure I-2 with additional data from manganese-boron solution activations. These are cross plotted showing gross activities in 40-ml to 11-liter volumes of pure manganese, manganese-cadmium, and manganese-boron solutions as a function of macroscopic absorption cross section. At low cross sections in the range of 2.24 to 4.4×10^{-2} barn per cm^3, the detectable difference in the absorption characteristics of the pure manganese and manganese with cadmium or boron solutions is very small. The cutoff at 2.22×10^{-2} barn per cm^3 is due to the macroscopic cross section of pure water. At the higher cross sections there is an apparent difference in the absorption characteristics of boron and cadmium. However, these differences are not large, and the deviations are within the experimental error.

In Figure I-4 an attempt was made to obtain a plot which compares two isotopes directly and which could be of great utility if valid. Here gross indium and manganese activities, divided by their respective disintegration constants, were plotted as a function of macroscopic cross section in three volumes. The manganese values are based on a larger number of activity determinations than the indium values and are,

therefore, more reliable. Also contributing to the apparent differences is the larger uncertainty in the dip-counter efficiency for indium. In order to make the manganese and indium data directly comparable, the indium activities were corrected for the epithermal-neutron contribution using the cadmium ratios reported previously.[1] The indium activity was additionally corrected for the absorption cross section of indium-115 by multiplying by 190/145 (ratio of the total indium cross section to the cross section for production of indium-116m only). An examination of the results shows a similarity in the two sets of curves, but the indium values are lower by approximately 50 per cent. Different neutron-absorption modes would not account for such a large discrepancy in results; therefore, the dip-counter efficiency used for indium is the most likely source of error.

Figure I-6 shows the specific manganese and manganese equivalent activity as a function of distance from the source – the source being surrounded with either 1/2 in. of paraffin or 1/2 in. of lead. An inspection of the four sets of curves shows the shift in the activation peak toward the source with the paraffin moderator. Of greater significance, however, is the difference in the observed activation efficiencies. Thus in applications where small volumes of highly active solutions are required, the interposition of a high-Z moderator is not desirable. It may become useful where large volumes of solutions containing larger amounts of the target isotope are to be activated.

It can be concluded that the data presented will be useful in ascertaining optimum parameters for a given system in a real application. The simulated process experiments now being planned will rely heavily on the data presented in this report.

FUTURE WORK

A 50-curie polonium-beryllium neutron source is now on order with Mound Laboratory. This source will be used during the next quarter for simulated in-process activation experiments. Design and construction of the simulated process system is currently under way. Along with the process experiments, some time will be spent in summarizing the experimental results and outlining an applications guide for engineers.

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(1) McFarling, J. L., Gluck, P., Kircher, J. F., and Sunderman, D. N., "Use of Intrinsic Radiotracers for Industrial Process Control", BMI-1553 (November 9, 1961).

(2) "Neutron Sources and Their Characteristics", Atomic Energy of Canada, Ltd., Technical Bulletin NS-1.

(3) Hodge, N., and Sowden, R. G., "Neutron Shield Materials", Nucleonics 19 (11), 158 (November, 1961).

II. RADIATION-INDUCED GRAFT-POLYMERIZATION STUDIES

Francis A. Sliemers, Manfred Luttinger, Emir Gülbaran*,
William B. Gager, Robert Lieberman, John F. Kircher,
and Robert I. Leininger

SUMMARY

The study of the mechanism of free-radical formation and decay in polymeric materials has been continued. The dual emphasis employed during the present period of the investigation has involved (1) an examination of the effects of structure and configuration on free-radical formation, particularly in the acrylate and methacrylate polymers, and (2) an investigation of the potential application of this information to the development of novel graft copolymers.

INTRODUCTION

The objective of this research program is the determination of structural and configurational factors on the behavior of polymers subjected to gamma irradiation and the correlation of the radiation-induced changes which occur with the ability of the polymer to form graft copolymers. It is anticipated that a mechanism of radiation attack on the various polymer systems can be established.

In previous work a number of polyalkylmethacrylates were examined extensively. The data suggest that (1) free-radical formation is generally accomplished by means of an ester scission, (2) ester scission is accompanied, at least in the majority of cases, by a scission on the polymer backbone, (3) the size and configuration of the hydrocarbon tail of the ester group and of the group attached to the carbon and alpha with respect to the ester group influence the efficiency of site formation, and (4) the rate of formation and/or decay of free-radical sites is affected by polymer mobility and, perhaps independently, by polymer molecular weight.

EXPERIMENTAL WORK

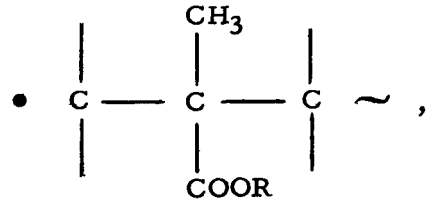
Unless otherwise noted, all polymers were prepared by radiation polymerization at the Battelle Cobalt-60 Gamma Facility. For the measurement of free-radical site concentrations, samples of deactivated polymer are reirradiated in vacuo to various total doses. Site concentrations are determined as a function of dose and, occasionally, as a function of dose rate using electron-paramagnetic-resonance (EPR) measurements.

* I. A. E. A. Fellow.

Vapor-phase chromatography and mass spectrometry are used to determine quantitatively the volatile fragments of the irradiation. Grafting techniques are being employed in an effort to correlate free-radical site concentrations with polymer reactivity.

Polymer Preparation

The preparation of an insoluble polymer of 2-hydroxypropylmethacrylate was described earlier.[1] Its insolubility was believed due to the known presence of dimethacrylate, a cross-linking agent, as an impurity in the monomer. This insoluble polymer produced a three-line EPR spectrum. The spectral shape may also have been the result of impurities. However, since the five-four spectrum characteristic of the unsubstituted methacrylates is generally attributed to the backbone free radical,



it is probable that the three-line spectrum of the hydroxypropyl polymer, if not due to impurities, is indicative of another species of free radical.

Recently, this problem has been pursued further. A well-controlled distillation of the monomer was carried out in an effort to remove impurities, and the polymer molecular weight was reduced by irradiating a highly dilute solution of the monomer to a relatively low percentage conversion. The resulting polymer is soluble in alcohol. The EPR spectrum of this "high-purity" material will be examined during the next report period.

Polystyrene was prepared from a solution of the monomer at 70 C using α, α'-azodiisobutyronitrile to initiate polymerization. The poly-α-methylstyrene was prepared by adding a mixture of monomer and dry pentane to a 6 to 1 volume ratio of pentane and methylene chloride containing boron trifluoride.

The dimethylaminoethylmethacrylate polymer was prepared by irradiation of a 10 per cent solution of the monomer in dry hexane. The polypropylene is a commercial resin prepared by Hercules.

Chemical Measurement of Free-Radical Concentration

A number of experiments have been performed to examine the effectiveness of iodine as a free-radical scavenger. This study, which has included an examination of other scavenger systems[1, 2], was undertaken primarily to establish if such a method might be applicable to the measurement of total site concentrations in the very low site-concentration range where sample size limits the applicability of the EPR instrument.

Using irradiated PMMA, iodine in carbon tetrachloride appears to be a good scavenger at high site concentrations, but at low radiation doses ($<10^6$ rads) the system is not sufficiently sensitive. Further, initial experiments indicate that radioactive iodine is also ineffective in the low site-concentration range.

Grafting Studies

A series of graft-polymerization experiments was completed in which acrylonitrile was used as graft monomer and several different base polymers were used. These included PMMA, polypropylene polystyrene, and poly-α-methylstyrene. The PMMA was soluble in the monomer whereas the polystyrene was only slightly soluble and the other polymers were only "wetted" by the acrylonitrile.

In the PMMA-acrylonitrile work, following grafting, the solution was poured into dimethylformamide to solubilize the excess monomer, and the polymer was precipitated with excess water and extracted 24 hr with water. Using this system it is theoretically possible to recover all of the copolymer and homopolymers and, at the same time, remove unreacted monomer.

The results from a series of grafting experiments, carried out at 25 C, are summarized in Table II-1. The data indicate that very little if any grafting occurred. Similar series of grafts have been completed in which (1) the grafting time has been varied at 25 C and (2) the irradiation and grafting temperatures have been reduced to -72 C.

TABLE II-1. RESULTS OF GRAFT-POLYMERIZATION STUDIES OF PMMA AND ACRYLONITRILE[a]

Run	Total Dose, 10^7 rads	Sites per Monomer Unit x 10^3 [b]	Nitrogen[c], per cent
G-67	--	--	0.16
G-68	--	--	0.17
G-69	0.02	0.3	0.27
G-71	0.02	0.3	0.15
G-70	0.08	0.9	0.23
G-72	0.08	0.9	0.14
G-73	0.32	2.0	0.22
G-74	0.32	2.0	0.33
G-75	0.48	3.2	0.23
G-76	0.48	3.2	0.16

(a) The grafting was carried out at 25 C for a period of 1 hr with approximately 75 cm^3 of monomer to approximately 5 g of polymer.

(b) These values were determined by EPR measurements.

(c) Multiplication of these data by 3.79 gives the percentage of acrylonitrile in the copolymers.

These data are listed in Table II-2. Again, very little grafting is indicated. Apparently, there is something inherent in the PMMA structure which, at least under the conditions employed, inhibits grafting.

TABLE II-2. RESULTS OF GRAFT-POLYMERIZATION STUDIES OF PMMA AND ACRYLONITRILE[a]

Run	Total Dose, 10^7 rads	Grafting Temperature, C	Grafting Time, hr	Sites per Monomer Unit x 10^3 [b]	Nitrogen[c], per cent
G-77	0.96	25	1	5.0	0.30
G-78	0.96	25	1	5.0	0.29
G-81	0.48	25	0.25	3.2	0.31
G-82	0.48	25	0.25	3.2	0.28
G-79	0.48	25	5	3.2	0.27
G-80	0.48	25	5	3.2	0.27
G-83	0.48	25	24	3.2	0.25
G-84	0.48	25	24	3.2	0.19
G-88	--	-72	1	--	(d)
G-91	--	-72	1	--	(d)
G-86	0.025	-72	1	0.3	0.10
G-87	0.025	-72	1	0.3	0.06
G-85	0.15	-72	1	1.3	(d)
G-92	0.15	-72	1	1.3	(d)
G-89	0.074	-72	2.5	0.8	0.10

(a) Approximately 75 ml of monomer was used with approximately 5 g of polymer for each grafting.
(b) These values were determined by EPR measurements.
(c) Multiplication of these data by 3.79 gives the percentage of acrylonitrile in the copolymers.
(d) These results are not yet available.

Since some solubility of the polystyrene in acrylonitrile was indicated, the grafting procedure described above was employed for this system. For the systems polypropylene-acrylonitrile and poly-α-methylstyrene-acrylonitrile, the procedure was simplified. The insolubles were merely removed from the excess monomer, washed with water, and extracted 24 hr with water. No effort was made, in these early runs, to remove acrylonitrile homopolymer.

An examination of Table II-3 reveals that there is some evidence for grafting at the higher dose in the case of the polypropylene although reproducibility is not good. However, it is apparent that little or no grafting occurred with the other two systems (Tables II-4 and II-5).

TABLE II-3. RESULTS OF GRAFT-POLYMERIZATION STUDIES OF POLYPROPYLENE AND ACRYLONITRILE[a]

Run	Total Dose, 10^7 rads	Sites per Monomer Unit x 10^3 [b]	Nitrogen[c], per cent
G-93	--	--	0.12
G-94	0.02	0.01	0.10
G-95	0.02	0.01	0.14
G-96	0.48	0.13	0.69
G-97	0.48	0.13	7.49

(a) Approximately 75 ml of freshly distilled monomer was used with approximately 5 g of polymer for each grafting. Grafting temperature was 25 C and grafting time was 1 hr.
(b) These values were determined by EPR measurements.
(c) Multiplication of these data by 3.79 gives the percentage of acrylonitrile in the copolymers.

TABLE II-4. RESULTS OF GRAFT-POLYMERIZATION STUDIES OF POLYSTYRENE AND ACRYLONITRILE[a]

Run	Total Dose, 10^7 rads	Sites per Monomer Unit x 10^3 [b]	Nitrogen[c], per cent
G-98	--	--	0.42
G-99	0.01	?	0.34
G-100	0.02	?	0.32
G-101	0.095	0.001	0.40
G-102	0.48	0.002	0.32
G-103	0.48	0.002	0.35

(a) Approximately 75 ml of freshly distilled monomer was used with approximately 5 g of polymer for each grafting. Grafting temperature was 25 C and grafting time was 1 hr.
(b) These data were determined by EPR measurements. The absolute values are somewhat uncertain because of a recent recalibration of the instrument.
(c) Multiplication of these data by 3.79 gives the percentage of acrylonitrile in the copolymers.

TABLE II-5. RESULTS OF GRAFT-POLYMERIZATION STUDIES OF POLY-α-METHYLSTYRENE AND ACRYLONITRILE [a]

Run	Total Dose, rads 10^7	Sites per Monomer Unit x 10^3 [b]	Nitrogen[c], per cent
G-104	--	Undetermined	0.16
G-105	0.02	"	0.13
G-106	0.02	"	0.05
G-107	0.08	"	0.13
G-108	0.48	"	0.13
G-109	0.48	"	0.13

(a) Approximately 75 ml of freshly distilled monomer was used with approximately 5 g of polymer for each grafting. Grafting temperature was 25 C and grafting time was 1 hr.
(b) These values were determined by EPR measurements.
(c) Multiplication of these data by 3.79 gives the percentage of acrylonitrile in the copolymers.

Free-Radical Formation in Polydimethylaminoethylmethacrylate and Polystyrene

Site concentration has been determined as a function of dose for polydimethylaminoethylmethacrylate and polystyrene. Interestingly, in the case of the DMAEMA polymer, no stable sites were formed even at total doses of approximately 4.3 x 10^7 rads. A higher molecular weight polymer is now being prepared for evaluation. The data obtained with polystyrene are listed in Table II-6. Little information as to radical position could be gained from spectral shapes. The spectra were quite diffuse, due at least in part to the high noise level present during measurements.

TABLE II-6. SITE FORMATION AS A FUNCTION OF DOSE IN POLYSTYRENE

Dose, rads	Sites per Monomer Unit x 10^3 [b]
2 x 10^5	?
5 x 10^5	?
1 x 10^6	1.23
3.2 x 10^6	2.74
4.8 x 10^6	2.29
9.6 x 10^6	3.12
1.9 x 10^7	5.80
3.4 x 10^7	4.19

(a) These values were determined using EPR measurements. The absolute values are somewhat uncertain because of a recent recalibration of the instrument.

Quantitative Examination of EPR Spectra in Several Polymers

Results from a detailed examination of the EPR spectra of several polymers are given in Table II-7. The quantity "g" in the table is the splitting factor and "A_1" and "A_2" are the hyperfine coefficients. The methyl-, ter-butyl-, and cyclohexylmethacrylate polymers showed the usual five-four spectrum, while the poly-2-hydroxypropylmethacrylate and the polymethacrylamide showed three- and five-line spectra, respectively. There were also hints of a four-line spectrum in the case of the polymethacrylamide. However, its intensity relative to the five-line spectrum was too weak for any measurements to be made.

A detailed examination of the spectra produced by those polymers which show the normal five-four pattern indicated that the same radical is being seen in all cases.

TABLE II-7. SPLITTING FACTORS AND HYPERFINE COEFFICIENTS FOR SEVERAL POLYMERS

Polymer	Dose, rads	Splitting Factor (g)	Hyperfine Coefficient, gauss A_1	Hyperfine Coefficient, gauss A_2
Polymethylmethacrylate	3.4×10^6	2.002 ± 0.001	22.7 ± 0.5	22.7 ± 0.5
Polymethylmethacrylate	1.4×10^7	2.002 ± 0.001	22.7 ± 0.5	22.7 ± 0.5
Poly-t-butylmethacrylate	3.4×10^6	2.002 ± 0.001	22.7 ± 0.5	22.7 ± 0.5
Polycyclohexylmethacrylate	3.4×10^6	2.002 ± 0.001	22.7 ± 0.5	22 ± 1
Poly-2-hydroxypropylmethacrylate	3.4×10^6	2.003 ± 0.001	8.5 ± 0.5	--
Polymethacrylamide	3.4×10^6	2.003 ± 0.001	22.6 ± 0.5	--

Effect of Dose Rate on Site Formation in Polymethylmethacrylate

Data from a study of the effect of dose rate on site formation in PMMA are presented in Table II-8. Dose rates of 1×10^4, 2×10^5, and 1×10^6 rads per hr were used in this work. The data indicate, as might be expected, that the measured site concentration for a given dosage increased with increasing dose rate. This is logically explained by the fact that a higher concentration of short-lived free radicals is "builtup" during high-dose-rate irradiation.

TABLE II-8. THE EFFECT OF DOSE RATE ON SITE FORMATION IN POLYMETHYLMETHACRYLATE

Dose Rate, rads per hr	Dose, rads	Sites Per Monomer Unit, x 10^{6}(a)
1×10^{4}	1.7×10^{5}	3.15
	4.8×10^{5}	6.58
	1.7×10^{6}	20.5
	3.4×10^{6}	27.8
2×10^{5}	2×10^{5}	3.76
	5×10^{5}	11.2
	1.2×10^{6}	28.0
	3.4×10^{6}	46.1
1×10^{6}	2.5×10^{5}	4.54
	5×10^{5}	12.5
	2×10^{6}	41.7
	3.5×10^{6}	63.4

(a) These values were determined using EPR measurements. The absolute values are somewhat uncertain because of a recent recalibration of the instrument.

CONCLUSIONS

Several conclusions can be justified on the basis of the work reported here:

(1) The use of iodine in carbon tetrachloride as a free-radical scavenger has proven ineffective. At high site concentrations the correlation with EPR measurement is good, but at low radiation doses the scavenger system is not sufficiently sensitive.

(2) The postirradiation grafting of acrylonitrile to a number of polymers has been investigated. There appears to be something inherent in the structure of PMMA which inhibits solution grafting. Postirradiation grafting to polypropylene has shown some promise.

(3) A detailed examination of the EPR spectra produced by several methacrylate polymers which show the normal five-four pattern indicates that the same radical is being seen in all cases.

(4) A study of the effect of dose rate on site formation has shown that the measured site concentration for a given dosage increases with increasing dose rate.

FUTURE WORK

The anticipated program for the April 1 to June 30, 1962, period includes:

(1) Continuation of the examination of polymer structure and its relationship to radiation susceptibility

(2) Examination of the effects of crystallinity and molecular-weight distribution on free-radical formation

(3) Determination of the effect of the temperature of irradiation on the types and concentration of free-radical sites formed

(4) Continuation of the grafting studies, including an investigation of peroxide-initiated grafting procedures.

REFERENCES

(1) "Quarterly Progress Report on Radioisotope and Radiation Applications", to the Division of Isotopes Development from Battelle Memorial Institute (January, 1962).

(2) "Quarterly Progress Report on Radioisotope and Radiation Applications", to the Division of Isotopes Development from Battelle Memorial Institute (October, 1961).

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