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APPLICATIONS OF NUCLEAR RADIATION AND RADIOISOTOPES TO TEXTILE MATERIALS AND PROCESSES

by

Arthur A. Armstrong, Jr. and Henry A. Rutherford

Prepared for

The Office of Isotopes Development
United States Atomic Energy Commission

November 1, 1960

The School of Textiles
North Carolina State College of Agriculture and Engineering
of the
University of North Carolina
Raleigh, North Carolina

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This work performed for

The Office of Isotopes Development
United States Atomic Energy Commission
Contract No. AT-(40-1)-2477

Annual Report for the period
November 1, 1959, to November 1, 1960

by

The School of Textiles
North Carolina State College of Agriculture and Engineering

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University of North Carolina

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ABSTRACT

Studies of possible applications of nuclear radiation and radioisotopes to textile materials and processes were undertaken. A broad study was made covering (1) the modification of fibers by exposure to radiation, (2) the modification of fibers by *in situ* polymerization and/or graft polymerization of vinyl monomers, (3) the application of beta gauges to textile processes, and (4) the use of tracer and activation analysis techniques.

Various vinyl monomers were added to textile yarns by gamma radiation using a vapor phase technique. The vapor phase technique was useful only for the volatile monomers acrylonitrile and vinyl acetate at 70°F. and one atmosphere pressure. Acrylonitrile and vinyl acetate were readily added to cotton, rayon, acetate, polypropylene and nylon. Small amounts were added to polyesters and none to acrylics.

Activation analysis was proposed for fiber identification and process studies. For fiber identification gamma-ray spectra were presented for most of the commercial textile fibers. A preliminary study was made of fiber blending in the cotton spinning process using activation analysis with manganese as the tracer.

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APPLICATIONS OF NUCLEAR RADIATION AND RADIOISOTOPES TO TEXTILE MATERIALS AND PROCESSES

Contract No. AT-(40-1) - 2477

1959-60 Final Report

INTRODUCTION

Studies of possible applications of nuclear radiation and radioisotopes to textile materials and processes were undertaken under contract with the Isotopes Applications Division of the U. S. Atomic Energy Commission in November 1958. The institution's share (N. C. State College) of about 20% of the total cost was provided by Burlington Industries, Inc., Cone Mills Corporation, Reeves Bros., and J. P. Stevens and Company.

The program under the contract envisioned a broad study dealing with (1) the modification of fibers by exposure to radiation, (2) the modification of fibers by in situ polymerization and/or graft polymerization of vinyl monomers, (3) the application of beta gauges to textile processes, (4) and the use of tracers and activation analysis techniques. The major emphasis during the first year was placed on the development of techniques for fiber modification (points 1 and 2), and on the application of beta gauges for the measurement and control of certain textile processes (point 3). During the second year, the emphasis was placed on activation analysis and on the modification of fibers through grafting techniques. It was decided to discontinue experiments dealing with the modification of fibers by radiation alone, and to discontinue, at least temporarily, further work with beta gauges. The present report, which deals with the work conducted during the second year of a proposed three-year program, is divided into four sections in which each of the above subjects is discussed separately.

PART I. FIBER MODIFICATION RESEARCH

All fibrous polymers used as textile materials, whether natural or man-made, have deficiencies of one kind or another. Much research effort has been and is being directed toward overcoming those properties of fibers that tend to limit their utility. One technique for improving the performance of textile materials is through fiber modification.

In the instance of the natural fibers, two approaches are used. One relies on additive materials mechanically deposited on the fibers; the other employs chemical means for fiber modification. The first procedure results in materials that are of a non-durable type; and, although additive treatments are widely used and have received consumer acceptance, the lack of durability toward water (laundering) and dry-cleaning procedures places a serious limitation on their usefulness. The treatment of cotton, rayon, and wool fabrics with wax emulsions for water repellency, cotton with borax-boric acid mixtures for fire resistance, or cotton with pentachlorophenol for mildew resistance, all exemplify the additive type.

The principle of the chemically reactive systems is to change the chemical nature of the fiber so that it will inherently possess the desired characteristics. This method is usually more costly, but, generally speaking, the products are more durable. Moreover, some properties cannot be achieved except by chemical modification. In most instances, however, the fibers are not entirely resistant to the environment required to cause the chemical modification. Thus, many treatments that have a satisfactory end result suffer some limitation or are not practical because of fiber damage caused during the chemical treatment, generally by catalysts or highly acid systems. Examples in this category are the cross-linking of cotton and rayon with resins to produce dimensional stability ("wash and wear"), the esterification of cotton with phosphorus compounds for fire resistance, the reaction of cellulosic fibers with stearic-acid derivatives for water resistance, or the catalytic deposition of reaction products of acrylonitrile in cotton for mildew resistance. It is of interest to note that the bulk of the research being widely conducted involves chemical modification and is concerned with cellulosic fibers, which constitute nearly 90% of the total fiber consumption in the U. S. A.

The properties of a synthetic fiber may be controlled to a great degree by the structure of the polymer. However, synthetic fibers are plagued with such problems as lack of stability toward heat, low softening points, poor dyeability, development of static, creep under tension, etc. Modification of the structure of the polymer after it is in the fibrous form might be an answer to some of the problems.

While much progress in improving fibers has been made in recent years, the shortcomings of the present methods for modification of fibers for specific end-use requirements, as well as interest in developing new products, leave much to be desired. Improved means of fiber modification through finishes are the focal point of a vast amount of development work. However, little effort making use of nuclear techniques, radiation, or radioisotopes, is being expended, outside of the present investigation.

All fibers are ultimately degraded by exposure to radiation. However, the rate of change in properties differs from fiber to fiber. Some materials, at intermediate points of exposure and prior to showing signs of degradation, undergo changes that may be desirable. The reactions responsible for this behavior (e. g., cross-linking) cannot, in most cases, be carried out by ordinary chemical means. Thus, because radiation can initiate or facilitate unusual chemical changes, it is evident that nuclear techniques might be employed for the modification of fibrous materials to make them more applicable in specific end uses.

How Radiation Might be Used

Because simple organic molecules, particularly those containing unsaturation, will undergo changes rather rapidly in the presence of radiation, some interesting possibilities for the modification of fibers are suggested. Some of the simple organic compounds are converted with a rather high order of efficiency. This is typified by ethylene polymerization, styrene polymerization, or the co-polymerization of butadience and styrene. Many vinyl polymerizations fit into this category. Thus, it would appear possible to polymerize certain selected materials either within fibers or on their surfaces. Further, the possibility of reacting certain substances with the fiber polymer, using radiation as the "catalyst" is not eliminated.

It is encouraging that some simple molecules may be converted at those levels of dosages that are not particularly damaging to the fibers themselves, even the relatively unstable cellulosic fibers. With respect to the synthetic polymers which are among the more stable types, the possibility of the exposure in media that will promote cross-linking or grafting is suggested.

During the first year of the project exposures of the various fibers were conducted in a cobalt-60 gamma radiation source of approximately 2300 curies, having a dose rate of 2×10^5 roentgens per hour. The source is so constructed that exposures may be carried out in air, in various gases, or in liquids. In preliminary work, the rate at which a number of textile fibers were changed by gamma radiation was determined. The effects on strength and elongation of rayon, acetate, polyester, nylon, acrylic, polypropylene, wool, and silk fibers were determined. All of the fibers that were investigated except acrylic, polyester, and wool were adversely affected by the gamma radiation at relatively low doses. The results obtained were consistent with the extent of degradation that was obtained in earlier work in this laboratory where other radiation facilities were used.

It was also necessary in preliminary work to investigate the behavior of vinyl monomers during exposure to gamma radiation. In general, the results with the monomers showed the following: (1), water accelerated the rate at which monomer was polymerized; (2), acrylonitrile and vinyl acetate polymerized most readily; (3), the presence of oxygen inhibited the polymerization; (4), the presence of some organic solvents apparently inhibited polymerization.

For several reasons, acrylonitrile was selected as the monomer with which to establish the principles and techniques for the application of vinyl compounds to fibers. Acrylonitrile polymerized most readily of all the substances tried and its presence could be detected very readily by a simple analysis of the final product for nitrogen.

Attempts were made to add acrylonitrile to cotton by irradiation of the samples in monomer solutions, samples first padded with monomer solutions, and samples in acrylonitrile vapors. As in the case of acrylonitrile alone, the presence of water was necessary for the polymerization. This suggests a free radical mechanism using the free radicals formed by the irradiation of water. All experiments on the irradiation of cotton samples in monomer solutions and samples padded with monomer solutions gave non-uniform distribution of polyacrylonitrile polymer. Moreover, the reproducibility of polymer concentration on the fibers under these conditions was very poor. A completely uniform addition of acrylonitrile was obtained by irradiation of cotton fiber in acrylonitrile vapors (in the presence of water vapor).

The preliminary studies on the vapor-phase addition of acrylonitrile addition to fibers were carried out by irradiating the samples in glass drying tubes in the presence of acrylonitrile vapors limiting the operating conditions to laboratory temperature and atmospheric pressure. The following apparatus was assembled for this study: oil-pumped nitrogen was used as the carrier gas and the gas flowrate was adjusted to 175 $cm.^3$/min. by a standard pressure-reducing and flow-control valve; various acrylonitrile vapor concentrations were obtained by passing the nitrogen through two gas bubble towers containing aqueous solutions of different acrylonitrile concentration; and the vapor was passed through a glass drying tube containing 1-2 grams of fiber during irradiation. A diagrammatic sketch of the apparatus is shown in Figure 1. A photograph of the gamma radiation source is shown in Figure 2.

Studies were made on the addition of acrylonitrile to cotton using 1, 5, and 10% acrylonitrile concentration in the vapor. The data showed that the rate of addition increased with increasing acrylonitrile concentration in the vapor. The rate of addition of acrylonitrile was constant for each vapor concentration and varied directly with the radiation dose. With our gamma radiation source the radiation intensity could not be varied so the effect of dose rate was not studied.

For the studies on acrylonitrile addition to the other fibers the highest acrylonitrile concentration in the vapor was used. The optimum conditions found at laboratory temperature and atmospheric pressure was a vapor concentration of 10% acrylonitrile and 2.2% water by volume. This condition was obtained by having the vapor in equilibrium with a water solution saturated with acrylonitrile or acrylonitrile solution saturated with water. In practice this was accomplished by placing the two saturated liquid phases in bubble towers and passing nitrogen through them. In this manner the vapor concentration remained constant as long as both liquid phases were present, and temperature and pressure were constant.

The data showed that acrylonitrile was readily added to cotton, mercerized cotton, rayon, acetate, polyvinylchloride, nylon, and polypropylene fibers, while very little was added to polyester and acrylic fibers. It is interesting to note that the behavior of the fiber toward the monomer appears to be related to the relative stability of the fibers to radiation. Cotton, mercerized cotton, rayon, acetate, polyvinylchloride, nylon, and polypropylene fibers are degraded very rapidly by gamma radiation while polyester and acrylic fibers are degraded very slowly. The rate of degradation may be a measure of the rate of formation of free radicals along the fiber polymer chain which may in turn influence the rate of polymerization of vinyl monomers on the fibers. Moreover, the addition of vinyl monomer (or polymer) is not influenced by the degree of crystallinity of the fiber. The highly crystalline fiber, native cotton, reacts just as readily as the less crystalline materials of the same chemical nature, namely, mercerized cotton (no tension) and rayon.

Vapor Phase Addition of Vinyl Monomers to Yarns

One of the biggest problems encountered in modifying fibers or fabrics by the grafting of vinyl compounds is to obtain a product of uniform composition. This was overcome by using the vapor phase technique, as discussed above and as presented in detail in the First Annual Report, Contract No. AT-(40-1)-2477, November 1959 for the addition of volatile monomers to staple fiber. The work has been extended to include yarns so that the effect of acrylonitrile addition on the breaking strength could be determined conveniently. For comparison, breaking strengths were made on unirradiated control samples and on samples which were irradiated in an atmosphere of nitrogen saturated with water only at 70°F. and 1 atm. pressure. The filament yarns used were cellulose acetate, rayon, nylon, a polyester, and an acrylic; staple yarns were of cotton and an acrylic.

The general procedure was as follows: small skeins of the yarns were placed in the one-liter stainless steel beaker fitted in the irradiation chamber. The system was flushed for one hour with 175 $cm.^3$/min. of nitrogen containing 10% acrylonitrile and 2.2% water. The beaker was then placed in the irradiation position in the Co-60 source and the flushing continued for the required length of time (1, 2, 4, 8, and 16 hrs.) The intensity of the gamma radiation inside the beaker was $3.8x10^5$ roentgens per hour. After irradiation, the acrylonitrile addition was determined from nitrogen analyses, except in the instance of the acrylic fiber. Here, the amount added was determined from the weight gain of the sample. The irradiated control samples were run in the same manner, omitting the acrylonitrile.

Values for the acrylonitrile addition are given in Table I and Figure 3. Breaking strengths of the irradiated controls are given in Table II and samples with acrylonitrile in Table III. Relative breaking strengths (relative to the unirradiated controls) for the irradiated control samples are given in Table IV and Figure 4 and for the samples with acrylonitrile in Table V and Figure 5. Relative breaking strength (relative to the irradiated controls) are given in Table VI and Figure 6.

Reporting the absorbed radiation dose presented a problem because of the different composition of the fibers. Radiation intensity in the radiation chamber was determined in roentgens per hour by chemical dosimetry using ferrous sulfate. The absorbed dose for different materials may be calculated by the method and data presented in the National Bureau of Standards Handbook 62. The exposure dose in roentgens may be converted to absorbed dose in rads for each material by multiplying the exposure dose in roentgens by a factor "f" which is the ratio of energy absorption coefficient of the fiber to the coefficient for air (rads per roentgen of exposure dose). The "f" factors for each fiber were calculated from the data in NBS Handbook 62 and are listed below:

fiber	f factor
cotton	0.93
polypropylene	1.00
rayon	0.93
acetate	0.93
nylon	0.96
polyester	0.91
acrylic	0.93

The "f" factors for the various fibers range from 0.91 for polyester to 1.00 for polypropylene. To simplify the presentation of results a "f" factor of 1.00 was used for calculating the absorbed dose for all the data in this report. If a more precise absorbed dose is needed the values given in the report should be multiplied by the "f" factor given above for each fiber.

Inspection of Table VI and Figure 6 shows that the acrylonitrile addition has little effect on the relative breaking strengths (relative to the irradiated controls) of rayon, nylon, and polyester; i.e., the change in strength caused by irradiation is the same in the presence and absence of the monomer. The relative breaking strength of cotton was decreased to approximately 0.9 for all the samples. The relative breaking strength of cellulose acetate increases significantly as the acrylonitrile addition increases.

In a previous report (November 1, 1959) the addition of acrylonitrile to fibers in stock form was discussed. The values obtained for the yarns shown here are significantly different from the values for the fibers in open form. This difference in behavior between the fibers and yarns may be due to dissimilarities in compactness (allowing better penetration in the stock) or to the past history of the samples. This point is being investigated.

In order to show the effect of acrylonitrile addition on the relative breaking strength of cellulose acetate, additional experimental runs were made until a maximum was obtained. Values of acrylonitrile addition, breaking strengths, and relative breaking strengths for the cellulose acetate samples are given in Table VII and Figure 7. Inspection of these data shows that the acrylonitrile addition increases with time of irradiation but the rate of addition decreases. Breaking strength increases with acrylonitrile addition and passes through a maximum at 122% acrylonitrile (72 hours of irradiation). The relative breaking strength (relative to the irradiated controls) increases with acrylonitrile addition and passes through a maximum also at 122% acrylonitrile (72 hours irradiation.) This indicates that the grafting of polyacrylonitrile to cellulose acetate has significantly increased the breaking strength of the yarn. Embrittlement also occurred. Whether the material is protected from degradation (i.e., chain scission) by the acrylonitrile is not yet clear. This behavior was not revealed in the earlier work with acetate fibers.

Other vinyl monomers were investigated for addition to yarns by gamma radiation using the vapor phase technique that was discussed in previous reports for the addition of acrylonitrile to staple fiber and textile yarns. The vinyl monomers and yarns studied are listed below:

Vinyl Monomers

acrylonitrile
vinyl acetate
vinyl crotonate
methyl methacrylate
vinyl propionate
vinyl butyrate
vinyl 2-ethyl hexoate
butyl methacrylate
divinyl sulfone

Yarns

cotton 30/1
polypropylene 350-70
rayon 60-10
acetate 100-28
nylon 210-34
polyester 70-34
acrylic 150-60
acrylic staple

The experimental procedure was as follows:

Small skeins of each yarn were placed in the one-liter stainless steel beaker. The system was flushed for one hour with 175 cm^3/min. of nitrogen which was in equilibrium with the two-phase monomer-water solution of the monomer being tested. The beaker was then placed in the irradiation position in the gamma radiation source and the flushing continued for the required length of time (1, 2, 4, 8, and 16 hrs.) The intensity of the gamma radiation inside the beaker was 3.8×10^5 roentgens per hour. After irradiation, the monomer addition to the yarns was determined from the weight gain of the sample. For comparison irradiated controls were run on each sample by irradiating the yarns in an atmosphere of nitrogen saturated with water (all other factors remained unchanged). The monomer addition to each textile yarn is given in Table VIII.

Breaking strength, elongation, and modulus were determined on the samples. The values of these properties were the average of 25 breaks on the Instron Tester. For the filament yarns the breaks were run on single filaments. Because of the large number of samples, it was decided to determine first the physical properties of the controls, 8-hour samples, and 16-hour samples, and later determine the physical properties of the other samples if the data indicated an improvement in properties. The physical properties of each yarn are listed in the following tables:

Table IX	Cotton 30/1
Table X	Polypropylene 350-70
Table XI	Rayon 60-10
Table XII	Acetate 100-28
Table XIII	Nylon 210-34
Table XIV	Polyester 70-34
Table XV	Acrylic 150-60
Table XVI	Acrylic Staple Yarn

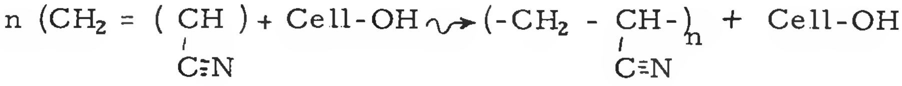
Inspection of the data in Table VIII shows that vinyl monomers are added to acetate yarns more readily than to the others. The monomers are added to nylon, polypropylene, cotton and rayon but less readily than with acetate. A very small amount of monomer may be added to polyester yarns and practically none to acrylic yarns. The more volatile monomers, acrylonitrile and vinyl acetate, are added from the vapor phase more readily than the less volatile monomers because of their higher concentration in the gas phase.

Inspection of the data in Tables IX and XVI shows only a few cases of improved physical properties produced by monomer addition. In the case of polypropylene, an increase in breaking strength is obtained with vinyl crotonate, vinyl propionate, vinyl 2-ethyl hexoate, and divinyl sulfone as compared to the irradiated control, but no increase if compared to the unirradiated control.

The foregoing may be summarized as follows. Acrylonitrile adds readily to cotton, acetate, rayon and nylon but not to the polyester or the acrylic fibers. It appears that the addition of this vinyl monomer occurs only on those polymer substrates that are unstable toward radiation. To an extent, the same is true of vinyl acetate except that this monomer adds much more readily to acetate than does acrylonitrile. The remaining vinyl monomers that were examined showed little ability to add to any of the fibers except to acetate. The monomers in this group did, however, polymerize when exposed to radiation by themselves. It would appear from the present data that a fairly high concentration of monomer is required for addition since those having a low vapor pressure failed to add appreciably from the vapor phase. Nothing outstanding was found concerning the physical properties of the fibers that exhibited monomer addition.

Mechanism of the Addition of Acrylonitrile to Cotton Cellulose

Previous investigations of the mechanism of addition of acrylonitrile to cellulose showed that a reaction did not occur through the hydroxyl groups. As all of the hydroxyl groups appeared available for acetylation, it was suggested that the mechanism favored the following reaction:



$$n\,(CH_2 = (\underset{\overset{|}{C\equiv N}}{CH}) + \text{Cell-OH} \rightsquigarrow (-CH_2 - \underset{\overset{|}{C\equiv N}}{CH}-)_n + \text{Cell-OH}$$

This may be referred to as in situ polymerization.

In an attempt to separate the polymer from the fiber, long-term extractions were carried out with boiling dimethyl formamide. Samples were extracted for 240 hours continuously, and analyzed for nitrogen content after every 24-hour period. The nitrogen content was found to decrease until the sample had been extracted 120 hours, after the value remained constant. At 120 hours, 37.5% of the original amount of polyacrylonitrile remained. (See Figure 8.)

To attempt separation by another method, samples of the nitrogen-bearing cellulose were acetylated in chloroform, the presumption being that the chloroform would dissolve all of the acetylated material and leave only the polyacrylonitrile, or cellulose grafted with polyacrylonitrile, as the insoluble material.

After acetylation and separation it was found that the chloroform contained a large amount of cellulose triacetate and a small amount of polyacrylonitrile. (3.5%). The residue was acetylated again and the nitrogen content was found to increase to 16.1%. Inasmuch as the theoretical nitrogen content of pure polyacrylonitrile is 26.42% the residue probably contained some cellulose which was not removable, i. e., in the grafted form.

A third method was investigated to separate cellulose from the poly-acrylonitrile, namely, biological attack. The presumption in this case was that micro-organisms would render the cellulose water-soluble and leave the polyacrylonitrile unaffected if the mechanism of addition were one of the in situ polymerization.

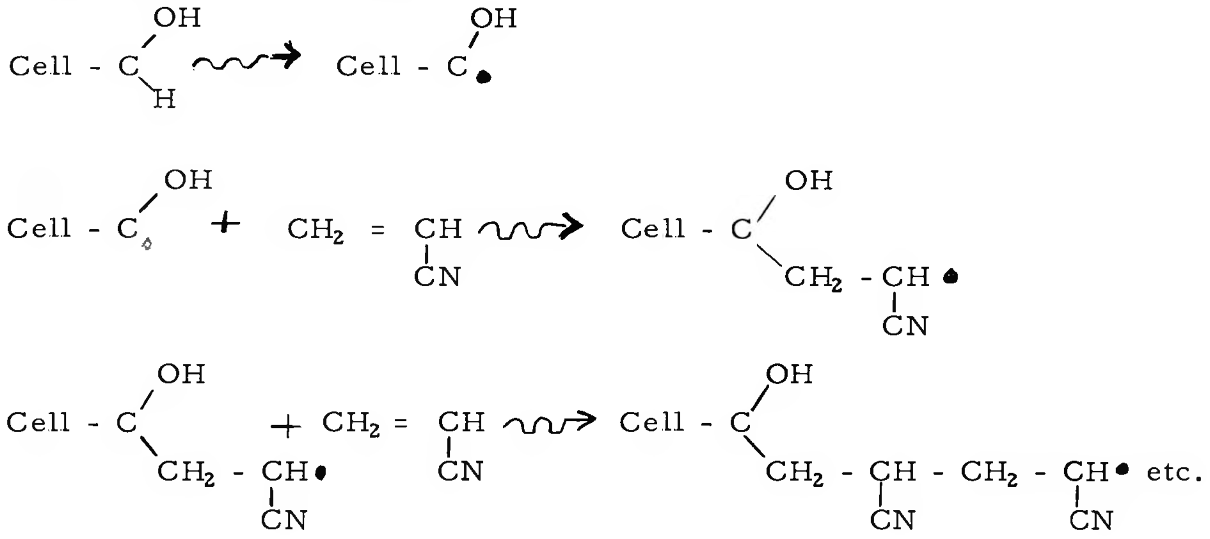
Preliminary tests were made on pads of scoured cotton, 48-hour gamma irradiated cotton, and samples of 80x80 print cloth. The pads and fabrics were placed on mineral salts agar and inoculated with spore suspensions of the following cultures:

Penicillium Oxalicum	Culture No. CF-8
Chaetomium Globosum	Culture No. CF-377
Chaetomium Globosum	Culture No. CF-490
Myrothecium Verrucaria	Culture No. F-721

After 21 days in an incubator maintained at 28°C. and 90% R.H., the untreated cellulose pads and cotton fabric showed maximum growth, and were completely destroyed, whereas the irradiated cotton did not support growth of any of the cultures.

Thus, it appeared that the cellulose in the irradiated samples could not be digested by these organisms; and as these are the best of the known cellulose destroyers, it did not seem feasible to attempt separation of the polyacrylonitrile from samples prepared by the vapor-phase irradiation of cellulose with acrylonitrile. It was interesting (but not surprising) that the irradiated pure cellulose was not destroyed by biological attack. Whether the time of irradiation bears any relationship to the resistance of the cellulose to attack is not known, but it may be possible to render cellulosic materials resistant to mildew by simple irradiation. This may possibly be investigated further.

From the foregoing it can be seen that it is very difficult to determine whether or not monomer (or polymer) is grafted to cellulose during exposure to gamma radiation. The possibility of grafting at the hydroxyl group has been ruled out, but the fact that a complete separation of cellulose and polyacrylonitrile by several methods was not possible suggests that at least a partial grafting (i. e., some of the total acrylonitrile added) occurred. The formation of a cellulose free radical might be postulated by the removal of a hydrogen attached to a carbon atom which, in turn, might initiate grafting of the vinyl compound as follows:



$$\text{Cell}-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}} \rightsquigarrow \text{Cell}-\overset{\text{OH}}{\text{C}}\bullet$$

$$\text{Cell}-\overset{\text{OH}}{\text{C}}\bullet + \text{CH}_2=\underset{\text{CN}}{\text{CH}} \rightsquigarrow \text{Cell}-\overset{\text{OH}}{\text{C}}-\text{CH}_2-\underset{\text{CN}}{\text{CH}}\bullet$$

$$\text{Cell}-\overset{\text{OH}}{\text{C}}-\text{CH}_2-\underset{\text{CN}}{\text{CH}}\bullet + \text{CH}_2=\underset{\text{CN}}{\text{CH}} \rightsquigarrow \text{Cell}-\overset{\text{OH}}{\text{C}}-\text{CH}_2-\underset{\text{CN}}{\text{CH}}-\text{CH}_2-\underset{\text{CN}}{\text{CH}}\bullet \text{ etc.}$$

In an attempt to determine whether cellulose forms free radicals in the presence of water (which is necessary for monomer additions) under the influence of gamma radiation, the stable free-radical diphenylpicryl hydrazyl (DPPH) was used. In organic solvents DPPH has a characteristic purple color, and since the absorption spectra of its reaction products with other radicals is quite different, a color change in the DPPH solution may be measured spectrophotometrically and used to indicate a decrease in concentration of DPPH. Because the DPPH solution itself was highly unstable to gamma radiation, it was not possible to irradiate the cotton in a solution of the free radical. Therefore, the solution was added to the cellulose after irradiation. The results consistently indicated that a small amount of DPPH (of the order of magnitude of 0.06 g per gm of cellulose) reacted with the irradiated cotton, but reproducibility was difficult due to the instability of DPPH toward oxygen, and to the extremely low concentration that had to be used.

Iodine in benzene solution was also employed in another attempt to detect free radicals in cellulose. The results were non-reproducible as in the case of the DPPH method.

A different approach to the problem of the detection of free radicals is through post-irradiation grafting. Although the experimental work is incomplete, the results have been encouraging. Cotton skeins were weighed and then irradiated for 1, 2, 4, 8, and 24 hours. The irradiated skeins were refluxed in liquid acrylonitrile (AN) and in AN vapor on a steam bath for 1, 2, 4, 8, and 16 hours. Polymer add-on was obtained to determine the effects of varying both the time of irradiation, the time of refluxing and the effect of contact with the liquid versus contact with the vapor. Dimethyl formamide (DMF) extractions were run on all of the skeins to remove in situ polymerized acrylonitrile (PAN). All the polymer on the samples which were refluxed in the AN vapor was removed by DMF extraction indicating in situ polymerization only, but those samples irradiated as long as 4 hours and refluxed in liquid AN showed a significant amount of polymer left after extraction. The cotton skeins containing the grafted PAN were yellowed evenly and showed little harshness of hand indicating uniform polymerization.

While the foregoing experiments have not proved beyond all doubt the free-radical mechanism for the grafting of AN to cellulose, they represent evidence in favor of the theory.

Post-Irradiation Grafting

The addition of vinyl monomers of low volatility to fibrous materials is impractical by the vapor-phase technique. Thus, other procedures must be investigated. One that has been used by other investigators is the so-called post-irradiation method for grafting. This technique is applicable to volatile, as well as the non-volatile vinyl monomers. The fibers or yarns are first irradiated in either an enert atmosphere or an oxidizing atmosphere and then placed in the monomer or in a solution of the monomer in a suitable solvent. In the case of irradiation in an inert atmosphere (nitrogen or vacuum), stable free radicals are formed in the fiber and these subsequently initiate graft polymerization. In the case of irradiation in an oxidizing atmosphere (air or oxygen), organic peroxides are formed in the fiber. On treating these fibers in a monomer solution, the peroxides form free radicals which initiate graft polymerization.

Some preliminary work has been done, using this technique, with a number of different fibers and acrylonitrile. The data indicate that the monomer can be readily added, giving a product of a fair degree of uniformity. However, it is anticipated that difficulties will be encountered in making uniform products with some of the other monomers by the post-irradiation technique. Efforts are, therefore, being directed toward the improvement of uniformity.

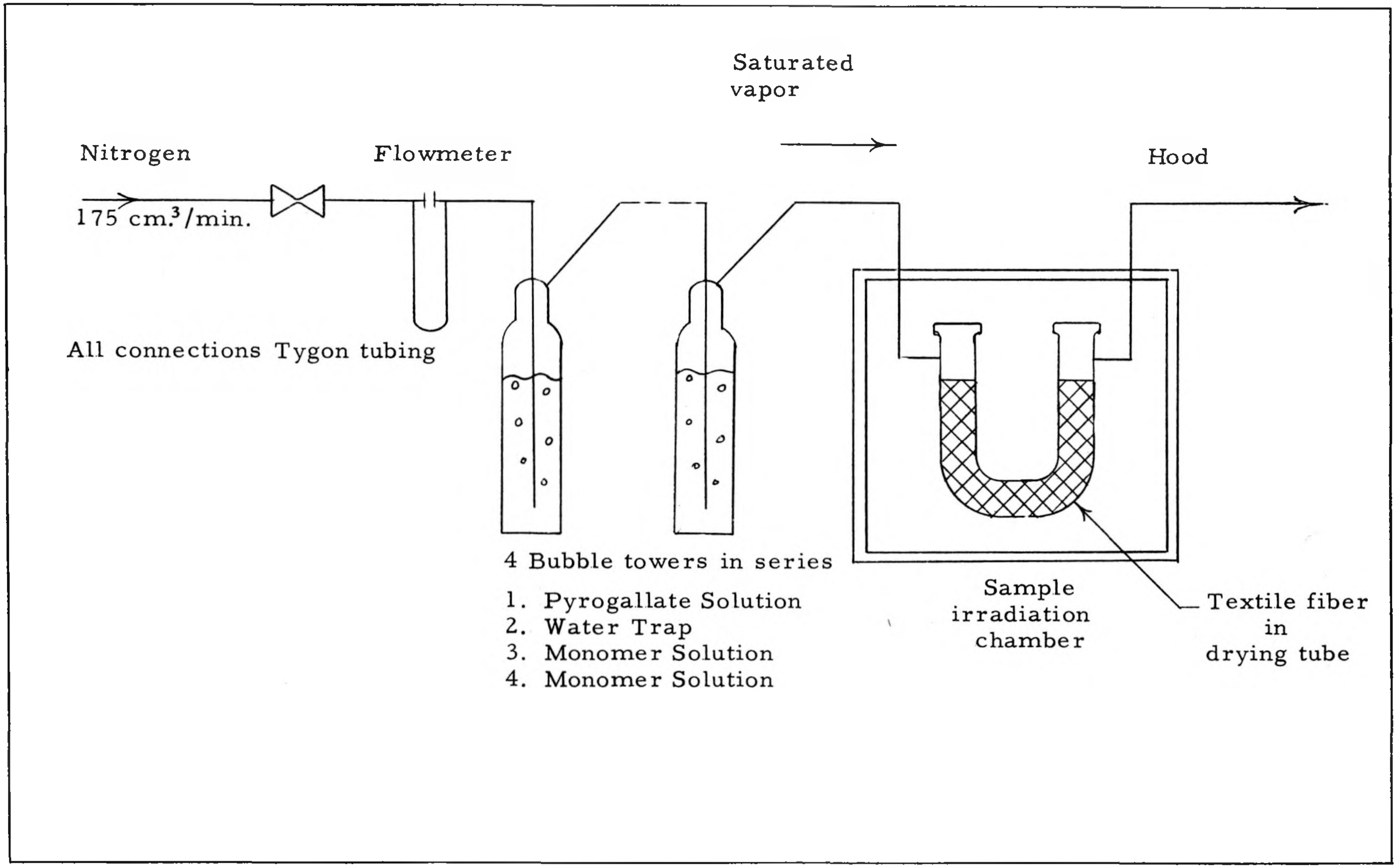


Figure 1 Diagrammatic sketch of vapor-phase irradiation apparatus

Figure 2

Photograph of Gammacell

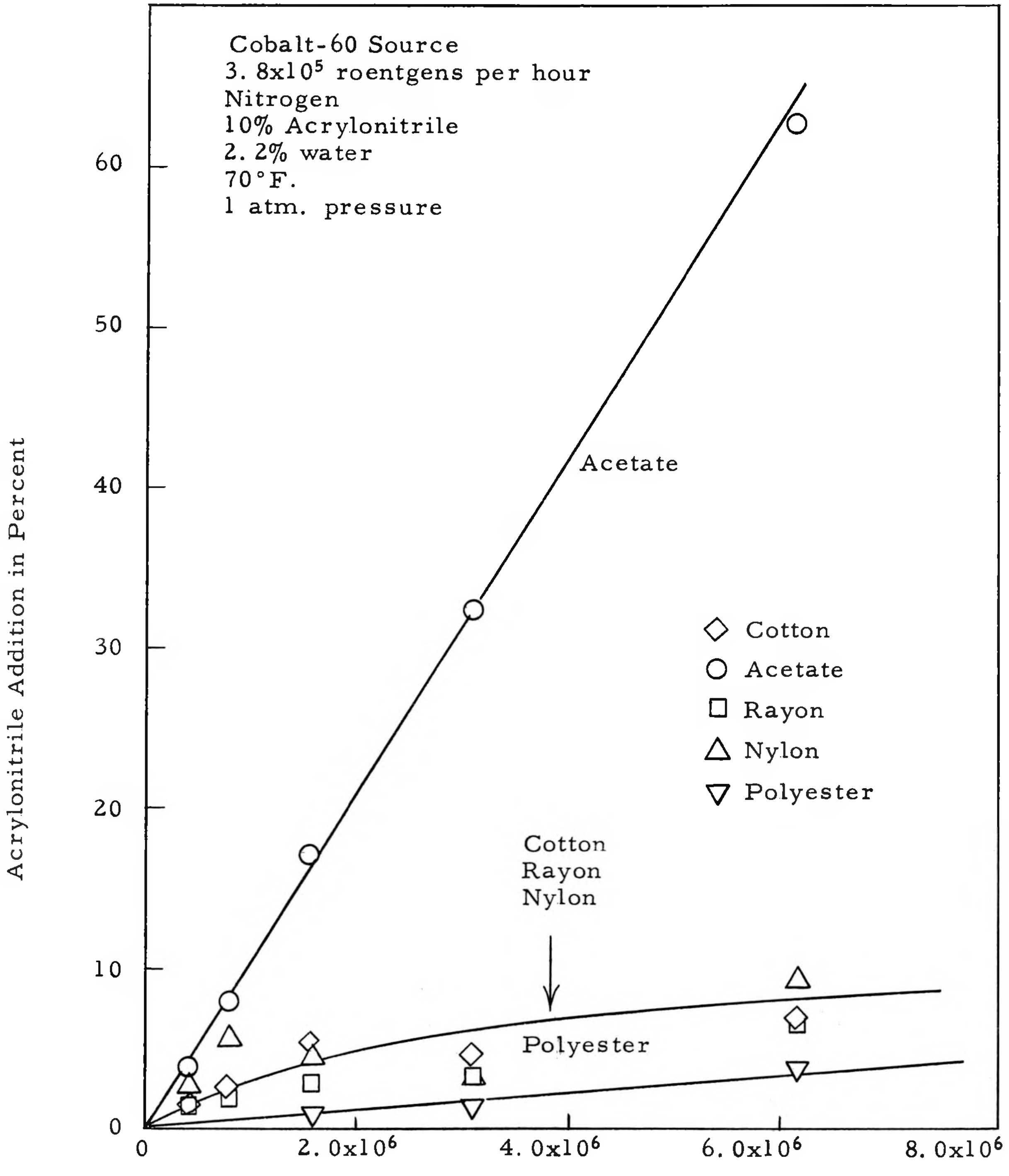


Figure 3

Vapor Phase Addition of Acrylonitrile to Textile Yarns

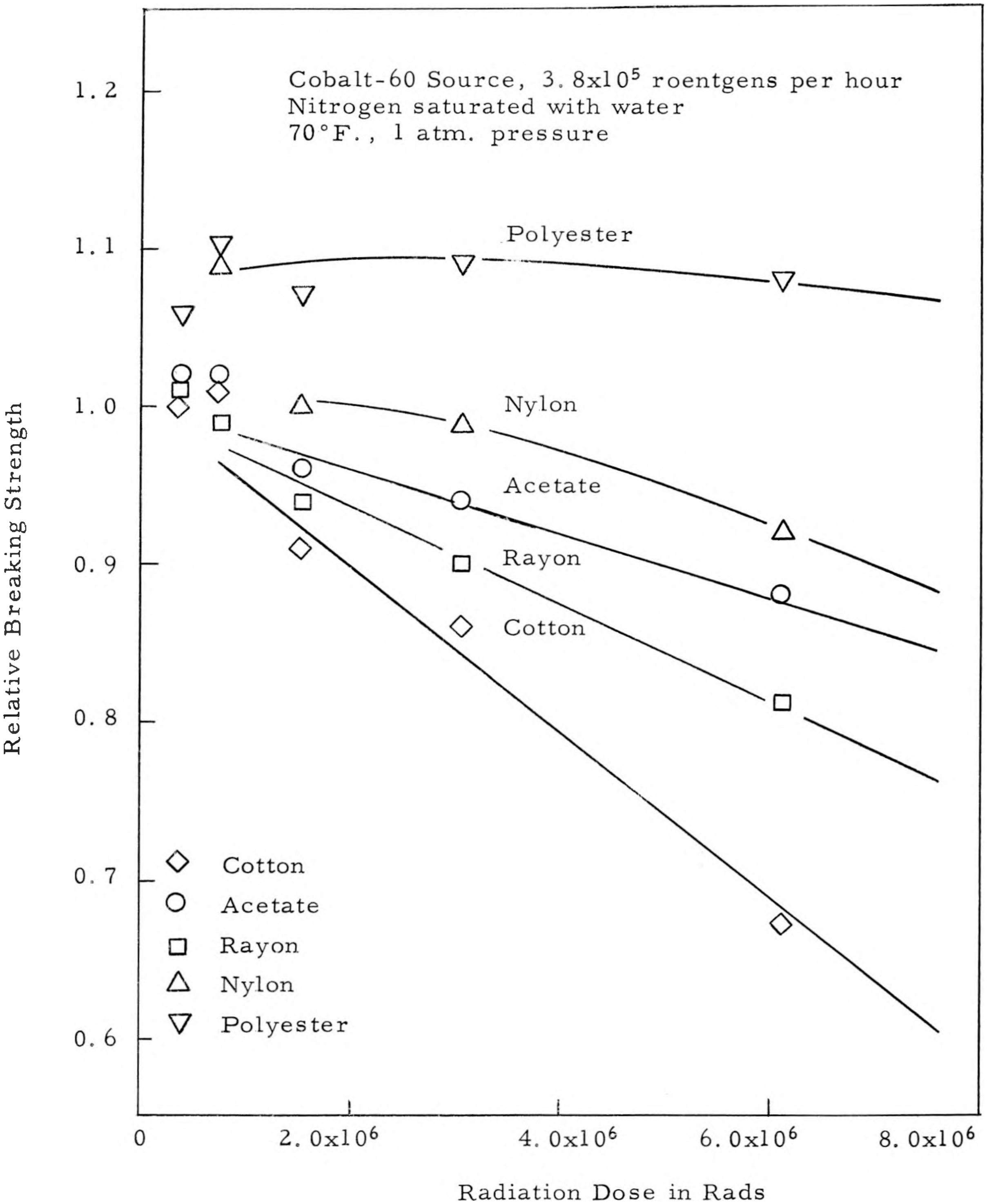
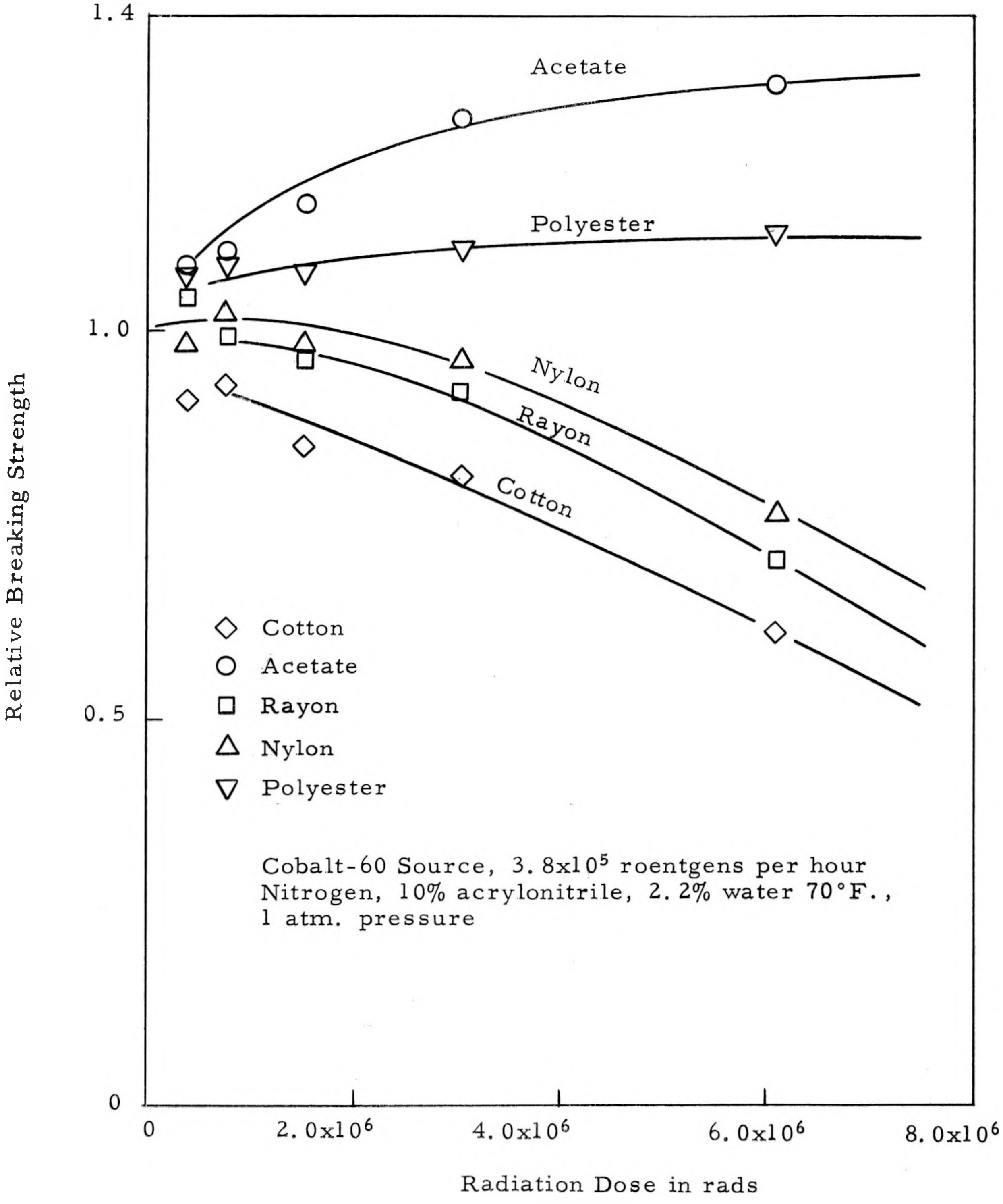


Figure 4

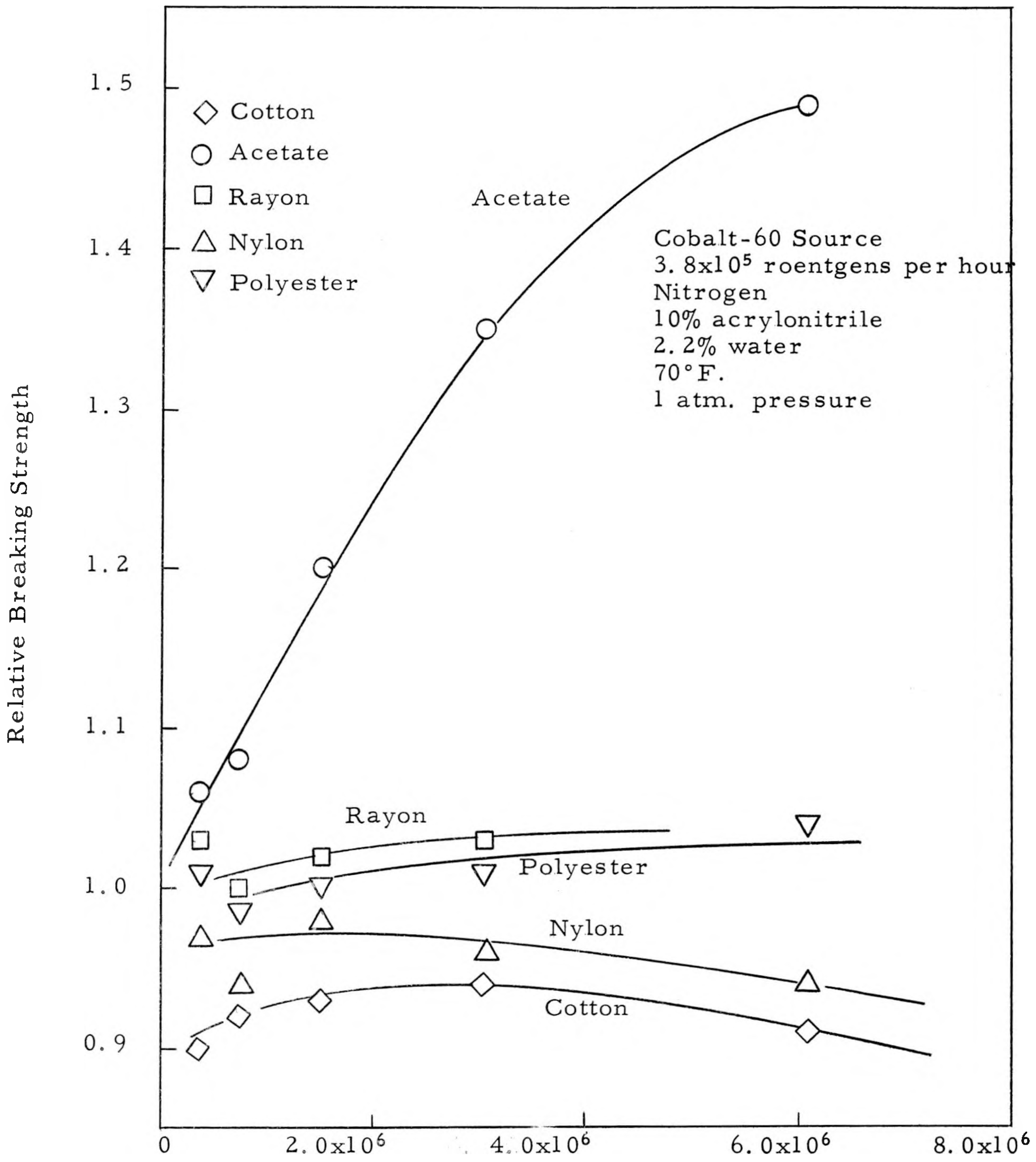
Relative Breaking Strengths of Textile Yarns
(relative to unirradiated control samples)



Cobalt-60 Source, 3.8x10^5 roentgens per hour
Nitrogen, 10% acrylonitrile, 2.2% water 70°F.,
1 atm. pressure

Figure 5

Relative Breaking Strengths of Textile Yarns
(relative to unirradiated control samples)



Radiation Dose in Rads

Figure 6

Relative Breaking Strengths of Textile Yarns
(relative to irradiated control samples)

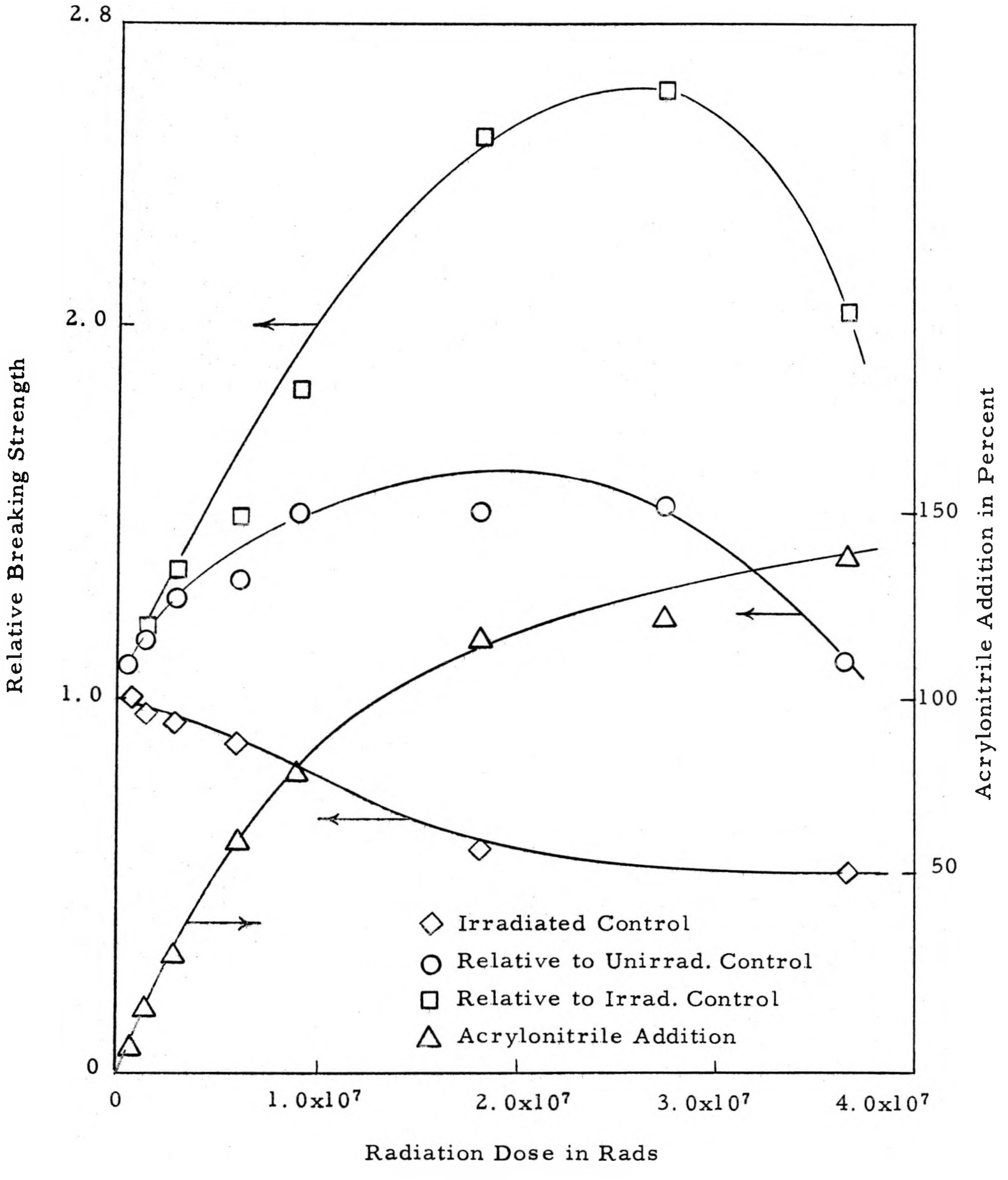


Figure 7

Cellulose Acetate Yarn: Relative Breaking Strength and Vapor Phase Addition of Acrylonitrile

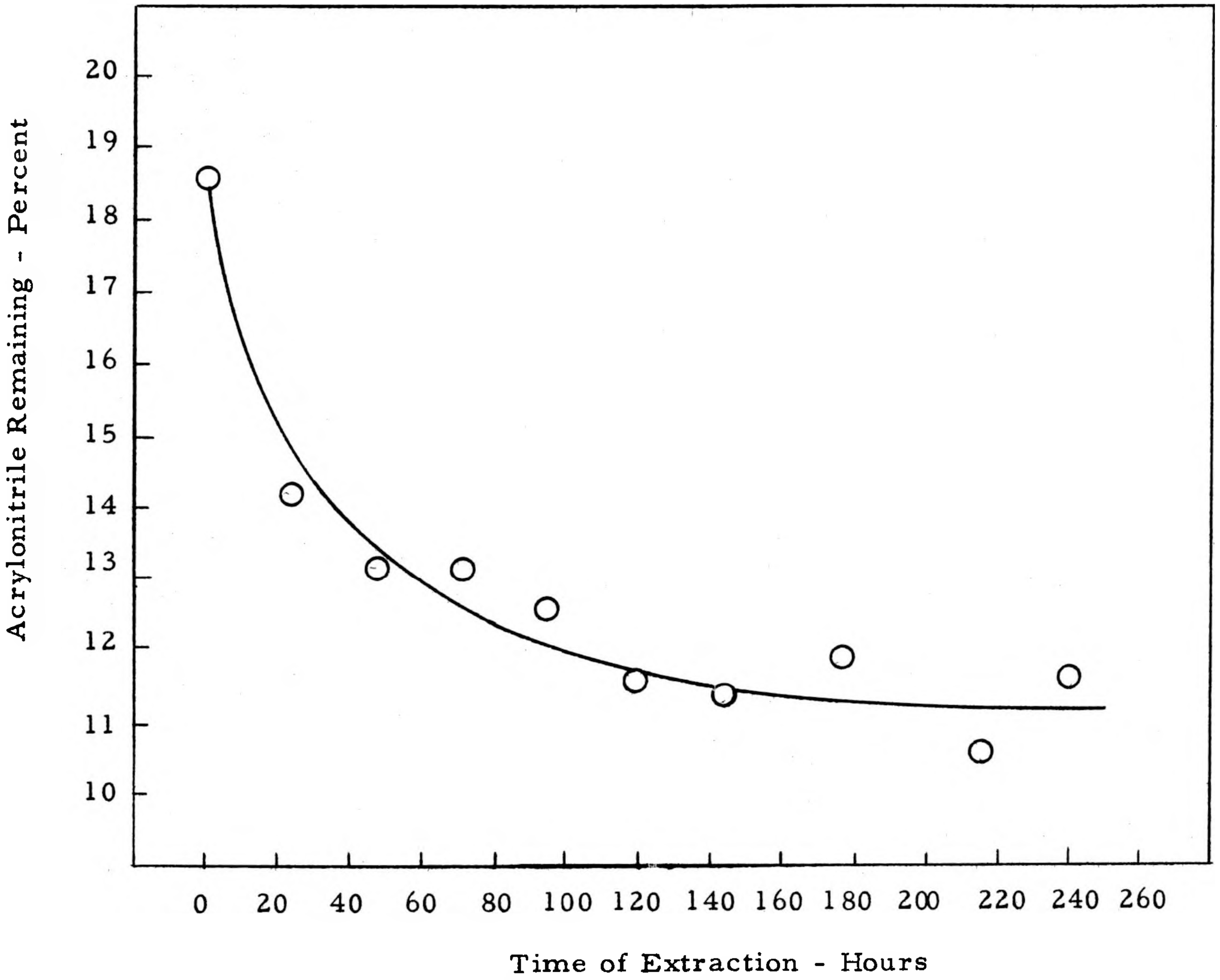


Figure 8. Percent acrylonitrile remaining as a function of extraction time.

TABLE I

VAPOR PHASE ADDITION OF ACRYLONITRILE TO TEXTILE YARNS

Cobalt-60 Source, 3.8 x 10^5 roentgens per hour. Atmosphere: nitrogen, 10% acrylonitrile, 2.2% water; 70°F., 1 atm. pressure

Radiation Dose	Cotton 30/1	Acetate 100-28	Rayon 60-10	Nylon 210-34	Polyester 70-34	Acrylic 150-60	Acrylic Staple Yarn
			Acrylonitrile Addition				
rads	%	%	%	%	%	%	%
3.80×10^5	1.4	3.7	1.2	2.4	0.4	0.0	0.0
7.60×10^5	2.5	7.8	1.8	5.8	0.0	0.0	0.0
1.52×10^6	5.2	17.0	2.8	4.4	0.4	0.0	0.0
3.04×10^6	4.5	32.1	3.4	3.0	1.1	0.0	0.0
6.08×10^6	6.6	62.5	6.1	9.3	3.5	0.0	0.0

TABLE II

BREAKING STRENGTH OF TEXTILE YARNS

Cobalt-60 Source, 3.8x10^5 roentgens per hour
Atmosphere: nitrogen saturated with water
70°F., 1 atm. pressure

Radiation Dose	Cotton 30/1	Acetate 100-28	Rayon 60-10	Nylon 210-34	Polyester 70-34	Acrylic 150-60	Acrylic Staple Yarn
				Breaking Strength			
rads	grams	grams	grams	grams	grams	grams	grams
0	246.2	5.1	10.5	31.4	8.9	14.4	849
3.80x10^5	245.9	5.2	10.6	31.9	9.4	13.5	1030
7.60x10^5	249.1	5.2	10.4	34.1	9.8	12.4	1000
1.52x10^6	223.6	4.9	9.9	31.3	9.5	13.1	958
3.04x10^6	210.9	4.8	9.4	31.2	9.7	14.6	880
6.08x10^6	164.6	4.5	8.5	29.0	9.6	14.4	853

TABLE III

BREAKING STRENGTH OF TEXTILE YARNS

Cobalt-60 Source, 3.8x10^5 roentgens per hour
Atmosphere: nitrogen, 10% acrylonitrile, 2.2%
water, 70°F., 1 atm. pressure

Radiation Dose	Cotton 30/1	Acetate 100-28	Rayon 60-10	Nylon 210-34	Polyester 70-34	Acrylic 150-60	Acrylic Staple Yarn
	Breaking Strength						
rads	grams	grams	grams	grams	grams	grams	grams
0	246.2	5.1	10.5	31.4	8.9	14.4	849
3.80x10^5	223.4	5.5	10.9	30.9	9.5	13.4	884
7.60x10^5	229.4	5.6	10.4	32.0	9.6	12.1	908
1.52x10^6	209.3	5.9	10.1	30.8	9.5	14.0	971
3.04x10^6	198.1	6.5	9.7	30.1	9.8	14.8	994
6.08x10^6	150.0	6.7	7.3	27.1	10.0	12.6	922

TABLE IV

RELATIVE BREAKING STRENGTH OF TEXTILE YARNS
(relative to unirradiated control samples)

Cobalt-60 Source, $3.8\mathrm{x}10^{5}$ roentgens per hour
Atmosphere: nitrogen saturated with water
70°F., 1 atm. pressure

Radiation Dose	Cotton 30/1	Acetate 100-28	Rayon 60-10	Nylon 210-34	Polyester 70-34	Acrylic 150-60	Acrylic Staple Yarn
		Relative Breaking Strength					
rads							
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$3.80\mathrm{x}10^{5}$	1.00	1.02	1.01	1.02	1.06	0.94	1.21
$7.60\mathrm{x}10^{5}$	1.01	1.02	0.99	1.09	1.10	0.86	1.18
$1.52\mathrm{x}10^{6}$	0.91	0.96	0.94	1.00	1.07	0.91	1.13
$3.04\mathrm{x}10^{6}$	0.86	0.94	0.90	0.99	1.09	1.01	1.04
$6.08\mathrm{x}10^{6}$	0.67	0.88	0.81	0.92	1.08	1.00	1.01

TABLE V

RELATIVE BREAKING STRENGTH OF TEXTILE YARNS
(relative to unirradiated control samples)

Cobalt-60 Source, $3.8x10^5$ roentgens per hour
Atmosphere: nitrogen, 10% acrylonitrile, 2.2%
water; 70°F. 1 atm. pressure

Radiation Dose	Cotton 30/1	Acetate 100-28	Rayon 60-10	Nylon 210-34	Polyester 70-34	Acrylic 150-60	Acrylic Staple Yarn
			Relative Breaking Strength				
rads							
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$3.80x10^5$	0.91	1.08	1.04	0.98	1.07	0.93	1.04
$7.60x10^5$	0.93	1.10	0.99	1.02	1.08	0.84	1.07
$1.52x10^6$	0.85	1.16	0.96	0.98	1.07	0.97	1.15
$3.04x10^6$	0.81	1.27	0.92	0.96	1.10	1.03	1.17
$6.08x10^6$	0.61	1.31	0.70	0.86	1.12	0.88	1.09

TABLE VI

RELATIVE BREAKING STRENGTH OF TEXTILE YARNS
(relative to irradiated control samples)

Cobalt-60 Source, 3.8x10^5 roentgens per hour
Atmosphere: nitrogen, 10% acrylonitrile 2.2%
water; 70°F., 1 atm. pressure

Radiation Dose	Cotton 30/1	Acetate 100-28	Rayon 60-10	Nylon 210-34	Polyester 70-34	Acrylic 150-60	Acrylin Staple Yarn
			Relative Breaking Strength				
rads							
0	0.90	1.06	1.03	0.97	1.01	0.99	0.82
3.80x10^5	0.92	1.08	1.00	0.94	0.98	0.98	0.91
7.60x10^5	0.93	1.20	1.02	0.98	1.00	1.07	1.02
1.52x10^6	0.94	1.35	1.03	0.96	1.01	1.01	1.13
3.04x10^6	0.91	1.49	0.86	0.94	1.04	0.88	1.08
6.08x10^6	1.00	1.00	1.00	1.00	1.00	1.00	1.00

TABLE VII

CELLULOSE ACETATE YARN: RELATIVE BREAKING STRENGTH AND VAPOR PHASE ADDITION OF ACRYLONITRILE

Cobalt-60 Source, 3.8×10^5 roentgens per hour

Radiation Dose rads	Acrylonitrile Addition percent	Breaking Strength in Grams		Relative Breaking Strength		
		Nitrogen Saturated with water	Nitrogen 10% Acrylo 2.2% water	Nitrogen-Water Relative to Unirradiated Control	Nitrogen-Water Acrylonitrile Relative to Unirrad. control	Nitrogen-Water Acrylonitrile Relative to Irradiated control
0	0	5.1	5.1	1.00	1.00	1.00
3.80×10^5	3.7	5.2	5.5	1.02	1.08	1.06
7.60×10^5	7.8	5.2	5.6	1.02	1.10	1.08
1.52×10^6	17.0	4.9	5.9	0.96	1.16	1.20
3.04×10^6	32.2	4.8	6.5	0.94	1.27	1.35
6.08×10^6	62.5	4.5	6.7	0.88	1.31	1.49
9.12×10^6	80.5	4.1	7.5	0.82	1.50	1.83
1.82×10^7	117	3.0	7.5	0.60	1.50	2.50
2.73×10^7	122	2.9	7.6	0.58	1.52	2.62
3.65×10^7	138	2.7	5.5	0.54	1.10	2.04

TABLE VII

Vapor Phase Addition of Vinyl Monomers to Textile Yarns

Cobalt-60 Source: 3.8 x 10^5 roentgens per hour

70°F. and 1 atm. pressure

Atmosphere: nitrogen in equilibrium with the two-phase, monomer-water solution

Gas flow rate: 175 cm^3 per min.

Acrylonitrile Addition - (gm. per 100 gm. yarn) at various radiation doses in rads

Yarn	3.80×10^5	7.60×10^5	1.52×10^6	3.04×10^6	6.08×10^6
cotton	1.4	2.5	5.2	4.5	6.6
polypropylene	0.5	1.2	2.6	5.1	11.2
rayon	1.2	1.8	2.8	3.4	6.1
acetate	3.7	7.8	17.0	32.1	62.5
nylon	2.4	5.8	4.4	3.0	9.3
polyester	0.4	0.0	0.4	1.1	3.5
acrylic filament	0.0	0.0	0.0	0.0	0.0
acrylic staple	0.0	0.0	0.0	0.0	0.0

TABLE VIII (cont'd)

Vinyl Acetate Addition -(gm. per 100 gm. yarn)
at various radiation doses in rads

Yarn	3.80×10^5	7.60×10^5	1.52×10^6	3.04×10^6	6.08×10^6
cotton	0.1	0.1	0.3	0.7	0.8
polypropylene	0.4	0.6	1.3	4.1	7.3
rayon	0.0	0.0	0.1	0.2	0.6
acetate	3.0	6.9	13.0	34.2	114.0
nylon	0.3	0.5	1.0	2.3	18.8
polyester	0.0	0.0	0.2	0.3	0.8
acrylic filament	0.0	0.0	0.0	0.0	0.0
acrylic staple	0.0	0.0	0.0	0.0	0.0

Vinyl Crotonate Addition - (gm. per 100 gm. yarn)
at various radiation doses in rads

Yarn	3.80×10^5	7.60×10^5	1.52×10^6	3.04×10^6	6.08×10^6
cotton	0.0	0.0	0.0	0.0	0.0
polypropylene	0.0	0.0	0.0	0.6	0.8
rayon	0.0	0.0	0.0	0.0	0.0
acetate	0.0	0.0	0.0	1.0	1.1
nylon	0.0	0.0	0.0	0.3	0.1
polyester	0.0	0.0	0.0	0.0	0.0
acrylic filament	0.0	0.0	0.0	0.0	0.0
acrylic staple	0.0	0.0	0.0	0.0	0.0

TABLE VIII (cont'd)

Methyl Methacrylate Addition - (gm. per 100 gm. yarn)
at various radiation doses in rads

Yarn	3.80×10^5	7.60×10^5	1.52×10^6	3.04×10^6	6.08×10^6
cotton	0.0	0.0	0.0	0.0	0.0
polypropylene	0.8	1.1	1.8	2.6	5.8
rayon	0.0	0.0	0.0	0.0	0.9
acetate	0.3	0.8	3.5	3.1	11.0
nylon	0.0	0.0	0.1	0.1	0.4
polyester	0.0	0.0	0.0	0.0	0.2
acrylic filament	0.0	0.0	0.0	0.0	0.0
acrylic staple	0.0	0.0	0.0	0.0	0.0

Vinyl Propionate Addition - (gm. per 100 gm. yarn)
at various radiation doses in rads

Yarn	3.80×10^5	7.60×10^5	1.52×10^6	3.04×10^6	6.08×10^6
cotton	0.0	0.0	0.1	0.2	0.3
polypropylene	0.2	0.3	0.5	1.7	2.7
rayon	0.0	0.0	0.0	0.3	0.0
acetate	0.6	1.1	5.5	7.6	27.4
nylon	0.1	0.1	0.3	0.6	1.1
polyester	0.1	0.0	0.0	0.1	0.3
acrylic filament	0.0	0.0	0.0	0.0	0.0
acrylic staple	0.0	0.0	0.0	0.0	0.0

TABLE VIII (cont'd)

Vinyl Butyrate Addition - (gm. per 100 gm. yarn)
at various radiation doses in rads

Yarn	3.80×10^5	7.60×10^5	1.52×10^6	3.04×10^6	6.08×10^6
cotton	0.0	0.0	0.0	0.0	0.0
polypropylene	0.2	0.2	0.6	1.3	2.9
rayon	0.0	0.0	0.0	0.0	0.0
acetate	0.0	0.1	0.5	1.5	4.8
nylon	0.0	0.0	0.0	0.1	0.3
polyester	0.0	0.0	0.0	0.0	0.0
acrylic filament	0.0	0.0	0.0	0.0	0.0
acrylic staple	0.0	0.0	0.0	0.0	0.0

Vinyl 2-Ethyl Hexoate Addition-(gm. per 100 gm. yarn)
at various radiation doses in rads

Yarn	3.80×10^5	7.60×10^5	1.52×10^6	3.04×10^6	6.08×10^6
cotton	0.0	0.0	0.0	0.0	0.0
polypropylene	0.0	0.0	0.0	0.2	0.6
rayon	0.0	0.0	0.0	0.0	0.0
acetate	0.0	0.0	0.0	0.2	0.4
nylon	0.0	0.0	0.0	0.0	0.0
polyester	0.0	0.0	0.0	0.0	0.0
acrylic filament	0.0	0.0	0.0	0.0	0.0
acrylic staple	0.0	0.0	0.0	0.0	0.0

TABLE VIII (cont'd)

Butyl Methacrylate Addition - (gm. per 100 gm. yarn)
at various radiation doses in rads

Yarn	3.80×10^5	7.60×10^5	1.52×10^6	3.04×10^6	6.08×10^6
cotton	0.0	0.0	0.0	0.0	0.2
polypropylene	0.0	0.3	0.2	0.4	0.9
rayon	0.0	0.0	0.0	0.0	0.0
acetate	0.0	0.0	0.0	0.0	0.4
nylon	0.0	0.0	0.0	0.0	0.3
polyester	0.0	0.0	0.0	0.0	0.2
acrylic filament	0.0	0.0	0.0	0.0	0.0
acrylic staple	0.0	0.0	0.0	0.0	0.0

Divinyl Sulfone Addition -(gm. per 100 gm. yarn)
at various radiation doses in rads

Yarn	3.80×10^5	7.60×10^5	1.52×10^6	3.04×10^6	6.08×10^6
cotton	0.2	0.1	0.0	0.1	0.9
polypropylene	0.1	0.1	0.0	0.7	1.4
rayon	0.4	0.1	0.0	0.0	0.9
acetate	0.2	0.3	0.6	1.5	6.4
nylon	0.1	0.1	0.1	0.3	1.4
polyester	0.5	0.1	0.1	0.2	0.4
acrylic filament	0.0	0.0	0.0	0.0	0.0
acrylic staple	0.0	0.0	0.0	0.0	0.0

TABLE IX

Effect of Monomer Addition on Physical Properties of 30/1 Cotton Yarn

Cobalt-60 Source
$3.8x10^5$ roentgens per hour
70°F. and 1 atm. pressure

gas flow rate: 175 $cm.^3$/min.
atmosphere: nitrogen in
equilibrium with two-phase
monomer-water solution

Radiation Dose rads	Control	Vinyl Acetate	Vinyl Crotonate	Methyl Methacrylate	Vinyl Propionate	Vinyl Butyrate	Vinyl 2-Ethyl Hexoate	Butyl Methacrylate	Divinyl Sulfone
				Breaking Strength in grams					
0	305	305	305	305	305	305	305	305	305
$3.04x10^6$	241	160	194	190	180	159	176	176	175
$6.08x10^6$	221	144	153	163	160	154	162	154	161
				Elongation in percent					
0	76.6	76.6	76.6	76.6	76.6	76.6	76.6	76.6	76.6
$3.04x10^6$	68.7	51.1	56.0	58.2	54.9	50.1	58.0	49.3	55.6
$6.08x10^6$	63.7	53.3	47.2	54.5	51.4	48.4	60.0	58.3	49.1
				Modulus in gm./inch					
0									
$3.04x10^6$					none				
$6.08x10^6$									

TABLE X

Effect of Monomer Addition on Physical Properties of Polypropylene 350-70 Yarn

Cobalt-60 Source
3.8x10^5 roentgens per hour
70°F. and 1 atm. pressure

gas flow rate: 175 cm.^{3}/min.
atmosphere: nitrogen in
equilibrium with two-phase
monomer-water solution

Radiation Dose rads	Control	Vinyl Acetate	Vinyl Crotonate	Methyl Methacrylate	Vinyl Propionate	Vinyl Butyrate	Vinyl 2-Ethyl Hexoate	Butyl Methacrylate	Divinyl Sulfone
				Breaking Strength in grams					
0	16.9	16.9	16.9	16.9	16.9	16.9	16.9	16.9	16.9
3.04x10^6	12.9	12.4	13.6	13.2	14.7	11.2	13.8	12.7	15.2
6.08x10^6	11.5	12.0	11.5	11.8	11.3	10.9	11.6	11.4	10.0
				Elongation in percent					
0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0
3.04x10^6	23.1	18.0	21.9	19.8	22.4	21.0	22.8	21.1	25.5
6.08x10^6	19.1	18.6	17.6	18.2	17.6	16.9	18.3	18.1	18.0
				Modulus in gm./inch					
0	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2
3.04x10^6	15.4	12.6	12.3	13.5	12.3	11.2	13.6	12.1	13.1
6.08x10^6	16.3	12.4	12.3	14.0	11.3	12.4	13.9	12.7	10.8

TABLE XI

Effect of Monomer Addition on Physical Properties of Rayon 60-10 Yarn

Cobalt-60 Source
3.8×10^5 roentgens per hour
70°F. and 1 atm. pressure

gas flow rate: 175 $cm.^3$/min.
atmosphere: nitrogen in equilibrium with two-phase monomer-water solution

Radiation Dose rads	Control	Vinyl Acetate	Vinyl Crotonate	Methyl Methacrylate	Vinyl Propionate	Vinyl Butyrate	Vinyl 2-Ethyl Hexoate	Butyl Methacrylate	Divinyl Sulfone
				Breaking Strength in grams					
0	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.4
3.04×10^6	6.0	5.5	6.0	5.7	5.9	5.2	5.7	5.7	6.0
6.08×10^6	5.2	4.7	5.2	5.1	5.1	4.8	5.2	5.3	5.2
				Elongation in percent					
0	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5
3.04×10^6	15.4	14.0	15.4	14.4	13.7	12.7	18.5	15.1	15.6
6.08×10^6	11.5	10.9	13.4	18.8	13.2	12.1	15.5	13.7	13.5
				Modulus in gm. /inch					
0	19.7	19.7	19.7	19.7	19.7	19.7	19.7	19.7	19.7
3.04×10^6	19.4	23.0	23.6	22.4	17.3	19.1	20.7	21.0	20.5
6.08×10^6	22.8	24.6	19.3	12.4	22.3	21.5	20.8	21.4	21.4

TABLE XII

Effect of Monomer Addition on Physical Properties of Acetate 100-28 Yarn

Cobalt-60 Source
3.8x10^5 roentgens per hour
70°F. and 1 atm. pressure

gas flow rate: 175 cm.^{3}/min.
atmosphere: nitrogen in equilibrium with two-phase monomer-water solution.

Radiation Dose rads	Control	Vinyl Acetate	Vinyl Crotonate	Methyl Methacrylate	Vinyl Propionate	Vinyl Butyrate	Vinyl 2-Ethyl Hexoate	Butyl Methacrylate	Divinyl Sulfone
Breaking Strength in grams									
0	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7
3.04x10^6	4.4	3.5	4.1	4.2	3.9	3.7	4.1	4.0	4.1
6.08x10^6	4.1	*	3.9	3.8	3.2	3.2	3.5	3.7	4.0
Elongation in percent									
0	28.1	28.1	28.1	28.1	28.1	28.1	28.1	28.1	28.1
3.04x10^6	24.4	4.1	28.5	25.3	22.0	20.0	28.3	22.2	24.4
6.08x10^6	22.0	*	23.8	18.0	12.0	16.4	21.8	21.9	22.7
Modulus in gm./inch									
0	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8
3.04x10^6	12.5	7.7	12.4	11.1	13.5	12.2	12.1	12.9	12.2
6.08x10^6	12.9	*	12.5	15.0	12.0	13.5	12.9	13.5	12.6

* Sample too brittle to test

TABLE XIII

Effect of Monomer Addition on Physical Properties of Nylon 210-34 Yarn

Cobalt-60 Source
3.8×10^5 roentgens per hour
70°F. and 1 atm. pressure

gas flow rate: 175 $cm.^3$/min.
atmosphere: nitrogen in
equilibrium with two-phase
monomer-water solution

Radiation Dose rads	Control	Vinyl Acetate	Vinyl Crotonate	Methyl Methacrylate	Vinyl Propionate	Vinyl Butyrate	Vinyl 2-Ethyl Hexoate	Butyl Methacrylate	Divinyl Sulfone
				Breaking Strength in grams					
0	37.4	37.4	37.4	37.4	37.4	37.4	37.4	37.4	37.4
3.04×10^6	33.5	28.0	31.8	33.2	31.9	29.4	32.7	33.0	33.1
6.08×10^6	33.1	26.0	30.0	30.2	31.5	30.1	32.0	31.9	29.8
				Elongation in percent					
0	83.3	83.3	83.3	83.3	83.3	83.3	83.3	83.3	83.3
3.04×10^6	79.2	70.3	76.8	89.0	79.5	63.5	87.1	82.4	93.0
6.08×10^6	76.4	46.7	73.1	74.8	79.1	70.7	85.9	84.4	77.7
				Modulus in gm./inch					
0	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5
3.04×10^6	22.9	23.5	25.0	24.4	23.5	25.6	25.6	25.0	25.6
6.08×10^6	25.4	25.6	25.6	25.6	25.6	25.0	26.9	24.7	24.4

TABLE XIV

Effect of Monomer Addition on Physical Properties of Polyester 70-34 Yarn

Cobalt-60 Source
3.8×10^{5} roentgens per hour
70°F. and 1 atm. pressure

gas flow rate: 175 $cm.^{3}$/min.
atmosphere: nitrogen in
equilibrium with two-phase
monomer-water solution

Radiation Dose rads	Control	Vinyl Acetate	Vinyl Crotonate	Methyl Methacrylate	Vinyl Propionate	Vinyl Butyrate	Vinyl 2.-Ethyl Hexoate	Butyl Methacrylate	Divinyl Sulfone
				Breaking Strength in grams					
0	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1
3.04×10^{6}	9.8	10.2	10.2	9.9	10.1	10.0	10.0	10.1	10.3
6.08×10^{6}	9.5	9.9	9.7	9.7	9.9	9.8	9.8	10.1	10.4
				Elongation in percent					
0	26.9	26.9	26.9	26.9	26.9	26.9	26.9	26.9	26.9
3.04×10^{6}	24.5	31.3	31.5	30.0	32.3	33.9	34.4	32.6	34.2
6.08×10^{6}	24.6	28.5	32.5	32.2	31.4	31.7	34.5	31.0	34.8
				Modulus in gm. /inch					
0	17.9	17.9	17.9	17.9	17.9	17.9	17.9	17.9	17.9
3.04×10^{6}	17.3	13.8	13.3	14.7	13.3	15.7	11.8	14.7	14.7
6.08×10^{6}	17.9	13.8	14.1	12.0	12.4	13.1	13.1	14.0	12.4

TABLE XV

Effect of Monomer Addition on Physical Properties of Acrylic 150-60 Yarn

Cobalt-60 Source
3.8x10^5 roentgens per hour
70°F. and 1 atm. pressure

gas flow rate: 175 cm.^{3}/min.
atmosphere: nitrogen in equilibrium with two-phase monomer-water solution

Radiation Dose rads	Control	Vinyl Acetate	Vinyl Crotonate	Methyl Methacrylate	Vinyl Propionate	Vinyl Butyrate	Vinyl 2-Ethyl Hexoate	Butyl Methacrylate	Divinyl Sulfone
Breaking Strength in grams									
0	13.1	13.1	13.1	13.1	13.1	13.1	13.1	13.1	13.1
3.04x10^6	12.7	12.9	12.3	12.3	13.2	12.9	13.5	13.8	12.6
6.08x10^6	12.1	12.8	13.8	12.9	13.9	13.7	13.6	14.4	13.7
Elongation in percent									
0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0
3.04x10^6	13.9	15.3	14.4	14.4	15.3	13.1	15.5	16.3	15.2
6.08x10^6	13.3	15.1	15.9	15.4	16.1	15.9	15.9	16.6	15.6
Modulus in gm./inch									
0	23.1	23.1	23.1	23.1	23.1	23.1	23.1	23.1	23.1
3.04x10^6	22.5	21.9	19.3	18.0	23.8	24.3	23.3	22.7	23.6
6.08x10^6	22.1	21.3	23.3	22.4	25.0	24.3	24.3	22.0	21.2

TABLE XVI

Effect of Monomer Addition on Physical Properties of Acrylic Staple Yarn

Cobalt-60 Source
$3.8x10^5$ roentgens per hour
70°F. and 1 atm. pressure

gas flow rate: 175 $cm.^3$/min.
atmosphere: nitrogen in
equilibrium with two-phase
monomer-water solution

Radiation Dose rads	Control	Vinyl Acetate	Vinyl Crotonate	Methyl Methacrylate	Vinyl Propionate	Vinyl Butyrate	Vinyl 2-Ethyl Hexoate	Butyl Methacrylate	Divinyl Sulfone
Breaking Strength in grams									
0	708	708	708	708	708	708	708	708	708
$3.04x10^6$	731	720	816	798	727	775	764	774	882
$6.08x10^6$	681	751	856	770	789	791	773	766	691
Elongation in percent									
0	24.6	24.6	24.6	24.6	24.6	24.6	24.6	24.6	24.6
$3.04x10^6$	25.3	24.5	25.2	25.4	24.7	24.4	24.5	25.0	25.2
$6.08x10^6$	25.1	24.2	24.8	23.8	24.8	24.5	24.5	24.5	23.7
Modulus in gm./inch									
0	772	772	772	772	772	772	772	772	772
$3.04x10^6$	715	605	653	597	634	604	592	609	867
$6.08x10^6$	663	841	836	710	870	794	582	624	751

PART II. ACTIVATION ANALYSIS

Fiber Identification

A problem frequently encountered in textile manufacturing and quality control is the identification of the source of supply of various textile materials, especially fibers and yarns. This situation poses difficulties for man-made fiber producers who may make similar fibers at different plants, fiber producers who make fibers similar in composition to that of other manufacturers, or spinners of yarns from cotton or other staple fibers.

The method of activation analysis is a technique that has gained increasing usage for determination of trace elements or impurities in a variety of materials. Since, in general, all textile fibers contain some trace impurities, or lend themselves to the incorporation of a preselected known impurity, activation analysis may present a means of fiber and yarn identification. A program was, therefore, initiated to apply this method to a large number of commercially available natural, regenerated and synthetic fibers in order to establish characteristic gamma spectra for each material. The chemical separation and quantitative determination of trace impurities in these materials is not, for the present, included in the objectives of this program.

As a preliminary step toward the development of a program of fiber identification, using activation analysis, it is necessary to obtain gamma-ray spectra for the different fibers. Gamma-ray spectra must be obtained to show the presence of the short, medium, and long half-life isotopes produced by the neutron activation of each material. These spectra will be used to determine some of the elements present and indicate if there is sufficient difference between fibers for identification. Gamma-ray spectra have been obtained for most of the commercial fibers by activating a one-gram sample in a nuclear reactor for one hour at a neutron flux of 10^{11}n. /cm.^{2}/sec. A 256-channel analyzer was used to obtain the spectra. Figure 1 is a photograph of the 256-channel analyzer used in this investigation. Figures 2 through 8 are photographs of the gamma-ray spectra obtained for one minute counting time.

These samples were irradiated in positions machined in the graphite reflector of the 10 KW heterogeneous reactor in the Physics Department. A delay of 2-3 hours is necessary in removing the samples from the reactor so that some of the intense radiation may decay. This delay eliminates the detection of the short half-life materials. Moreover, the irradiation time of one hour was not sufficient to activate the long half-life isotopes. Therefore the spectra obtained included only some medium range half-life isotopes. No attempt was made at quantitative interpretation of these gamma-ray spectra. Detailed data on the activation analysis for each spectra are listed in Table I if quantitative evaluation is desired.

Figure 2 presents the gamma-ray spectra for the five acrylic fibers used in this investigation. Inspection of these spectra show that the gamma-ray spectrum for acrylic fiber A is identical with the gamma-ray spectrum for acrylic fiber E (except for the magnitudes of the photopeaks). Detailed data for each spectrum are given in Table I if comparison of the magnitudes of the photopeaks is desired. The gamma-ray spectrum for acrylic fiber D is similar to the spectra for acrylic fibers A and E with the exception of the larger photopeak at 0. 51 Mev. This indicates that acrylic fiber D contains Cu-64 not present in the other fibers. The gamma-ray spectra for acrylic fibers B and C are entirely different from the spectra of the other acrylics.

The spectrum for acrylic fiber B shows large photopeaks for Cu-64 and Mn-56 while the spectrum for acrylic fiber C shows smaller photopeaks for Zn-69, Cu-64, and Mn-56. All the acrylic fiber spectra show large photopeaks for Na-24.

Figure 3 presents the gamma-ray spectra for three polyester fibers. The spectrum for polyester fiber A shows large photopeaks for Sb-122 and Mn-56. The photopeak for Sb-122 is the only large peak for polyester fibers B and C and polyester fiber C contains a much larger amount of antimony than polyester fiber B.

The spectra for five nylon fibers are given in Figure 4. All the spectra for nylon are quite similar in that they have large photopeaks for Na-24 and small peaks for Mn-56. The magnitudes of the photopeaks are slightly different and some of the spectra show slight differences. These differences are the faint peaks of Zn-69 in nylon fibers B and E and of Cu-64 in nylon fiber E.

Figure 5 presents the gamma-ray spectra of three rayon fibers. All the rayon fiber spectra are similar; they contain the strong photopeaks of Na-24 and a very faint photopeak for Mn-56 at 0. 84 Mev. The magnitudes of the Na-24 photopeaks are much larger for rayon fiber C.

Gamma-ray spectra for four acetate fibers are presented in Figure 6. Acetate fibers A and B have spectra which are similar. Both contain strong photopeaks for Cu-64, Mn-56 and Na-24 and a weak photopeak for Sr-87. For acetate fiber A there is a photopeak at 1. 5 Mev. which was identified as K-42, and there are several other faint photopeaks which were not identified. The spectra for acetate fibers C and D are identical, showing the strong photopeaks of Na-24 and a faint photopeak for Mn-56. The spectra for acetate fibers C and D are very similar to the spectra for rayon fibers shown in Figure 5.

Figure 7 presents the gamma-ray spectra for four polypropylene fibers. These fiber samples were made by two different fiber manufacturers. They were spun from both stabilized and unstabilized polypropylene polymer made by the same manufacturer. Gamma-ray spectra for unstabilized polypropylene fibers A and B were identical and showed photopeaks for Cu-64, Mn-56 and Na-24. Also the gamma-ray spectra for stabilized polypropylene fibers A and B were identical and showed the photopeaks of Cu-64, Mn-56, Na-24 and several other faint photopeaks which were not identified. This indicates that polypropylene fiber spun from the same polymer contains the same trace elements as indicated by activation analysis.

Gamma-ray spectra for glass, wool, silk, cellulosic cotton, and scoured cotton fiber are presented in Figure 8. For the glass fiber the spectrum shows large photopeaks for Na-24 and a small photopeak for Mn-56. The spectra for wool and silk are very similar, showing the photopeaks for Na-24, Mn-56, and Cu-64. The cellulosic fiber spectrum shows the photopeaks for Na-24, Mn-56, Cu-64 and Sr-87. The spectrum for cotton fiber shows photopeaks for Na-24, Mn-56, K-42, Cu-64 and a faint unidentified photopeak. Scouring the cotton removed most of the trace elements except manganese as indicated by the spectrum for scoured cotton.

Inspection of Figures 2 through 8 shows differences between different groups of fibers and some differences between the same type fibers produced by different manufacturers. In most cases the differences in these spectra are not sufficient for positive identification of both fiber and manufacturer.

To get a complete picture, spectra for both the short half-life and long half-life isotopes will be obtained.

In order to obtain gamma-ray spectra for the short half-life isotopes a plastic sample holder for five samples was made for the core of the reactor. With this sample holder it is possible to remove the samples immediately after activation. A sample can be removed from the reactor and counting started in approximately five minutes after activation. Using this method, isotopes with half-lives down to approximately 5 minutes may be detected.

Gamma-ray spectra were obtained by this method on acrylic fiber E as shown in Figure 9. Inspection of this figure shows the photopeak of the 6 minute Ti-51 at 8 minutes and 33 minutes after activation.

For the long half-life isotopes it is planned to activate the samples for 10 hours and 50 hours and obtain the gamma-ray spectra for each textile fiber.

Process Studies Using Activation Analysis

It has been proposed that activation analysis might be used as a tool in studying the process of fiber blending. This would be done by tagging the fibers with a high cross section isotope whose presence and distribution in the fiber could be determined by activation analysis. Since the variability (or distribution) of the isotope in the fiber is thought to be a measure of the blending efficiency, it is desirable to be able to measure the variance due to sample variation as precisely as possible. To this end, work has begun to determine the variance inherent in activation analysis in order to account for it in measuring the fiber variance. Two sources of this variance were considered: variance in counting and variance in reactor flux.

In order to measure the counting variance, an activated gold foil was placed in the detector well of the analyzer and counted ten times, subtracting the background simultaneously. This was done at three levels: one thousand, ten thousand, and one hundred thousand counts in the gold peak. The data were analyzed by several different methods, and variances calculated for each, in order to find the method giving the lowest variance. The method giving the lowest variance was finding the average photopeak width for all ten counts. The integral count was determined under the photopeaks within the average peak width. This gave the advantage of having the same number of channels for each photopeak. This method gave results comparable to those expected from theoretical considerations. (The theoretically expected variance from counting random events, assuming a Poisson distribution, is equal to the total number of counts). The results are as follows:

Average Peak Count	Variance		Standard Deviation		Coefficient of Variation	
$\bar{x}$	σ^2		σ		v= $(100\sigma / \bar{x})$	
	Actual	Theoretical	Actual	Theoretical	Actual	Theoretical
1,182	1,172	1,182	34.3	34.4	2.90%	2.91%
10,881	4,666	10,881	68.3	104.3	0.63%	0.96%
93,418	118,570	93,418	344.2	305.6	0.37%	0.33%

It was concluded that this method was satisfactory and that no variance above that expected theoretically would be introduced by counting procedures.

The variance in reactor flux was found to be much more significant. The reactor has four removable stringers in the graphite reflector. Four sample holes were machined in each of these stringers giving a total of 16 positions for irradiation next to the core. Sixteen samples containing a known amount of gold were placed in the sample positions and irradiated. The samples were counted and the variance calculated. The results after subtracting the variance due to counting by using the equation

$$\sigma^2_{\text{flux}} = \sigma^2_{\text{total}} - \sigma^2_{\text{counting}}$$

are as follows:

	Average Count $\bar{x}$	Coefficient of Variation $v = (100\ \sigma / \bar{x})$
Total	332, 300	3. 69%
Stringers 15	337, 300	0. 46%
14	346, 750	1. 33%
13	315, 300	1. 35%
12	330, 000	1. 09%
Between Stringers	332, 300	3. 97%

As can be seen, these variations are too high for any sensitive work in variance measurement. If the relative flux for each sample position were constant, these variations could be eliminated. Because of changes in control rod positions, however, the flux distribution in the reactor is probably not constant. It was thought that the relative fluxes might be more nearly constant if all sixteen positions were in the same stringer. In order to investigate this, twelve more sample holes were machined in stringer No. 13 to give four rows of four positions each for a total of 16. These were tested in the same manner and the results are as follows:

	Average Count $\bar{x}$	Coefficient of Variation $v = (100\ \sigma / \bar{x})$
Total	225, 697	13. 20%
Row 1	263, 889	1. 38%
2	239, 848	1. 31%
3	211, 336	0. 63%
4	187, 716	1. 49%

These data indicate that the coefficient of variation in any row of four sample positions is approximately 1. 3%. This means that for any one determination the value of the counting rate will be within ± 1. 3% of the true mean value 70% of the time. It is necessary now to calibrate all 16 sample positions very precisely and determine a coefficient of variation for the flux distribution.

To determine the actual variability of the samples, the variability due to counting and to flux distribution must be removed from the total variability. Assuming that these variances are additive the equation for the variances is

$$\sigma^2 \text{(total)} = \sigma^2\text{(counting)} + \sigma^2\text{(flux)} + \sigma^2\text{(sample)}$$

Then the variance due to the sample can be calculated from the above equation.

The variance due to counting has been established as the total number of counts. The variance due to the flux is now being evaluated by precise calibration of the 16 sample positions. After this variance has been established, then the sample variance can be determined from the total variance of an experimental run. This method can be used to determine variances in a number of process studies. An experiment is being set up to determine the efficiency of blending in the spinning process for cotton yarn. The cotton yarn will be tagged with a metallic element, probably manganese, copper or gold, and variances determined at different points in the process. The sample variances will indicate the degree of blending.

Activation Analysis of Manganese - Labeled Cotton

The applicability of activation analysis to the identification of textile fibers and yarns is based on the premise that these materials contain characteristic impurities which, when transformed into their radioactive isotopes by bombardment with neutrons, emit gamma-rays of discrete energies and thus form characteristic, identifying spectra. However, in the case of cotton, identification cannot depend upon the naturally-occurring impurities, since these arise from environmental conditions such as soil, fertilizer, water supply, etc., and probably vary considerably. Thus, with natural materials, identification might better be accomplished by labeling the fiber with a substance that can be readily transformed into a radioactive isotope. Based on preliminary experiments, manganese, which has a short half-life and a relatively simple decay scheme, was selected for the series of experiments on tagging cotton with non-radioactive cations.

The detailed experimental procedures that were used to prepare the various samples are shown in Appendix I. Briefly, about 1.4 ounces of labeled cotton was mixed with 20 pounds of untreated fiber and the mass converted to yarn and fabric by conventional methods. The fabric was desized, scoured, bleached, and dyed on pilot-scale equipment using procedures that duplicated normal plant practices. At all steps in both the dry and wet processing of the material, samples were taken to check the level of retention of the manganese label. The preparation and handling of samples, the gamma-ray spectrometer with associated instrumentation used for analysis of the irradiated samples as well as the technique of labeling cotton with manganese was described previously (Annual Report, November 1, 1959, Contract No. AT-(40-1)-2477).

Typical spectra of raw-stock samples containing various amounts of the labeled fiber were shown in a previous report (Annual Report, November 1, 1959, Contract No. AT-(40-1)-2477). Although the feasibility of the method was demonstrated, several important and practical questions remained unanswered. These are listed below and constitute the basis for the present series of experiments.

A. How reliable is the method used for evaluating the manganese content of the samples and how do experimental values for activity compare with theoretical calculations?

B. Does additional dilution of a fixed-ratio mixture of untreated and labeled raw stock occur during the conversion of the raw material into yarn?

C. Does preferential elimination of the labeled fibers occur during processing?

D. What is the sample size required for detection of the manganese at any stage of yarn processing?

E. How homogeneous are the products at the various stages of processing, i. e., what is the blending efficiency?

F. Does the label remain in the yarn once woven into cloth and subjected to wet processing?

G. Does the manganese cause undue tendering in bleaching?

H. Do the impurities in the dyestuffs and auxiliary chemicals interfere with the determination of manganese in the event that analysis of finished materials is required?

As a first approach to quantitative interpretation of the analysis, it was decided to use the peak height of the characteristic 0. 84 Mev. photopeaks of Mn-56 as a measure of the manganese concentration. Cotton was tagged with manganese by ion exchange to a concentration of approximately 6×10^{-4} grams of manganese per gram of cotton. A one gram sample of the tagged cotton was activated for four hours at a flux of 10^9 n. /cm.^{2} sec. A gamma-ray spectrum was obtained for this sample and the peak height was 1.2×10^4 cpm. /gm. cotton corrected to a time 15 minutes after activation. The peak height for untagged cotton was 120 cpm. /gm. cotton.

Calculations were made to estimate the peak height of any one gram sample randomly selected at any stage of processing. A chart showing the different stages of processing is given in Table II. The ratio of tagged to untagged cotton was approximately 1 to 170 (38 grams of tagged cotton to 6356 grams of untagged cotton). Therefore, the expected peak height for one gram sample of blended cotton, assuming complete homogeneity, was approximately 190 cpm. /gm. cotton. By comparing this number with the specific activities (peak heights) actually obtained, shown in Table III, it can be concluded that complete homogeneity or blending was not achieved at any stage of processing.

The analyses of the waste collected in picking and carding indicate that preferential elimination of the labeled fibers did not occur. The results are tabulated in Table IV. The specific activities of the waste from the card cylindery, flats and doffer are lower than those from some lap samples, the material which is fed into the card. The waste from the blending reserve on the picker showed a very high specific activity. However, this was not unexpected since this type of waste contains much of the vegetable matter associated with the raw cotton, and it is naturally rich in manganese. This manganese does not originate from the labeled fibers. Similarly, the fly and motes from the card as well as the fly at the card doffer showed a high manganese content, again due to vegetable matter that is eliminated from the raw stock in the carding process.

From every stage of processing samples were randomly withdrawn from the production line and subdivided into 0. 4, 1. 0, 2. 0, 5. 0, and 10. 0 gram portions. A detailed flow chart is given in Table II and the processes schematically illustrated in Figure 10. These samples were irradiated and subsequently analyzed for manganese. The criterion used in evaluating the results was the height of the characteristic peak associated with the label, i. e., the 0. 84 Mev. primary photopeak of Mn^{56}, in the manner described earlier. The data are shown in Table III and illustrated in Figure 11.

In all cases the amount of manganese was readily estimated. All samples containing the labeled fibers showed about twice the manganese activity of the untreated control raw stock. As expected, the lap exhibited a large variation in manganese content since thorough mixing at this first stage of processing had not yet occurred. With each additional step, however, the amount of manganese in a given sample increased, reaching a saturation point after the second drawing and only exceeding this level in the case of plied yarn. The average specific activity of samples from each stage of processing, plotted in Figure 12, demonstrates the above quite clearly.

The data in Table III show further that even a one-half gram sample was sufficient for the detection of the label. However, when the individual specific activities are taken into consideration (they can be computed from Table III it is found that the optimum sample weight for analysis lies between two and ten grams.

The labeled yarn was made into a plain-woven fabric which was subjected to the usual wet-processing operations, namely, desizing, scouring, bleaching and dyeing. In order to detect any possible adverse effects of the added manganese on the material, the bleach bath was monitored for changes in the pH and the fluidity of the material before and after bleaching measured. The possibility of contamination from impurities in the dyestuffs was also recognized. This could either make the detection of the label difficult or yield erroneous results because of the presence of additional manganese. However, the dyeing process was not investigated thoroughly. Only one direct dye and one vat dye was considered.

Several samples (6, 9, 10, 12 (about 1 g) and 24 (about 2 g) square inches in area) were taken from the grey cloth and after each step in wet-processing for analysis. The results are compiled in Table V and illustrated in Figure 13. By in spection of the data listed in Table V, it is immediately evident that almost all of the manganese added as label was removed in desizing and scouring. This can be accounted for by the fact that the manganese reacted primarily with the acid groups in the pectic matter of cotton which, as a rule, is largely removed by enzyme desizing and normal scour. The increase in fluidity during bleaching was normal.

The grey cloth exhibited an activity that was predictable from the yarn data (Table III), i. e., the one-gram yarn sample showed an activity of 260 cpm, while the 12 in^2 sample, also about one gram, assayed 276 cpm. After desizing, the activity of cloth samples dropped to about half of the above and remained at this level throughout the other stages of wet processing, although the vat dyed samples, in general, had somewhat higher counts. From the data available, however, it appears that dyeing did not introduce complicating factors.

Cotton yarns may be successfully labeled with a small amount of an "impurity" such as manganese. It was shown that the manganese could be subsequently detected and quantitatively estimated at all stages of yarn processing even when the randomly-selected samples were small in size. No evidence was found that preferential elimination of the treated fibers occurred or that the original ratio of treated to untreated raw stock is further diluted in the course of processing. The analysis of the cloth woven from the labeled yarns and subjected to wet processing showed that almost all of the manganese was removed in desizing. Thus, the identification of tagged yarns in finished products would be rather questionable when using manganese as the tracer.

In this experiment the ratio of the labeled to untreated fiber was approximately 1:170 using cotton that had only 6×10^{-4} grams of manganese per gram of cotton. The results showed that if analyses are to be made on samples in excess of two grams, the ratio could have been increased to 1:400 without imparing the detection. Ultimately, such ratio depends mainly on the degree to which manganese or, for that matter, any other chosen label can be substituted into cellulose.

There are two more aspects of this problem to be pursued in the near future: (1) repeat the experiments described in this report, using cotton fibers labeled after the pectic matter was removed, and (2) investigate a series of elements in addition to manganese which may eventually be used for labeling cotton yarns.

Figure 1.
Photograph of 256-Channel Analyzer

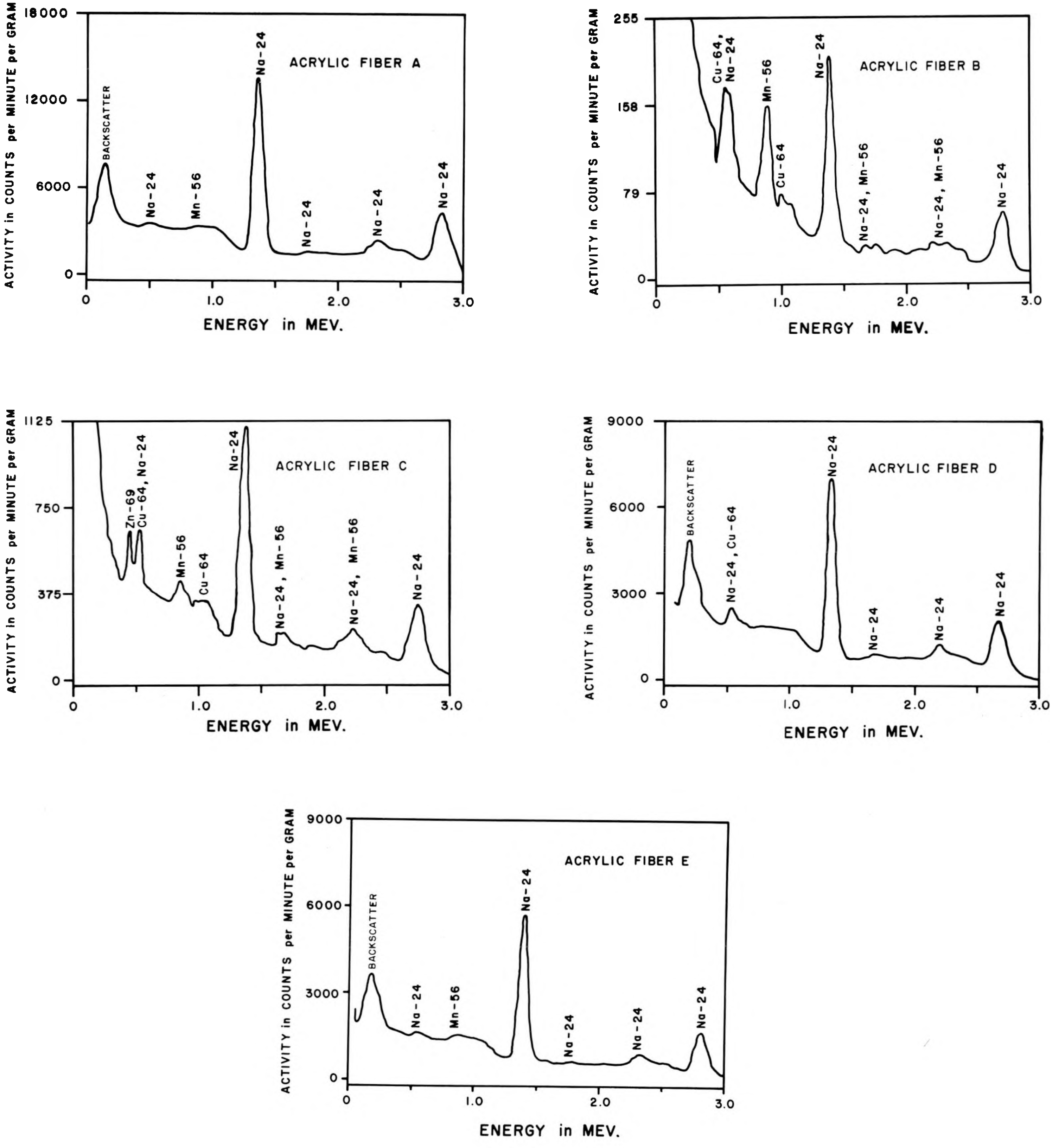


Figure 2.

Gamma Ray Spectra of Acrylic Fibers

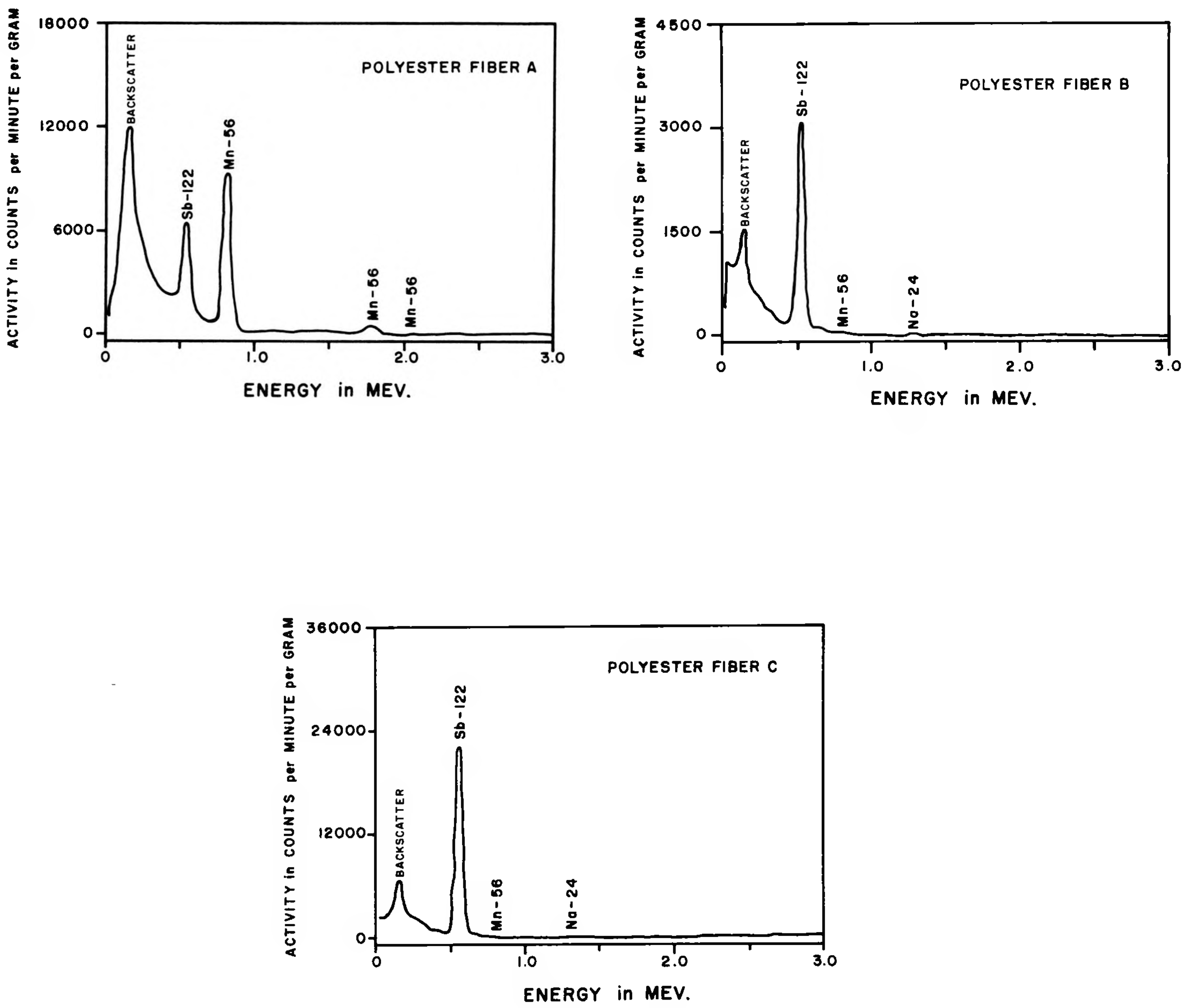


Figure 3.

Gamma Ray Spectra of Polyester Fibers

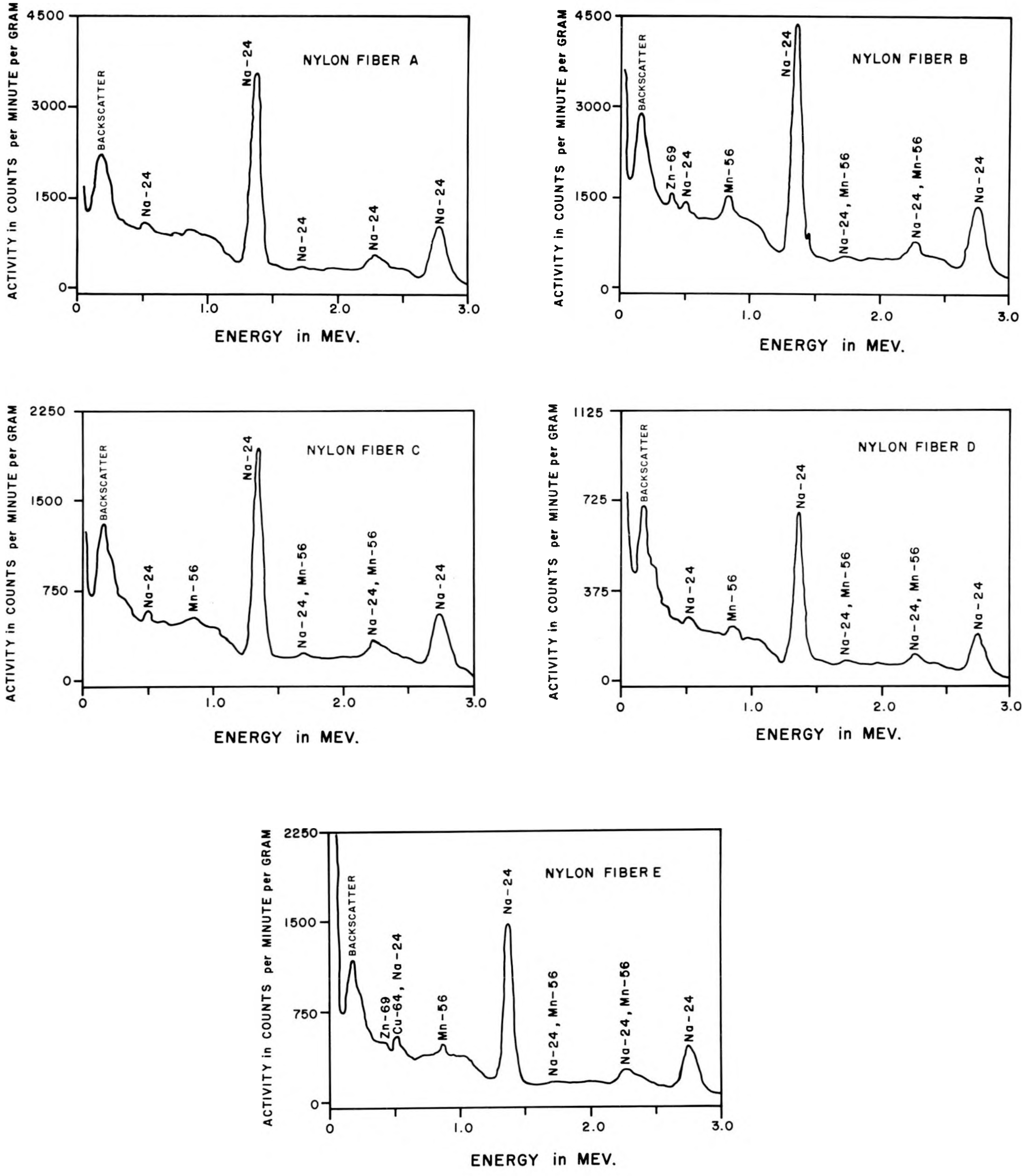


Figure 4.
Gamma Ray Spectra of Nylon Fibers

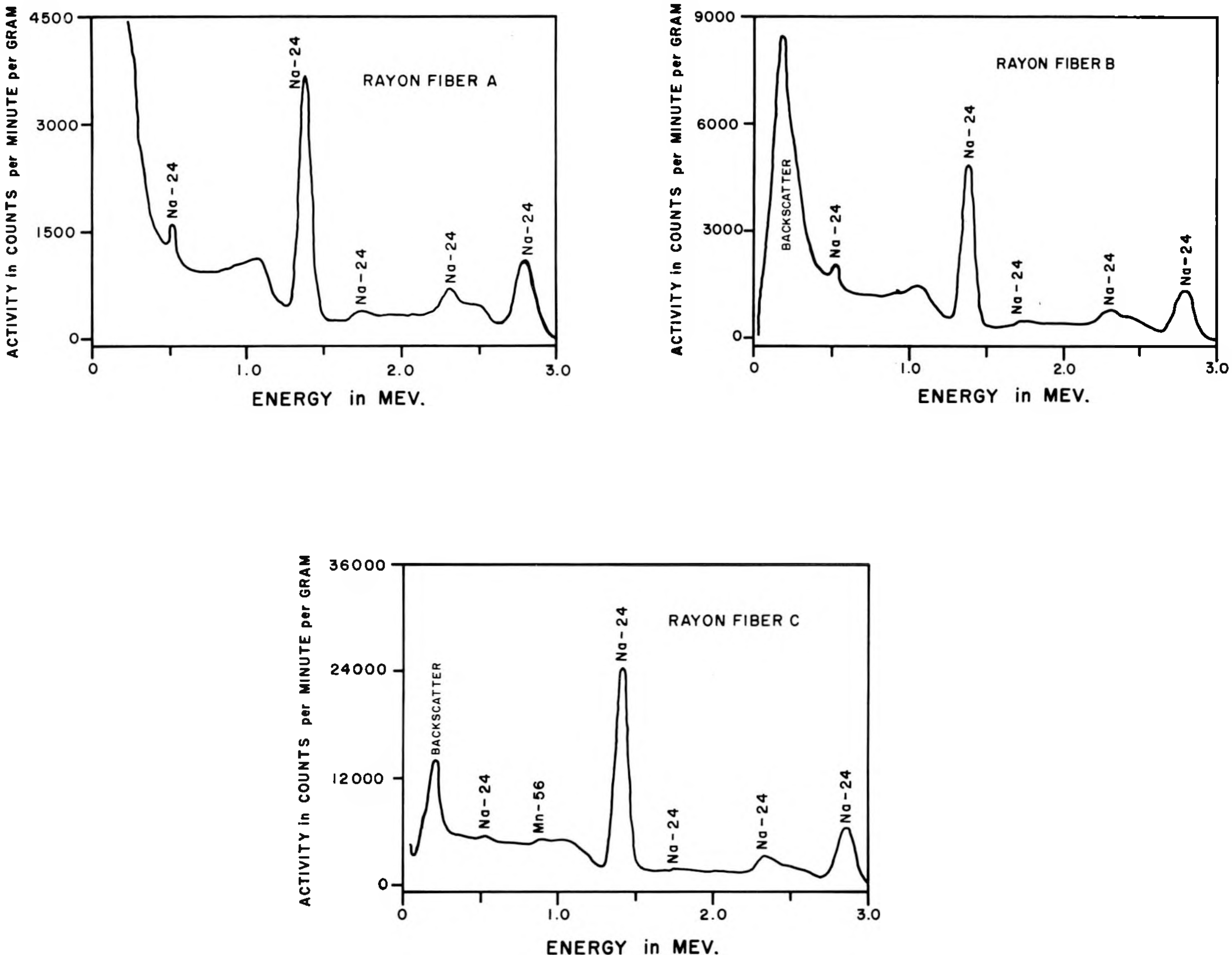


Figure 5.

Gamma Ray Spectra of Rayon Fibers

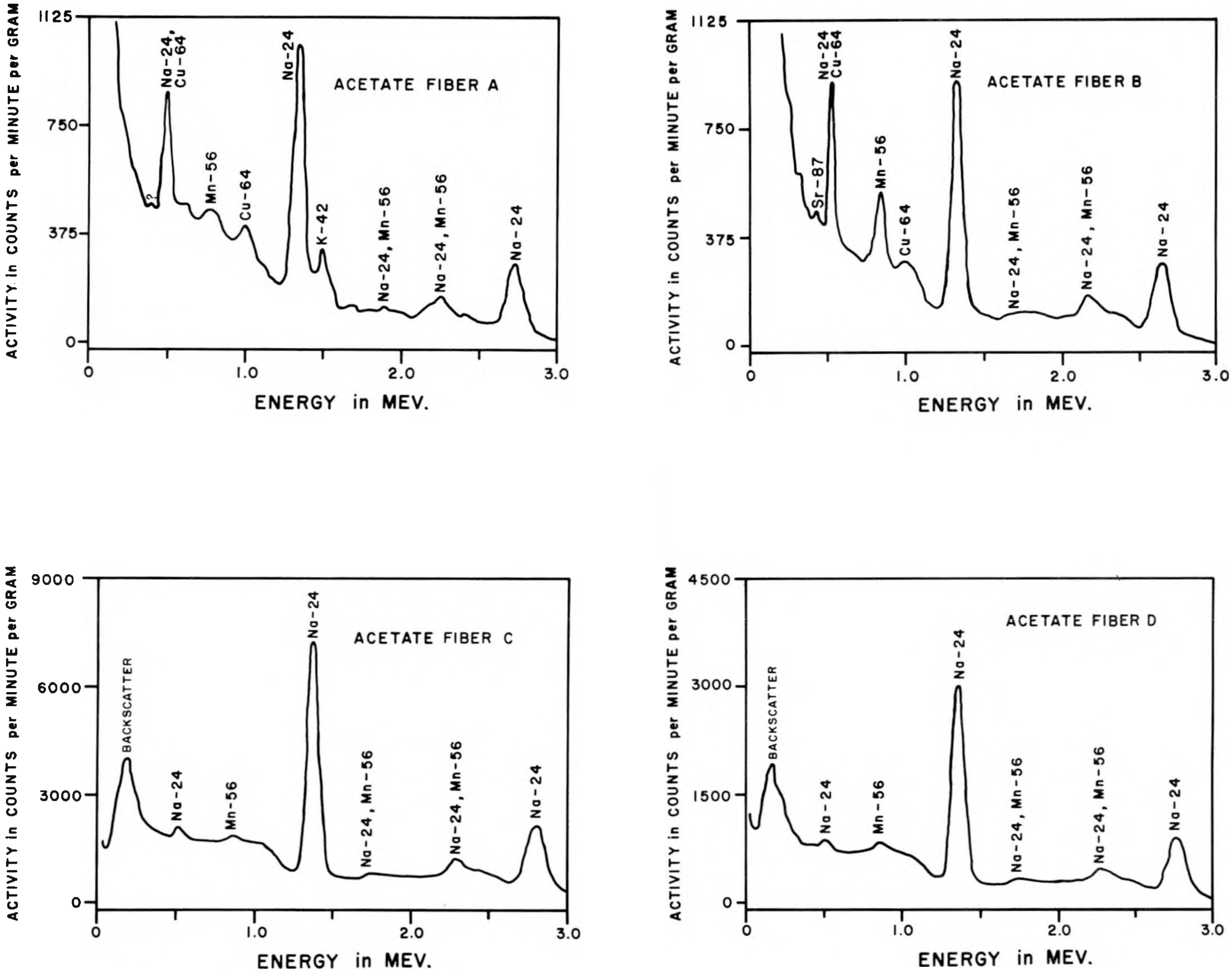


Figure 6

Gamma Ray Spectra of Acetate Fibers

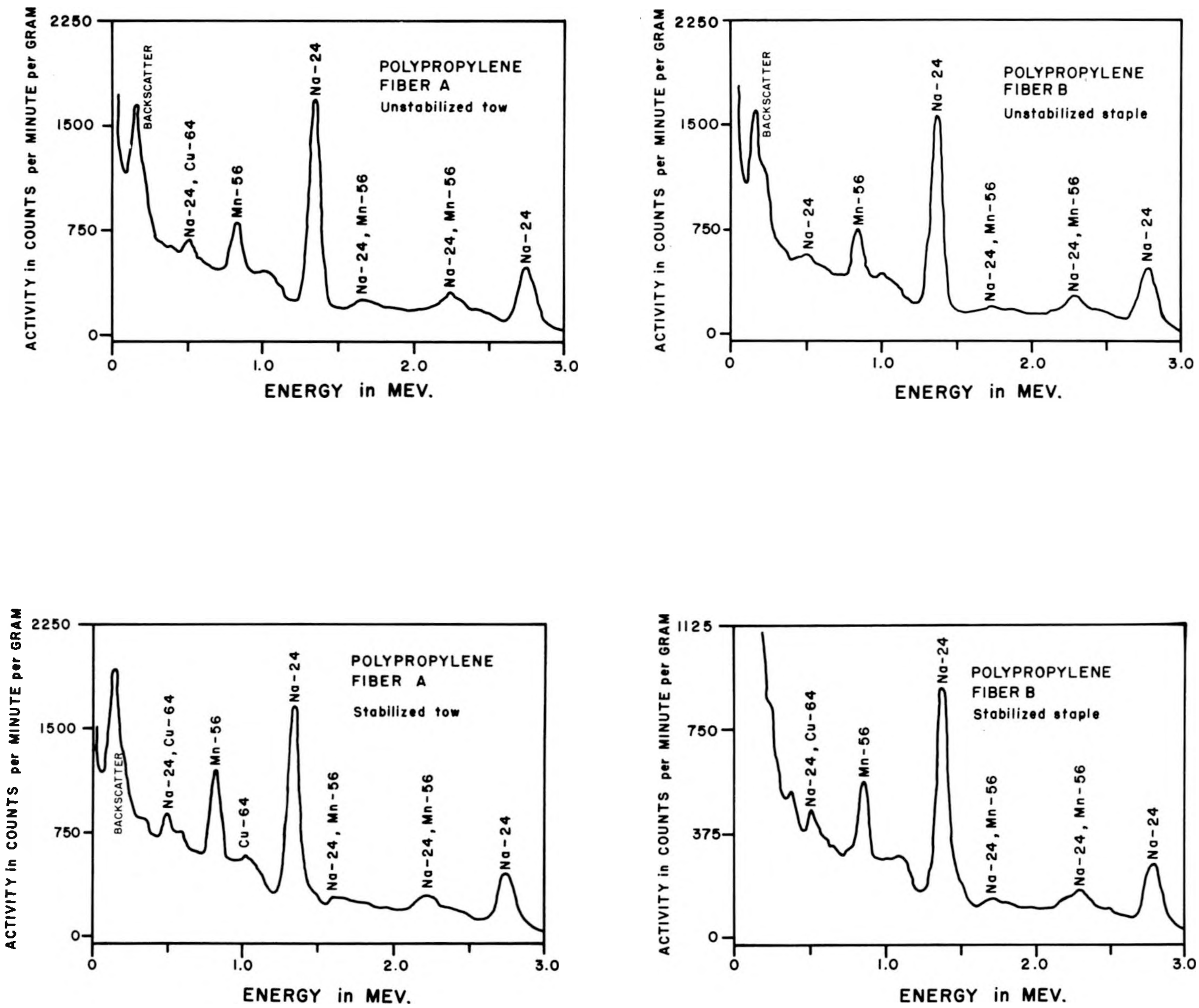


Table 7.

Gamma Ray Spectra of Polypropylene Fibers

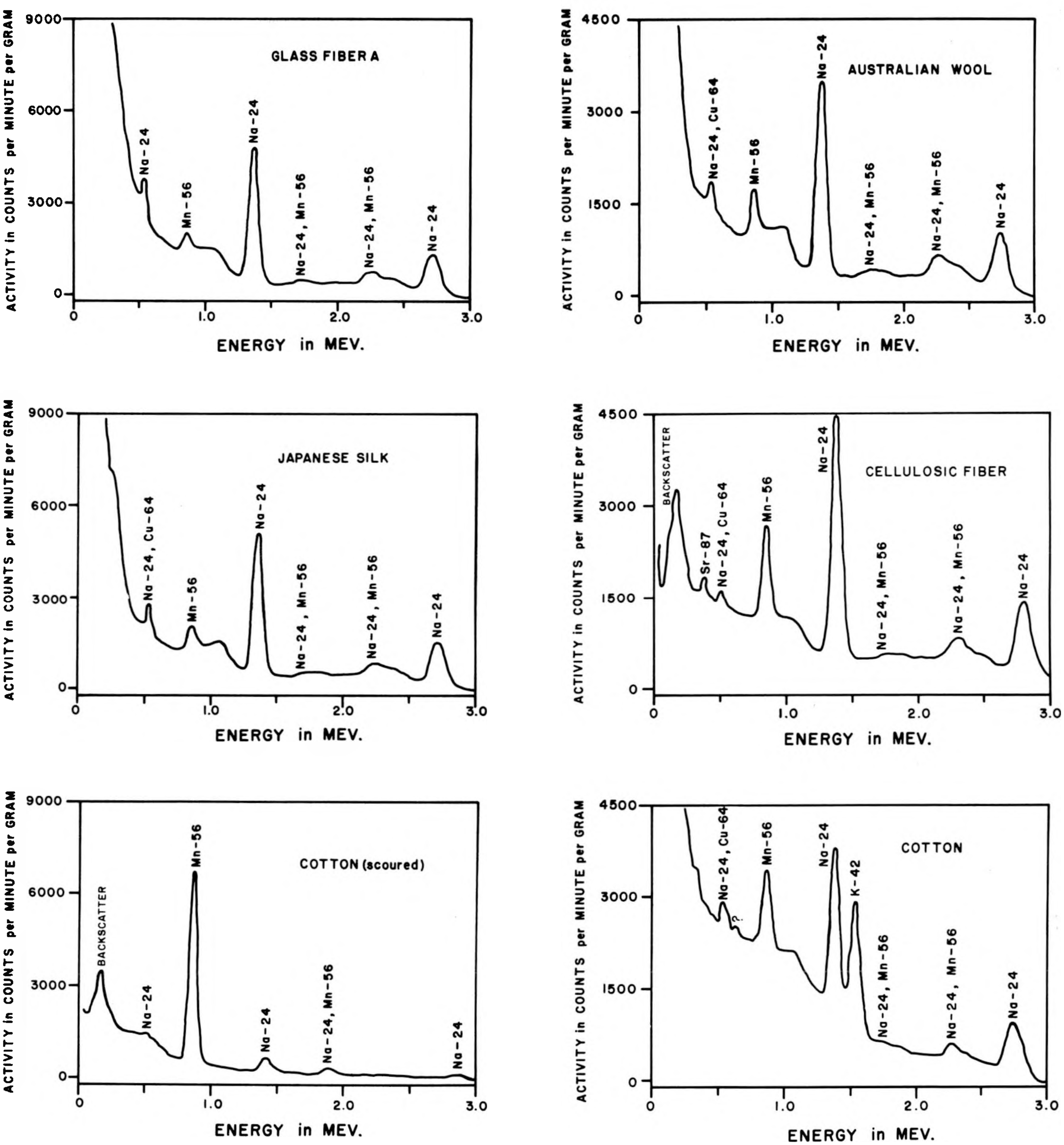


Figure 8.

Gamma Ray Spectra of Various Fibers

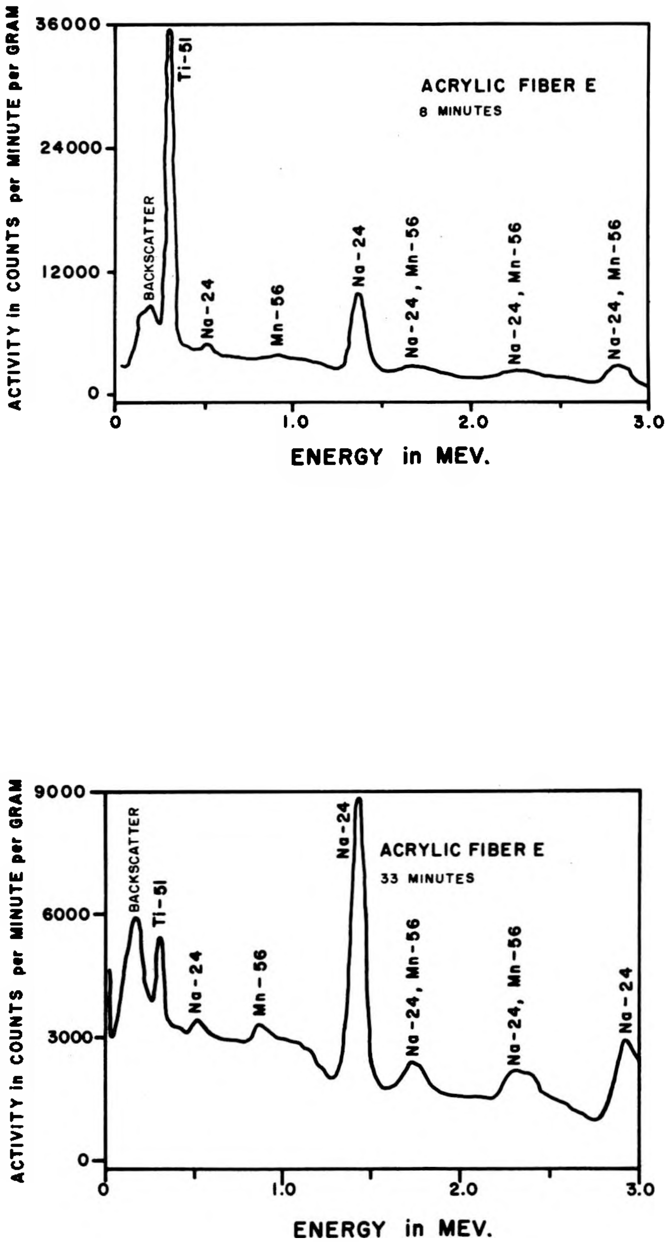
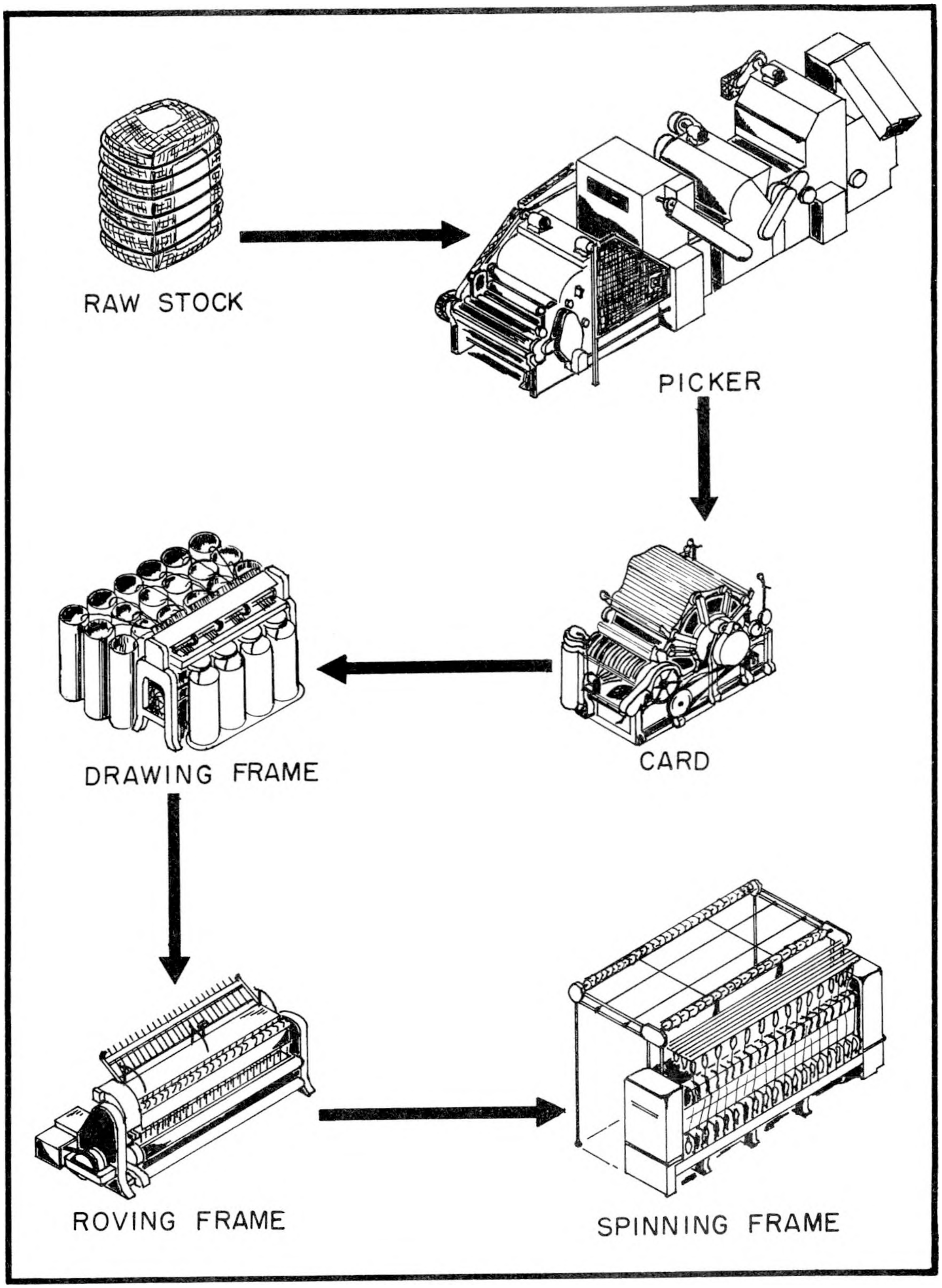


Table 9.

Gamma Ray Spectra of Acrylic Fiber E


RAW STOCK
PICKER
CARD
DRAWING FRAME
ROVING FRAME
SPINNING FRAME

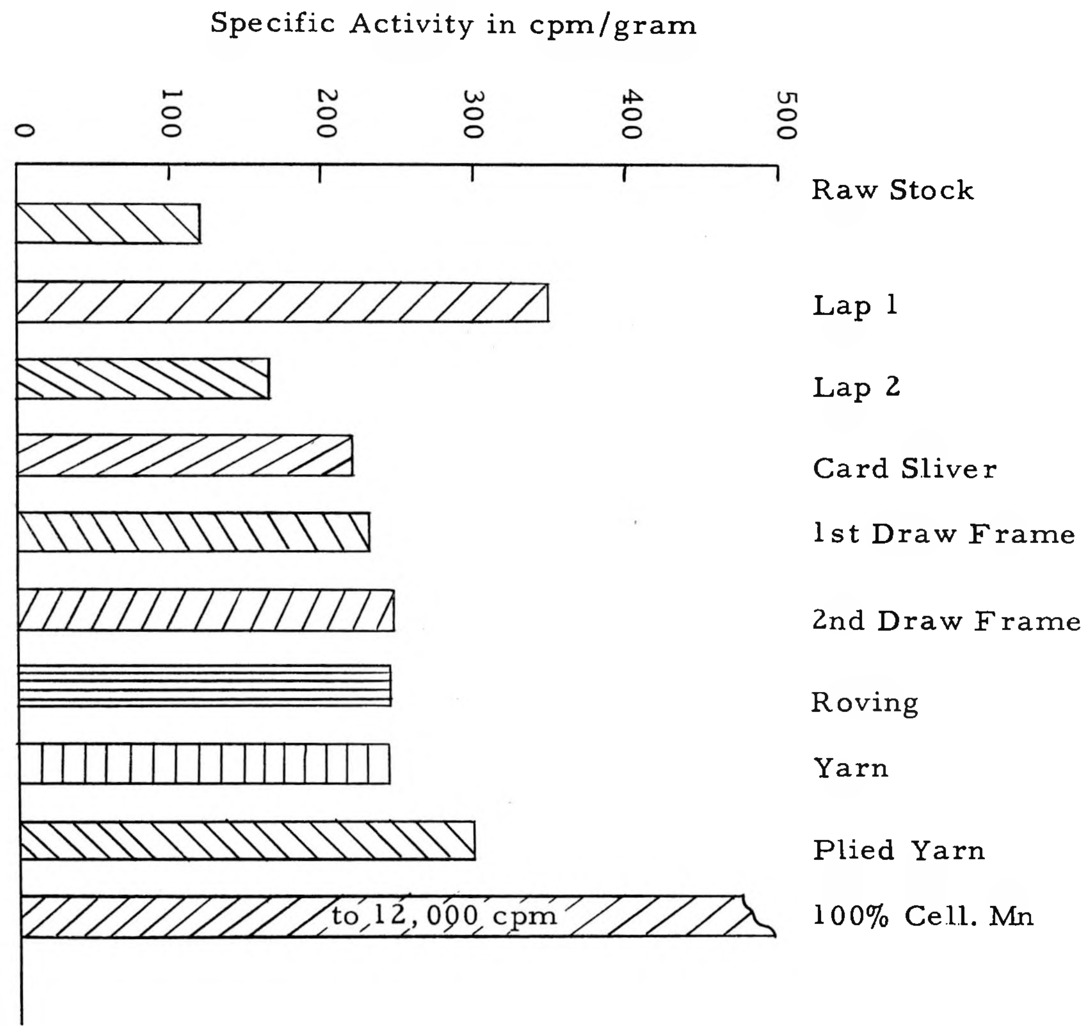
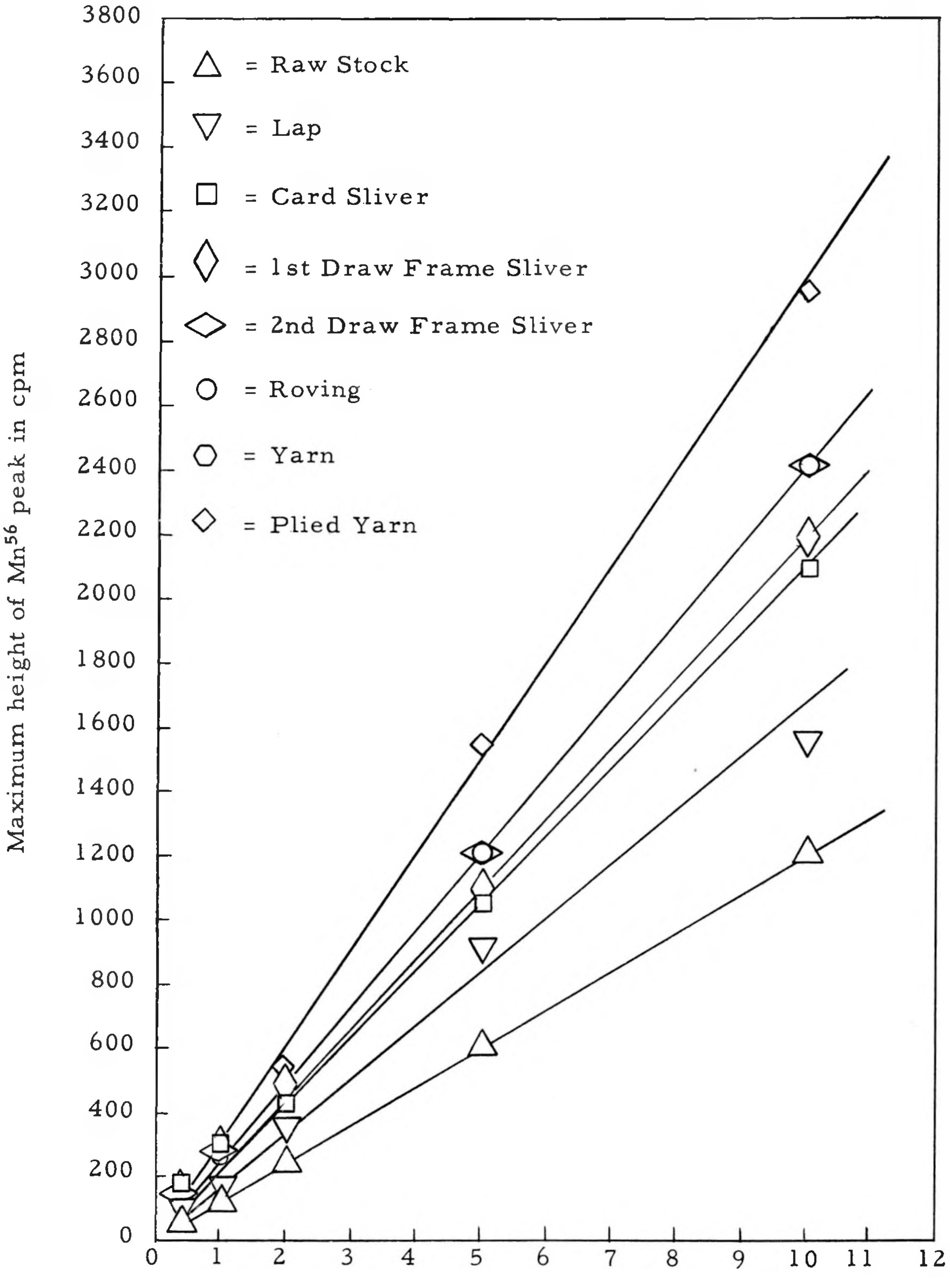

Specific Activity in cpm/gram
0
100
200
300
400
500
Raw Stock
Lap 1
Lap 2
Card Sliver
1st Draw Frame
2nd Draw Frame
Roving
Yarn
Plied Yarn
100% Cell. Mn
to 12,000 cpm

Figure 11



3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
△ = Raw Stock
▽ = Lap
□ = Card Sliver
◊ = 1st Draw Frame Sliver
◇ = 2nd Draw Frame Sliver
○ = Roving
⬡ = Yarn
◇ = Plied Yarn
Maximum height of Mn^{56} peak in cpm
0
1
2
3
4
5
6
7
8
9
10
11
12
Weight of sample in grams

Figure 12

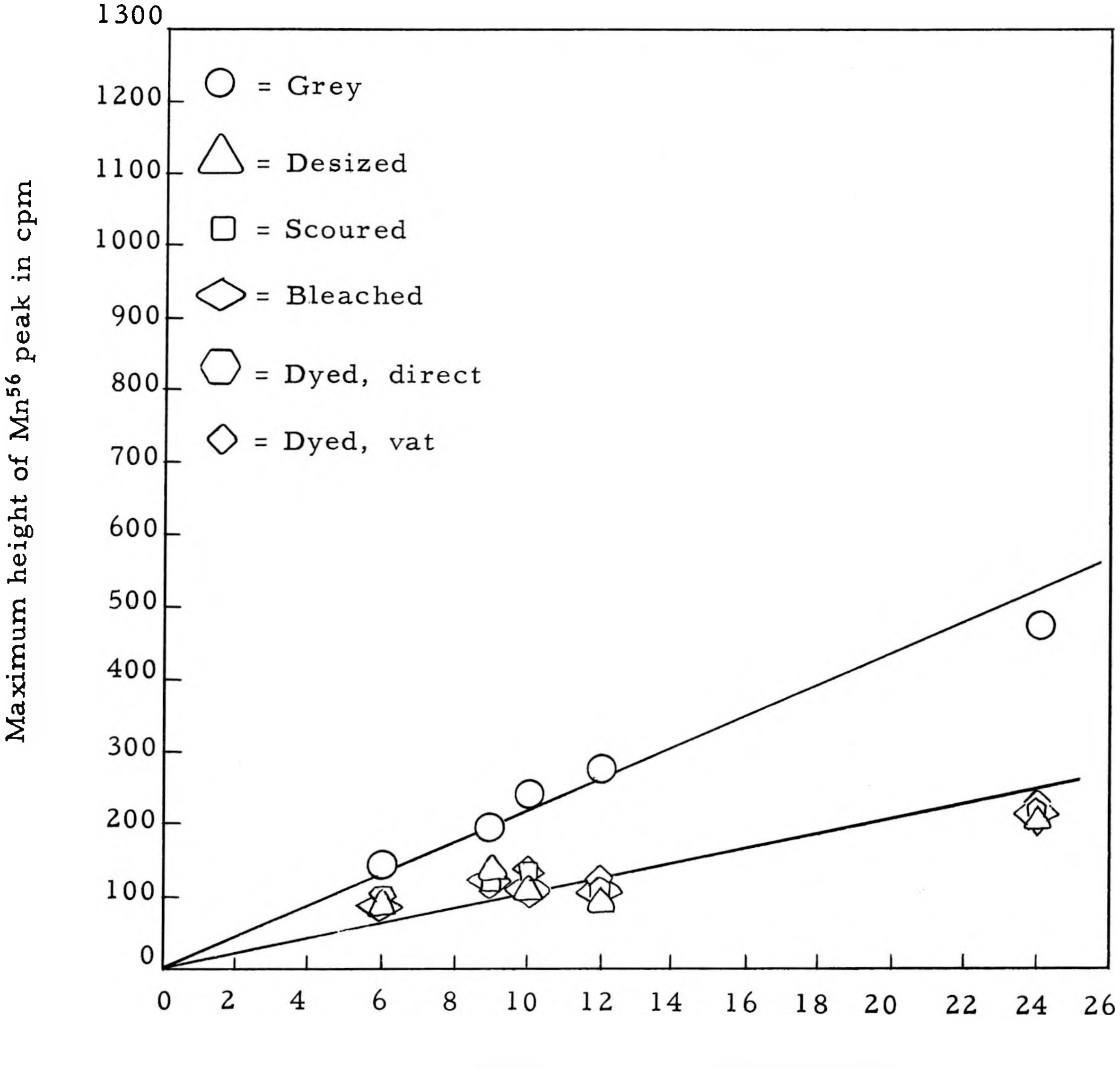

Maximum height of Mn^{56} peak in cpm
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
○ = Grey
△ = Desized
□ = Scoured
◇ = Bleached
⬡ = Dyed, direct
◇ = Dyed, vat
0
2
4
6
8
10
12
14
16
18
20
22
24
26
Sample size in square inches

Figure 13

TABLE I

DATA FOR ACTIVATION ANALYSIS

neutron flux - 10^{11}n. /cm.^{2} sec. sample size - 1 gram
activation time - 1 hour

Fiber	Time after activation	Fiber	Time after Activation
Acrylic A	3 hr. 17 min.	Acetate A	6 hr. 10 min.
Acrylic B	5 hr. 40 min.	Acetate B	8 hr. 10 min.
Acrylic C	4 hr. 52 min.	Acetate C	6 hr. 4 min.
Acrylic D	9 hr. 53 min.	Acetate D	6 hr. 15 min.
Acrylic E	3 hr. 5 min.		
		Polypropylene A	2 hr. 33 min.
Polyester A	8 hr. 55 min.	(stabilized) B	3 hr. 37 min.
Polyester B	8 hr. 20 min.	Polypropylene A	2 hr. 37 min.
Polyester C	3 hr. 5 min.	(unstabilized) B	3 hr. 41 min.
Nylon A	5 hr. 23 min.	Glass A	8 hr. 16 min.
Nylon B	5 hr. 44 min.		
Nylon C	6 hr.	Wool	8 hr. 50 min.
Nylon D	5 hr. 54 min.		
Nylon E	5 hr. 50 min.	Silk	8 hr. 28 min.
Rayon A	6 hr. 25 min.	Cellulosic	3 hr. 13 min.
Rayon B	6 hr. 20 min.		
Rayon C	2 hr. 59 min.	Cotton	8 hr. 41 min.
		Cotton (scoured)	4 hr.

Table II. Processing Flow Chart

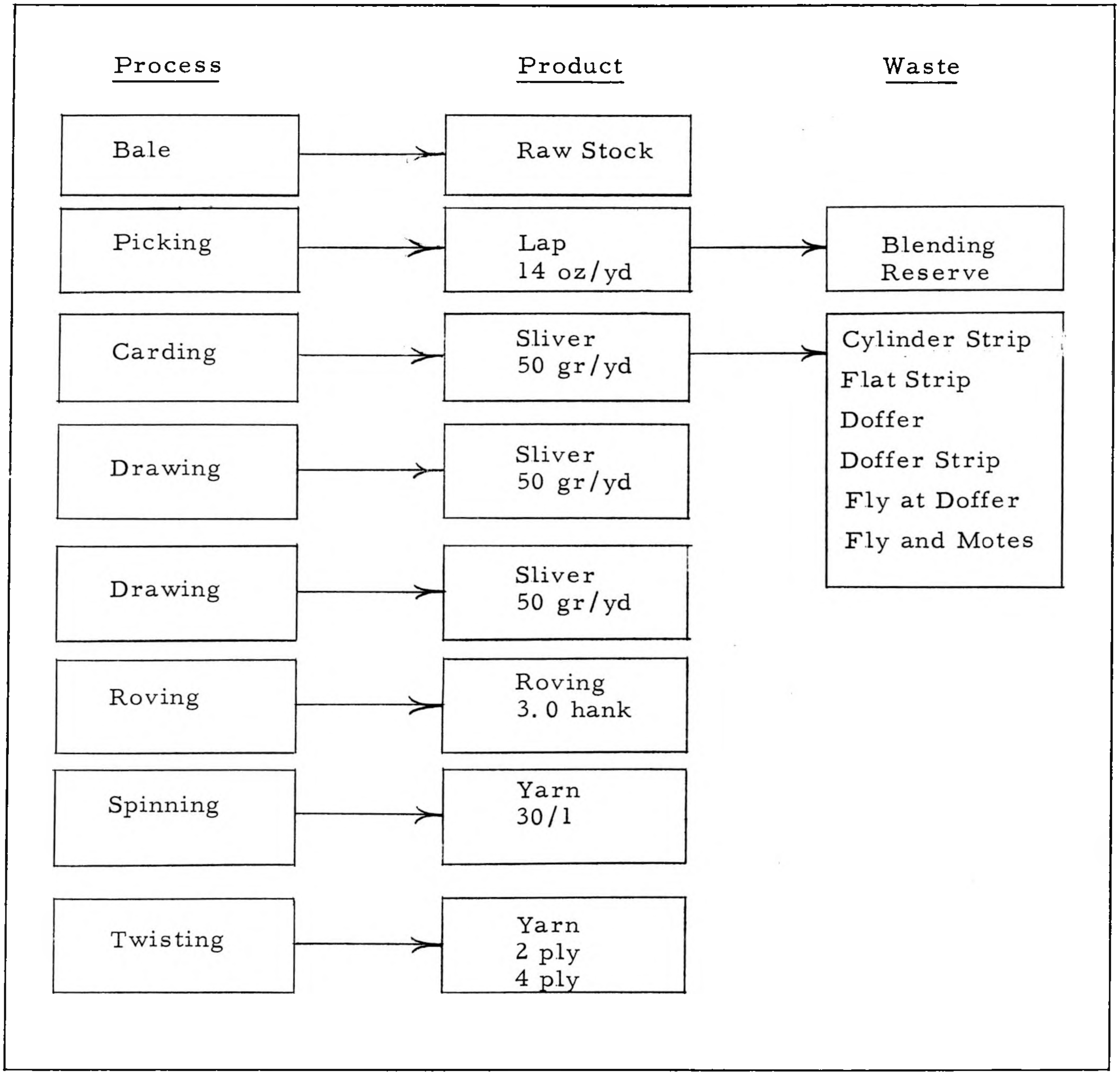


Table III. Analysis of Mn labeled cotton, yarn-processing operations

Sample Weight grams	Peak height of Mn^{56} 0.84 Mev photo-peak in counts per minute (cpm)									
	Raw Stock	Lap 1	Lap 2	Card Sliver	1st Draw Frame Sliver	2nd Draw Frame Sliver	Roving	Yarn	Plied Yarn	100% Cell. Mn
0.4	50	204	103	180	172	168	150	132	150	4800
1.0	120	345	147	310	300	288	270	260	305	12000
2.0	240	705	348	432	492	-	470	-	560	24000
5.0	600	1775	914	1043	1100	1200	1200	1200	1552	60000
10.0	1200	3470	1545	2090	2190	2400	2400	2400	2498	120000
Average Specific Activity cpm/g	120	353	166	220	231	247	244	243	300	12000

Table IV. Analysis of processing waste

Sample Weight grams	Maximum height of Mn^{56} Peak in counts per minute (cpm)						
	Raw Stock	Blending Reserve Strip	Cylinder Strip	Flat Strip	Doffer Strip	Fly at Doffer	Fly and Motes
1. 0	-	660	-	-	-	-	-
2. 0	240	-	550	580	-	1170	2000
5. 0	-	-	-	-	1568	-	-
Specific Activity cpm/g	120	660	275	290	314	585	1000

Table V. Analysis of Mn labeled cotton, wet-processing operations.

Sample Size inch^2	Maximum height of Mn^{56} peak in counts per minute (cpm)					
	Grey	Desized	Scoured	Bleached	Dyed Direct	Dyed Vat
6	144	79	78	72	90	72
9	190	137	114	116	116	114
10	242	104	137	114	104	142
12	276	101	107	109	116	138
24	472	202	219	208	206	233
Avg. Spec. Act. cpm/cm^2	22	10	11	10	10	11

PART III. FIBER MODIFICATION BY GAMMA RADIATION

In the first annual report the behavior of a number of textile fibers during exposure to gamma radiation from a cobalt-60 source was described. The only fibers showing good stability toward the radiation were the acrylic and polyester types. In this work the dose rate used was about 2×10^5 roentgens per hour. The experiments were repeated, using a dose rate of about 4.4×10^5 roentgens per hour. The effect on the physical properties of the fibers at equal doses of radiation was the same in the two cases. These results were not unexpected and served to confirm the conclusions reached earlier, namely, that there is little possibility of modifying fibers in a direction to make them better or more useful by radiation alone. With all of the fibers in common use, degradation reactions predominated over any other effects. While this conclusion may be valid in other radiation systems, it must be emphasized that it is based on the results obtained with gamma radiation from a cobalt-60 source using dose rates in the range of 2 to 4×10^5 roentgens per hour. Whether low doses of radiation obtained at low dose rates may accomplish some useful purpose is a question not yet answered. This will be investigated in future work, but no special emphasis on fiber modification in this way is planned.

PART IV. THE USE OF THE BETA GAUGE FOR MEASUREMENT AND CONTROL

An attempt has been made to show the usefulness of a beta gauge as a means for measuring weight (mass per unit area) non-destructively. Experiments were conducted using the beta gauge for measurements of wet pick-up, extent of drying, fabric uniformity, and fabric abrasion or wear (Annual Report, November 1, 1959, Contract No. AT-(40-1)-2477). Emphasis was placed on the establishment of principles which would lead to the development of systems for measurement and automatic control of several textile processes. A paper dealing with this subject has been accepted for publication by the AMERICAN DYESTUFF REPORTER. Publication date has not yet been announced.

The various operations in textile manufacturing which could conceivably benefit from beta-gauge control systems were reviewed. The warp-sizing operation which incorporates padding, and drying, was considered from both the technical and economic points of view, as the most suitable selection for the first complete study. A proposed system of beta gauges and auxiliary instrumentation for measurement and control of sizing is shown in Figure 1. It consists of four gauges and strip-chart recorders, one analog-proportional memory with two line delays, two subtraction networks, two-ratio-computing networks and recorders, and finally, two proportional automatic controls.

Gauges A, B, and D (Figure 1) are used to measure wet pick-up and final add-on. The information from Gauge A, which measures the yarns entering the slasher, is subtracted from measurements at B and D through the memory and subtraction networks; the resulting information is fed into the respective ratio-computing networks which then yield the desired wet and dry pick-up data. System A-B activates automatic control No. 1 which compensates for short term variations in the (B-A)/A ratio by changing the pressure on the squeeze rolls; system A-D operates on automatic control No. 2 which compensates for long trends in the (D-A)/A ratio by changing the set-point of the first automatic control. Finally, Gauge C located after the drying cans and before the lease rods, is used to obtain information, (1), as to possible dimensional changes in the materials as a result of exposure to heat, moisture and stress, (2) on the amount of shed, and (3) on the drying process when used in conjunction with recorded measurements from Gauges A, B, and D. Gauge C is for the present independent of the system and does not contribute to the control.

It was suggested that the described systems be studied in four separate phases. Figure 2 illustrates proposed phases 1 and 2, Figure 3, depicts phase 3; phase 4 represents the entire system and is shown in Figure 1.

Instrument manufacturers werecontacted, and the various layouts were discussed with them. No major modification in the proposed systems were made as a result of these discussions. However, the prices quoted on even the minimum system for a thorough investigation of the use of beta gauges in warp sizing, were prohibitive. After a thorough discussion of the situation with the cooperating mills on this project, it was decided to discontinue this aspect of the work.

It also became obvious that for economic reasons, all studies regarding beta gauges should be discontinued under this contract. The textile industry could possibly use beta gauges for measurement and control, but only if the instrumentation for this purpose were not costly. Low cost beta-gauge systems apparently would find wide application, but such is not the case with the high-cost custom-made systems.

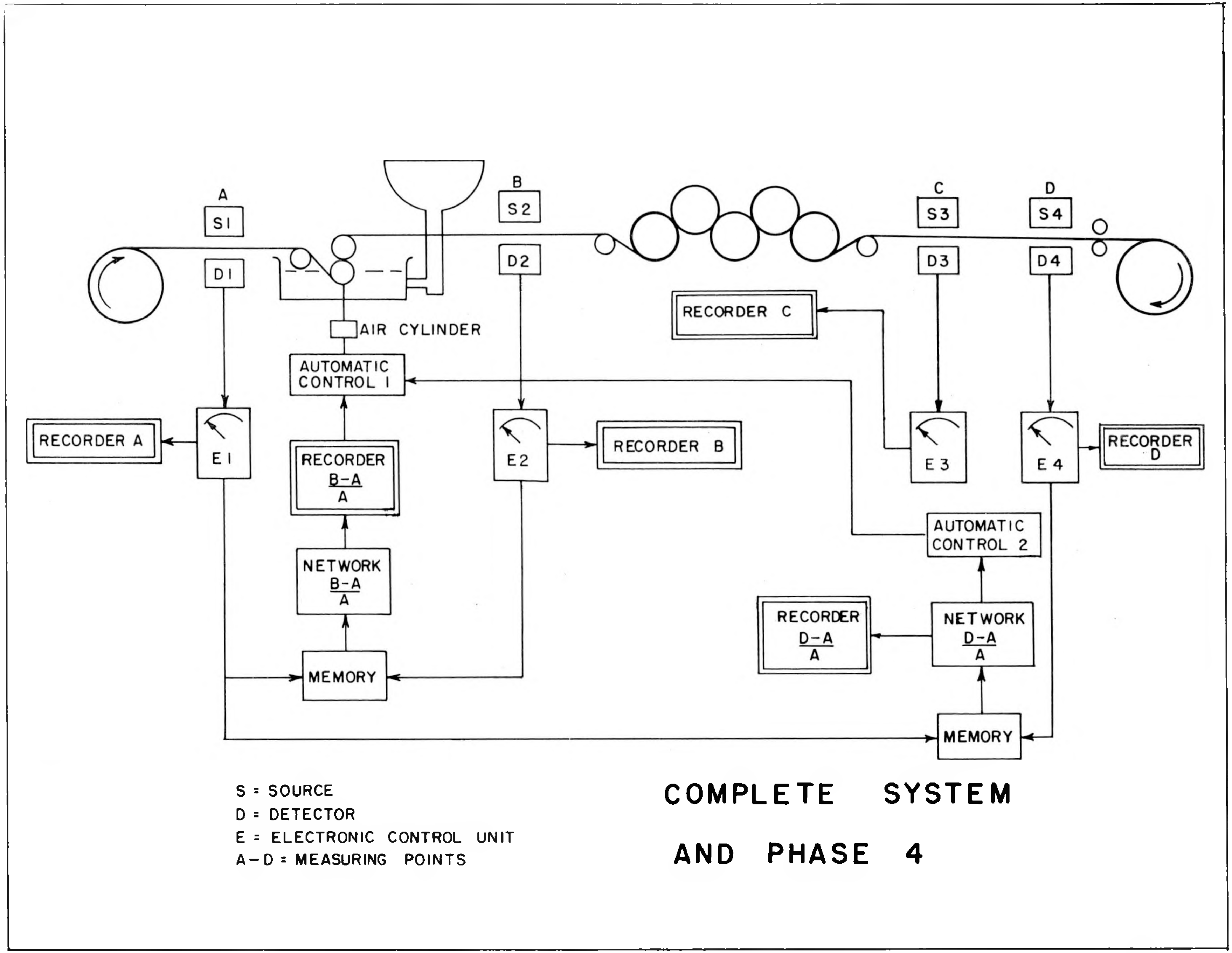


Figure 1. Beta Gauge System - Phase 4

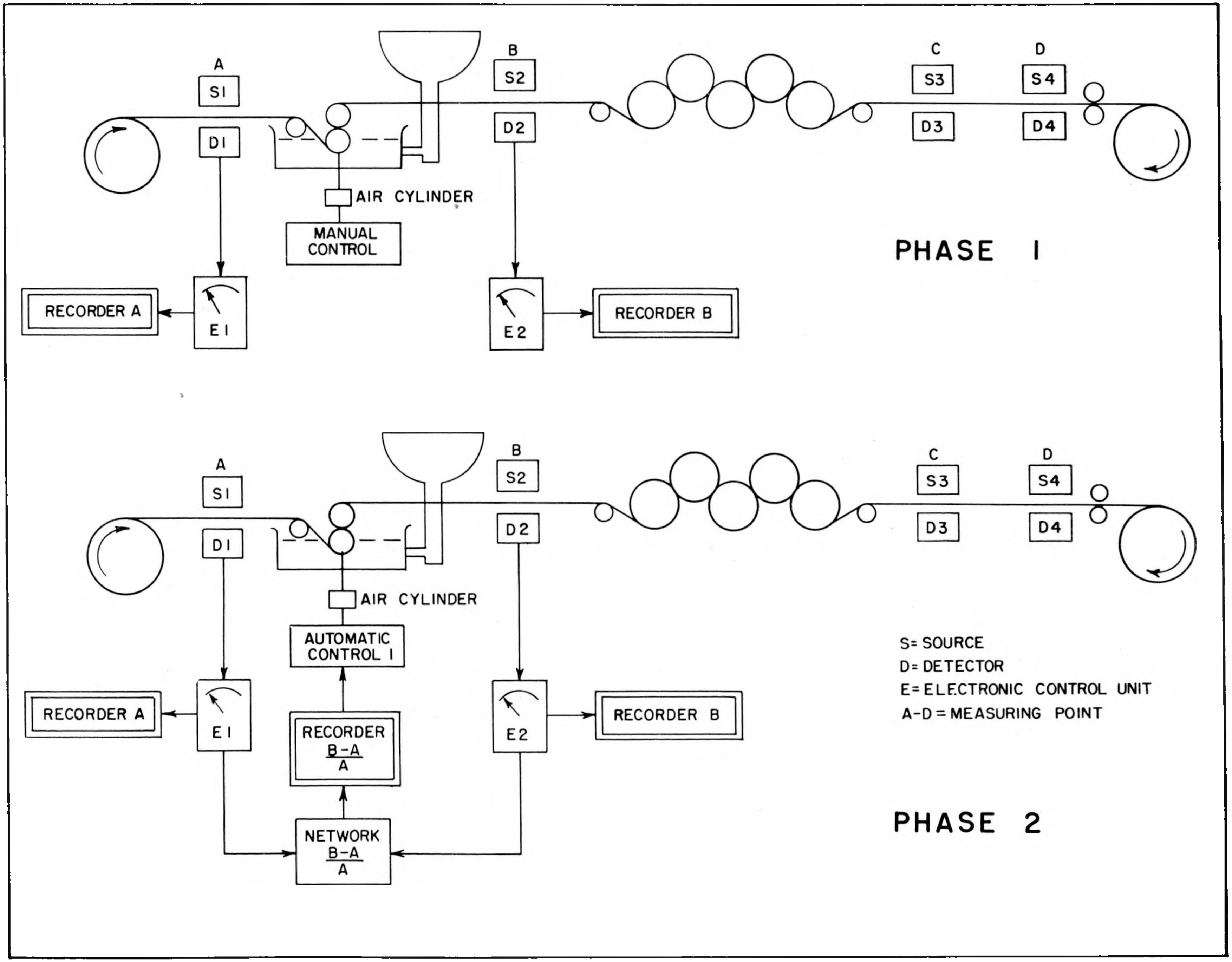


Figure 2. Beta Gauge System - Phases 1 and 2

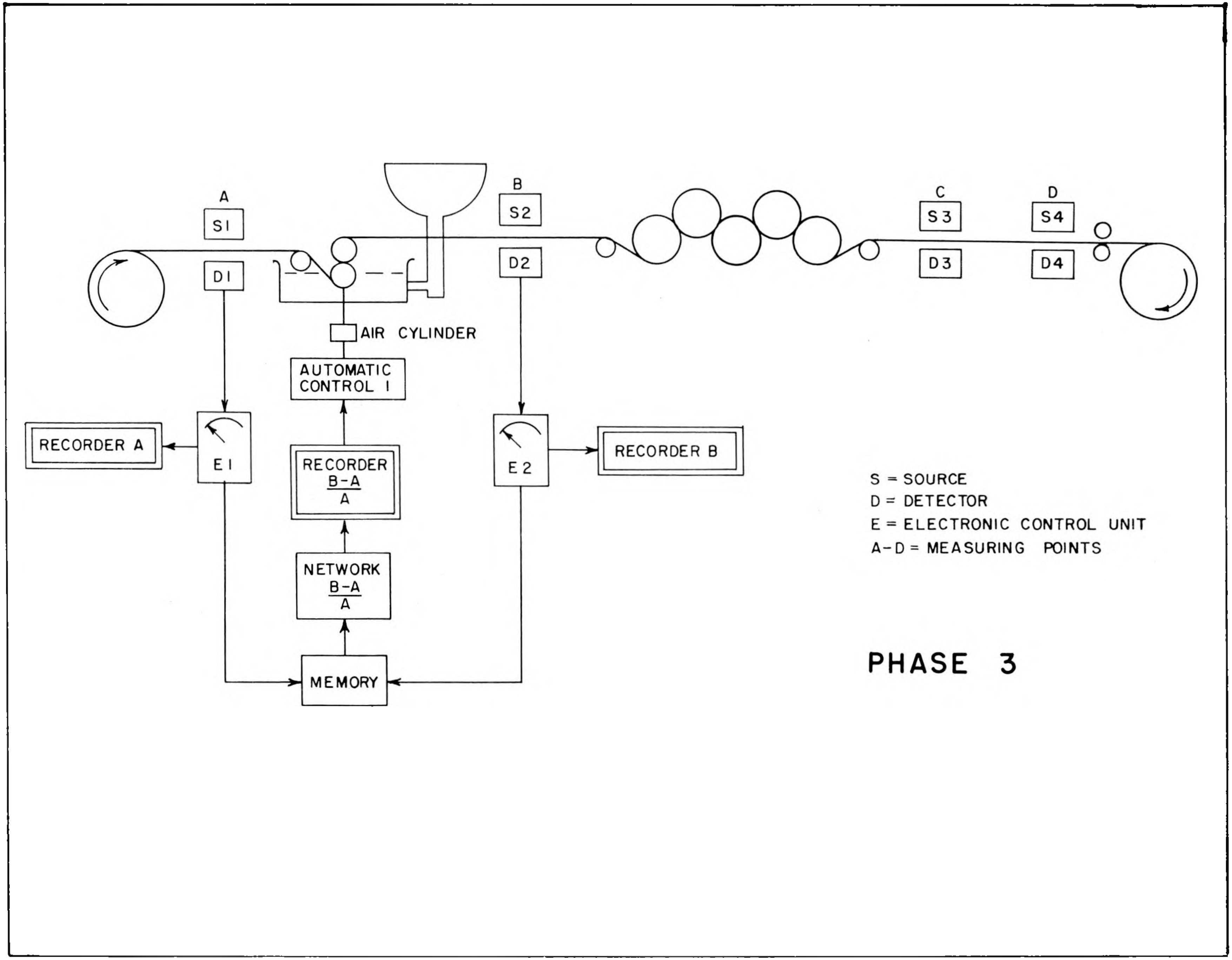


Figure 3. Beta Gauge System - Phase 3

APPENDIX I

EXPERIMENTAL DETAILS

The labeled yarn was produced in the following manner. Twenty pounds of raw stock (1-7/16 inch American Egyptian Cotton) were fed into the hopper of a Saco-Lowell one process picker. At the feeding apron preceeding the breaker beater, 38 grams of manganese-labeled cotton (1-7/16 inch American Egyptian, $6x10^4$ g Mn/g cotton) was dispersed by hand into the raw stock. Due to this mixing procedure only 14 pounds of the lap (14 oz/yd) produced on the picker contained the labeled cotton. Waste was collected from the breaker beater, blending reserve and finisher beater.

The lap was transferred to a Saco-Lowell card and made into 50 gr/yd sliver. The waste was collected from the cylinder, flats and doffer, and included the fly at the doffer and fly and motes in general. All of the sliver produced on the card was divided into six equal portions and fed into a Whitin 4 over 4 draw frame. The resulting 50 gr/yd sliver was again subdivided into six parts and fed into another Whitin 4 over 4 frame. This sliver (50 gr/yd) was spun into 3-hank roving on a Whitin Woonsocket G-2 roving frame, and then into 30/1 yarn on the Saco-Lowell SZ-2 spinning frame. A small amount of the singles yarn was converted into plied yarn on a Whitin twister.

Samples from all stages of processing (raw stock, lap, card sliver, 1st draw frame sliver, 2nd draw frame sliver, roving, and yarn) ranging in weight from 0.4 to 10 grams were collected and prepared for irradiation.

A portion of the yarn was wound on a Whitin-Schweiter Winder on filling bobbins. The remainder was warped on the Benninger (35-yard warp consisting of 27 bands each having 100 ends) and slashed on the Callaway Slasher. The sizing formulation consisted of a 40-gallon mix containing 60 lbs. of Penford Gum No. 280, 16 lbs. of Elvanol 72-60, 12 lbs. of Texize Wax W-20, 2 lbs. of Pentex No. 40, and 12 oz. of Non-stick Oil. After slashing, the yarn was made into plain-woven fabric on a Draper XD loom.

The grey material was subjected to the following wet-processing operations. First, the material was desized twice using 5.0% Rhozyme DX and 1.0% Triton X-100 at 180°F. for one hour. Since not all of the size was removed, a third desizing was necessary which was carried out using 1 lb. of Diastafor L3 in 56 gallons of water and 0.5% Triton X-100 at 180°F. for one hour.

The desized material was scoured with 2.0% soda ash and 1.0% Naccanol NR at 210°F. for 20 minutes.