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A STUDY OF THE FREE RADICAL YIELD PRODUCED IN 1-BROMOBUTANE BY IRRADIATION WITH MONOCHROMATIC X-RAYS OF DIFFERING PHOTON ENERGIES

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I. INTRODUCTION

A. Purpose of the Study

It is the purpose of this study to determine whether the radiation effect yield per unit of energy absorbed in certain chemical systems is a function of the photon energy of the radiation. Monochromatic x-rays were used to irradiate 1-bromobutane in the liquid state. The free radical yield per unit of energy absorbed in the target compound has been determined for various x-ray wavelengths in the region of the photoelectric cross section K edge discontinuity for bromine. For convenience, the curve resulting from a plot of radiation effect per unit of energy absorbed vs. incoming photon energy will be referred to as the action spectrum in the remainder of this paper. This definition is consistent with terminology employed by previous workers in this laboratory(1,2). It should be noted that the action spectrum is based on energy absorption rather than on the energy incident. Thus the data points as plotted have already been corrected for differences in absorption cross section.

The present study is motivated by some very interesting and largely unexpected results from two recent studies with monochromatic x-rays(1,3). The results of these past studies will be discussed in detail in Section I C. The action spectrum resulting from these past studies exhibits sections of high radiation effect yield (or resonances as they are termed in the references) for certain energies in the region of the K absorption edge of the target material as compared to the yield for adjacent energies. The literature searches conducted in these studies, as well as the search reported in this paper have not revealed many studies utilizing monochromatic radiation reported in the literature. The use of monochromatic x-rays as the source for radiation studies may reveal effects dependent on photon energies which have not been observed in past studies due to the spread of photon energies present in the radiation sources used.

Both of the recent studies utilized rather complex compounds and the results are not completely understood. It is hoped that by choosing a similar but less complex system, as has been attempted here, results may be obtained which may help explain some of the earlier observations. It is anticipated that the system developed in these studies can be used to study the energy dependence of radiation effects in many other liquid compounds.

B. Description of the System Studied

Throughout this paper the system is intended to include all of the components of the radiation effects experiment: a calibrated source of radiation, a target material whose radiation effects are to be determined and a method of reproducibly irradiating the target material and determining the particular effects produced. The criteria for selecting a system are numerous, and will be discussed more fully in Sections II A and D.

The radiation source for this study was monochromatic x-radiation produced by the fluorescent re-emission of characteristic radiation from various elements in the form of radiators which were subjected to bombardment by the continuous x-radiation spectrum from a standard tungsten target x-ray tube.

The target material for these studies was purified 1-bromobutane in a liquid state containing a very small concentration of stable free radical material (diphenyl-picryl-hydrazyl, hereafter abbreviated as in the literature as DPPH). The liquid was contained during irradiation in an irradiation cell of special design containing thin windows for low radiation attenuation and a maximum surface to volume ratio. The mechanical placement of the cell was designed to ensure reproducibility of radiation absorption by the target material (see page 106). The radiation path length in the target material was selected for approximately 98% absorption of the incident beam for all photon energies to be studied (see page 110). The atomic constituency of the target material and the photon energy determine the fraction of the initial energy absorption which will occur in the target atom (bromine in this case). In these studies more than 95% of the absorbed energy is initially absorbed in bromine atoms (see page 26) for all photon energies studied.

For the purposes of this study radiation effect is measured as the free radical yield from the radiation induced reaction, and this terminology will be retained unless otherwise noted. The free radical yield was determined from the quantity of DPPH expended in the course of the irradiation since DPPH reacts quantitatively with the 1-bromobutane radicals produced by irradiation (see page 88). The disappearance of DPPH was determined spectrophotometrically. The use of DPPH to determine radical yield was adapted primarily from the work of Chapiro(4).

After suitable calibrations, corrections and conversion of units have been made, the final result of this study will be the action spectrum of 1-bromobutane for photons of energies ranging from 6 to 25 Kev.

C. Review of the Pertinent Literature

The literature relevant to this study has been reviewed in two recent previous studies(1,2) which will not be repeated here, although the more pertinent results will be mentioned. Certain aspects of the subject were approached from a different viewpoint in this study and will be reviewed in more detail.

1. Summary of Studies on the Dependence of Radiation Effects on the Quantum Energy of the Radiation

Previous studies which are most related to this study are the investigations of Garsou, Emmons and Atkins. These three studies along with the present study were all conducted at the same laboratory. Since all four studies have had a common objective of determining radiation effect yields as a function of the photon energy of the irradiation source, they constitute a distinctive series of radiation effects studies.

Study of Organic Halides. Garsou(3) completed his study on the effects of monochromatic x-rays on several organic halogenated solids and liquids at the Phoenix laboratory in 1959. He irradiated thin plastic films containing dissolved halogen compounds and a leuco-base dye p,p;p"-methylidynetris- (N,N'-dimethylaniline) (MTD) which reacted with the radiation products of the halogen to produce a highly colored dye crystal violet. The radiation source used in this study was diffracted x-radiation produced by a crystal spectrometer. X-rays of differing photon energies in the region of the K edge of the halogen compound were used to irradiate the compounds. The quantity of crystal violet produced during irradiation (determined spectrophotometrically) was used to compute the radiation yield per photon absorbed.

Garsou reported that regions of high radiation effect yield existed for specific energies near the K edge energy of the target atom. He concluded that the effectiveness of the different x-ray wavelengths formed a spectrum with maxima and minima and that the variation of the action spectrum was not dependent on the photoelectric absorption spectra of the target atom. He reported that radiation of wave lengths in the region of the K_α emission energy of bromine gave the highest yield of any photon energy. In attempting to explain his results he was unable to reconcile the results with existing theories and as a consequence he suggested that possibly some process might be occurring which had not been observed previously. Several possibilities were presented and discussed. It was suggested that further studies should be conducted with higher radiation intensity and better energy resolution.

Subsequent work has raised some questions about the energy resolution obtained in Garsou's studies(5). It is felt that although there are some uncertainties about certain aspects of Garsou's studies, the possibility of the existence of an energy dependence in the system studied has been raised and that this work has pointed up the current lack of information in this field.

Catalase. The study of the effects of radiation on the catalase system by Emmons(1) was underway in this laboratory when the present study was begun. Emmons sought to determine whether x-radiation of wavelengths near the iron K absorption edge would be more effective in deactivating the ability of catalase to catalytically decompose hydrogen peroxide as compared to other x-ray wavelengths. The important function of the four iron atoms contained in the high molecular weight (250,000) catalase molecule had been established previously and it was felt that the initial deposition of energy in the immediate region of the iron atom might produce deactivation of the molecule more effectively than the expenditure of an equal quantity of energy elsewhere in the molecule.

Figure 1 shows the curve obtained in that study using the crystal spectrometer as the source of monochromatic radiation. It should be noted that although the ordinate values of loss of catalase activity appear to follow the iron absorption curve, each data point actually represents the loss of activity for the same amount of energy absorption and at equal absorption dose rates. Thus it would appear that radiation of energies above the iron K edge are considerably more efficient in producing loss of activity. Similar results were obtained by irradiations of dry catalase. Emmons also found that iron fluorescent radiation gave the highest yield of any energy studied.

The catalase system is very complex and very tedious experimental techniques are required for good results, thus the analysis of Emmons' work was not straightforward. In order to explain his results Emmons advanced the possibility that some type of preferential energy transfer from catalase molecule to catalase molecule might account for the high number of inactivations (23) observed per initial photon absorbed. He was unable to explain his results with existing theories and known

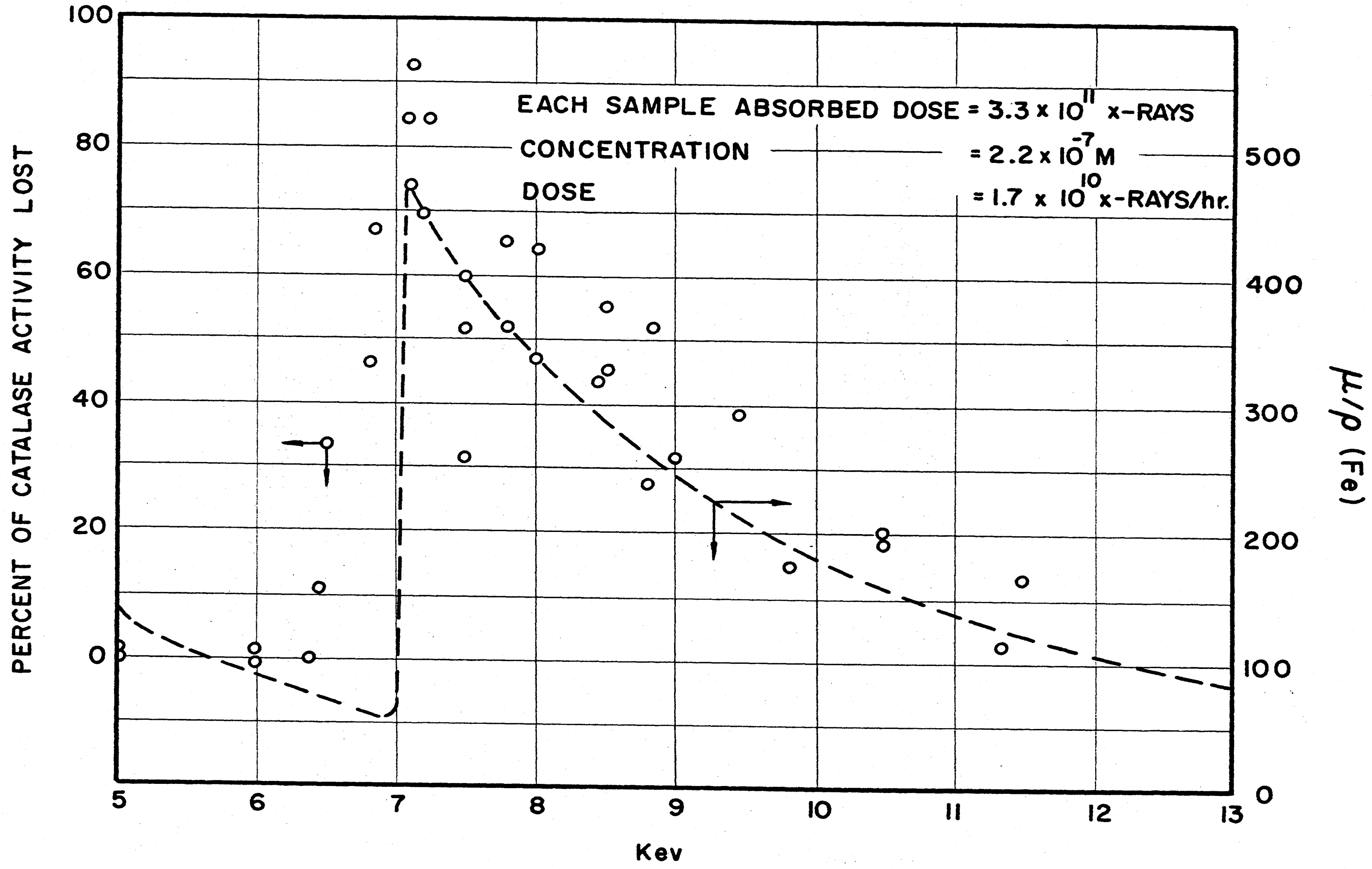

Figure 1. Catalase Solution Loss of Function at Selected X-Ray Energies [from Emmons(1)].

mechanisms, but was forced to recognize the possibility of the existence of some new process or processes.

The work of Garsou and Emmons has been recently summarized in a report by Gordus(6).

Organic Mercury Compounds. In a study conducted concurrently with this one, Atkins(2) irradiated an organic compound of mercury (α-acetoxymercuri-β-methoxy hydrocinnamic ethyl ester) as a solid with varying photon energies around the L edge of mercury. The radiation yield was determined as the quantity of inorganic mercury released during irradiation per unit of energy absorbed in the compound. The mercury yield was determined with standard chemical techniques and the dosimetry used to determine absorbed dose was identical with the techniques used in this study. Atkins' results were very similar to those of this study, i.e. the radiation yield of the mercury compound studied was independent of the photon energy of the radiation over the range of photon energies studied. Atkins concluded that although the simple mercury system studied showed no energy dependence, more complex systems (e.g. biological systems which are known to have radiation effects which are LET dependent) might have a discontinuous action spectrum for radiation with wavelengths in the region of an absorption edge of a heavy atom.

Other Studies. Only three other studies were found in the literature in which varying photon energies were used to determine whether the radiation effects yields observed were dependent on the photon energy of the radiation source. In 1952 Guild(7) studied the inactivation of bacteriophage and catalase by soft x-rays. His investigation attempted to determine whether the x-ray action spectrum differed from the absorption spectrum. His studies were conducted with direct beam (heterogeneous energy) x-rays with differing maximum photon energies, obtained by varying the accelerating potential of the electrons bombarding the x-ray target material. By irradiating with potentials of less than, equal to and greater than the absorption edge energy of phosphorous (2.14 Kev) he concluded that "the absorption of a photon by a phosphorus atom in nucleic acid is no more effective for inactivation of T-1 bacteriophage than absorption by any other atom." The results of his study are not completely clear since the radiation used in the study was not monochromatic.

Manoilov(8) irradiated grass frog hearts with direct x-ray beams generated in anodes of iron, copper, nickel and cobalt. He sensitized the hearts to effects on the iron bearing cytochrome molecules by lowering the available oxygen supply to the organism immediately following irradiation. He irradiated the hearts with identical dose rates and total incident dose (measured in roentgens) and observed that the control hearts and the hearts irradiated with x-rays from iron and cobalt anodes survived for 20-30 minutes while 70-86% of the hearts irradiated with x-rays from the nickel and copper anodes ceased to function within 3-15 minutes following irradiation. He speculated that "...if during the action of x-rays together with general ionization of the substance, there is actually a direct action on the iron atom forming part of the enzyme, corresponding to the characteristic radiation, and the latter is connected with an increased absorption of photon energy, then we would expect different biological effects in the irradiation of objects with x-rays emitted by iron and cobalt anodes, in comparison with x-rays emitted by nickel and copper anodes." He further concluded that "...during the irradiation of organisms with x-rays, the direct action of radiation on cytochrome molecules plays a definite part." Analysis of Manoilov's conclusions is difficult because of the sparseness of details in the article; however, several questions arise:

(1) It appears that absorbed dose is based on roentgen measurements. Making roentgen measurements of a direct heterogeneous energy x-ray beam is not difficult; however, the determination of energy absorption in the sample based on knowledge of the energy absorbed in air for mixed x-ray energies is not simple. The article did not mention any conversion of r measurements to actual energy absorption, so it is assumed that the author related the biological effect produced to the r measurements of the beam. Assuming the r measurement is dominated by the K_α emission of the anode, the energy in ergs/cm^2 per r varies from 4.5 for iron to 8.5 for copper (Figure 21), thus the actual energy delivered to the organism may have increased with the Z of the target material.

(2) Maloinov's conclusion that direct action on cytochrome is involved seems premature until it can be established that cytochrome damage produced the effects observed and that the relative yields of indirect action on cytochrome are sufficiently low that the direct action could be detected under the experimental conditions reported.

Several studies have been made of the sensitivity of photographic film to varying photon energies and different local ionization density produced by different types of radiation(9-11). The most significant work of this type related to the present study is the work of Seeman(12). Seeman irradiated two commercial types of x-ray film at 11 different photon energies (5-67 Kev) obtained by a fluorescence technique similar to that used in the present study. Selective filtration was used to attenuate the K_{β}, thereby producing sources of almost completely monochromatic radiation. Absorbed dose was computed from absorption cross sections and incident dose measurements were made with a special ionization chamber.

Seeman found that the effectiveness per unit of energy absorbed increased with decreasing photon energy with sudden drops in effectiveness as the absorption edges of bromine and silver were crossed from low to higher energies. The sudden jumps in effectiveness above the absorption edges were attributed to the sudden loss of photoelectrons occurring at the K edge energy and the loss of K fluorescence which occurs for photon energies greater than the K edge energy. The gradual decrease of effectiveness which occurred for higher photon energies was attributed to effects of the energy distribution of photoelectrons.

Since the reduction of a single silver atom can render a grain developable(13), the effectiveness of photoelectrons in producing developable grains depends strongly on the grain size and nature of the emulsion. Seeman felt that low energy photoelectrons would be effective in producing perhaps several grains at the end of a track, whereas more energetic electrons might spend considerable energy in each of several grains while slowing down. Thus the energy expended in excess of that required to produce one free silver atom would not contribute to the observed yield. No information is given in the article about the absolute yield of the process thus the relative importance of secondary electrons and Auger electrons cannot be compared to the effects of the photoelectrons.

This concludes the review of studies of the effects of monochromatic radiation on chemical and biological systems. Monochromatic radiation has been used as an analytical or experimental tool in many studies which will not be discussed here (e.g. use of fluorescence radiation to calibrate scintillation detectors for energy dependence(14-17) and the use of fluorescence radiation to induce Auger transitions in order to determine fluorescence yields and the energy distribution of Auger electrons(18)). One use of monochromatic radiation not usually associated with studies of the effects of radiation on organic materials is the determination of w, the average energy required to produce one ion pair in the material being irradiated. As will be discussed in Section I D it is believed that further analysis of experimental and theoretical determinations of w might produce some useful information about the effects of x-radiation on organic materials. Work which is related to the present study was done by Kulenkampff(19,20) in 1926. He determined the value of w for air with x-rays of differing energies almost monochromatic characteristic x-radiation was obtained from the direct x-ray beam by using different anode materials and by selective filtration. Absolute energy absorption was obtained through the use of an x-ray calorimeter similar to the one used in this study. Subsequent work by

Gaertner(21-24) and by Crowther and Orton(25) determined the values of w for a number of monatomic, diatomic and polyatomic gases for one or two wavelengths. No systematic study of a single organic compound using a number of monochromatic wavelengths could be found.

2. Summary of Studies of Radiation Effects in Related Systems

This section reviews the radiation effects studies of alkyl halides and similar materials using mixed beam radiation.

Much of the work done in this study would be considered as a part of the broad field of radiation chemistry. Many excellent reviews of radiation chemistry studies are available(26-38). Several articles review radiation effects studies on organic materials more extensively(39-45). Many studies of the effects of radiation on organic materials have been conducted recently; a few typical studies are listed(45-54). A considerable number of radiolysis and photolysis studies have been conducted with organic halides and related compounds(55-70). The only specific reference to a study of 1-bromobutane found was a study of the radiolysis of butyl bromides with gamma rays by Wilcox(71).

Wilcox irradiated samples of the butyl bromides (both highly purified and as-received; both with and without dissolved oxygen) with cobalt-60 radiation and determined the gross decomposition yield of the sample by gas chromatographic analysis. He found that breakage of the halogen-carbon bond was the predominant reaction and in the case of 1-bromobutane the major product was n-butane. Some 1,2-dibromobutane was also formed, apparently by the abstraction of hydrogen atoms by energetic bromine atoms. The G value (molecules produced per 100 ev of energy absorbed) for n-butane production was 3.4. This value would be approximately equal to the G value for decomposition since no other major reaction products were found. No appreciable differences in product distribution or yield were observed due to the presence of impurities (including both dissolved oxygen and the as-received impurities in the organics). Since gross decomposition was always produced in order to obtain sufficient products for identification no observations were made of products, yields, or the effects of impurities which might occur in the initial stages of the reaction.

Many parallels have been drawn between the effects of radiation and the results of photochemical reactions, thus some recent photochemical studies of the alkyl halides were reviewed(72-86). Alkyl halides have been used extensively in hot atom chemistry studies. In those studies the atom to be studied is usually made radioactive by neutron capture or it is a radioactive daughter of another radioactive species and upon formation the atom becomes thermally hot from the recoil energy absorbed from the departing photon or particle (in order to conserve momentum). Since the hot atom is tagged radioactively its subsequent reactions can be followed with relative ease. Considerable progress toward understanding the basic types of reactions which occur to the hot atom while it possesses high kinetic energy, as it slows down and finally as a thermal species has been made by the additions of suitable materials which function as moderators or scavengers. Some of the work with alkyl halides is listed(87-90).

One phase of hot atom studies involves the use of compounds synthesized with bromine 80m. The decay of the isomeric state produces bromine

80 (which is radioactive) and the gamma ray emitted is highly internally converted in the bromine K shell. The excited atom thus produced is identical to the bromine atoms which have absorbed an x-ray photon in the K shell in the present study with one convenient exception: the radioactivity of the bromine atom facilitates the observation of the reactions of the original bromine atom without confusion due to the presence of other bromine atoms produced non-selectively in the sample by electron interactions. Thus the initial reaction which occurs following x-ray absorption can be studied and the nature of all subsequent reactions of the original excited atom can be studied. Several studies using isomeric transitions in alkyl halides were found in the literature(91-97). Gordus and Willard found that isomeric transitions in gaseous $C_2H_5Br^{80m}$ resulted in bond rupture of the original compound in greater than 96% of the molecules which suffered decay of the bromine atom(92). This result would seem to indicate that the disruption of the 1-bromobutane molecule which absorbs an x-ray would occur with high probability.

The initial charge and mass distribution of atoms and molecules which have undergone nuclear transformations (either beta decay or gamma ray emission with high internal conversion) with the subsequent Auger emission of electrons has been the subject of several studies(100-107). Snell and Pleasanton(108) report the buildup of positive charges as high as 22 in xenon ^{131} following the isomeric transition from xenon^{131m} which was allowed to decay in a specially designed mass spectrometer. Wexler and Hess(109), using similar techniques, studied the ion and mass distribution resulting from the beta decay of bromine^{82} synthesized into

1,2-dibromoethane. The predominant ionized species occurring was $C_2H_4Br^+$. Cantwell(110) has analyzed the dissociation of HT following the beta decay of tritium theoretically using hydrogen type wave functions.

One of the common methods used to determine the yield of radiation induced decomposition of organic materials is the use of scavenger materials which react with the radicals produced by the radiation energy absorption. Schuler(111) reviews the recent advances in the use of scavengers and compares some of the results obtained with different scavenger systems. Probably the most frequently used scavenger in organic systems is iodine. Iodine could not be used in the present study due to its high x-ray absorption cross section. Schuler concluded, however, that approximately the same estimates of radical production are obtained from studies using DPPH scavenger as are obtained with iodine. Some typical studies which used iodine (both radioactive and stable isotopes) as a scavenger were reviewed(112-129). Triphenylmethane(130,131), radiobromine(132), p-benzoquinone(133), erioglaucine(134) and other materials have also been used as scavenging agents.

The use of DPPH as a free radical counter was first suggested by Chapiro(135) in 1951. Many of the techniques developed by Chapiro were used in this study and are discussed in more detail in Section II D. In addition to many studies using DPPH(136-151), Chapiro and his colleagues have also used polymerization initiaion to measure radical yields(152). Several other laboratories have used DPPH to measure the free radical yields produced by the decomposition of organics by radiation(153-157).

3. Miscellaneous Literature Consulted

A large effort in the literature search was directed toward finding and reviewing any experimental or theoretical studies of the energy dependence of radiation effects which had been made in the past. The results of the experimental studies were described in the first part of this section. The following discussion includes all the other references which were found pertinent to the current study.

Interaction of Radiation with Molecular Species. Many general discussions of radiation chemistry theory were found(158-185). The initial event and the species produced by the primary act are discussed in particular in three articles(186-188). The distribution of reaction products along the path of an ionizing particle has been the subject of several recent studies(189-200). The rate of energy loss (usually abbreviated LET) has been determined experimentally and theoretically, particularly for water and tissue(201-206). Lea(207) has studied several biological systems which have a radiation yield that is dependent on energy (e.g. chromosome breakage in the spore Tradescantia) and concludes that the energy dependence can be explained in terms of sensitivity of the system to the local ionization density changes resulting from the different electron energies produced by differing types of radiation and different photon energies. Lea found that differences in the local ionization density could produce different effects in these systems due to the particular molecular arrangement. The same effects could be produced with different types of radiation if the local ionization produced was the same; thus the system was not directly dependent on the photon energy or the type or location of the initial event but was dependent on the density of primary and secondary electrons produced by the radiation.

The local ionization density resulting from the absorption of different types of radiation in water is shown in an excellent chart(202). Several reviews of LET dependent systems are available(208-209). The sensitivity of the Fricke dosimeter to LET (in addition to the effects of varying oxygen and acid concentrations) was studied recently(210).

The production of energetic secondary electrons (delta rays) is an important factor in determining the local ionization density which will occur when different types of radiation are absorbed(211-213). Electron scattering and impact studies have been very useful in determining the nature of the ionized species produced by radiation(214-220). The sequence of events following the initial absorption event and the approximate lifetimes of the different species has been discussed(221-223). Reactions between ions and molecules are known to occur and the results of some reactions are largely dominated by ion molecule reactions(224-227). In condensed media many organic ions will decompose following neutralization with a free electron or another molecule which has captured an electron(228-233).

Much of the energy which is absorbed from secondary electrons produces excited molecules. Since the energy of the lowest lying excited state is often greater than the bonding energy of complex organic materials, molecular dissociation is a common product of excited states(234-239). Other methods of de-excitation can occur including energy transfer, quenching, protection and sensitization(240-248).

An important quantity which is related to the distribution of ionized species vs. excited species formed by the secondary electrons is w, the average energy absorbed to produce one ion pair(249-264). Measurements of w can be made conveniently only for gases; however some measurements have been made with liquids(260) and with solids(249). The approximate constancy of w for most materials is surprising in view of the rather large differences often observed for radiation product yields but has been qualitatively explained(257).

Properties of DPPH. DPPH was first synthesized in 1922 by Goldschmidt and Renn(265). Many of its chemical properties, reactions and derivatives were studied at that time. The preparation and purification are straightforward except that DPPH can form complexes with some organic solvents (including benzene) and special care is required to obtain the pure DPPH without solvent(266,267). Some general chemistry of DPPH and its derivatives was reviewed(268-272). The infra red and ultraviolet absorption spectra of DPPH and some derivatives are reported(273-274). Some experimenters have had difficulties with fading of the optical density of DPPH solutions(275). One possible source of difficulty is that DPPH reacts with unsaturated organics, organic acids and some alcohols(4). DPPH has been used as a primary standard for calibration of Electron Paramagnetic Resonance equipment because of its well defined EPR spectra, good stability and complete dissociation even in solid form, thereby producing a definite quantity of free spins per gram(276-284).

Prior to its use in radiation chemistry studies DPPH was used as a radical counter and scavenger in other types of reactions(285-287).

The efficiency of radical production of various polymerization catalysts was determined with DPPH(288-293). DPPH was also used to determine the rate of polymerization initiation and other kinetics of the reaction(296-304). DPPH has been used in some radiation chemistry studies to scavenge the free radicals produced in order to study certain reactions without interference(305-306). The possibility of occurence of DPPH reactions with excited states of benzene, cyclohexane and several other compounds was suggested from the work of Griffith(307). This work is discussed in more detail in Section II D.

A limited survey of some of the chemical properties and reactions of the alkyl halides was conducted(308-315).

References on Irradiation Techniques. Several references were found for the design of high intensity x-ray machines which would be useful for future radiation studies with monochromatic radiation(316,317). Several sources of experimental and calculated values for absorption cross sections for 5-35 Kev x-rays were used(318-323). The fine structure of the absorption cross section of some materials near absorption edges was discussed in several references(324-326). The range, energy loss and energy spectrum of electrons while slowing down were contained in several references(327-331). The widths of x-rays emission lines and the relative intensities of the various fluorescence lines were found in several references(332-334) although there are considerable gaps in the information available (for example the total x-ray power emitted by an x-ray target as characteristic radiation compared to the power emitted in the continuous spectrum could not be found). A compilation of x-ray emission line energies and absorption edge energies in Kev for all elements by Fine and Hendee(335) was used throughout the study and was found to be particularly useful.

No reference to the use or design of x-ray filters of the type needed for this study was found. Several references were found for techniques which were somewhat applicable(336-342). Fluorescence yields and Auger electron yields were obtained from several references(343-349).

A number of sources of information on x-ray dosimetric measurements were consulted(350-367). Few applications of calorimetric techniques for the measurement of low energy x-ray power could be found(368-371). Many recent applications of calorimetric techniques were found for measuring the power output of high intensity accelerator and gamma ray beams(372-378). The most sensitive thermocouples and thermopiles available commercially which were found were those of the Charles M. Reeder Co.(379).

The need for a krypton radiator necessitated the synthesis of a krypton clathrate since no commercial supplier could be found. Some of the properties and uses of clathrates are described in the references(380-383).

Several references were found which discussed improvements in techniques for colorimetric analysis(384-386).

Other Chemical Systems for Further Study. The early work in this study included a brief survey of several other chemical systems which were felt to show promise for further study. Some of the references are listed in hopes that they may be of future use. A review of general chemical systems sensitive to radiation was reported in the literature but was not readily accessible(387). The bond energies of common organic compounds were given in several articles(388-390). Properties of free radicals were discussed(391-400). The use of electron paramagnetic resonance techniques to determine the number and types of free radicals produced by monochromatic radiation was considered(401-407). Two references were found of the production of free radicals by irradiation of stable free radical materials(408-409). Radiation studies using dyes as the target materials were considered because of the high detection sensitivity for many dyes(410-439). Several references to the use of dyes mixed in plastics similar to the work of Garsou(3) were found(440-446). The use of organometallic compounds would be desirable for studies like the present one since the initial x-ray energy absorption could be preferentially directed to the metal atom in many cases(447-464). The use of chemiluminescent materials to detect radiation products was considered(465-472).

D. Discussion of the Applicable Theory

The purpose of this section is to examine the available experimental and theoretical information on radiation interaction mechanisms in an attempt to determine whether the action spectrum of the present system should be energy dependent. No attempt will be made to discuss radiation effects mechanisms comprehensively except those which might be expected to show energy dependence. The discussion will also be limited to the radiation effects produced by the absorption of low energy (5-35 Kev) monochromatic x-radiation and the various forms of degraded energy which are produced as a result of the initial absorption.

The three studies in this series preceding this study(1,2,3) have discussed the basic interactions of radiation and matter. Those discussions will not be repeated here except in review and a few additional points will be discussed.

1. Initial X-Ray Absorption Event

X-ray interactions occur by three basic mechanisms: pair production, Compton and other forms of scattering and photoelectric absorption(204). Pair production cannot occur for photon energies below 1.02 Mev(204), consequently this process can be eliminated from consideration. The total contribution of the cross section for all scattering processes for bromine computed at the energy (13.475 Kev) for which the minimum photoelectric cross section exists (within the range of energies studied) is less than 6%(319). The scattering component will be considerably less for most of the energies used in this study. The average fractional energy change experienced by the scattered photon for Compton scattering at the low energies used in this study will always be small (less than 5%)(206). The energy imparted to the electrons in this scattering process will form a continuous distribution of energies with no selective production of scattered electrons with certain energies. In most cases the scattered photon will be absorbed photoelectrically in the sample since it is thick for photons of the energies which will result from scattering. The final result is that the photon which is scattered initially will produce essentially the same effects as photons which are absorbed initially by the photoelectric process. Thus the predominant initial event is photoelectric absorption.

Photoelectric absorption is a very selective process as employed in this study since only bromine atoms will be responsible for (effectively) all of the x-ray energy absorption. The selective energy absorption which can be obtained with the photoelectric process was the primary reason for choosing monochromatic x-rays as the radiation source for this study and for previous studies in the series. It seemed reasonable to expect that materials would be most likely to show an energy dependence of radiation effects in the photoelectric absorption region if any energy dependence on the initial photon energy was to be observed at any energy.

The cause of the specificity of absorption can be seen in Figure 2 which shows the absorption coefficient for 1-bromobutane and its constituent elements. Since the photoelectric cross section varies as the fifth power of the atomic number(206) effectively all initial x-ray absorptions will occur in bromine atoms. The site of the initial energy deposition then is well defined and the process is well understood.

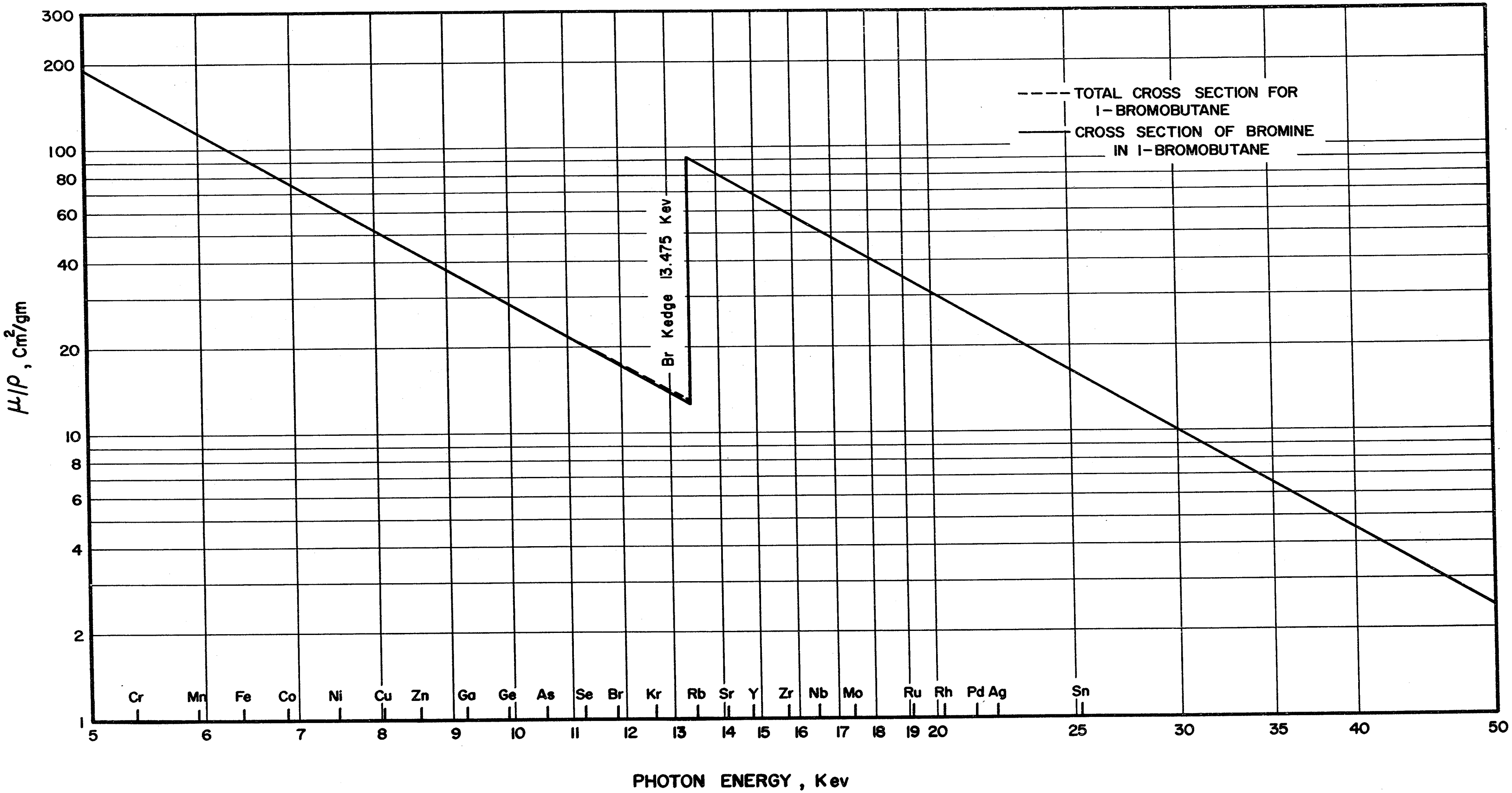

Figure 2. Absorption Cross Section of 1-Bromobutane.

In a large complex molecule it would seem that considerable variations might occur in the location and effectiveness of the <u>initial</u> absorption event depending on the initial photon energy. Whether the radiation effect which is observed will retain the specificity of the initial absorption event is the main question to be resolved. The predominance of events which follow the initial absorption, if independent of the initial photon energy, might tend to obscure the energy-dependent initial event. It is the purpose of the following sections to explore the different mechanisms in which the radiation energy can interact with the sample as the energy is degraded until equilibrium is reached. It would seem that in most instances the effect produced by the initial absorption event would be obscured by the large number of effects produced by degraded radiation since the energy deposited in the initial absorption is not retained in the absorbing atom but is emitted as fluorescence radiation or produces energetic electrons. The radiation effects produced by these species would be expected to obscure the energy dependent effects of the initial event unless: (1) The ratio of observed effects produced by the initial event to those produced by the subsequent events is large enough to permit detection. (2) The effects produced by the subsequent events are dependent on the initial event because of a spatial or geometric effect of the location of the initial event. (3) The effects of the subsequent events are dependent on the initial event because of the nature (type of radiation and photon energy) of the secondary radiation produced from the initial event. These alternatives assume that only one radiation effect is detected or that the same effects are produced by the initial and subsequent events. Experiments could be designed which would delineate between the effects produced by the initial and final events (e.g. hot atoms studies(87-90) or the mass spectrographic studies of Wexler(109)). However, the detection methods used in this study and previous studies in this series would not be expected to distinguish between the effects produced by the initial and final events.

2. Photoelectric Absorption

This line of reasoning can be seen more clearly by a closer examination of the details of the photoelectric absorption process. Following the initial interaction of the photon with the target atom an electron is ejected from the atom with a kinetic energy equal to the difference between the incoming photon energy and the binding energy of the electron which has been ejected from the atom. An insignificant amount of kinetic energy is imparted to the atom as the photoelectron leaves in order to conserve momentum in the reaction. The interaction of the photon with electrons in different energy shells will depend on the coupling between the two particles and results predominantly in K and L shell reactions for the photon energies and elements used in the present study. Since the probability of interaction is zero for a photon to eject an electron with a binding energy greater than the photon energy, the absorption probability for interaction with the electron exhibits a discontinuous increase from zero to some finite value at the photon energy equal to the electron binding energy. This energy is usually called the critical absorption energy and the jump in the cross section value is usually called the K (or L) edge. The ratio of the cross section values above and below this energy determines the ratio of absorption in each shell at the critical energy and for nearby energies greater than the critical energy. Thus as photons of increasing energies are absorbed photoelectrically, traversing* the K edge will not alter the nature of the L shell reactions. Since the ratio of absorption cross sections across the K edge is about 8 for the materials used in this study, K reactions will be eight times more prevalent than L and M reactions for photon energies greater than the K edge energy. The fraction of the initial photon energy which is given to the photoelectron thus varies considerably as the K edge is traversed.

A curve showing the fraction of initial photon energy which is given to the photoelectron for a bromine target atom for the x-ray energy range used in this study was calculated and is shown in Figure 3.

3. Fluorescence Yield and Auger Electrons

Auger Electrons. Following the ejection of the photoelectron into the continuum of unbound states the atom is left in a highly excited state with an excess energy corresponding to the binding energy of the ejected electron. The initial vacancy will be filled by an electron from one of the outer shells. Simultaneous emission of a discrete amount of energy equal to the difference between the binding energy of the two electronic shells involved will occur by one of two competing processes:

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* For convenience the terminology "traversing the K edge" which has meaning for crystal spectrometric work in which different energies can be swept out by the rotation of the crystal, will be retained for the fluorescence radiator studies in which successively higher energies are obtained by using different radiators.

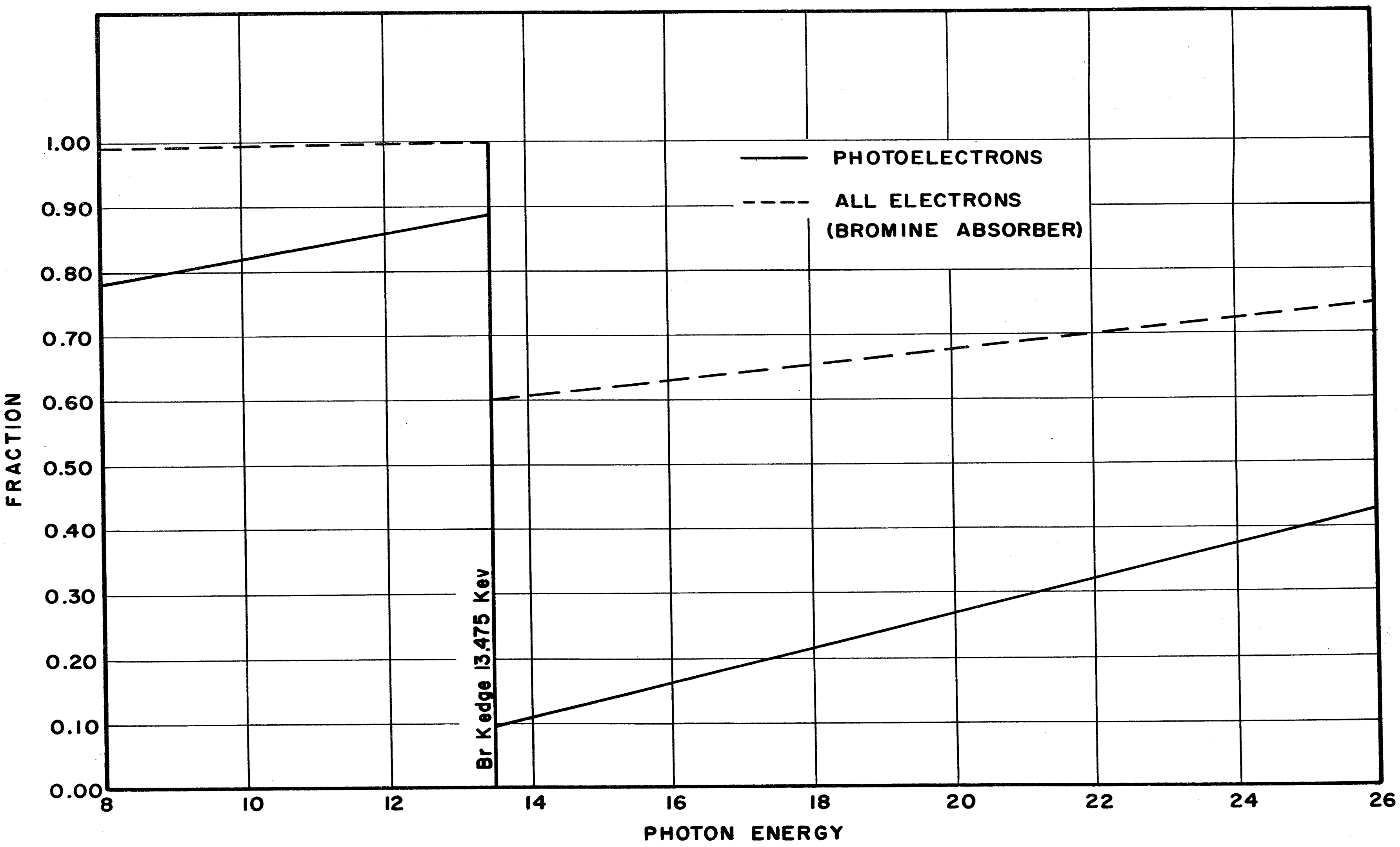


Figure 3. Fraction of Original Photon Energy Given Initially to Photoelectrons and to All Electrons.

(1) A fluorescence photon of discrete energy will be emitted (i.e. the characteristic radiation which makes possible the use of radiators to obtain different monochromatic radiation). (2) Another electron will be ejected from a lower energy position with a discrete kinetic energy corresponding to the difference in binding energy between the initial vacancy and the sum of the binding energies computed for the excited atom of the other two electrons reacting. The former process is called fluorescence emission and is governed by selection rules as to which shells and subshells can interact and the relative probabilities of interaction. The latter process is called Auger emission and corresponds to true coupling of the electronic states of the excited atom (rather than internal conversion of the photon) since electron energies corresponding to forbidden transitions have been observed(473).

Fluorescence Yield. The fluorescence yield w_n is defined as the fraction of vacancies in the n-th shell in which a fluorescence photon is emitted as the vacancy is filled compared to the total number of vacancies filled by all means. The fluorescence yield is a strong function of atomic number ($w_K, w_L \propto (1+CZ^{-4})^{-1}$), increasing with Z and decreasing considerably for lower energy shells ($K \gg L \gg M$)(343). The values of w for bromine are $w_K = 0.56$ and $w_L < 0.05$(343). The fluorescence yield is independent of the energy of the incoming photon. Auger electrons are produced with discrete energies; neither the allowed electron energies nor the distribution of the number of electrons with particular energies changes with the energy of the incoming photon(343).

An important result of the lower fluorescence yields for outer electronic shells is that essentially all photoelectric absorptions (including those which emit fluorescence radiation) will result in the ejection of several electrons from the target atom. It would be anticipated that the efficiency of decomposition of the molecule containing the target atom would be very high due to the loss of binding electrons. Experimental results of this process were discussed on page 16. Thus it is seen that as different monochromatic energies are used for the irradiation of a sample the only change occurring in the initial interaction mechanism is the energy of the ejected photoelectron and the fraction of initial photon energy which is given to the photoelectron, unless an absorption edge is traversed.

Effects of Crossing an Absorption Edge. An interesting feature of the role of Auger electrons and photoelectrons is the comparison of electron energies as the K edge of the target atom is traversed. Bromine will be used as a numerical example but the essential features will be the same for other target atoms. Consider the absorption of a K_α photon from rubidium (13.39 Kev) or from strontium (14.16 Kev) in a bromine atom. In the former case a photoelectron of 11.6 Kev will be emitted and the remainder of the energy will be dissipated as weak L fluorescence or a collection of low energy Auger electrons. Many alternative methods of de-excitation are possible for the latter case; only the most probable ones will be considered since no large deviations from the two cases cited will occur. A photoelectron of 0.685 Kev will be ejected and either (1) fluorescence (56% of the time) or (2) an L Auger transition can occur. (1) Fluorescence will produce a K_α photon (84% of the time(474)) which will most likely be absorbed in the sample and produce an absorption in the L shell resulting in the emission of a photoelectron of 10.13 Kev and some low energy fluorescence and/or Auger electrons. (2) The most likely Auger transition following a K shell vacancy(475) is the $K \rightarrow L_{II}L_{III}$, i.e. an electron is emitted with the energy of approximately $K \leftarrow L_{II}$ (i.e. K_{α_2}) less the binding energy of an L_{III} electron, which equals 10.32 Kev for bromine. Other low energy fluorescence and/or Auger electron emission will dissipate the remainder of the energy. Thus it is seen that although the detailed electron energy distribution changes as the K edge is traversed the major portion of the initial photon energy is given to a single high energy electron (either Auger or photoelectron). As a result of these processes the maximum change in energy of the energetic electron is only 10% as the K edge of bromine is traversed.

4. Fluorescence Radiation

As the absorption edge (always the K edge in this study) is crossed the number of absorptions in the L shell will decrease to a fraction, 1/1(1+jump ratio) = 1/9 of the number of L events occurring for photons with energies below the K edge(476). This statement assumes that the sample was totally absorbing for the photons of energies less than the K edge for all samples and that the same radiation intensity is used below and above the K edge energy. The difference in absorption is due to the competing process of K shell absorption and the characteristic K shell processes will occur. Due to the thickness of the samples used in this study compared to the mean free path for L fluorescence radiation essentially all of the L fluorescence radiation will be absorbed in the sample whereas much of the K fluorescence radiation will be able to escape the sample. The necessary corrections for fluorescence escape in the final action spectra curves obtained in this study are discussed in Section II D.

There is no preferential absorption of fluorescence radiation after the photon has left the atom according to the standard references on photoelectric cross section(18,319). In order to ensure that no narrow resonance-type of absorption was occurring for fluorescence emission radiation which might have been unobserved with crystal spectrometric techniques in past studies, the absorption cross section of a zirconium foil was determined using filtered K_{α} fluorescence radiation from a zirconium radiator and other radiators with emission energies near zirconium K_{α}. No deviation of the cross section from reported values was observed for any of the radiators. No additional experimental evidence was found in the literature which would support or deny the existence of resonance-type of absorption of fluorescent radiation.

It would appear that the only function of fluorescence radiation in this study is to relocate the point of absorption of a large portion of the energy of the initially absorbed photon to another point (inside the sample in the case of L fluorescence and occasionally outside the sample in the case of K fluorescence radiation). The possibility of a resonance type of transfer of fluorescence radiation from one atom to another would thus seem to be excluded on both theoretical and experimental bases.

5. Energy Dissipation by Electrons

At this point in the sequence of events all of the initial photon energy has been converted into kinetic energy of electrons except for the energy lost by K fluorescence escape from the sample and the small recoil energy imparted to the initial atom upon emission of fluorescence radiation and/or electron ejections. At the time of ejection from the atom the energetic electrons have two characteristics which are related to the initial absorption event: (1) The spatial distribution of the electrons is inhomogeneous since they are all emitted from target molecules and most frequently from the target atom. (2) The energies of the Auger electrons are characteristic of the target atom and whether the energy of the initial photon was greater or less than the K edge energy of the target atom (but not otherwise dependent on the energy of the initial photon). Note that the photoelectron is specific in both spatial distribution and energy, depending directly on the photon energy and the target atom location.

Slowing Down of Electrons. The slowing down of electrons is a well known phenomena, although experimental verification of many reactions is sparse. High energy electrons are slowed down by inelastic collisions with atomic electrons. For this study electron-nucleus and electron-electron bremsstrahlung can be neglected since for the photon energies used these processes occur only rarely compared to inelastic collisions. If the energy imparted to the electron is less than its binding energy it can be elevated to an excited state. The electron may be ejected from the atom if the impact energy from the collision is greater than the binding energy. Occasionally a collision of the latter type will produce a very energetic secondary electron (or δ ray) which can have enough energy to produce several ionizations. On the average about half of the initial energy of the original electron will be expended in forming δ rays(477). The role of δ rays in radiation chemistry is discussed in more detail in Reference (163). As the velocity of the charged particle decreases the probability of interaction increases; thus the collision density along the path of an individual particle increases to a maximum near the end of travel of the particle.

Energy Distribution from Electron Interactions. No theoretical or experimental information about the point by point distribution of energy between ionic and excited species along the path could be found in the literature. Some related calculations have been made of the probability of excitation versus ionization of helium atoms for low energy electrons(219) (see Figure 4). Two features of this figure are particularly significant for this study: (1) As might be expected from optical spectra, excitation probability maxima (shown on the chart as a maximum value for w the average energy required to produce an ion pair, thus a measure of the energy input into excited states which do not produce ionized species) occur for energy input into excited states. (2) The probability for input of energy to produce ionization is a slowly varying function which decreases monotonically for higher electron energies. There are no preferential energies above the optical levels of the atom which have large reaction probabilities. This analysis is further corroborated by the experimental measurements of electron collision cross sections by Lassettre(218) which do not show the

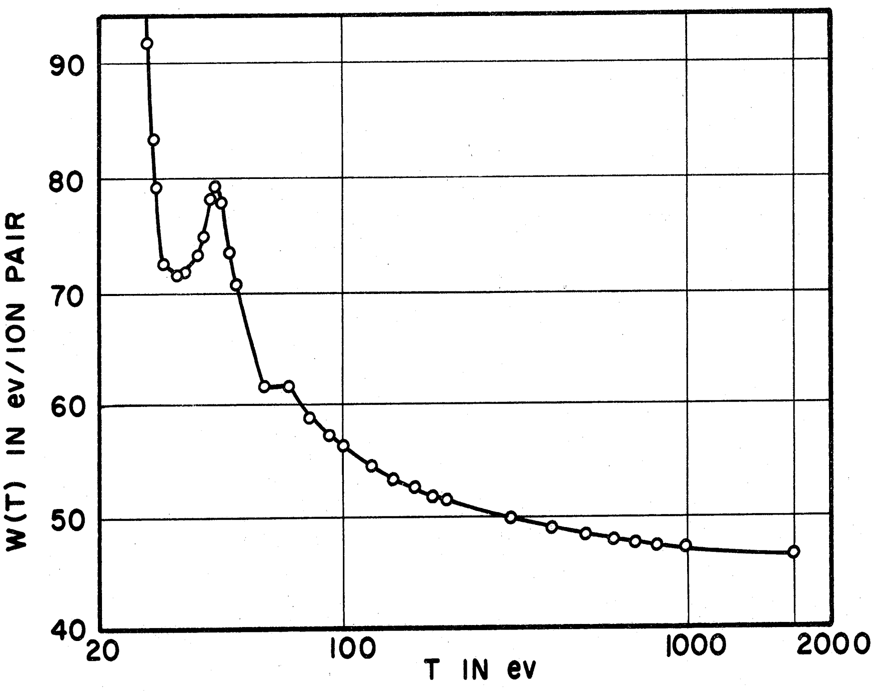


Figure 4. Mean Energy Required to Produce One Ion Pair in Helium [from Miller(219)].

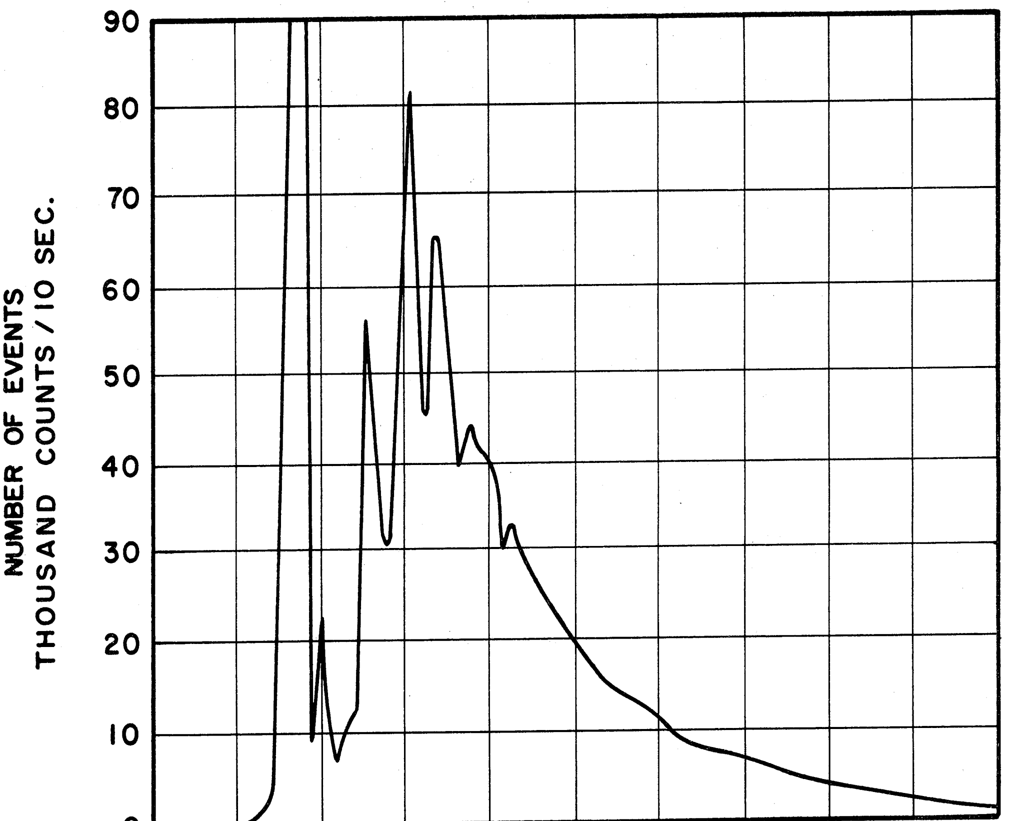


Figure 5. Mean Energy Loss per Collision for 500 ev Electrons in Oxygen [from Lassettre(214)].

occurrence of any discontinuous reaction probabilities for energy losses greater than the optical levels of the scattering material. A typical curve of Lassettre's data is shown in Figure 5.

In view of the information on electron scattering it would seem reasonable to assume that although the Auger electrons are generated with distinct energies the statistical nature of the scattering processes would tend to randomize the electron energy distribution so that an electron slowing down from an energy of several Kev to an energy corresponding to the energy of the optical level resonance absorptions would have lost all characteristics of its original energy. The final energy distribution of the low energy electrons which cause most of the excitations and ionizations in the material is a product of the thermalization process and does not retain the characteristics of the initial electron energy distribution.

Reviewing the dissipation of energy by electrons it is seen that although the initial energy distribution of Auger electrons is distinctive (depending on the electron energy levels of the target atom and on the type K, L, etc. of initial photon absorption event): (1) The difference in the electron energy distribution which will occur depending on whether the initial photon ejects a K electron or an L electron is small and (2) the initial energy distribution of the Auger electrons is randomized before the electrons slow down sufficiently to be scattered inelastically by the excitation energy levels of specific atoms.

The initial energy of the photoelectron is also dependent on the photon energy and the energy levels of the target atom but the same analysis as above would apply. Thus it would appear that based on present information the production of specific radiation effects due to the distinctive initial energy distribution of electrons would be unlikely.

6. Significance of the Spatial Distribution of Energy Deposition

The most significant innovation in this study and preceding studies of this series is the specificity of the spatial distribution of the initial absorption of energy within the target molecule. Photoelectric absorption localizes the deposition of tremendous energies (compared with the energy of chemical bonds of the molecule) to a specific target atom within the target molecule. If (1) the target atom constitutes a sensitive site in the molecule (for some particular molecular function such as the iron atom in the catalase molecule studied by Emmons(1)) and if (2) sufficient energy from the initial absorption could be expended in the sensitive site; the radiation effects produced in the material would be expected to exhibit considerable sensitivity to the initial photon energy. Whether the initial reaction can be detected in the presence of similar events is discussed on page 41.

Quantum Yield Greater than One. If the quantum yield of the observed radiation reaction is considerably greater than one because the degraded radiation is producing more reactions than the initial reaction it is difficult to see how the spatial distribution of the initial absorption could cause any energy dependence of the reaction. The major production of radiation effects would be caused by electrons ejected in random directions from the initial molecule and reacting with other molecules at random; thus there should be no extra-molecular coupling between molecules which would allow the degraded radiation from one molecule to react preferentially with the sensitive sites of another molecule due to the initial distinctive spatial origin of the degraded radiation. The possibility of a resonance type of coupling between molecules which would allow the preferential transfer of energy from one sensitive site to another because of the distinctive energy of the degraded radiation was discussed on page 38.

Quantum Yield Less Than One. If the quantum yield of the observed radiation effect is less than one the specificity of monochromatic irradiation might be expected to produce a radiation effect which would be dependent on the photon energy of the radiation. The loss of binding electrons which occurs during the Auger transitions following the initial x-ray absorption would most likely result in molecular disruption at the site of the target atom. The extremely high local ionization density which occurs in the immediate vicinity of the target atom might be of significance in large complex molecules (such as might be encountered in a biological system) where the sensitive site consists of several adjacent atoms surrounding the target atom. The high local ionization density might destroy the sensitive site more efficiently than random ionizations since several random events might be required to produce sufficient damage to destroy the sensitive site. The sensitive site in this example would correspond to the multi-hit target in biological materials observed by Lea(163) and others.

This type of reaction has been proposed previously by Platzman(478) but no experimental tests of this hypothesis could be found in the literature. The lack of experimental verification is not surprising in view of the experimental difficulties which would be encountered in such a test. With the fluorescence equipment used in this study the highest monochromatic intensity achieved was about 1.33×10^{12} photons per minute thus a quantum yield of unity would produce only 7×10^{15} events in 100 hours of irradiation assuming total absorption of the x-ray beam. The detection of such a small quantity of reaction products in a sample large enough to be totally absorbing to the x-radiation would probably be very difficult except in special cases.

A necessary condition for this type of reaction to occur is that the efficiency of production of radiation effects by degraded radiation must be considerably lower than the efficiency of production of radiation effects by the initial absorption event since much more energy is transferred to the sample by degraded radiation than from the target atoms.

Since the quantum yield for 1-bromobutane is on the order of 35 molecules disrupted per photon absorbed the energy-dependent reaction of the type proposed by Platzman would not be expected to be detectable for 1-bromobutane. It would appear that based on present knowledge the free radical yield of 1-bromobutane should not be dependent on the spatial distribution of energy deposition by electrons.

7. Significance of Radiation Yield

The magnitude of the radiation yield is an important piece of information since some inferences about the nature of the reaction process can be made once the yield is known. In particular a quantum yield (number of effects produced per photon initially absorbed) value greater than one would seem to indicate either:

(1) that much of the observed effect was caused by degraded radiation;

(2) in some manner the initial event produced a species which was able to initiate a large chain reaction; or

(3) some other undefined phenomena associated with and specific to the initial event was able to produce the observed effect (even though the actual quantity of energy retained by the initial atom is very small compared to the energy content of the degraded radiation).

A reaction of type (2) is eliminated for 1-bromobutane since a chain reaction with the alkyl bromide is too endothermic to occur appreciably(479). Reactions of type (1) would not be expected to produce radiation effects which depended on the initial photon energy according to the discussion of pages 38 and 41 except in the case of LET dependent reactions (see the next section). Reactions of type (3) cannot of course be excluded or accepted without further information about the phenomena involved.

In order for reactions of type (2) and (3) to be detected in the presence of reactions from degraded radiation the efficiency of production of the radiation effect by the initial absorption event must be considerably higher than the production of the same effect by degraded radiation. This statement is based on conclusions made in the preceding parts of this section; i.e., (1) most of the energy which is ultimately absorbed by the sample is transferred to the sample by interactions with degraded radiation, and (2) the radiation effects produced by degraded radiation are not dependent on photon energy.

8. Discussion of LET Sensitive Reactions

The only type of reaction which had been shown to be energy dependent which was found in the literature is usually described as a LET dependent reaction. LET in this case is used to denote the differential energy loss per unit path length but is occasionally used in the literature as the average energy loss per unit path length for the entire path of the particle. In order to avoid this difficulty the term local ionization density will be used in this thesis to denote the differential $-\frac{dE}{dX}$. This difficulty was recognized by Lea who used the term ion-density or specific density for the number of ionizations produced per micron of path length(480).

LET dependent reactions have been discussed in detail in the literature(481-483). One common theory of LET dependence(483,484) attempts to correlate the radiation yield with the volume of the sensitive site as compared to the number of ions produced in similar volumes along the path of the ionizing particle. In some cases (certain strains of mosaic tobacco virus for example(485)) one ionization per sensitive volume is sufficient to produce the radiation effect, while in other systems (Tradescantia chromosome breakage for example(486)) several ionizations per sensitive site may be required to produce the radiation effect. In the former case an increase in ion density would be expected to decrease the radiation yield since any increase of ion density in excess of the minimum density required to deactivate the sensitive site would be ineffective. For Tradescantia however, the radiation yield increases with increasing ion density since the production of ion densities less than the minimum ion density required to deactivate the sensitive site are ineffective. Experimental evidence for reactions of the types mentioned is ample and well substantiated; however, other mechanisms have been proposed in addition to the one advanced here and no one explanation is felt to be completely satisfactory(481). The need for a sensitive site and a definite number of events to disable the site is shared by all of the theories reviewed.

It would be anticipated that LET sensitivity might be observed due to the variations in x-ray photon energies used in the studies of this series. Two variations might be expected: (1) The change in local ionization density due to the variation in the energy of the photoelectron which is ejected in the photoelectric capture of the x-ray photon. (2) The variation in local ionization density in the immediate region of the target atom as the K edge is traversed due to changes in the Auger shower of low energy electrons.

Upon closer examination it would seem that neither of the above situations should result in very large changes in local ionization densities for the x-ray energies used in this study. Figure 6 shows the variation in ion density for electrons in tissue for different energies in the region of the present study. As is seen the variations in ion density are not large between 6 and 25 Kev. Since this figure is for electrons it is representative of the variations in the ion density resulting from x-rays of similar energies but the actual variations in the ion density resulting from x-radiation are smaller(487). Lea states(488),

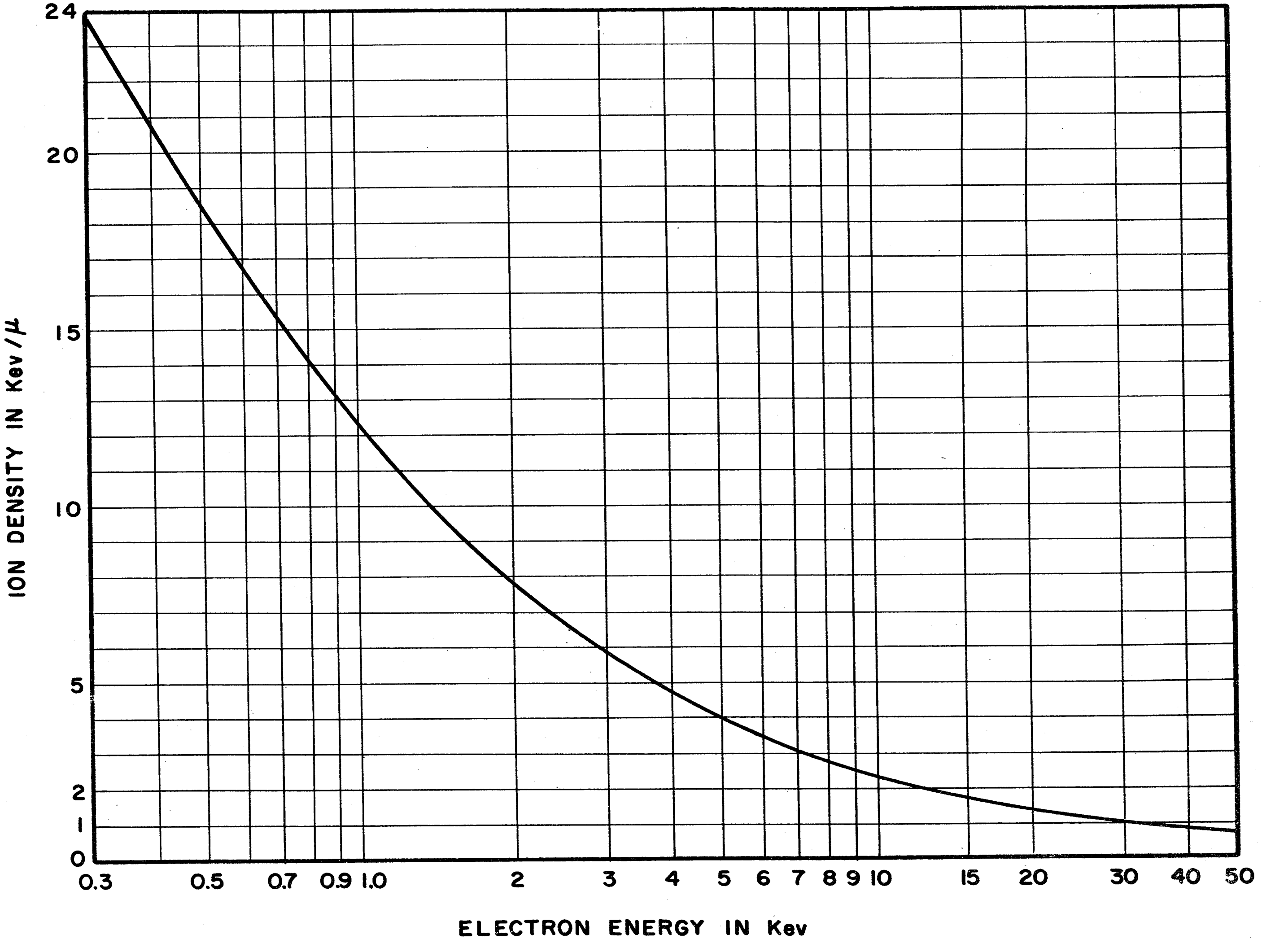


Figure 6. Ion Density in Tissue Produced by Electrons of Different Energies [drawn from data given by Lea(163)].

> "Thus the yield of the reaction studied for a given number of ionizations per unit volume of irradiated tissue is practically independent of wave-length over the range of wave-lengths most easily accessible, viz. γ-rays and x-rays down to say 50 Kev. It is usually only when soft x-rays of wave-lengths exceeding 1Å are used, or neutrons or α-rays, that a significant variation is found."

It would seem that since the local ionization in the region of the target atom is so high, that photons with energies above and below the K absorption limit might produce considerably different local ionization densities in the region of the absorbing atom (case (2) above). The discussion on page 33 shows, however, that the energy distribution of low energy electrons following a photoelectric absorption will be almost the same regardless of whether the initial absorption ejects a K or L electron. The energetic photoelectron produced by absorption of radiation below the K edge will be replaced by an Auger electron of almost equal energy for absorptions which occur for energies greater than the K edge.

In summary it would appear that no significant differences in local ionization density should be encountered in studies of the present type using monochromatic x-radiation with photon energies between 6 and 25 Kev. Thus a molecular system would have to be very sensitive to LET differences in order to show any variations in yield due to the small LET differences encountered in this study.

9. Summary

This analysis has been made in an attempt to develop a qualitative understanding of the various radiation degradation processes which precede the occurence of radiation effects in order to determine whether the energy dependent characteristics of the initial photon absorption event are preserved as the energy is degraded and the radiation effects occur. No attempt was made here (and none was found in the literature) to develop a theory which would predict from basic principles the nature and quantity of radiation effects which should occur during irradiation. It would appear that the knowledge of the amount of energy expended in matter by radiation and the mechanisms of formation of excited and ionic species (on a macroscopic scale) are known. However, the detailed information about the actual distribution of energy among the different possible excited states, the stabilities of the different excited states and the nature of the ion neutralization processes is not known well, or at all.

It seems contradictory that although the initial yield of ionic states (and apparently also complementary information on the yield of excited species by inference) from ionization chamber experiments among all of the gases tested (including both monatomic and polyatomic species) differs in general by less than a factor of two; the gross yields of decomposition and/or radical yields of the same materials may differ by as much as several orders of magnitude. The usual explanation of this behavior is that the initial formation of ionic and excited states is rather unselective since such large energies are encountered in radiation exposures compared to the normal chemical reactions(489). After the initial species are formed normal chemical processes proceed until equilibrium is reached. The differences in final yields are thus determined by the specific nature of the chemical reactions which follow the initial indiscriminate formation of excited species.

It has been the purpose of this analysis to determine whether the formation of the excited species was dependent only on the energy absorption of the sample or whether the photon energy of the radiation could be expected to produce different results. Based on the analysis of present theory given in this section the yield of the 1-bromobutane system should not be dependent on the photon energy of the radiation.

The following quotations are typical of current thinking on the energy dependence of radiation effects.

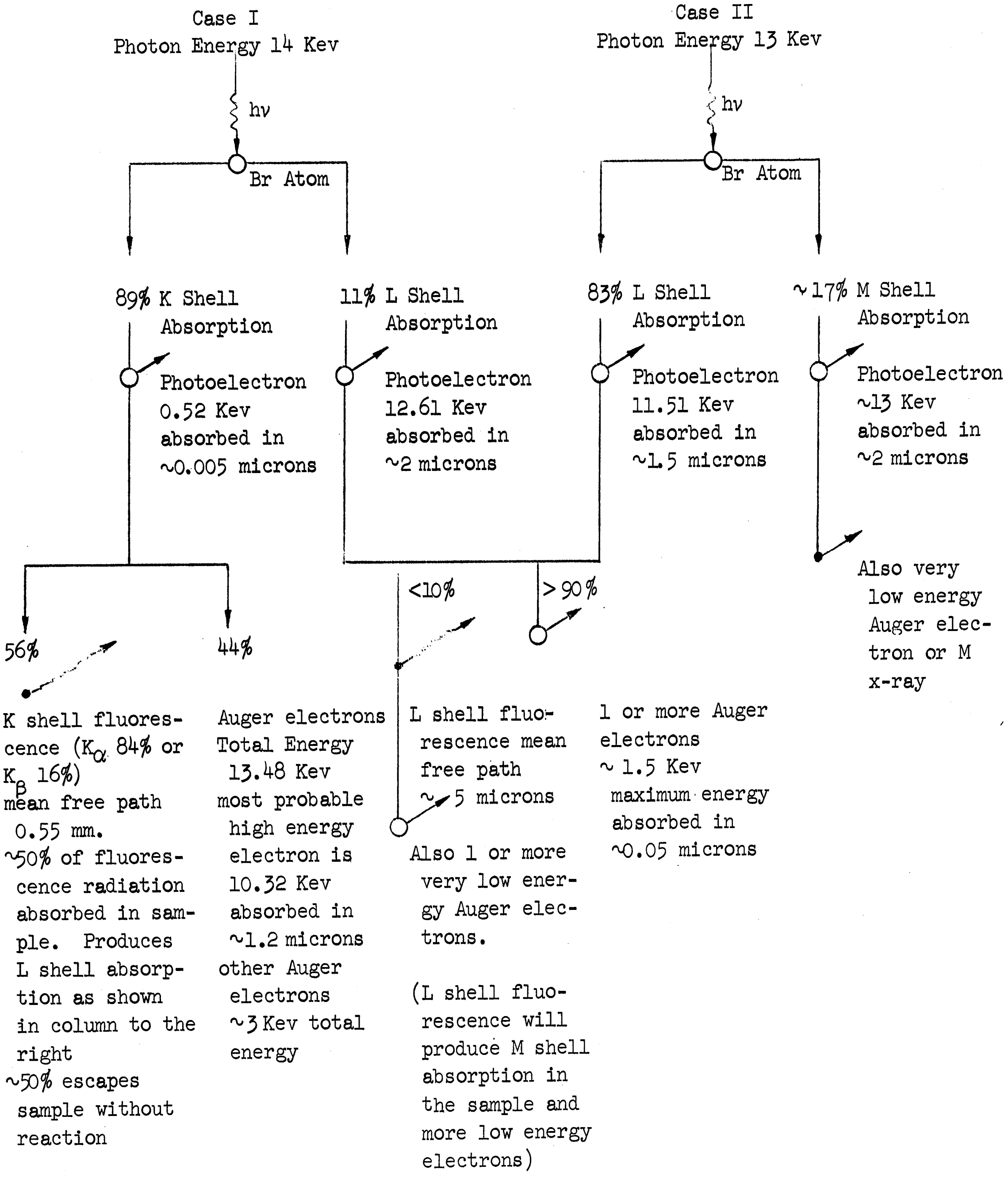
> Zirkle(490) stated, "So far as is known, the properties of the ions which are produced along an ionization track are independent of the properties of the high energy particle. This is also true of the excited molecules, i.e., those activated to states lower than ionization."

> Burton(37) stated, "The chemical effects of high energy radiation on matter are due almost exclusively to electrons."

> Fano(492) stated, "All processes produced by x-rays have therefore the main effect of replacing x-rays with fast electrons. The chemical action of x-rays is exerted almost entirely through secondary fast electrons...the inelastic collisions experienced by secondary electrons affect solely the external electrons of atoms within a limited radius of action. The qualitative effect of these collisions differs somewhat from the effect of collisions by very fast particles, in so far as the secondaries produce comparatively more ionizations and fewer excitations. Nevertheless, this circumstance does not affect the great similarity of action of different ionizing radiations, since the secondaries themselves are produced according to the same pattern no matter what the primary radiation."

> Walling(132) stated, "Exposure of organic materials to high-energy particles, e.g., α, β and γ rays, results in the introduction of energy locally far in excess of that associated with ordinary chemical bonds. Although the processes by which energy is degraded are complex and obscure, a large portion of it goes into a rather indiscriminate breaking of chemical bonds. As a result, the consequences of such exposure are largely radical reactions, although often of a very complicated kind."

SUMMARY OF RADIATION PHENOMENA WHICH OCCUR
FOLLOWING THE ABSORPTION OF AN X-RAY PHOTON IN A BROMINE ATOM



Photoelectron 0.52 Kev absorbed in ~0.005 microns

Photoelectron 12.61 Kev absorbed in ~2 microns

Photoelectron 11.51 Kev absorbed in ~1.5 microns

Photoelectron ~13 Kev absorbed in ~2 microns

Also very low energy Auger electron or M x-ray

K shell fluorescence (K_α 84% or K_β 16%) mean free path 0.55 mm. ~50% of fluorescence radiation absorbed in sample. Produces L shell absorption as shown in column to the right ~50% escapes sample without reaction

Auger electrons Total Energy 13.48 Kev most probable high energy electron is 10.32 Kev absorbed in ~1.2 microns other Auger electrons ~3 Kev total energy

L shell fluorescence mean free path ~5 microns

Also 1 or more very low energy Auger electrons.

(L shell fluorescence will produce M shell absorption in the sample and more low energy electrons)

1 or more Auger electrons ~ 1.5 Kev maximum energy absorbed in ~0.05 microns

II. EXPERIMENTAL TECHNIQUES

A. Availability of Radiation Sources

1. Use of Cobalt-60 Gamma Rays

Although the photon energies of cobalt-60 are so high that the predominant reaction with the target atom is Compton scattering rather than photoelectric absorption, the use of cobalt irradiations is still useful in this study for certain comparative measurements. The high photon intensities, considerable range of dose rates available, large volumes of radiation space available and the simplicity of operation of the cobalt source made its use very attractive for screening studies. Much of the preliminary work of this study was conducted in the cobalt source. The effects of various impurities on the system, of the radiation dose rate, scavenger concentration and linearity of effect with total absorbed dose were studied. The use of cobalt radiation provided a fast and convenient check of the techniques of sample preparation, handling, irradiation and optical density measurements. Most of the cobalt irradiation results were also verified with x-ray studies. to ensure that the results were consistent. However, it was felt that the time spent for cobalt studies was very useful in orienting the x-ray studies.

2. Use of the Crystal Spectrometer

From the beginning of the study it was anticipated that the major portion of the radiation studies would be conducted with monochromatic x-rays. High intensities of mixed radiation are readily obtained from standard x-ray equipment; however, specialized techniques must be used to obtain high intensities of monochromatic x-rays. The restrictions on the selection of a system to be studied which are imposed by the lack of sufficient radiation beam intensity will be discussed in detail in Section II D. The necessity of obtaining high beam intensities was one of the early problems which required a considerable expenditure of effort and which resulted in the development of a technique to use fluorescence radiation as the source of monochromatic radiation.

Earlier studies at this laboratory used a standard x-ray crystal spectrometer to obtain monochromatic radiation(1,3). The equipment used was a General Electric Company XRD-5 x-ray diffraction unit, shown in Figure 7. On the left is shown the scaler, rate meter, timer, and recorder assembly; in the center, the goniometer assembly with the tube mounted and the SPG-1 proportional counter detection unit in position; and on the right is the stabilized high voltage power supply for the unit.

Extremely good energy resolution can be obtained with the crystal spectrometer by using very narrow beam defining slits, by careful selection of the diffraction crystal, by etching the diffraction crystal, by meticulous alignment of the equipment and by the application of very careful experimental techniques. Double crystal spectrometers have been used to measure the line widths of x-ray emission lines (for example Reference (493) gives the width of ZrK_{α_1} at half maximum as 6 ev and shows the resolution of absorption edge fine structure of less than 2 ev). Unfortunately the radiation intensity which can be obtained with these techniques is often so low that special counting techniques are needed, thus only the most sensitive systems could be irradiated with this technique (e.g., photographic films).

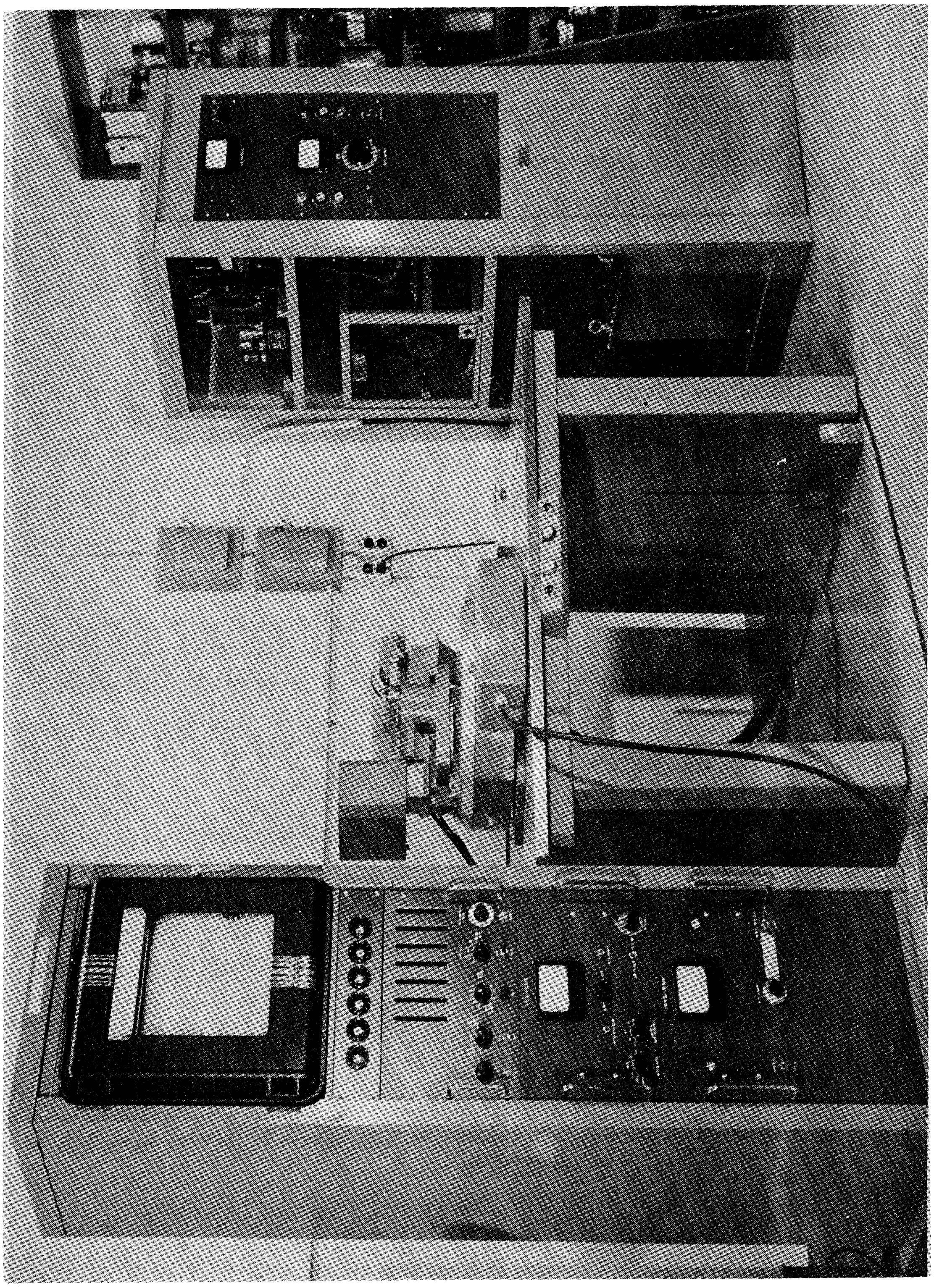


Figure 7. Photograph of General Electric XRD-5 X-ray Diffraction Unit.

As successively higher intensity exit beams are obtained from the crystal spectrometer by increasing the collimator width, the energy resolution worsens rapidly. Calculations and an experimental analysis(5) have shown for example that to obtain the source intensity used by Garsou in his study the effective width at half maximum of the photon energy spectrum centered on the bromine K edge is almost 1 Kev. Since Garsou's system was extremely sensitive compared to most other systems which one would like to study, it is apparent that the difficulties of obtaining sufficient intensity with good energy resolution are severe with the crystal spectrometer. One possible solution is the use of higher intensity x-ray tubes. The Machlett AEG-50 T tube used in these studies is one of the highest intensity tubes available commercially. As a result of these difficulties the use of the crystal spectrometer in the present study was limited to supporting studies.

Several measurements of absorption spectra were made with the crystal spectrometer using the maximum resolution alignment. Early preliminary studies of the ionization yield of methyl bromide were made with the crystal spectrometer aligned for maximum intensity output as discussed in Appendix B.

3. Use of Monochromatic Fluorescence X-Rays from Various Radiator Elements

The XRD-5 unit is also equipped with accessories which enable the unit to be used for fluorescence analysis. A typical setup of the equipment to perform fluorescence analysis is shown in Figure 8. The equipment was used as shown in Figure 8 to perform the numerous emission spectral analyses of the different radiator elements as described in Section II C.

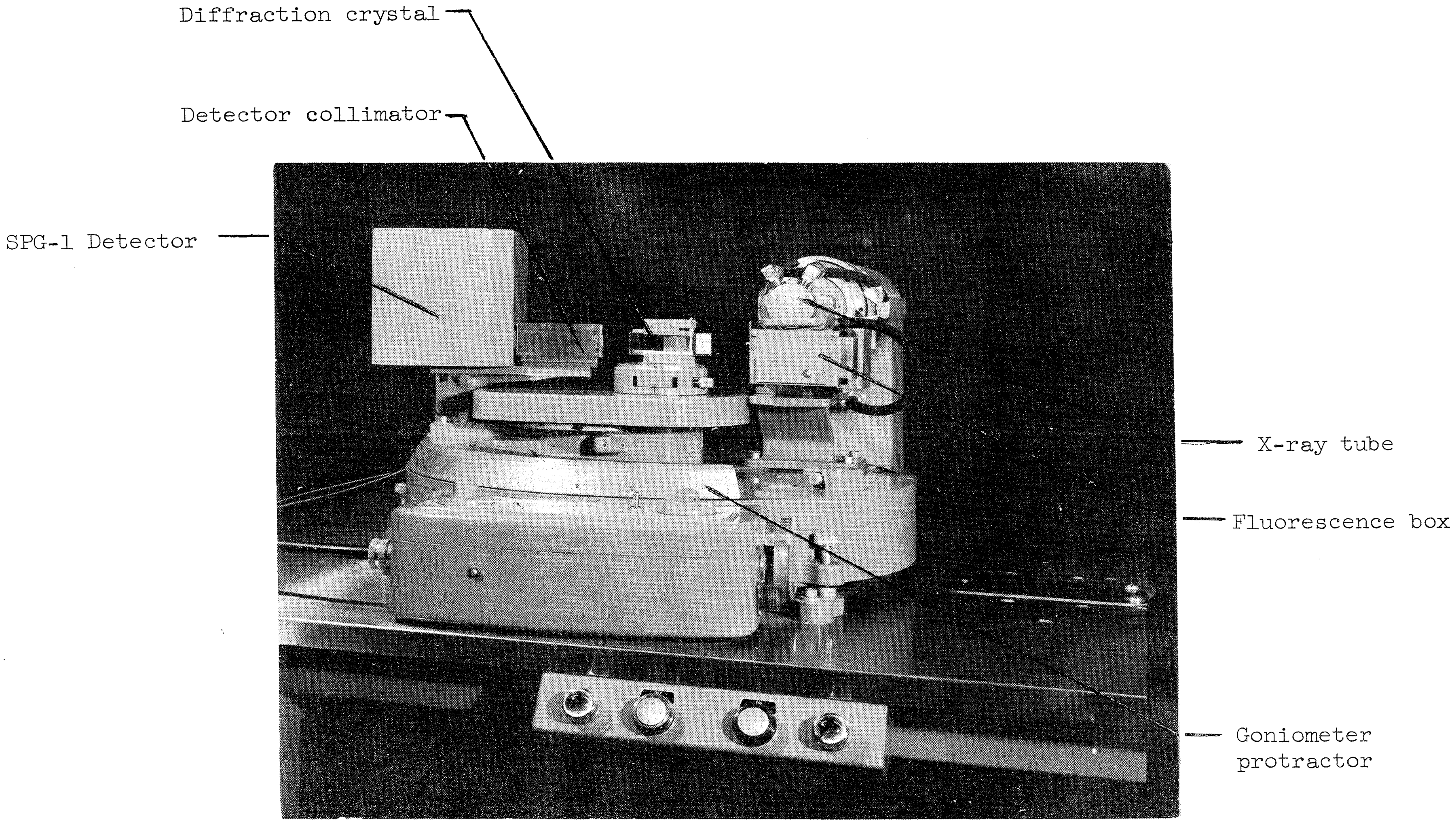


Figure 8. Arrangement of XRD-5 Equipment for Fluorescence Analysis.

Figure 9 shows the XRD-5 unit altered for use as a radiation source. To the knowledge of the author this application of fluorescence x-ray equipment has not been reported previously. Although this innovation is very simple in concept the advantages to be gained are considerable.

Production of Direct Beam Fluorescence Radiation. Several previous studies have used the direct beam characteristic spectra of the x-ray tube for an irradiation source. The intensities which are obtained by this technique are very high but the source radiation is heavily contaminated by the continuous spectrum from the x-ray tube. A rough estimate of the fraction of energy contained in the the characteristic spectra vs. the continuous spectra was given in Reference (494). The total ionization produced by a molybdenum target x-ray tube with an unspecified anode potential was determined and compared to the ionization produced by the K_α characteristic radiation, i.e., 1000 compared to 350. Since filtration can be used to attenuate preferentially the wavelengths shorter than the K_β, the contribution of the continuous spectrum for short wavelength radiation can be lessened. However, a larger fraction of the continuous spectrum is comprised of wavelengths longer than the K_β and cannot be attenuated without attenuating the K_α intensity severely. Thus any use of direct beam characteristic radiation will introduce errors due to the contamination of the radiation spectrum by the continuous radiation, even if filtration is used. Another disadvantage of the preceding method is that a different anode material is required for each different photon energy to be used. Replaceable anodes or multiple tubes will have to be used, and many of the elements needed cannot be obtained in convenient form for anode construction.

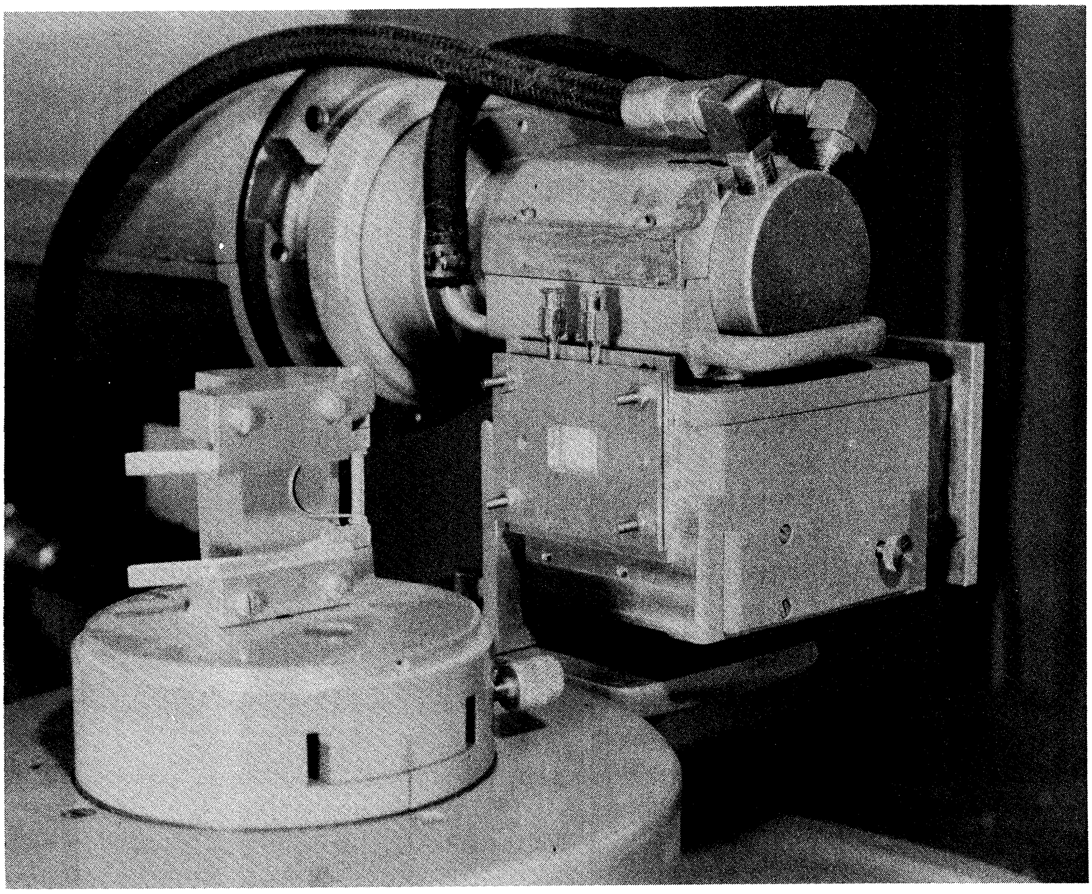


Figure 9. Adaptation of XRD-5 Unit for Use as a Radiation Source for Irradiation Studies.

Production of Fluorescence X-Radiation by Re-Emission from Radiator Elements. A very useful compromise between the high intensity available from filtered direct radiation and the high energy resolution obtained with the double crystal spectrometer is the use of fluorescence radiation re-emission from various radiators. The fluorescence irradiation technique, shown schematically in Figures 10 and 11 makes use of the standard arrangement of the apparatus for fluorescence analysis except that the sample position is occupied by the particular element whose characteristic radiation is to be used for irradiation and the appropriate filter is interposed between the radiator and the sample to be irradiated. The geometrical arrangement of the equipment used in these studies was by no means optimized, since only a small fraction of the fluorescence radiation reaches the sample. The radiation intensities were adequate for the system under study and the convenience of using the equipment as supplied without extensive modification was considerable.

The resulting radiation was pure K_α (or K_α and K_β in the case no filtration was used) with less than 3% contamination by continuous radiation (resulting chiefly from Compton and Thomson scattering of the direct beam by the radiator) and less than 2% contamination due to $K\beta$ radiation. The choice of radiator elements and the construction of the filters are described in Section II B.

Some Advantages of the XRD-5 Unit for Use as a Fluorescence Radiation Source. The use of the XRD-5 equipment for this study presented several advantages which should be mentioned. The sample drawer shown in Figure 12 was fitted with a spring loaded tongue which held the radiators

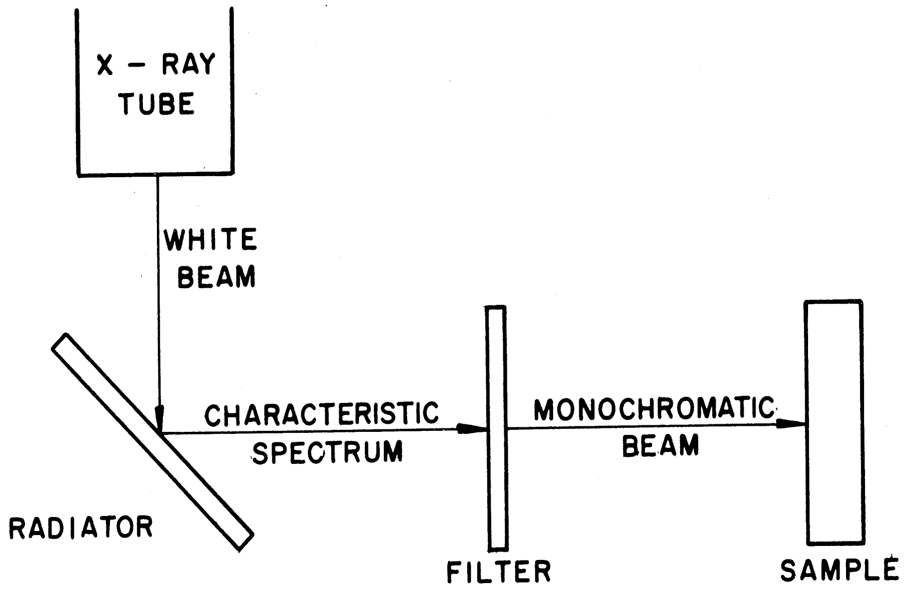


Figure 10. Schematic Diagram of Irradiation Arrangement for Using Fluorescence Radiation.

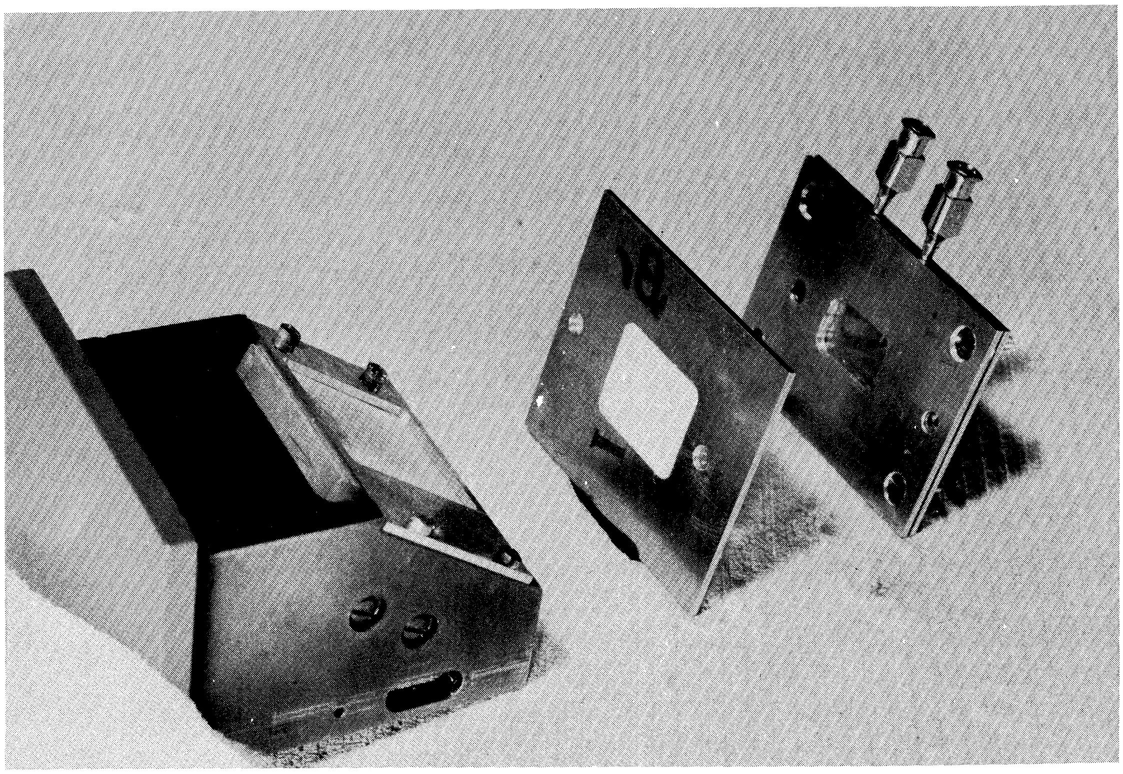


Figure 11. Blown-Up View of Equipment Used for Irradiations with Fluorescence X-Radiation.

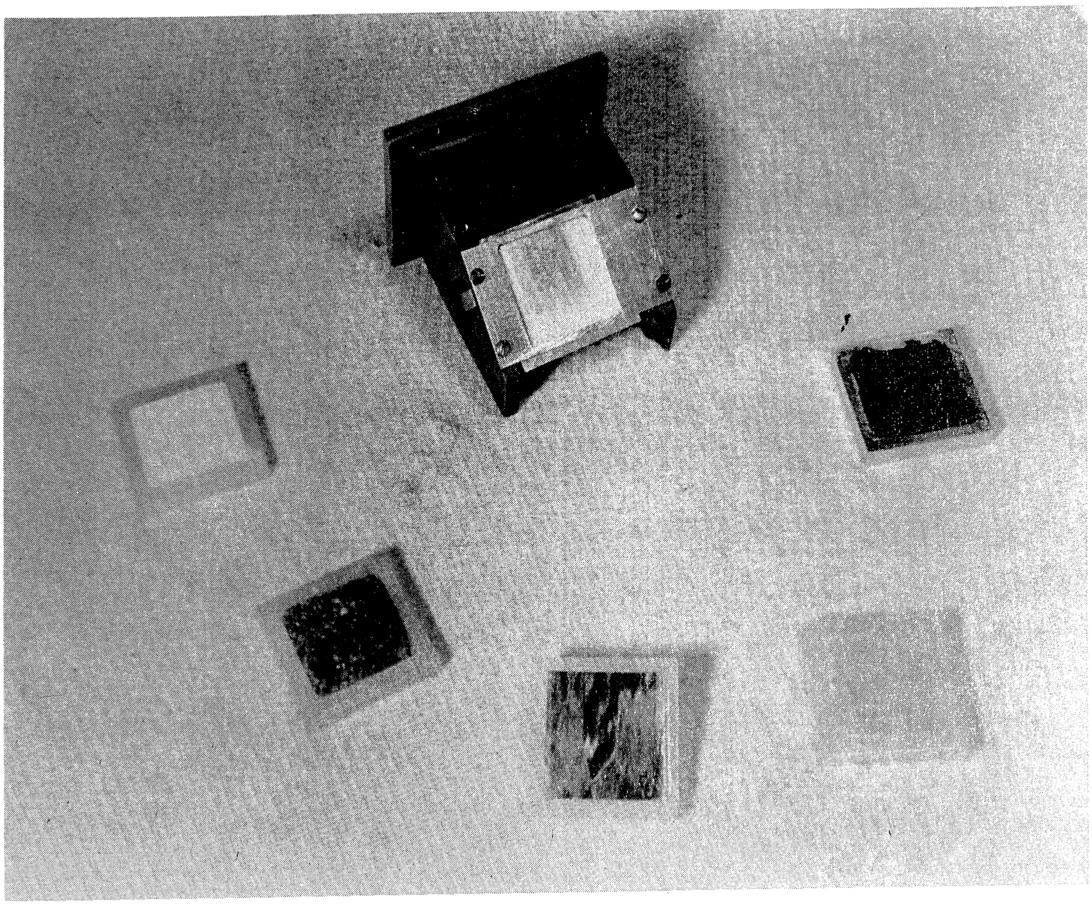


Figure 12. Sample Drawer and Typical Radiator Elements.

rigidly in place yet radiators could be changed very easily. The drawer assembly contained an automatic shutter which covered the x-ray tube beam tunnel and which opened only as the sample drawer was fully inserted. This feature was an important safety device and allowed the entire experiment to be set up including stabilization of the x-ray power supply before the x-ray beam was allowed to fall on the sample.

The irradiation intensity could be constantly monitored by transmission measurements through the sample by placing the goniometer table at 0^o with the proportional counter in the standard position. The XRD-5 was equipped with a digital printer which could print interval or cumulative counts for convenient preset periods in the absence of an operator to facilitate monitoring of long irradiations. The use of fluorescence radiation as a source of radiation for radiation effects studies is discussed in more detail in Reference (5).

B. Construction and Use of Radiators and Filters

Radiators. Typical radiators are shown in Figure 12, and Figure 13 shows several filter elements. Forty-five different radiator elements were constructed, including every element from Z of 22 (Titanium) through Z of 51 (Antimony) with the exception of Technetium. High Z elements with L emission spectra in the range of 10 to 15 Kev were also made. Within the range of energies 5 to 35 Kev, thirty-five K_α emission energies are available for use as irradiation sources, and an equal number of K_β energies can be used by irradiating with K_α and K_β mixed and then subtracting the K_α contribution based on previous pure K_α irradiations. Whenever possible pure elemental forms were used as foils or powders contained in plastic planchettes. Non-toxic and unreactive chemical compounds were used when the elemental form could not be used. In all cases the extraneous cation or anion was chosen to have as low a Z as practible in order to prevent contamination of the desired radiation by characteristic radiation from the cation or anion. Krypton was badly needed since its emission lines have energies very near the bromine K edge. An organic clathrate of β-quinol containing about 17% krypton by weight was synthesized and used successfully. A more detailed description of the construction of the radiator elements is given in Reference (5).

After each radiator was made a fluorescence analysis of the element was made using the standard fluorescence setup of the XRD-5 unit to insure that no unknown impurities were present which could contribute significantly to the radiator spectrum. A typical analysis is shown in Figures 14 and 15. Note that intensity is shown on a log scale in order

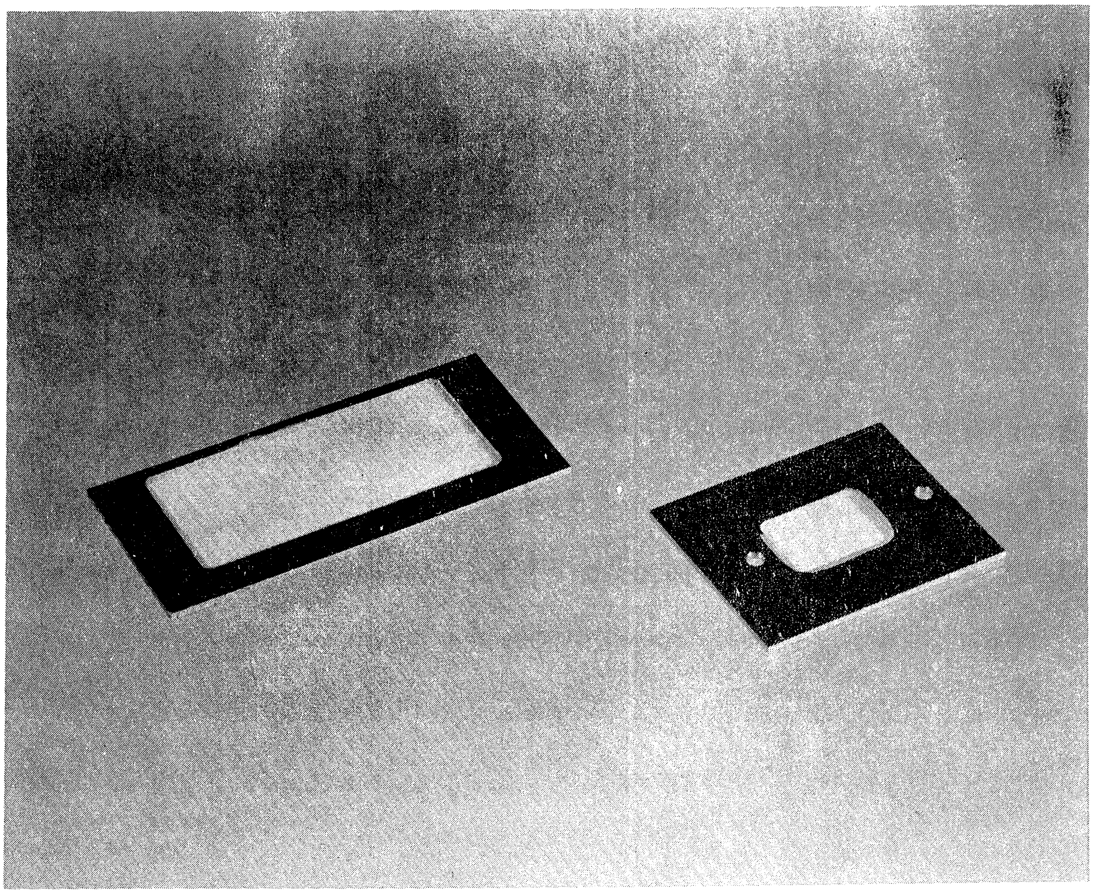


Figure 13. Typical Filter Elements.

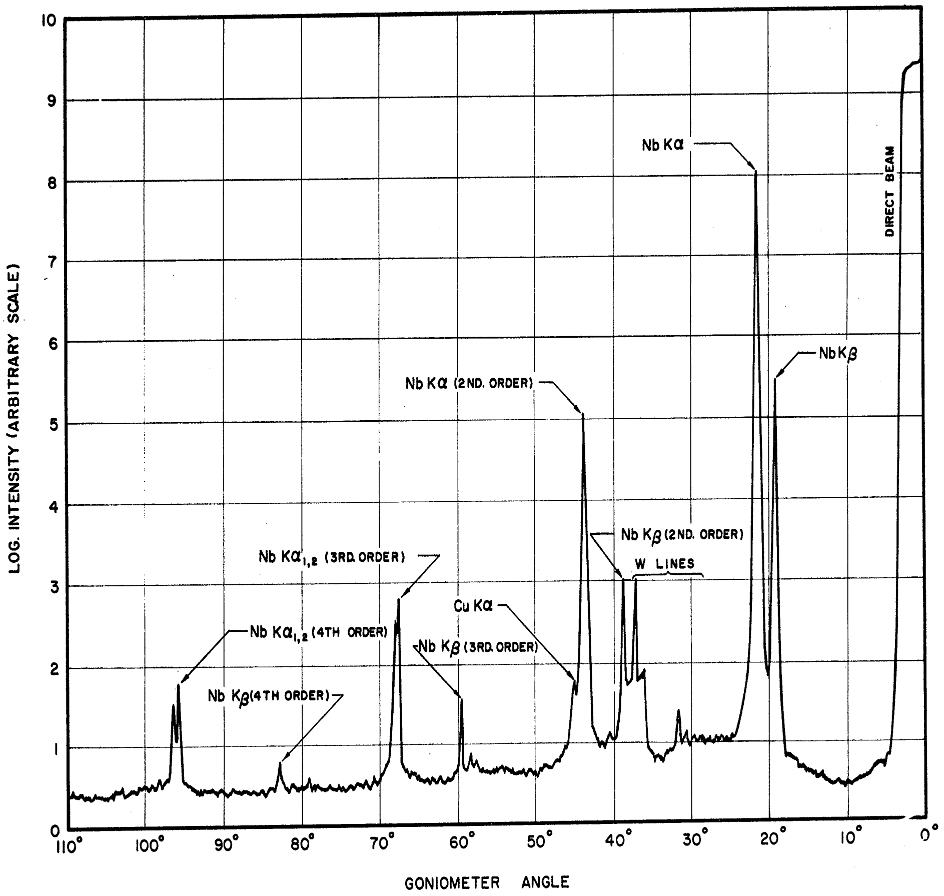


Figure 14. Typical Photon Energy Spectrum Obtained from Unfiltered Radiator Element.

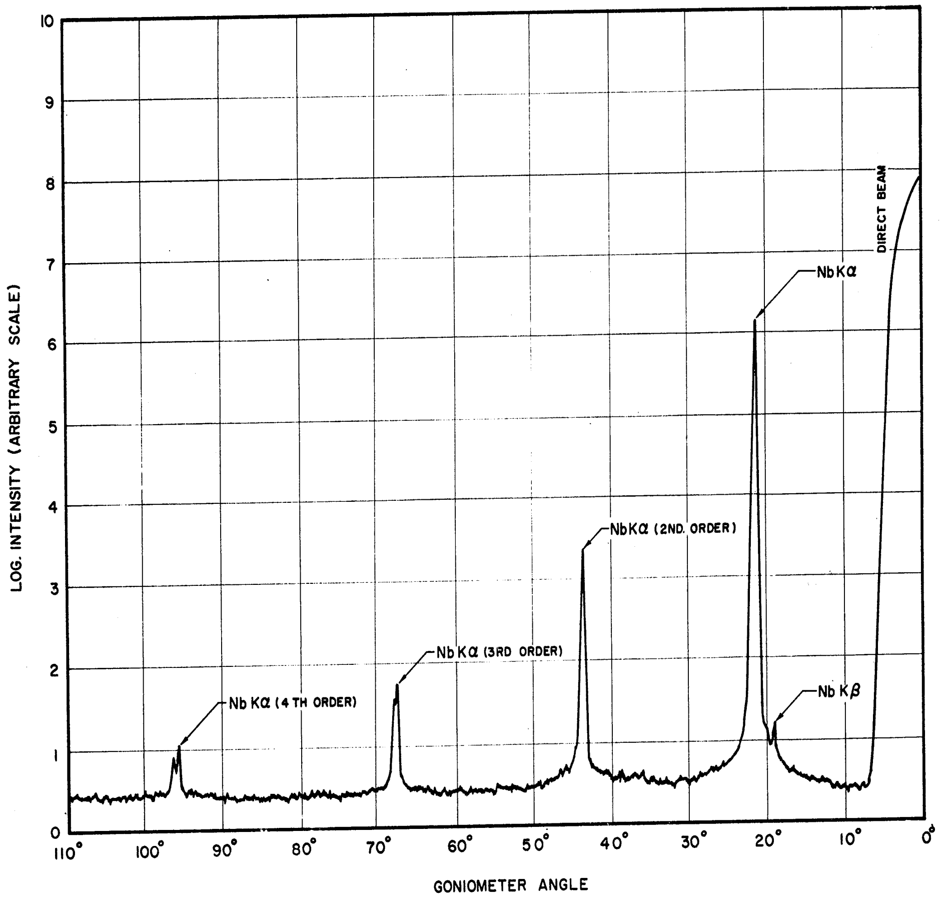
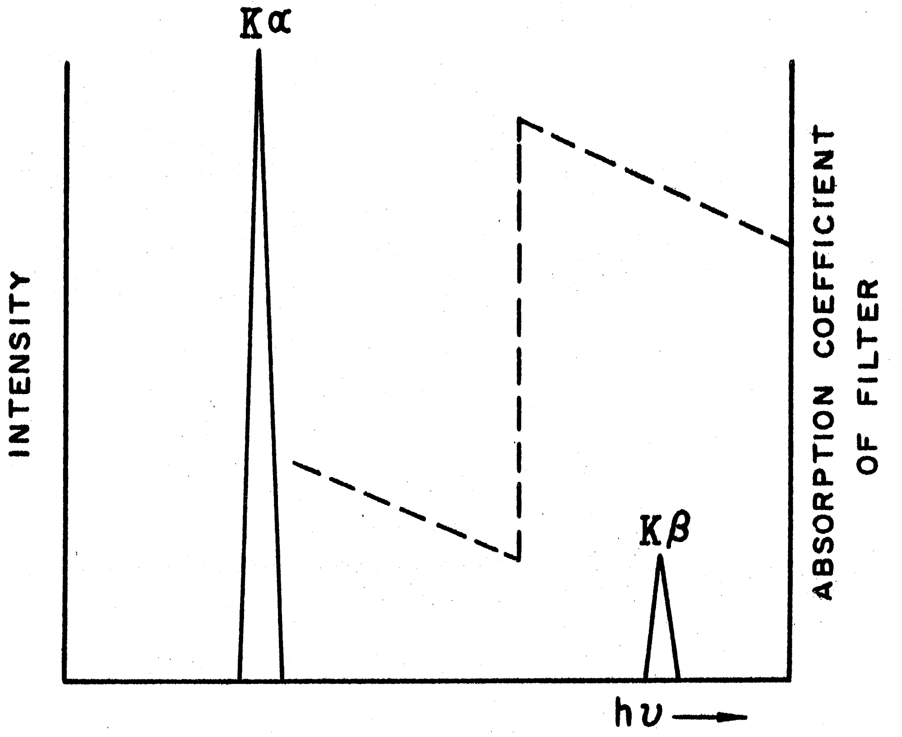


Figure 15. Typical Photon Energy Spectrum Obtained from Filtered Radiator Element.

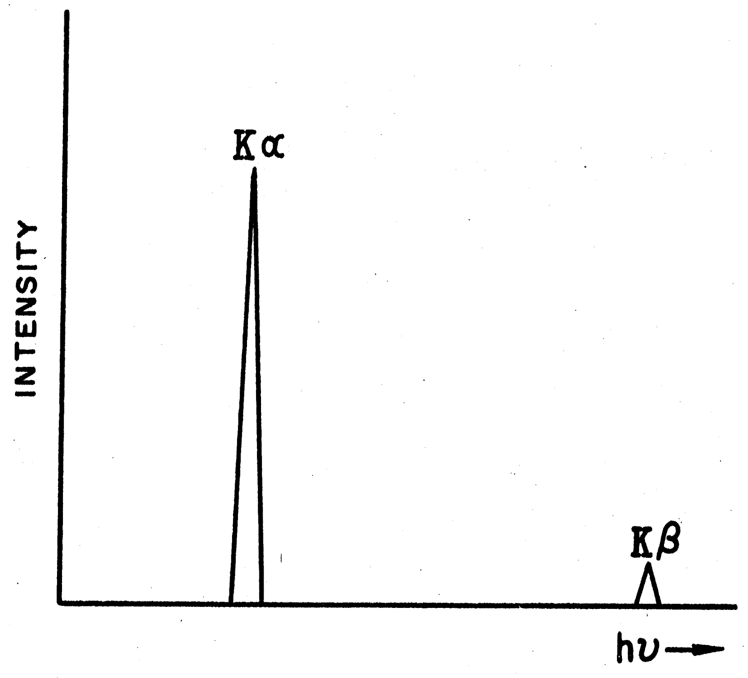
to be able to identify the impurities. In all cases iron and copper fluorescence from the sample box were observed as were the tungsten characteristic and continuous spectra which were scattered into the beam by the radiator. The total intensity of the extraneous radiation was kept below 5% of the total intensity except in the case of the high Z radiator elements. Since these elements were used for their L spectra which had a lower fluorescence yield in most cases compared to the K yield obtained with the lower Z elements, the scattered intensity in some cases would be as high as 5% of the total intensity. In no case was any significant contamination observed except for a sample of pure zirconium obtained from the local chemical supply house which was shown to be almost pure hafnium by fluorescence analysis.

Filters. Filters are used to attenuate K_β radiation selectively without much attenuation of the desired K_α radiation. Initially the ratio of K_α/K_β radiation intensity was about 5:1 for the elements used in this study(495). Selective attenuation of the K_β can be used to achieve a ratio of 50-100:1 without attenuating the initial K_α intensity by more than a factor of 3. The K_α and K_β photons of every element used in this study could be filtered by at least one and in some cases two or three elements by choosing a filtering element which had a K absorption edge of an intermediate wavelength between the K_α and K_β wavelengths to be filtered. This filtering technique is shown schematically in Figure 16.

In order to minimize parasitic absorption by the filter, the use of extraneous material should be avoided and any binder or support must be made of low Z material. Whenever possible thin foils were used. Powders were very finely ground while in solution and attached to 1 mil Mylar



UNFILTERED



FILTERED

Figure 16. Schematic Representation of X-Ray Filter Action.

sheeting with a minimum of rubber cement. The development of these techniques was rather time-consuming and represents the end product of considerable experimentation. Previous work reported in the literature described filters which were unacceptably thick or too thin to achieve the amount of filtration desired(336-342).

Most of the filter attenuations were within a factor of 1.5 compared to the theoretical ratios calculated for a pure filter material distributed uniformly. The deviations from theoretical values were caused by the non-preferential absorption of the supporting material and by non-uniform distribution of the filter material. The K_α and K_β intensities with and without filtration were determined with the x-ray unit in the standard setup for fluorescence analysis. This information was also used to calculate the absolute dose rates for filtered irradiations since most of the calorimetric determinations were made with unfiltered spectra. The higher source intensities gave more reproducible calorimeter values; also it was rather difficult to change filter elements during some of the calorimeter runs. The techniques developed in this study for making filters, as well as some of the unsuccessful attempts are described in more detail in Reference (5).

C. Calibration of the Radiation Sources and Determination of the Absolute Energy Content of the Incident Radiation

One of the major problems of the present study was the determination of the photon energy distribution and the intensity of the x-ray beam used as the radiation source. For the purposes of this study the relative accuracy of the calibration of the dosimetry system for different energies was felt to be considerably more important than the absolute calibration of the system. The dosimetry system as finally developed was satisfactory in both respects.

For simplicity the dosimetry problem was divided into three sections and a separate solution was sought for each section. The basic problems were:

(1) To obtain a simple, accurate and geometrically reproducible system to check for day to day source intensity, i.e., a secondary standard.

(2) To obtain a system possessing little or known energy dependence which could be used easily and frequently or at least could be used to calibrate the secondary system and furnish recalibration as needed.

(3) To obtain a system which could be used as an absolute energy calibration of the other systems, preferably with the same geometrical arrangement as the samples to be irradiated.

Item (1) was solved by using the standard proportional counter supplied with the x-ray unit positioned in a reproducible location. Because of the high intensity of the fluorescence beam a geometrical filter was used to obtain low enough count rates to avoid large coincidence corrections. The constancy of response of the photon counter was checked against an iron-55 source designed for easy removal and replacement. A picture of the iron-55 standard in position for counting is shown in Figure 17. The reproducibility of the system assuming complete disassembly and reassembly of the geometrical arrangement of the counter, sample holder and radioactive standard was better than 0.1%.

The need for a system of known energy dependence (2) was met by the development of an x-ray calorimeter which had total absorption for all of the photon energies studied. In addition the final model of the calorimeter was thermally stable enough that absolute energy determination could be made with the calorimeter in the same position as was occupied by samples under irradiation.

Separate intercomparisons of the absolute energy calibration by the calorimeter were made using an air ionization chamber (Victoreen Model 625 R meter); by using the SPG-1 photon counter and efficiency data furnished by the manufacturer with suitable geometric and air path absorption corrections; and by using the Fricke dosimeter in the same cells and identical position in which the samples were irradiated.

1. Development of the X-Ray Calorimeter and Its Use as a Primary Standard

Determination of x-ray dose rates presents a serious problem due to the high energy dependence of many conventional dosimetry systems. The energy response of many systems (e.g. the photon counter furnished with the XRD-5 unit) is obtained by calculation often using little or no

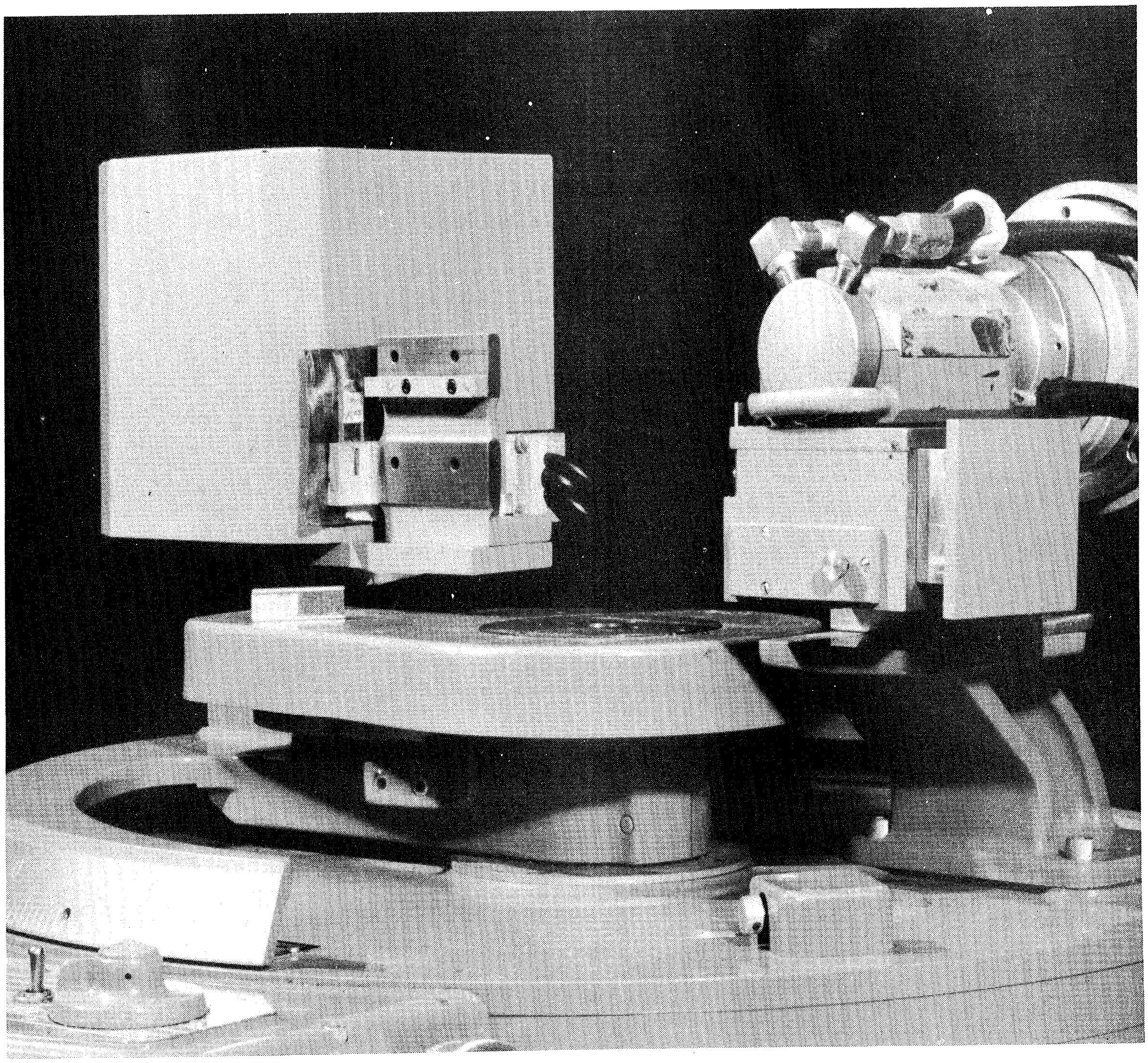


Figure 17. XRD-5 with Iron-55 Source Used for Standardizing the SPG-1 Counter.

experimental verification of energy dependence with monochromatic radiation. Other systems have been calibrated against a free air ionization chamber or against the Fricke dosimeter, but in most instances the energy comparison is done on the basis of "effective energies" obtained from mixed beam x-rays with aluminum or copper filtration. Thus any detailed energy dependence which might be present (e.g. the K edge absorption discontinuities caused by unknown impurities) might be obscured because of the large spread of wavelengths of the calibrating beam.

Other Dosimetry Systems Considered--Fricke Dosimeter. The absolute yield and energy response of the Fricke dosimeter for low energy x-rays have been determined only by comparison with an ionization chamber(360). Until 1954 most of the calibration studies of the Fricke dosimeter for other types of radiation were based on the ionization chamber(361). Recently several calorimetric calibrations of the absolute yield of the Fricke dosimeter with cobalt-60 radiation have been made(496,497) which agree with previous values, thereby giving a cross check of ionization chamber techniques.

Air Ionization Chamber. The absolute yield and energy dependence of the air ionization chamber depend on the absorption coefficient of air and the value of w, the average energy required to produce one ion pair (assuming that the chamber is properly designed and is used correctly). Experimental and theoretical values for the absorption coefficient of air for the energies of interest to this study are available and show reasonably good agreement(319). Attempts to predict w from theoretical considerations have been made(257), but the success has not been very gratifying. Experimental determinations of w have been numerous and in many cases agreement has been poor(19,25,214). Recent experiments have shown that the value of w of many gases is very sensitive to small concentrations of impurities(214). Using more rigid control of experimental conditions than was done in many of the earlier studies, recent determinations of w in air are felt to quite reliable(214).

Measurements of w as a function of photon energy for energies of 5 to 50 Kev have been made. In all studies which were found in the literature search the energy of the x-rays used was either assumed to be the effective energy obtained by varying tube potentials and using non-selective filtration, or K_α radiation obtained from the characteristic spectra of the tube target material (mixed with the continuous Bremsstrahlung contained in the direct beam)(19,21,25). There was considerable disagreement among early experimenters as to whether the value of w for air was dependent on wavelength(18). Most researchers today apparently agree that the value of w for air is independent of energy for x-rays and electrons from below 5 Kev to above 30 Kev(214,498,499).

It is of interest to note that the recent general acceptance of 34 ev per ion pair(500) agrees quite well with the value of 35 obtained in the very early (1929) studies of w by Kulenkampff(19). No reference was found in any recent literature to this excellent work which was based on a very elegant calorimeter design. This work also appears to contain the most convincing evidence of the absence of any photon energy dependence of the value of w in air for x-rays of energy 5 to 25 Kev since

Kulenkampff used the characteristic radiation from the target material of the x-ray tube (filtered to remove K_β radiation) as the radiation source. No reference to any determination of w using monochromatic radiation produced from fluorescence was found.

Design Criteria for Calorimeter. Although it was believed that the free air ionization chamber would be a satisfactory primary standard for this study it was felt that the direct determination of energy output for each radiator by a dosimetry system which had no energy dependence would present more convincing evidence for the lack or presence of energy dependence in the system under study. The development of an x-ray calorimeter was deemed desirable and after several preliminary models were made, a satisfactory design was achieved. The full details of the design and construction of the device are given in Reference (5).

The design of the calorimeter was predicated on the following criteria:

(1) The receiver plate of the calorimeter was to be effectively totally absorbing for all x-ray energies from 5-35 Kev.

(2) Corrections for window absorption, etc. were to be kept to a minimum and experimental determinations of the correction factors were to be made for each energy measured.

(3) The background thermal noise from the x-ray tube had to be kept to a very minimum since identical conditions would not be preserved for each radiator.

(4) It was desired that the geometrical arrangement of the device be identical to a sample under irradiation.

(5) A self contained heater was needed to provide absolute calibration.

(6) Long term stability without recalibration was desired.

(7) Short time stability and short time test durations were desired since no convenient method was devised for monitoring the output from the x-ray machine for stability during a test run.

Details of the Calorimeter Design. The calorimeter receiver plate was made of 2 mil gold foil. The thickness was chosen as the thinnest readily available foil thickness which would be totally absorbing to x-radiation of 5-35 Kev. The area of the plate was chosen as the smallest area which would intercept the total beam in the sample position (a safety factor was incorporated in all dimensions to allow for errors of alignment, etc.). Gold was chosen as the material with the best combined values of low specific heat, high thermal conductivity, high surface polish and reflectivity, low tarnish properties, high photoelectric cross section and low fluorescence escape probability.

The temperature rise of the receiver plate was detected by a commercial thermistor. The thermistor is a semiconductor device which has a very high negative temperature coefficient of resistivity and can be made in the form of a very small bead. Leads from the thermistor and a high resistance heater were brought to the outside of the calorimeter through a Kovar seal. The output signal was read as a highly amplified unbalance in a Wheatstone bridge circuit and was conveniently plotted continuously on a recorder. The slope of the line $-\frac{d\Omega}{dt}$ was directly proportional to energy absorption and was compared with the slope obtained by applying a known power input to the internal heater.

The receiver plate was insulated from the calorimeter box by means of thin silk threads to minimize heat conduction between the receiver and the environment. The thermistor and heater were rigidly attached to the receiver and were thermally insulated from the environment by means of heat sinks contained inside the calorimeter and attached to the very thin wire leads of the thermistor and heater. The heat sinks were insulated from the calorimeter box by the use of thin silk threads for support and the use of very thin wires between the heat sinks and the external terminals of the calorimeter. The receiver assembly was contained in a brass box which was evacuated to minimize convection and air conduction to the receiver. Radiation shields were also included to minimize radiant heat transfer. X-rays were admitted through the box and to the receiver by transmission through a 1 mil Mylar sheet attached to the calorimeter with a vacuum tight cement seal.

The exterior of the calorimeter box was covered with 2 inches of styrofoam insulation and the assembly was aligned visually to insure that the receiver plate would intercept the entire beam. Several thicknesses of aluminum leaf and 1/4 mil Mylar sheet were then inserted between the radiator and the window of the calorimeter to prevent thermal radiation from the x-ray tube target from streaming into the calorimeter with the x-ray beam.

Several complete runs were made, each consisting of three or more determinations of the energy output of each radiator spaced at more or less random intervals throughout the run. Heater calibrations were interspersed throughout the runs at frequent intervals.

The data were corrected for window absorption and averaged. The final beam intensity for each radiator for 50 Kvp and 50 ma x-ray output is listed in Table I. Figure (18) shows the calorimeter and the associated equipment. Interior views and close-up pictures of the receiver plate are shown in Reference (5).

TABLE I

SOURCE INTENSITIES

Radiator Element	Filter Element	K_α Energy Kev	K_β Energy Kev	Unfiltered Intensity		Filtered Intensity	
				K_α	K_β	K_α	K_β
				← erg/min x 10^4 →			
Iron	----	6.40	7.06	1.52	0.32	---------	
Copper	Nickel	8.05	8.90	1.86	0.39	1.24	0.038
Gallium	Zinc	9.25	10.26	1.13	0.24	0.48	0.011
Germanium	Gallium	9.89	10.98	1.45	0.31	0.49	0.0039
Arsenic	Germanium	10.54	11.73	1.36	0.29	0.49	0.0056
Selenium	Arsenic	11.22	12.50	1.97	0.42	0.67	0.0046
Bromine	Selenium	11.92	13.29	1.48	0.31	0.89	0.042
Krypton	Bromine	12.65	14.11	1.73	0.37	1.15	0.058
Rubidium	Bromine	13.39	14.96	1.56	0.33	1.09	0.069
Strontium	Rubidium	14.16	15.83	2.16	0.46	0.89	0.028
Ytterium	Strontium	14.96	16.74	1.36	0.29	0.77	0.029
Zirconium	Strontium	15.77	17.67	2.32	0.49	1.42	0.068
Niobium	Zirconium	16.61	18.62	2.31	0.49	1.28	0.035
Molybdenum	Zirconium	17.48	19.61	1.95	0.42	0.89	0.043
Silver	Palladium	22.16	24.94	1.91	0.41	1.68	0.24
Tin	Silver	25.27	28.48	1.59	0.34	0.51	0.0042

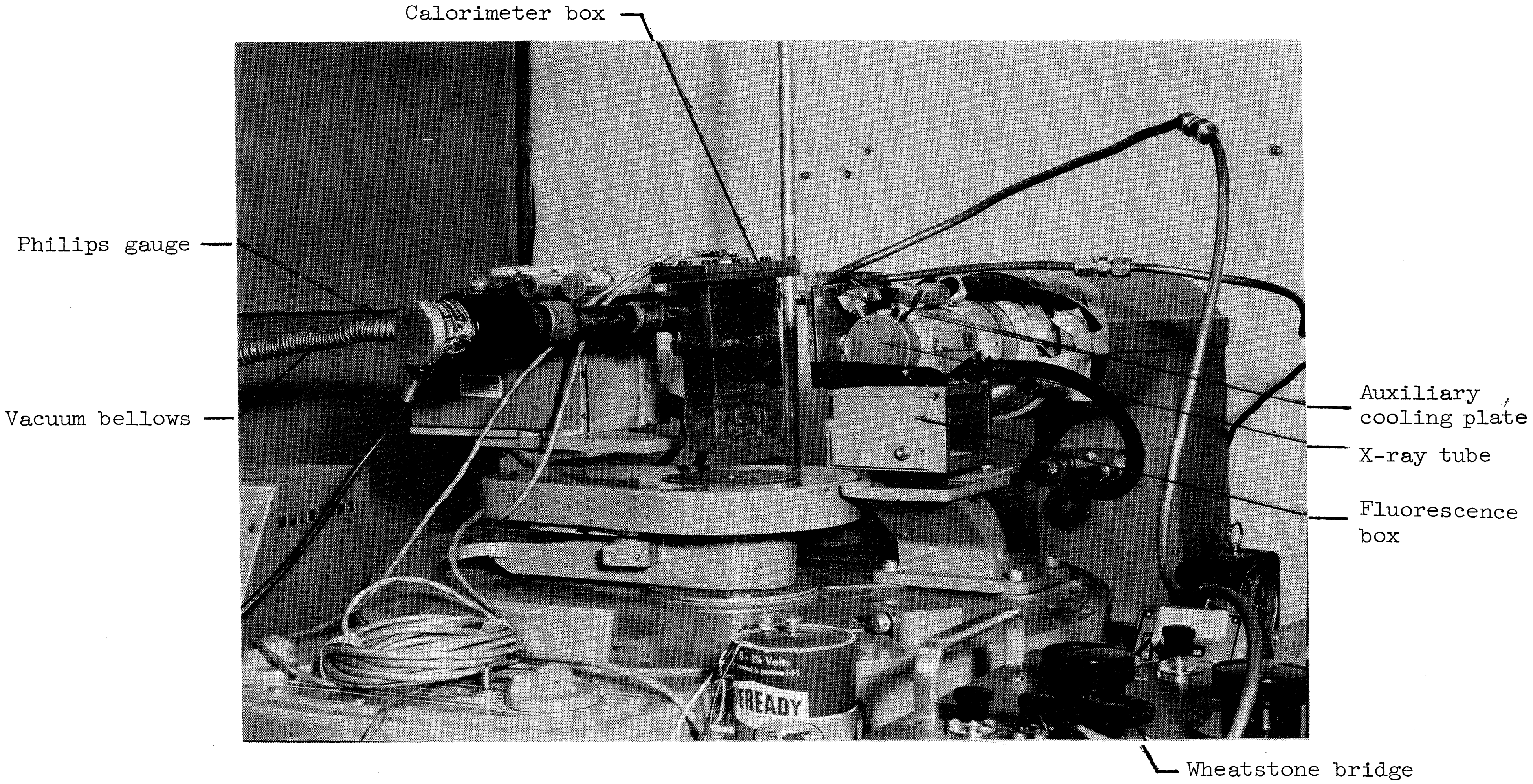


Figure 18. Low Energy X-Ray Calorimeter and Associated Equipment.

2. Secondary Standards: Photon Counter, Ionization Chamber and Fricke Dosimeter

SPG-1 Detector. The dosimeter which was used for measuring the source intensity of each irradiation and monitoring the source intensity during irradiation was the General Electric Company Model SPG-5 X-Ray Spectrometer. Since this counter was mounted on the goniometer table and was intended to be used for measuring the intensity of photons coming from the diffraction crystal it had several advantages for the present use. The unit can be completely dismantled and replaced reproducibly. The unit is designed for high counting rates without severe coincidence corrections, has high counting efficiencies for the photon energies of interest and the manufacturer furnished a curve of efficiency as a function of photon wavelength.

A response to an inquiry to the company indicated that the efficiency curve was calculated and that no experimental check was made for each unit, although some units had at one time been compared with a free air ionization chamber. A radioactive standard (iron-55) was used to check the reproducibility of the counter and associated equipment. Iron-55 was chosen as the standard because of its long halflife (2.9 years) and because its internal conversion photon emission gives characteristic manganese radiation which has approximately the same energy as the radiators used in the study. The SPG-1 detector was also used with the goniometer table and diffraction crystal to record the emission spectrum of each radiator element.

The photon efficiency of this counter was determined using the calorimeter data on beam intensities for each radiator. The ratio of the indicated intensity (using the G. E. efficiency curve) to the measured intensity (using the calorimeter data) is plotted as a function of energy in Figure 19. This curve is based on absolute efficiencies and includes the necessary correction factors for geometry, air absorption, etc.

Air Ionization Chamber. An independent check of the photon counter calibration was made with a small air ionization chamber designed especially for low energy x-radiation. The Victoreen R-meter was very convenient to use since it could be placed in the same position as the sample to be irradiated, thereby simplifying geometry and air absorption corrections. The Victoreen condenser R-meter, model 651 was equipped with a thin window of nylon and was supposed to read the true dose rate in roentgens within 5% for photon energies within the range of 6 to 35 Kev. The unit was a standard condenser type unit provided with an external reader. The range of 0-250 R was convenient since many of the dose rates to be measured were in the region of 100 r per minute. The reproducibility of this instrument was very good (better than 1% in most cases) when its geometric positioning was standardized. A picture of the R-meter (resting in a plastic cradle designed to position it accurately) in position to take a measurement is shown in Figure 20.

Using the relationship(1)

$$E(h\nu) = \frac{83.8}{(\mu/\rho)\mathrm{air}} \qquad \mathrm{ergs/cm^2}$$

where $E(h\nu)$ is the energy flux per Roentgen (in $\mathrm{ergs/cm^2}$ -r) and (μ/ρ) is the true mass absorption for air one can obtain energy fluxes from r measurements if the energy distribution of the photons is known. A graph of this function is shown in Figure 21.

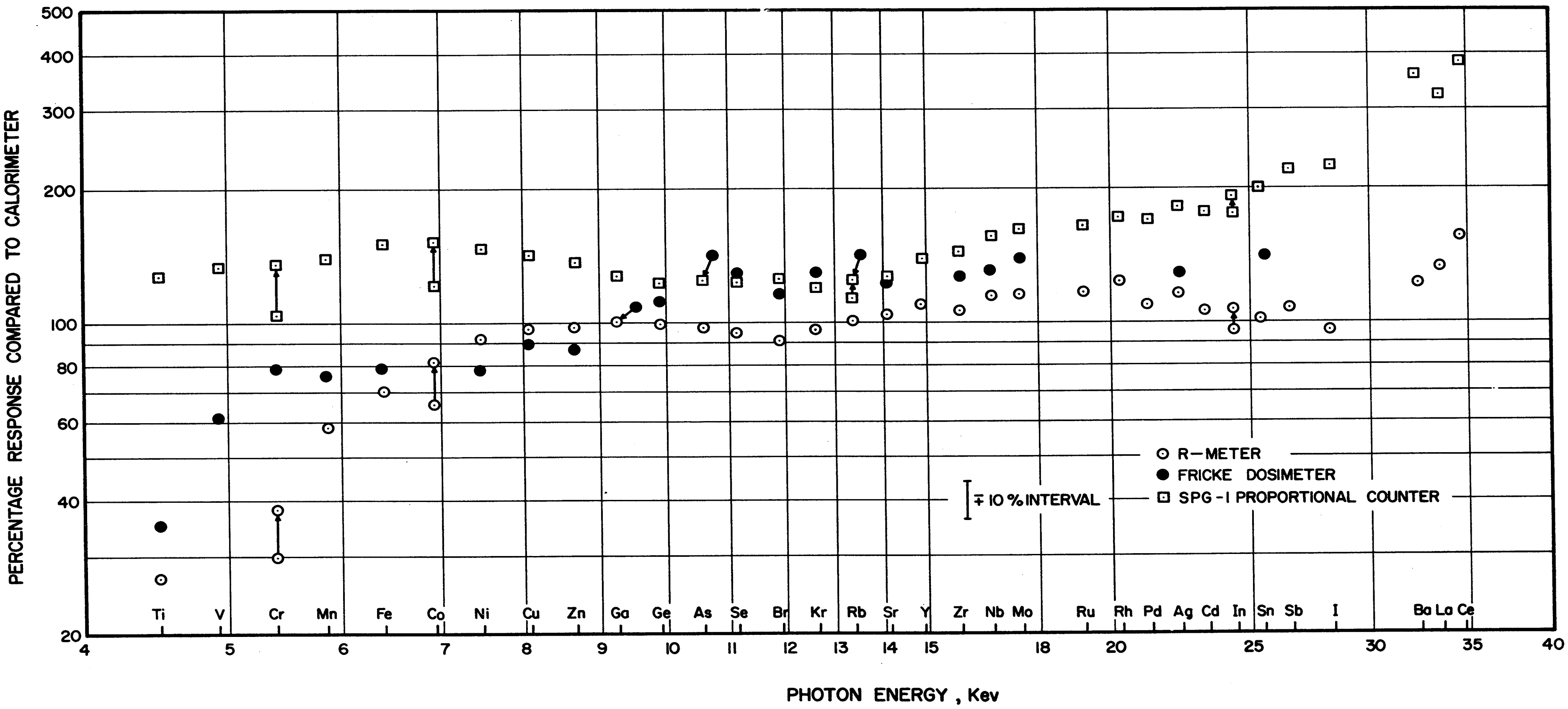


Figure 19. Results Obtained from Calibration of R-Meter, Fricke Dosimeter and SPG-1 Counter against the Low Energy X-Ray Calorimeter.

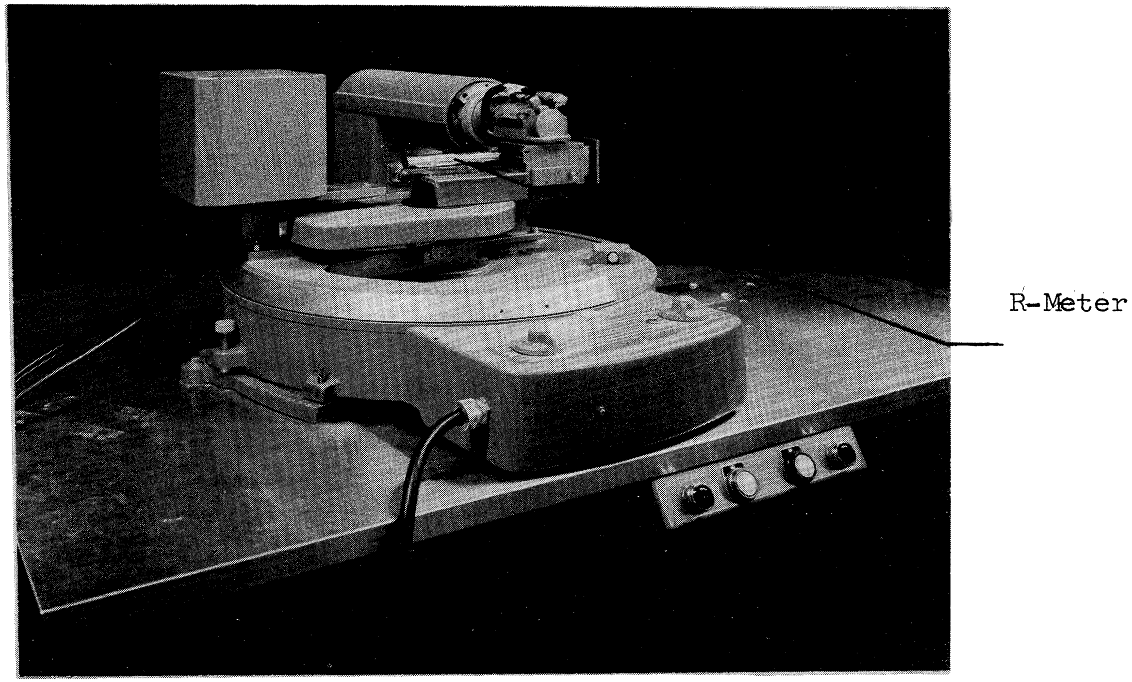


Figure 20. Victoreen R-Meter in Position to Make a Measurement.

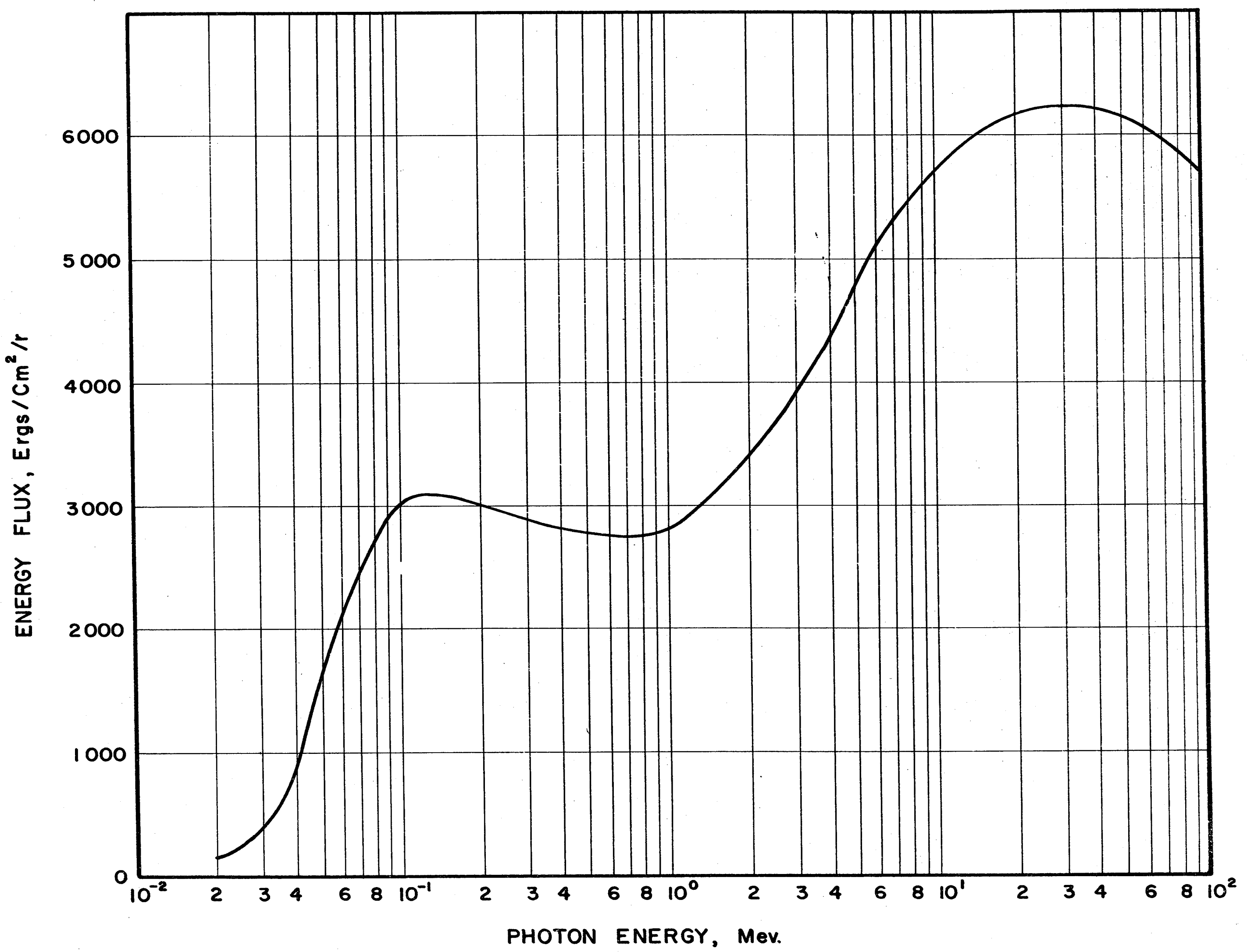


Figure 21. Conversion of Units of Roentgens Absorbed in Air to Ergs/cm^2 Incident Radiation Flux as a Function of the Photon Energy.

Figure 19 shows the plot of the ratio of intensity indicated by the r-meter to the intensity indicated by the calorimeter.

Fricke Dosimeter. The Fricke dosimeter was used as another independent check of the calorimeter values of source intensity. This calibration was felt to be of particular value since the dosimeter was a liquid and could be irradiated in the same cell in which the sample irradiations were made. The details of the use of this dosimeter are discussed thoroughly in the literature and will not be repeated here(350). This dosimeter provides fast reliable measurements and has become almost universally accepted as a standard dosimeter.

The action of the dosimeter depends on the oxidation of ferrous ions to ferric ions by the reaction products formed during the irradiation of an 8 N sulfuric acid aerated water (triple distilled) solution. The reaction is an indirect reaction and the rate is independent of ferrous and ferric ion concentrations, although the rate is somewhat dependent on the LET of the radiation. The yield of the reaction is determined as the ferric ion concentration which is read spectrophotometrically as an absorption peak at 305 millimicrons.

The yield of the reaction was taken as 15.4 molecules oxidized per 100 ev of energy absorbed in the solution. This value is an average of 15.1 and 15.7, the values reported recently by Rosinger(360) for molybdenum and silver K_α radiation respectively, obtained from the characteristic radiation from different anode materials and filtered to remove K_β radiation. The value of 2174 liter mole^{-1}cm^{-1} at 24.5°C was used as the best value of the molar extinction coefficient(350,366).

Irradiations were performed in a cell which was identical to the cell described in Section II C except that the thickness was increased to 0.7 cm in order to be more absorbing to x-radiation (due to the lower absorption coefficient of water compared to the 1-bromobutane solution).

Since the cell was not totally absorbing for all radiation used in the calibration, transmission measurements were made and the proper corrections factors were used to give total beam energy. The results of these measurements are shown in Figure 19.

Summary. As Figure 19 shows, the agreement of the four dosimetric methods within the energy range of most interest (9-25 Kev) is good. No sharp discontinuities or other unusual response with energy was noted for any of the methods. The final relative intensity values are believed to be correct within 10%. The absolute accuracy of the dosimetry measurements is ± 20%. Additional discussion of the accuracy of the dosimetric measurements will be found in Reference (5).

Dosimetry measurements of the cobalt-60 source were performed with the Fricke dosimeter and checked also with a cobalt-60 Victoreen R-meter condenser air chamber.

D. The 1-Bromobutane-DPPH System

The selection of the radiation source has been discussed previously; the selection of the remaining parts of the system, the target material and the detection method, will be discussed in this section.

1. Criteria for Selection of a Target-Detector System for Study

Target Material. One of the most important problems in selecting a target material and a detection method is to find a combination target and detector which will give significant indication of radiation effects for reasonably short irradiation periods of exposure to the very low source intensities which are associated with the use of monochromatic radiation. The low source intensity has tended to limit the selection of target material and detector to either (1) a target material which is very sensitive to radiation or (2) a target material for which a detection system is available which can detect very small changes in the target material caused by radiation. The development of the fluorescence techniques discussed previously has relieved this limitation considerably compared to the earlier work done with the crystal spectrometer. However, the selection of materials which can be studied by the new technique is still very limited compared to other types of radiation studies.

The next step was to choose a target material which might be expected to show the same type of energy response as those used in the earlier studies. The alkyl halides studied by Garsou(3) and catalase studied by Emmons(1) both had one or more high Z atoms which were contained in a molecule of predominantly low Z atoms. The high Z atom thus became a preferential target for the initial photoelectric absorption of photon energy and all subsequent events had to proceed from that specific location in the molecule. It was this general type of molecule which was felt most likely to show energy dependence effects upon irradiation with monochromatic x-radiation as was discussed in section I D.

Most of the compounds considered were alkyl halides or metal-organic compounds. Many interesting biological materials appeared to be suitable target materials but were not considered because of the high degree of complexity usually associated with the molecular structure of these materials. It was desired that a simple material-detector be developed to help interpret earlier results with more complex materials.

Detection Methods. Several detection concepts were investigated preliminarily for use with an alkyl halide or metal-organic compound. These detection concepts were quite specialized as compared to those used in many radiation effects studies since they were designed to detect extremely small quantities of radiation product.

The four detection methods considered were:

(1) The use of radioactive target atoms which could be separated and counted with standard radiochemical techniques.

(2) The trapping of radiation-produced free radicals by low temperatures and detection by electron paramagnetic resonance.

(3) The synthesis of target materials likely to give stable free radicals upon irradiation of liquids with minute concentrations of dissolved scavenger which could be detected with EPR or spectrophotometrically.

(4) The irradiation of liquids with minute concentrations of dissolved scavenger which could be detected with EPR spectrophotometrically.

Based on the intensity which would be obtained with the crystal spectrometer (10^5-10^6 photons incident per second), calculations indicated that the irradiation periods required to produce a detectable quantity of radiation product might be excessive with any of the four detection systems (greater than 100 hours). Since the analysis was based on the highest sensitivity values for each method which could be found in the literature, any significant increase in the irradiation periods required by any method due to unexpected difficulties would preclude success with that method. It was felt that considerable experimentation would probably be needed to determine whether any of the methods could be made to work. However, the preliminary analysis did not show that any of the methods definitely would not work.

With the intensities which can be obtained from fluorescence radiation (10^{10} photons incident per second) all of the methods appear to be quite feasible. Method (1) is very sensitive and some of the products of the reaction can be identified since tracer chemistry techniques can be performed on the material after irradiation. The choice of isotopes and compounds which can be used with this detection method is limited since the self damage of the material may be high due to the rather high isotopic specific activities which must be employed in order to obtain detection sensitivity (e.g., γ-emitting isotopes would in general be preferred instead of β-emitting isotopes).

Method (2) is being used in many radiation studies(44) but the problems imposed by the use of low temperatures during irradiation are particularly severe for low energy x-rays. Method (3) has been used with cobalt-60 γ-irradiations(409); however, the type of compounds which can be studied is rather specialized and the number of compounds which could be studied is limited. Method (4) is quite sensitive and many radiation effects studies have been made with scavengers(111). Unfortunately this method does not give much information about the nature of the radiation products since the scavenger is unselective in its reaction. This method of detection is however applicable to the study of many types of compounds thereby enabling the direct comparison of the radiation effects produced in different compounds since the rest of the system remains unchanged. Detection method (4) was chosen for use in this study.

Detection Methods for Gross Radiation Studies. Two other detection methods have been used commonly for gross* radiation studies in pure materials: (1) the composition of the final products; (2) initiation of reactions of known kinetics. Detection method (1) assumes that the final products are derived exclusively from a recombination of the primary radicals or from their reaction with the substance being irradiated without the intervention of any chain processes. The only radicals detected then, are those which react to give a product different from the starting material. A fraction of the primary radicals always recombines in the original form(173), thereby escaping detection and causing the determined radical yield value to be too small. By method (1) CH_3I gives a radical

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* The use of the term gross radiation effects studies is intended to include all studies which do not use monochromatic radiation sources; and in general produce large amounts (greater than 1%) of decomposition of the compound to be studied. Such studies would include cobalt γ-irradiations, high energy electron studies and mixed beam x-ray irradiation. The radiation sources used in such studies usually have intensities which are several orders of magnitude greater than those used in this study.

yield value of 5.08 compared to a value of 20.2 for other methods(501). For other materials the discrepancies are often not so large.

Method (2) is quite sensitive since chain reaction initiation is the reaction frequently employed; however, compounds to be studied must be good solvents of the monomer and polymer and often propagation and termination rates are not well known.

2. Choice of DPPH as the Detection System

The use of diphenylpicrylhydrazyl (DPPH) to react quantitatively with free radicals formed by thermal, photochemical, and radiation decomposition, is well known(285-307). The effectiveness of various initiators of polymerization reactions and the rates of polymerization reactions and the rates of polymerization reactions have been studied with DPPH as a radical counter or scavenger(288-304). DPPH has been used by several groups to determine the radiation sensitivity of a large number of organic compounds subjected to Co^{60} gamma radiation and to gross unfiltered x-radiation of differing anode potentials. The radiation yield values obtained by this method agree well with values obtained by other methods(111,139). DPPH is a stable crystallizable free radical, and is entirely dissociated both in the solid state and in solution. It reacts quickly with thermal radicals by decolorizing.

Properties of Effective Scavengers. The effective use of scavengers in radiation effects studies has been discussed in detail by Chapiro(139) and will be reviewed here. The scavenger must fulfill a certain number of conditions. It must (a) be readily measurable in low concentrations; (b) be sufficiently reactive to afford complete scavenging at concentrations low enough for the direct effect of radiation on the scavenger to be negligible; (c) have no protective or sensitizing action; (d) react with radicals in a nonselective fashion, but react neither with the substrate, nor with the ions, nor with the excited molecules; and (e) recombine with radicals in a known proportion.

The choice of DPPH as the scavenger to be used in this study was strongly influenced by the high degree of success achieved by Chapiro and his co-workers who used DPPH to study the radiosensitivity of a large number of organic compounds to gross cobalt and x-radiation.

Iodine, bromine, chlorine, the hydrogen halides and triphenylmethane have also been used as scavengers(112-134). Iodine has probably been used more than any other scavenger but was not acceptable to this study due to its high absorption cross section for low energy x-rays.

Use of DPPH as a Scavenging Agent. DPPH fulfills the requirement for a good scavenger listed above.

(a) Its very intense violet or purple hue makes colorimetric determinations possible at concentrations of less than 1 x 10^{-8} moles/cc.

(b) DPPH was used in this study at concentrations on the order of 1 x 10^{-7} moles/cc. This corresponds to a molar fraction of about 10^{-5}. The direct action of x-rays on DPPH is insignificant.

(c) No protective or sensitizing action has been reported for DPPH(4,139).

(d) The reaction rate between DPPH and the substrate material (1-bromobutane) is low. Suitable corrections can be made by the use of control solutions.

Lack of DPPH Reaction with Ionized Species. The reaction betwen DPPH and ionized species has been discussed by Chapiro(4). Radiation studies of some typical organic materials were made using the polymerization initiation method to determine the radical yield. Benzoquinone was added to some of the test, thereby inhibiting the polymerization completely. Since benzoquinone is known(4) to inhibit radical-induced polymerization reactions without affecting ion-induced reactions, it was concluded that the polymerization which occurred in the uninhibited test was not caused by ionic species. The results from radiation studies with the same organic materials using DPPH to determine the radical yield were identical to the results of the uninhibited polymerization initiation tests. Due to the similarity of test results it was asserted that DPPH did not react with ionized species.

Lack of DPPH Reaction with Excited Species. The possibility of a DPPH reaction with excited states has not been resolved(502). It is felt that this question is of interest to the present study, but not of vital importance because: (1) Many of the excited states formed will eventually produce a radical species during de-excitation. (2) Ionization studies (see Appendix B) have shown that the initial distribution of excited states does not vary with energy, thus any reactions with excited states which occurred would not be expected to be energy dependent.

Additional information on the reaction with excited states is contained in the following analysis of the work of Griffith (307).

The work of L. R. Griffith has been quoted frequently as an indication that DPPH may react with excited states. Griffith irradiated several organic compounds including benzene with mercury ultraviolet light filtered to transmit wavelengths 3126-3130 °A. He concluded that since a reaction between the solvent and DPPH occurred during irradiation (photodissociation of the solvent was not believed to occur at the wavelengths used), the first triplet excited state of the solvent was reacting with the DPPH.

This study was examined in some detail. Several questions arose; however, the following two were felt most pertinent: (1) In the references listed by Griffith as demonstrating the failure of the solvents to photodissociate at 3126°A no specific reference to the lack of photodissociation at 3126°A was found; rather the articles discussed photodissociation which occurred with good quantum yield at wavelengths of 2000°A and less. One article(503) predicted no decomposition of benzene at 2537°A because of the low extinction coefficient for that wavelength; however, measurements showed the reaction to occur with a small but observable quantum yield. (2) Probably the best data obtained to date which shows the relative unimportance of DPPH reactions with excited states for the purpose of high energy radiation studies is contained in the study by Griffith in the form of the overall quantum yields obtained in his studies.

The total quantum yield (molecules of DPPH reacted per photon absorbed in the solvent) for benzene was reported as only 0.01. On the other hand the reaction of DPPH with free radicals is effectively 100% efficient. Thus it would appear that measurements of the number of free radicals produced by radiation using DPPH will not be in error due to DPPH-excited state reactions unless the ratio of excited states to free radicals becomes very large. The initial ratio of excited states to ionized species in most materials is believed to be about 3 to 1(504,505).

<u>DPPH Reaction Kinetics</u>. In order to determine whether DPPH reacts with the radicals produced from irradiation in a known proportion (d, Page 89), the kinetic equations of the reaction should be examined. The following development is due to Chapiro(4).

A small quantity of DPPH (on the order of 40μ gm. DPPH/cc. of target compound, i.e. $\sim 10^{-7}$ mole/cc.) is dissolved in the target-solvent. The free radicals formed by radiation in the irradiated solvent will either recombine or react with DPPH, as in the following reaction scheme:

$$\begin{array}{lll} S \xrightarrow{h\nu} 2R^* & k_1\,\varphi & (1) \\ R^* + R^* \rightarrow X & k_2(R^*)^2 & (2) \\ R^* + DPPH \rightarrow R - DPPH & k_3(R^*)(DPPH) & (3) \end{array}$$

where S is a solvent molecule, R* the free radical formed by the flux φ with a radical yield k_1, X is a stable product molecule, and the k's are the rate constants as shown.

In the steady state the number of radicals produced equals the number of radicals which combine.

$$k_1\varphi = k_2(R^*)^2 + k_3(R^*)(DPPH) \qquad (4)$$

The rate of depletion of DPPH is then

$$V \equiv - \frac{d(DPPH)}{dt} = k_3(R^*)(DPPH)$$

but from (4)

$$(R^*)^2 + \frac{k_3}{k_2} R^*(\mathrm{DPPH}) - \frac{k_1}{k_2}\varphi = 0$$

$$R^* = \left(-\frac{k_3}{k_2}(\mathrm{DPPH}) \pm \sqrt{\left(\frac{k_3}{k_2}(\mathrm{DPPH})\right)^2 + 4\frac{k_1}{k_2}\varphi}\right)\Bigg/ 2$$

The negative solution is rejected since negative concentrations are physically meaningless.

$$V = \frac{k_3(\mathrm{DPPH})}{2}\sqrt{\left(\frac{k_3}{k_2}(\mathrm{DPPH})\right)^2 + \frac{4k_1}{k_2}\varphi} - \frac{k_3(\mathrm{DPPH})^2}{2k_2}$$

and

$$V = \frac{k_3^2(\mathrm{DPPH})^2}{2k_2}\left[\left(1 + \frac{4k_1k_2\varphi}{k_3^2(\mathrm{DPPH})^2}\right)^{1/2} - 1\right] \tag{5}$$

For high (DPPH) concentration

$$\left(1 + \frac{4\varphi k_1k_2}{k_3^2(\mathrm{DPPH})^2}\right)^{1/2} \approx 1 + \frac{2\varphi k_1k_2}{k_3^2(\mathrm{DPPH})^2} \tag{6}$$

and Equation (6) reduces to

$$V = k_1\,\varphi \tag{7}$$

Thus the rate of disappearance of DPPH is equal to the rate of production of free radicals for high DPPH concentrations.

For very dilute DPPH concentration Equation (5) can be simplified to

$$V = \frac{k_3}{k_2^{1/2}} \qquad (k_1\varphi)^{1/2}\ \mathrm{DPPH} \tag{8}$$

Thus at (DPPH) concentrations sufficiently higher than a given value $(\mathrm{DPPH})_{\mathrm{crit.}}$ the disappearance of DPPH is essentially independent of concentration, and proportional to the first power of the dose rate. At low concentrations the DPPH disappearance rate is proportional to the first power of the DPPH concentration and to the square root of the dose rate. Figure 22, plotted from the unpublished work of Boag, Chapiro, Ebert, and Gray shows these features.

Using the Arrhenius Equation an estimate can be made of $(\mathrm{DPPH})_{\mathrm{crit.}}$ from the activation energies involved, assuming that the collision factors are equal. Chapiro$^{(4)}$ assumed that the scavenging reaction (3) required an activation energy of 5 kcal. while the recombination reaction (2) required no activation energy.

Then for 99% complete scavenging

$$\begin{aligned} e^{-5000/RT}(R^*)(\mathrm{DPPH}) &\approx 100(R^*)^2 \\ (\mathrm{DPPH}) &\approx 10^5(R^*) \end{aligned} \tag{9}$$

Thus for a stationary concentration of R^* of the order of 10^{-12} mole/cc. the concentration of DPPH required would be only 10^{-7} mole/cc.; this concentration of DPPH is low enough to make the direct effect negligible.

From Equation (6) an expression can be obtained for $\mathrm{DPPH}_{\mathrm{crit.}}$, the minimum concentration for which essentially complete scavenging can be expected by determining when the approximation ceases to be valid.

$$\text{If} \qquad \frac{2\varphi k_1 k_2}{k_3(\mathrm{DPPH})} \approx 0.10 \tag{10}$$

then the error of the approximation is less than 0.5%.

Using (10) and (6)

$$(\mathrm{DPPH})_{\mathrm{crit.}} = \frac{2k_2^{1/2}}{k_3}\sqrt{10\varphi k_1}$$

or

$$(\mathrm{DPPH})_{\mathrm{crit.}} \propto \varphi^{1/2}$$

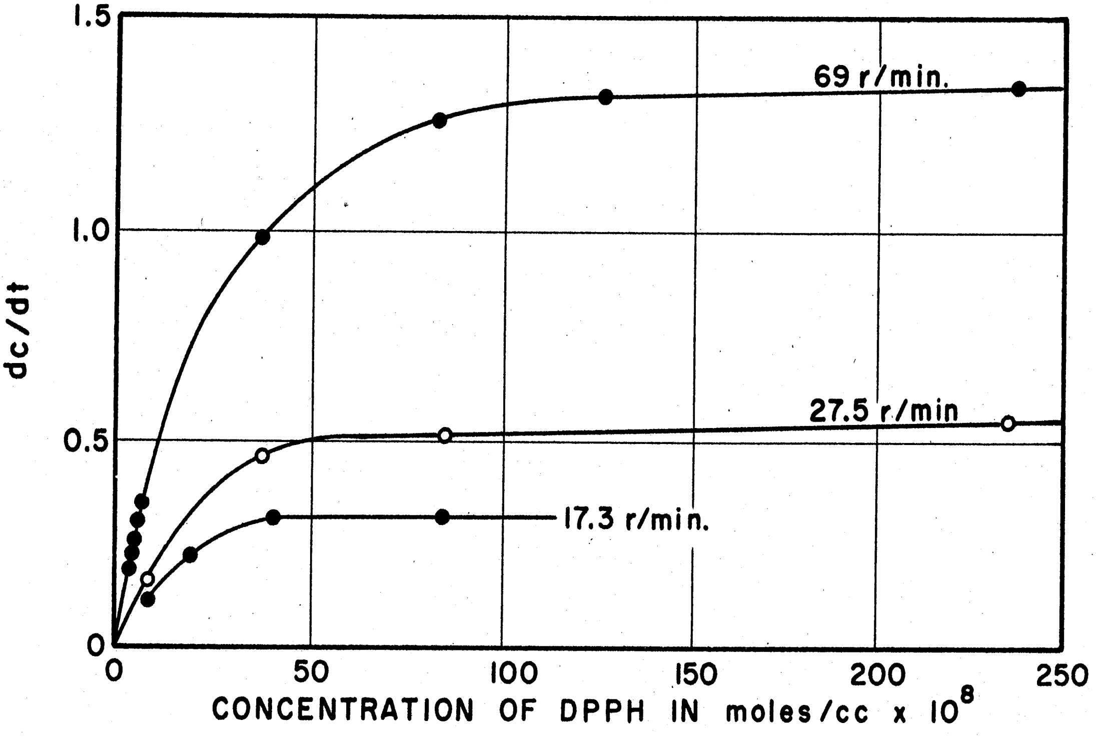


Figure 22. Rate of Loss of DPPH Concentration in Chloroform Irradiated with X-Radiation at Differing Dose Rates as a Function of the Initial DPPH Concentration [from Chapiro(139)].

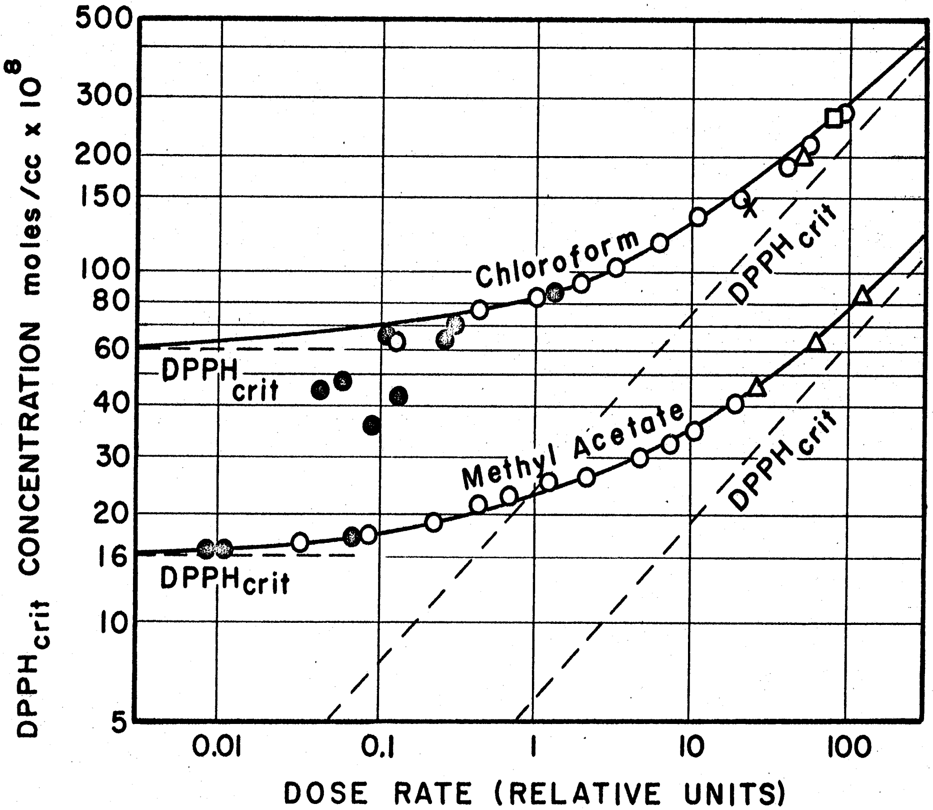


Figure 23. Variation of the Critical Concentration of DPPH as a Function of the Radiation Intensity [from Chapiro(139)].

Effects of Inhomogeneous Radical Distribution. The above analysis is based on a homogeneous distribution of radicals. This relationship has been observed at high flux intensities; however, for low intensities $(DPPH)_{crit.}$ attains a constant value rather than continuing to decrease with lower intensities. This behavior is shown in Figure 23. It is believed that this concentration corresponds to the minimum DPPH concentration which can effectively scavenge the high local radical concentrations which occur in delta tracks and spurs along the main ionizing path of the photon. The concentration of radicals in these local hot spots is, of course, independent of intensity except at very high intensities when the tracks overlap. The overlapping of paths is a function of the photon energy as well as photon intensity; however, the relatively small energy variations used in this study should not cause any significant changes in the $DPPH_{crit.}$-intensity relationship.

The limiting solutions to the above equations and the work of Chapiro with carbon tetrachloride and chloroform (using gross x-radiation and cobalt gamma radiation) were used to guide the preliminary experimental program. It was the purpose of the preliminary experimental study to show that DPPH could be used to effectively scavenge all of the radicals produced during irradiation in 1-bromobutane. Since the equations above predicted a region of DPPH concentrations for which the reaction would be independent of DPPH concentration and dose rate it was deemed desirable to conduct all x-irradiations under these conditions. The results of the experimental study are described in Sections III A and III B.

3. Choice of 1-Bromobutane as the Target Material

Target Atom. Section (1) indicates the desirability of choosing either an alkyl halide or metal-organic compound for this study. Several metal-organics were considered for the study; however, the more readily available compounds (e.g. tetraphenyltin) are solids and would have to be studied as a solute dissolved in a solvent. Many alkyl halides are available which are liquid at room temperature and which can be handled without excessive hazard and difficulties. Bromine and iodine are the most practical halogen target atoms for irradiation with x-rays using the x-ray equipment available for this study. Bromine was chosen as the target atom in preference to iodine for the fluoroscence studies since more radiators were readily available with emission energies near the bromine K edge than were available for iodine. Figure 2 shows the bromine K edge, bromine absorption cross section and the energies of all the radiators used in the study.

Target Compound. The choice of 1-bromobutane was rather arbitrary among the many bromine compounds with similar characteristics. It was felt that results obtained by using simpler molecular forms would be more easily explained and would be more appropriate for an initial study. Preliminary screening tests were also conducted with bromoform, 1-bromoethane and 1,2-bromoethane. Both bromoform and 1,2-bromoethane were considerably more sensitive to background reactions (sensitivity to temperature, light, impurities or other causes which resulted in decomposition of the material). 1-bromoethane was less desirable than 1-bromobutane because of its higher vapor pressure which caused excessive evaporation from the cell.

The 1-bromobutane used for all of the irradiation was purified according to the methods used by Griffith(307). Eastman white label

1-bromobutane was contacted with an excess of DPPH and fractionally distilled in an all-glass column. The final product was tested for purity by measurements of density, index of refraction, infra-red and ultraviolet absorption measurements and by gas chromatographic analysis. The total concentration of impurities was less than 0.5% based on the chromatographic analysis. Impurities which could be identified by gas chromatography included 1-chlorobutane, primary and secondary butyl alcohol and n-butyl ether.

The radical yield of 1-bromobutane as determined in preliminary screening studies was in the region of interest, i.e. not too high as to require excessive DPPH concentrations for complete scavenging yet high enough to give easily measurable reaction rates.

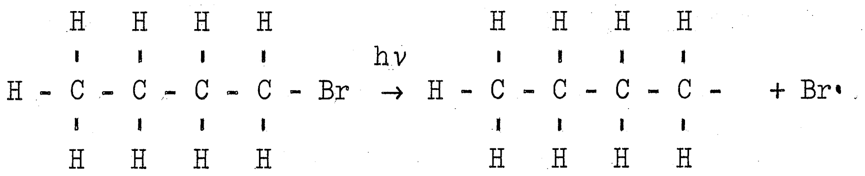
Some of the materials studied by Chapiro(506) were found to give erratic yields upon irradiation due to the presence of water and/or oxygen. No sensitivity of radiation yields of 1-bromobutane was found due to air saturation or to small additions of water. Similar results were obtained by Wilcox(71) who found no changes in product yield from 1-bromobutane due to air saturation or as-received impurities in the organic.

Several experimenters(4,307) have observed post irradiation changes in the optical density of other DPPH solutions. No post irradiation changes in optical density of DPPH solutions in 1-bromobutane were observed.

Observations of the background reaction between 1-bromobutane (including the impurities remaining after purification) and DPPH were made periodically. Although the reaction rate changed somewhat from one batch of 1-bromobutane to another the overall reaction rate was quite low. The average reaction rate corresponded to a reaction of less than 1% of the DPPH per day and at no time exceeded 5% per day. Solutions which had accumulated 10% or more background reaction were not used for irradiation and were reprocessed. The errors incurred by background reactions were limited by using control solutions with every sample irradiation. The background reaction rate was not found to be particularly sensitive to variations in room lighting and room temperature.

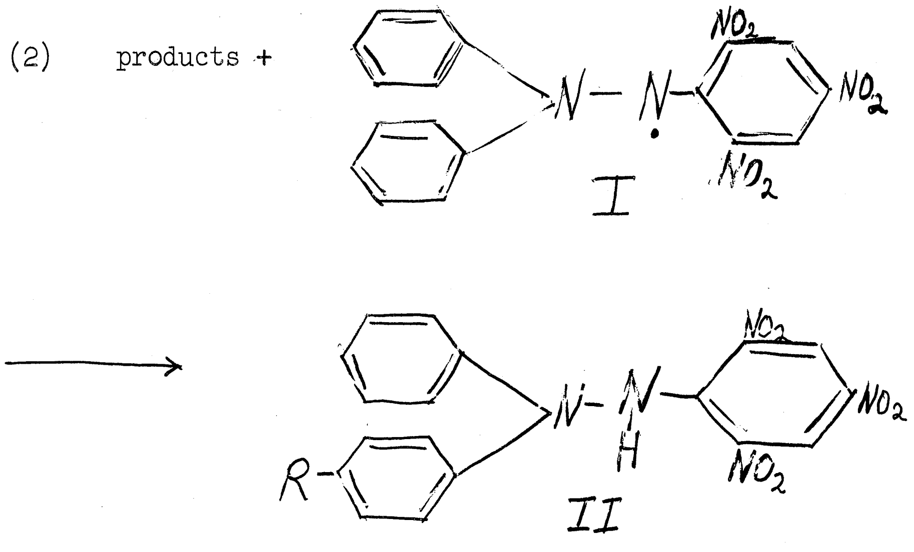
Reactions Produced by Irradiation. The following reactions are expected to occur during the irradiation of 1-bromobutane. The work of Wilcox(71) has shown that greater than 95% of the reaction products of 1-bromobutane irradiation result from the scission of the halogen carbon bond.

(1)



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-Br \xrightarrow{h\nu} H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}- \quad + Br\cdot$$

(2) products +



where R = Br or C_4H_9

The final product structure II is predicted from the work of Goldschmidt and Renn(265) and the work of Poirier, Kahler and Benington(266,270-272). The loss of absorptivity at 520 millimicrons is directly due to the loss of the free electron in structure I according to Poirier, Kahler and Benington(271).

4. DPPH Concentration Determination

In order to utilize the disappearance of DPPH molecules as the measure of the number of radicals produced by radiation it is necessary to be able to determine the DPPH concentration readily before and after irradiation. The high extinction coefficient of DPPH in most solvents makes possible the use of spectrophotometric techniques which are simple, fast, accurate and very sensitive. Extremely small quantities of DPPH can be determined by Electron Paramagnetic Resonance (10^{12}-10^{13} molecules) because of the unpaired electron in the free radical. DPPH crystals are frequently used in calibrating EPR equipment(276-385) because DPPH remains in the free radical state quantitatively even as a solid and the sensitivity for detection of the DPPH spectra is great. EPR techniques were not required in this work since the quantities of DPPH used were always within the range of detection of the spectrophotometric equipment.

DPPH Extinction Coefficient in 1-Bromobutane. The extinction coefficient of DPPH in 1-bromobutane was measured with a Beckman DU Spectrophotometer and adherence to Beer's law was verified for DPPH concentrations of 10^{-9} to 10^{-6} moles per cc (corresponding to an optical density for 1 cm light path of about 0.010 to 10) at 520 millimicrons.

Absorption maxima were observed with the Cary Recording Spectrophotometer at 523 and 332 millimicrons as shown in Figure 24. The extinction coefficient of pure 1-bromobutane at these wavelengths was negligibly small.

From the definition of ϵ, the molar extinction coefficient(507), and optical density (or absorbence)(508)

$$\epsilon = \frac{M}{cd} \log_{10} \frac{I_o}{I} \quad \text{where } \log_{10} \frac{I_o}{I} = \text{Optical Density}$$

M is the molecular weight of the solute (394.34 for DPPH),

c is the concentration in gm/liter,

d is the thickness of the light path in cm.

I_o is the unattenuated beam intensity,

I is the attenuated beam intensity.

From Figure 25 the OD for a DPPH concentration of 10^{-7} moles per cc is 1.16. Then

$$\epsilon = \frac{394.34 \times 1.16}{1 \text{ cm} \times 394.34} \times 10^{-4} \text{ gm/l} = 11{,}600 \text{ (520 millimicrons).}$$

This value compares favorably with the values of 11,900 for benzene(307) and 11,500 for chloroform(509) given in the literature.

Preparation of Samples for Optical Density Measurements. DPPH crystals were weighed on a Cahn Electrobalance Model M-10 and mixed with the required volume of 1-bromobutane in volumetric flasks in order to obtain solutions of known DPPH concentration. The optical density measured in balanced quartz 1 cm square cells was plotted vs μ gm/cc of DPPH as shown in Figure 26 to determine whether Beer's law applied to the

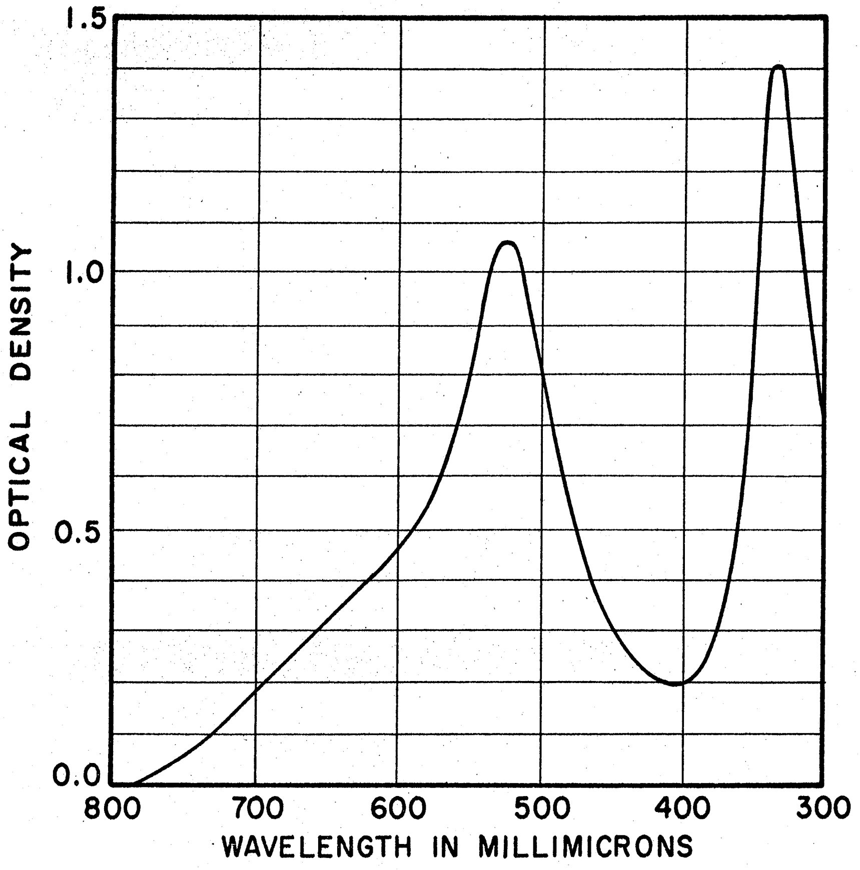


Figure 24. Absorption Spectra of DPPH in 1-Bromobutane.

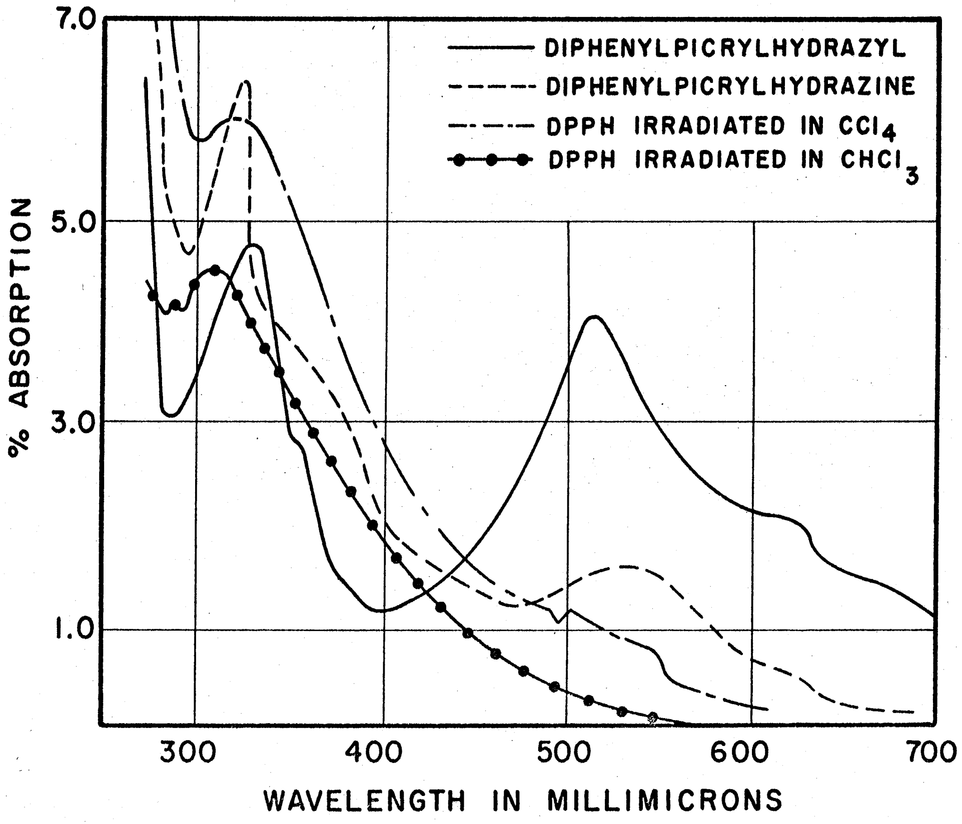


Figure 25. Absorption Spectra of DPPH and the Products Produced by Irradiating DPPH in Chloroform [from Chapiro(4)].

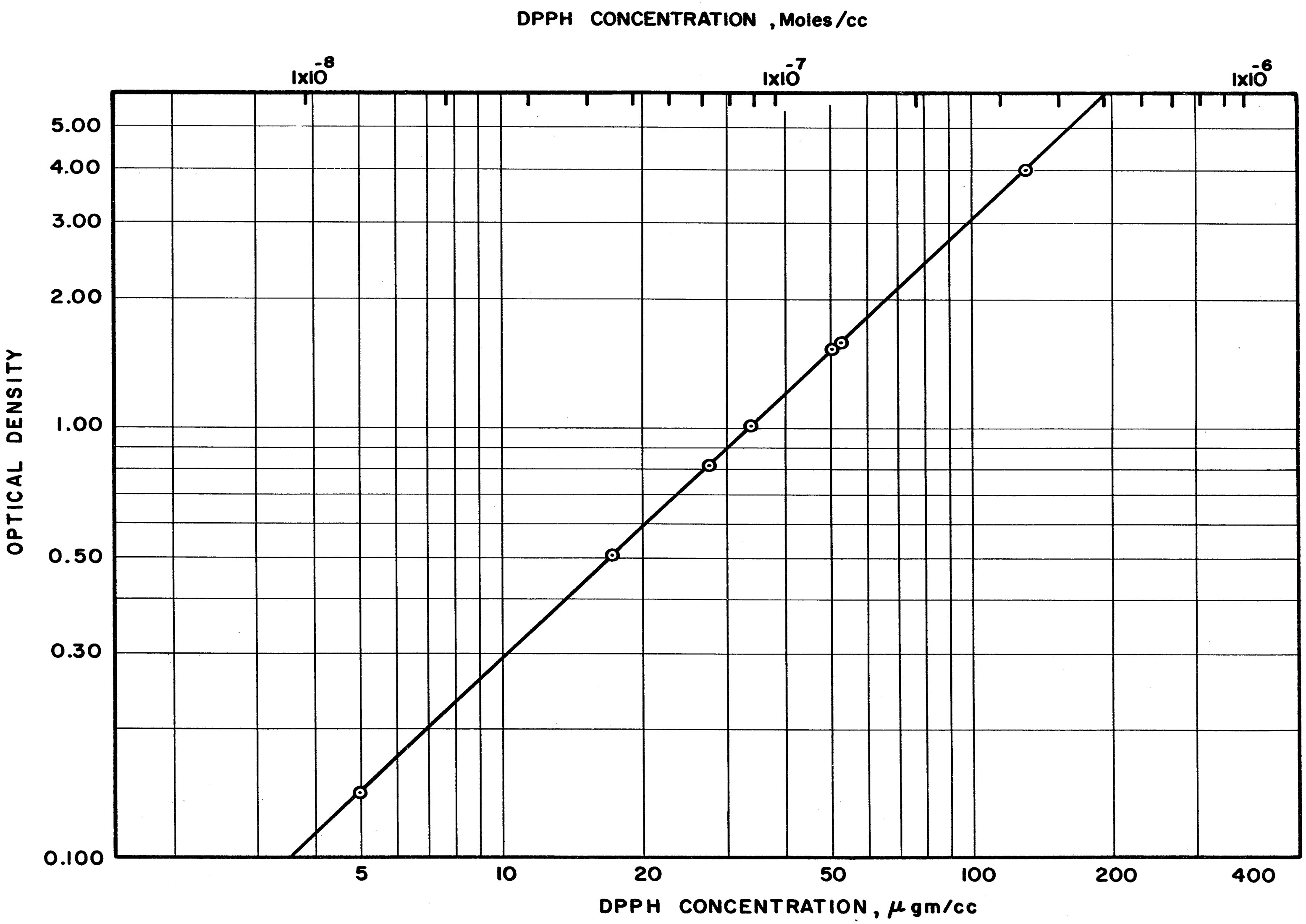


Figure 26. Optical Density of DPPH Dissolved in 1-Bromobutane as a Function of DPPH Concentration.

solution. Weighing was done most frequently on the 0-1 mgm balance scale where an accuracy of ± 0.2% of full scale reading was obtained. The overall accuracy obtained from a series of such measurements including weighing, mixing, dilution and optical density was ± 0.8%.

Absorbtivity of the Products of Irradiation. Since most of the data taken in this study were used for intercomparison any absorptivity of reaction products should not affect the comparison of data taken with different radiation sources but would affect the absolute yield.

The absorption spectra of DPPH and of the final products remaining after consumption of all DPPH in a solution of chloroform irradiated with x-radiation was obtained by Chapiro(510) and is shown in Figure 25. Chapiro determined that the reaction products produced 15% absorption at 520 millimicrons wavelength as compared to the original DPPH absorption at that wavelength(511). He also compared the absorptivities at 800 millimicrons where the products absorb less than 5% as strongly as DPPH.

The optical density of a few samples of 1-bromobutane which had absorbed high x-ray doses in this laboratory gave values of about 16% compared to the original OD due to DPPH. This value corresponds to the asymptotic value of optical density obtained in Figure 36. This correction factor of 1/.84 has been used only in the determination of the absolute yield of 1-bromobutane irradiated with monochromatic x-rays on page 134. The action spectra curves given in Section III were plotted without this correction for simplicity since no attempt was made to determine it accurately.

minor alterations of the instrument. These alterations included the installations of a Lowery-Bessy pinhole in front of the cells to mask down the light beam of the spectrophotometer(512); the installation of a special "slotted and keyed" sample carrier (distributed by Aloe Scientific Co.) which provided accurate alignment of the cell holder with the light beam; and a special carriage designed for the microcells (made by Pyrocell) which provided accurate alignment of the cells with the light beam of the spectrophotometer. The cells, pinhole attachment and carriage are shown in Figure 27.

When the cells were balanced and carefully cleaned the errors in measuring optical density values in the region of 1.0 were less than 0.5%. Successive measurements in a particular series of 7 control determinations gave an error (for one standard deviation) of ± 0.22%.

5. Construction of the Irradiation Cell

Several irradiation cells which were used in this study are shown in Figure 28. The following criteria were considered in the design of the cell:

(1) The cell should be chemically inert to the reactants and products produced in the reaction.

(2) The cell should be equipped with windows which are thin to x-rays.

(3) The cell should have a minimum volume to surface ratio, with a minimum thickness designed to achieve essentially complete absorption of the incident radiation.

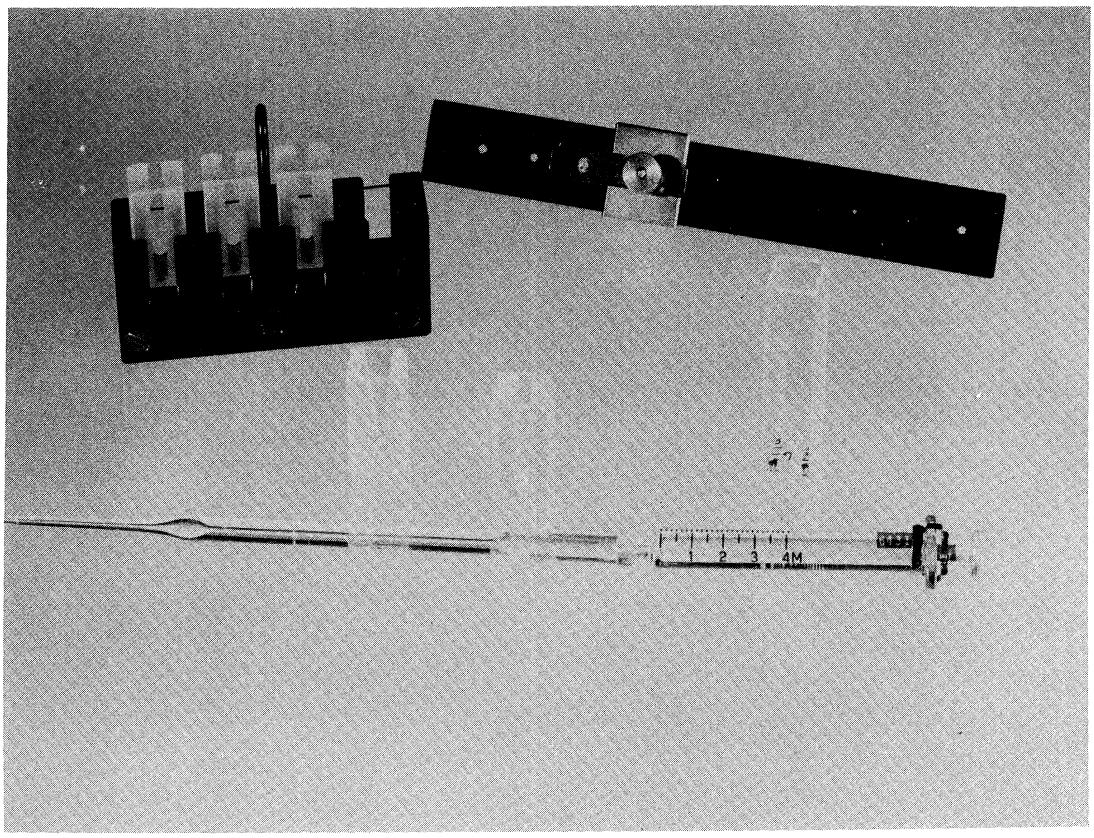


Figure 27. Microcells and Associated Equipment.

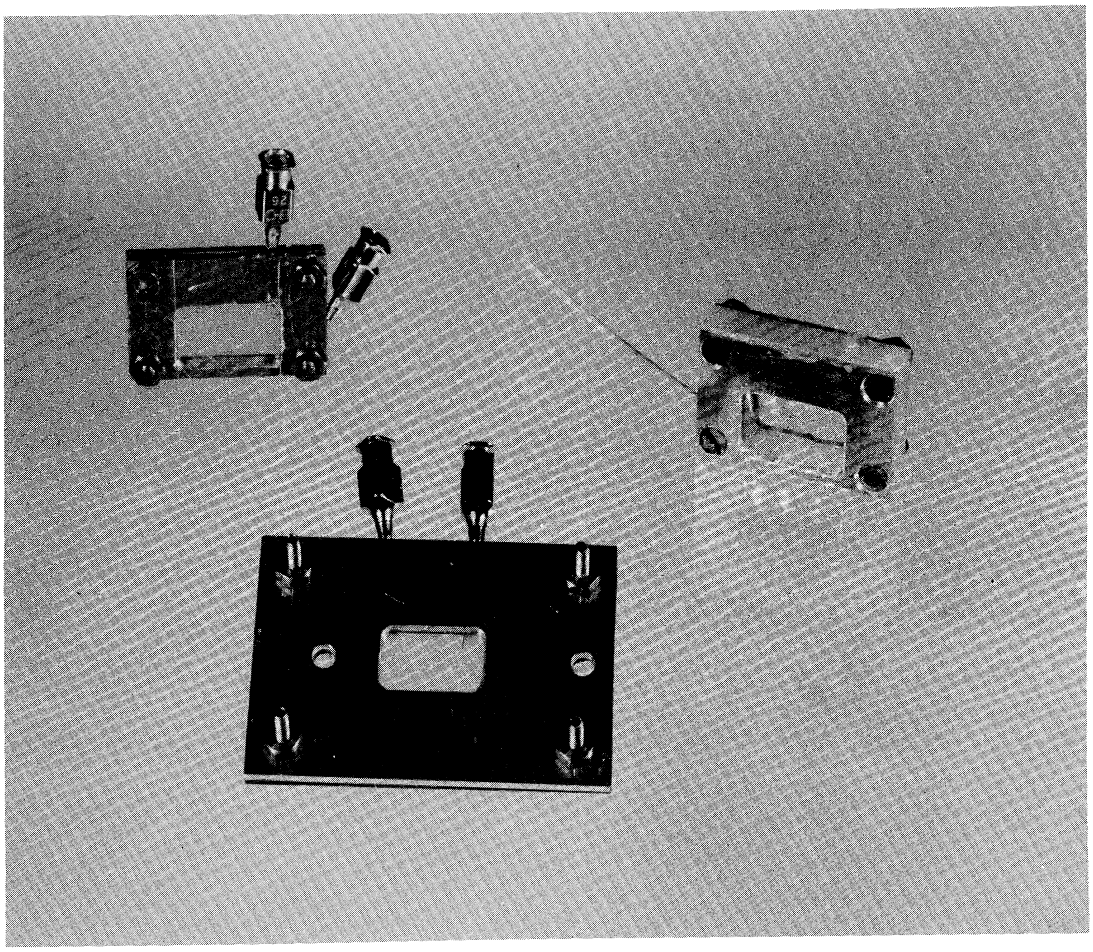


Figure 28. Irradiation Cells.

(4) The cell should be easy to fill and empty.

(5) The cell should be vapor tight or maintain a very low rate of evaporation of the target material.

(6) The entire radiation beam should always be absorbed in the target material.

Construction Details. The cell consisted of two 1/16 inch thick plates of aluminum which clamped two 1 mil Mylar sheet windows tightly against the surface of a 60 mil sheet of polyethylene. The polyethylene filler had a rectangular hole cut out to form the reaction chamber (about 0.8 x 0.5 inches). The interior surface in contact with the sample liquid was either Mylar or polyethylene and was thus unreactive with the sample. The Mylar sheets were coated on the outer side with a small amount of stopcock grease to assist in filling small surface defects which might otherwise allow a leak. The Mylar was pliable enough so that it formed a leaktight seal when clamped tightly and uniformly against the polyethylene liner of the cell. A small chamber in the top corner of the polyethylene reaction chamber served as a bubble trap and simplified the loading of the cell considerably. The small chamber is shielded from any radiation by the 1/16 inch aluminum sheet so that the presence of a small bubble there did not alter the energy absorption by the sample. The sample is inserted and removed by means of two #27 hypodermic syringe needles which are inserted through the liner into the reaction chamber. The hypodermic needles are very convenient for transferring the sample without holdup or loss and can be easily connected to the syringe in which the sample is placed for storage or transfer. The pressure drop through the needles allows small pressures to be built up in the cell during loading and unloading which helps void the cell of air. The needles also act as an effective trap to prevent excessive evaporation of the sample. The evaporation rate of 1-bromobutane was less than 0.1% per hour.

Cell Alignment and Beam Absorption. The cell was made with two holes which keyed onto two studs mounted in the face of the radiator box. The area of the beam (2.47 cm^2) was smaller than the window area of the cell, thus the energy input to the sample was always constant within limits of detection. The attenuation of the radiation beam by the window is of the order of 1% or less for all wavelengths used in this study. Due to the expansion of the windows when a sample is inserted into the cell the path length through the sample is $\sim$ 3 mm. The sample thickness will absorb 97% or more of the initial beam intensity at all wavelengths. This is seen from the attenuation by photoelectric absorption where

$$I = I_0 e^{-\mu/\rho \, \rho t}$$

I is the intensity remaining at a thickness t traversed by the beam, I_0 is the initial intensity incident on the sample, μ/ρ is the mass absorption coefficient for the target material and ρ is the density of the material. The minimum cross section for bromine encountered in this study is for K_α radiation from a rubidium radiator (13.394 Kev). μ/ρ for this energy is 17 cm^2/gm. The density of bromine in 1-bromobutane is 79.92/137.03 x 1.299 gm/cm^3.

$$I = I_0 e^{\frac{17 \times 79.92 \times 1.299 \times 0.3}{137.03}}$$

$$I/I_0 = 2.2\%$$

As a further check, the transmitted intensity was read for each sample.

6. Irradiation Procedure

The detailed irradiation procedure is presented in Appendix A. A brief synopsis of the irradiation procedure will be given here for clarity.

The starting materials (1-bromobutane and DPPH) are purified. A dilute concentration of DPPH in 1-bromobutane is prepared (usually about 1 x 10^{-7} moles/cc with an initial optical density of about 1.5) and the optical density is measured.

The proper radiator is inserted into the fluorescence box (see Figure 12) and the proper filter is placed over the beam tunnel of the fluorescence box. The filter and irradiation cell are held in place by two studs which project from the fluorescence box. Figure 29 shows a filter in place and Figure 9 shows a filter in place with the irradiation cell in position for an irradiation.

The irradiation cell is filled with the solution and the sample is irradiated for a predetermined period (usually about 30 minutes). Figure 28 shows some of the irradiation cells used in the study. The cell to the extreme left was used for all irradiations of 1-bromobutane. The cell on the right was used for the Fricke dosimeter studies.

After irradiation the cell is removed and the sample volume is measured. The sample is inserted into a photometric cell and the optical density of the irradiated solution is measured. A small volume of the unirradiated solution is used as the control for the optical density measurement and pure 1-bromobutane is used as the blank for the measurement. Periodically a sample is inserted into the irradiation cell and the entire

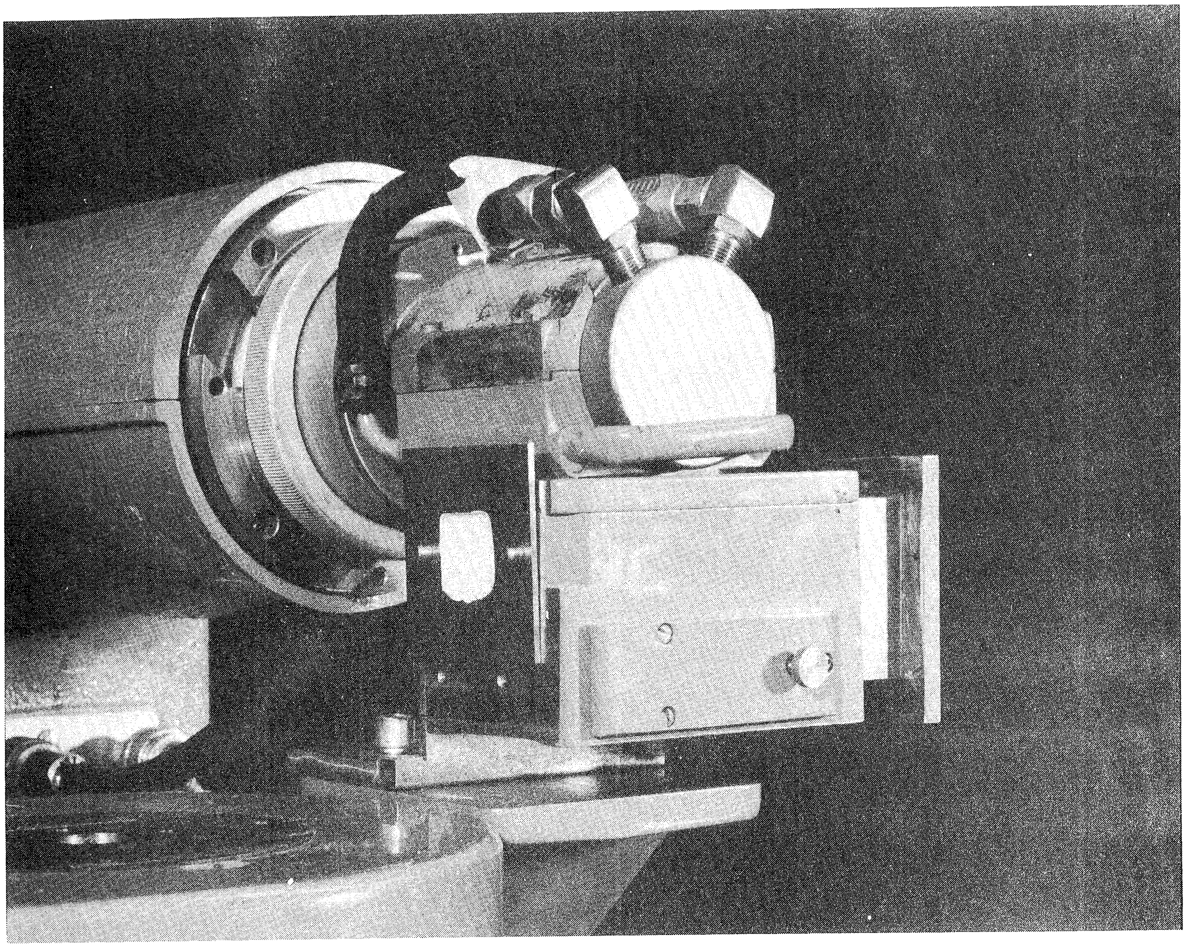


Figure 29. XRD-5 Unit with Filter Element in Place.

procedure is repeated except that the fluorescence box is not pushed in to open the x-ray beam shutter. Thus the irradiation control solution is exposed to the same environmental conditions as the irradiated sample for radiation.

III EXPERIMENTAL PROGRAM

The major portion of the experimental studies was divided into two phases. The preliminary studies included both Cobalt γ-irradiations and x-irradiations at several photon energies. The final phase of the study was the irradiation of samples with monoenergetic x-rays of differing photon energies.

A. Cobalt-60 Irradiations

Cobalt-60 irradiations were used as preliminary test of the effectiveness of DPPH to scavenge the radicals produced by irradiating 1-bromobutane. The work of Chapiro et al(4) as discussed in Section II D has shown that DPPH can be used successfully with compounds which are similar to 1-bromobutane (ethyl bromide and bromoform). Because of the large radiation space available in the cobalt irradiation facility and the simplicity of making the irradiation, most of the preliminary testing was done with cobalt-60 radiation. After the techniques were verified the tests were repeated with monochromatic x-radiation.

Irradiation Techniques. Small glass vials such as those shown in Figure 30 were used as the containers in the cobalt γ-irradiations. Purified 1-bromobutane with the required concentration of DPPH was placed into the vial with a micro pipette and the vial was placed in the cobalt facility at the proper height and distance from the source to obtain the desired dose rate. Irradiation times varied from several minutes to several days and dose rates from 0.1 r to 1000 r per minute were used.

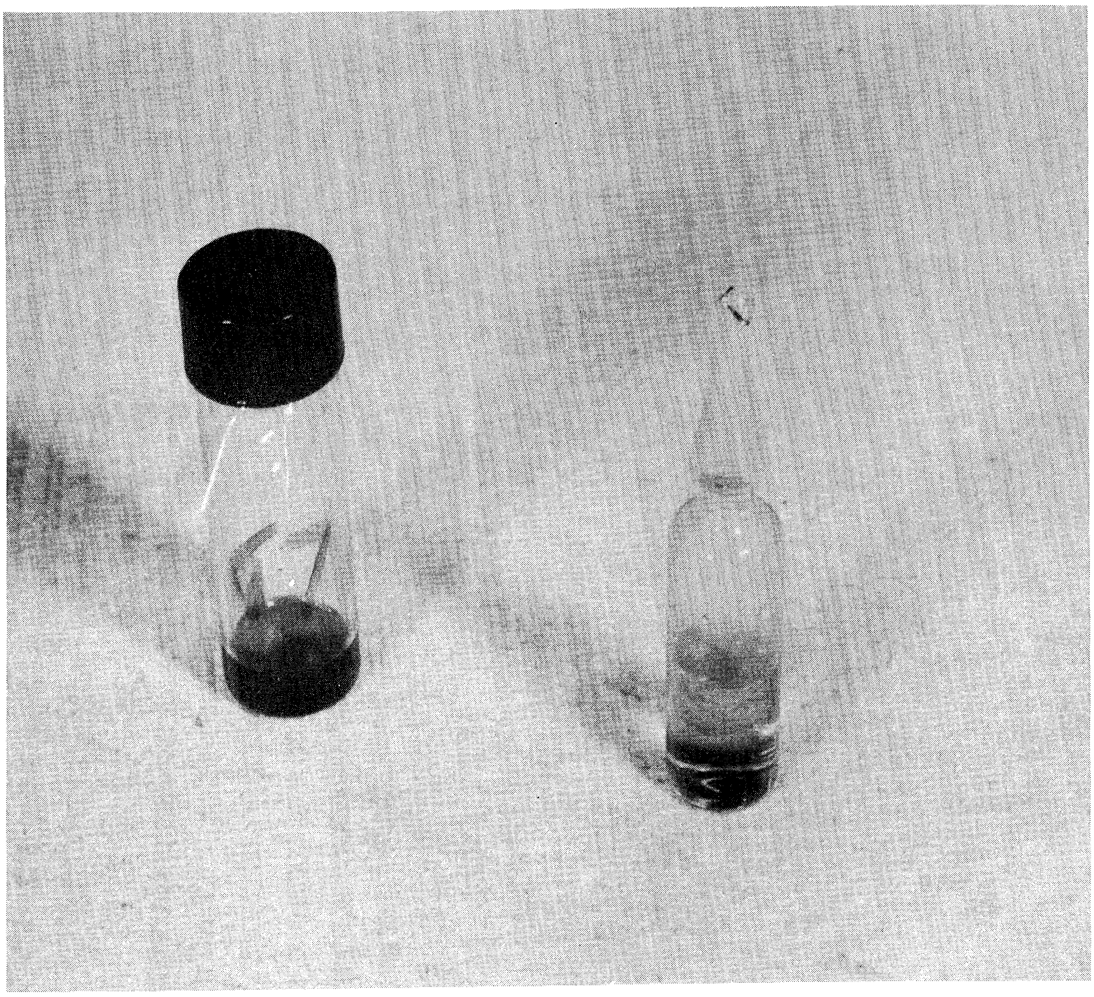


Figure 30. Vials Used in Cobalt γ-Irradiations.

In general three samples were irradiated at each condition and the results were averaged. Agreement among the three samples was usually ± 5%; however, in a number of instances one of the replicates might differ appreciably from the other two. The exact nature of this difficulty was not determined completely; however, more refined techniques reduced the incidence considerably.

Several difficulties were encountered in early tests which might be of interest. The first series of tests was conducted with the vials which had screw type bakelite caps with wax impregnated paper inserts. Some of the compounds tested (particularly ethyl bromide) had such a high vapor pressure that leakage occurred in some of the vials. Efforts to cap the vials more tightly resulted in a number of breakages but the leakage still occurred intermittently. It was observed that the wax impregnation of the cap reacted rapidly with DPPH. Apparently this was caused by the presence of unsaturated hydrocarbons which are known to react with DPPH(4). Vials with pressfit polyethylene caps were also tried but the cap was not vapor tight for any of the compounds tested. Two types of caps were used successfully: (1) The bakelite caps were used with a thin (1/4 mil) sheet of Mylar covering the vial and screwed down tightly with the bakelite cap and liner. (2) Screw caps were obtained which had cone-type polyethylene liners which wore vapor tight and unreactive with the DPPH and alkyl halides.

Some of the scatter of data in the early tests was attributed to small quantities of impurities remaining in the vials following routine cleaning of the vials. The final cleaning procedure included a thorough washing in hot water with Alconox detergent, soaking overnight in a chromic acid cleaning solution followed by a multiple rinse in tap water and a triple rinse with double distilled water. The vials were dried in an oven and stored in a dust-free location until used. Several samples were irradiated in flame-sealed vials as shown in Figure 30. The results of these tests were consistent with the other irradiations.

Effects of Dose Rate and DPPH Concentration. In order to use DPPH as a radical counter it was necessary to show that the yield of the reaction was independent of dose rate and DPPH concentration, and that the yield was proportional to the total absorbed dose over the range of doses used in the study. Numerous combinations of the three variables were tested and typical results are given in Figures 31-33.

Figure 31 shows the effect of dose rate on the radiation yield as determined by the decrease in optical ddnsity of DPPH dissolved in the 1-bromobutane. The yield varies by less than 20% with a dose rate variation of a factor of about 16. Experimental errors in these tests were not sufficiently small to determine whether the small variation shown was real or the result of statistical variation of the data. All dose rates used in the final x-ray studies were confined to variations of less than a factor of 3. This test was conducted at a single initial DPPH concentration and the total consumption of DPPH was limited to 20% or less to minimize any variations of yield with concentration.

Figure 32 shows the effect of DPPH concentration on yield. Since the concentration of DPPH was decreasing during the course of the irradiation the total change in concentration allowed in these tests was limited to 20%

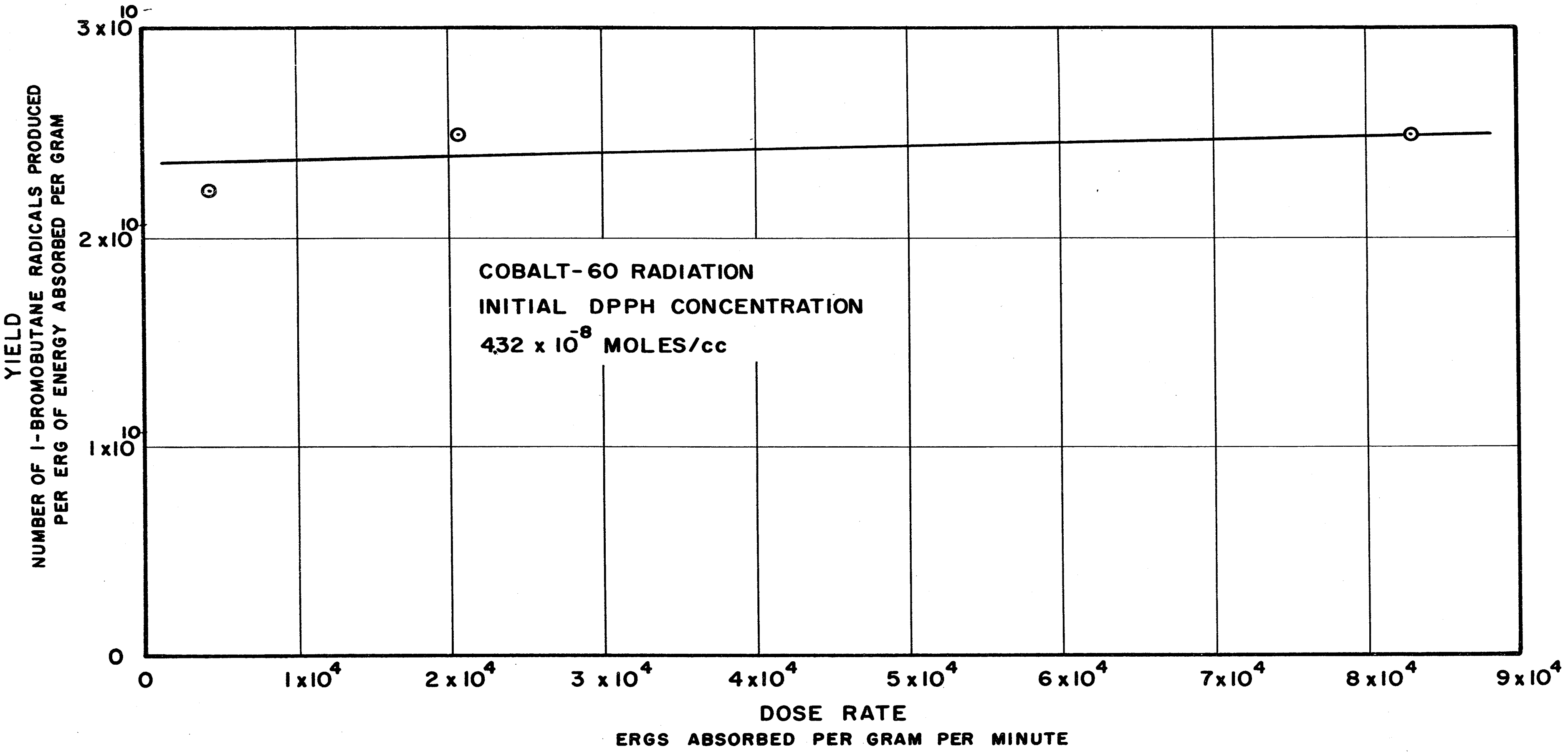


Figure 31. Effect of Dose Rate on Free Radical Yield--Cobalt γ-Radiation.

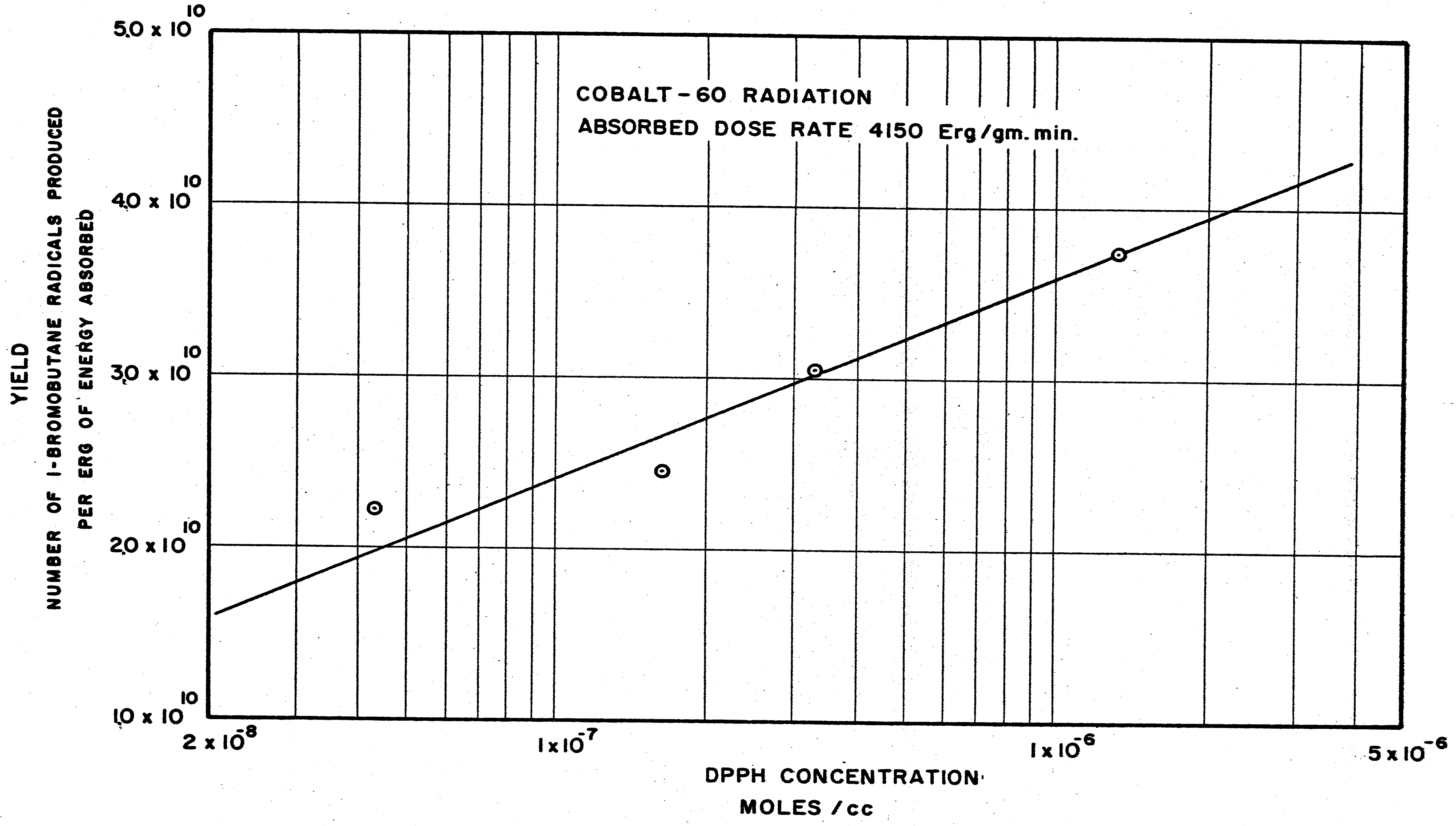


Figure 32. Effect of DPPH Concentration on Free Radical Yield--Cobalt γ-Radiation.

or less. Tests were also made with the concentration change limited to 5% and less, which confirmed the order of magnitude of the results obtained with the 20% limit. The percentage error for the 5% tests was largely due to the small changes in optical density which had to be measured. When the results of the test (with the 20% limit) were plotted, it became evident that variations in concentration occurring in the course of a test with concentration variations up to 50% would have little effect on the observed yield.

Linearity of Yield with Total Absorbed Dose. Figure 33 shows the linearity of observed yield with total absorbed dose. This curve represents samples which were irradiated up to a DPPH depletion of 42% without the appearance of any observable non-linearity due to the decrease in the DPPH concentration. Thus it would appear that considerable ranges in dose rate, DPPH concentration and total energy absorption can be used without appreciable error.

Absence of Critical Concentration. Since Figures 31 and 32 do not show any appreciable effects of DPPH concentration and dose rate on yield within the ranges studied, no minimum concentration of DPPH was found which was required to scavenge completely the radicals produced in the cobalt-60 irradiation of 1-bromobutane. Thus no "$DPPH_{crit.}$" was found which would correspond to the work of Chapiro with chloroform (see page 93). As was mentioned in Section II D, $DPPH_{crit.}$ corresponds to the minimum concentration of scavenger for which the yield of the reaction will be independent of dose rate and DPPH concentration. For concentrations below $DPPH_{crit.}$

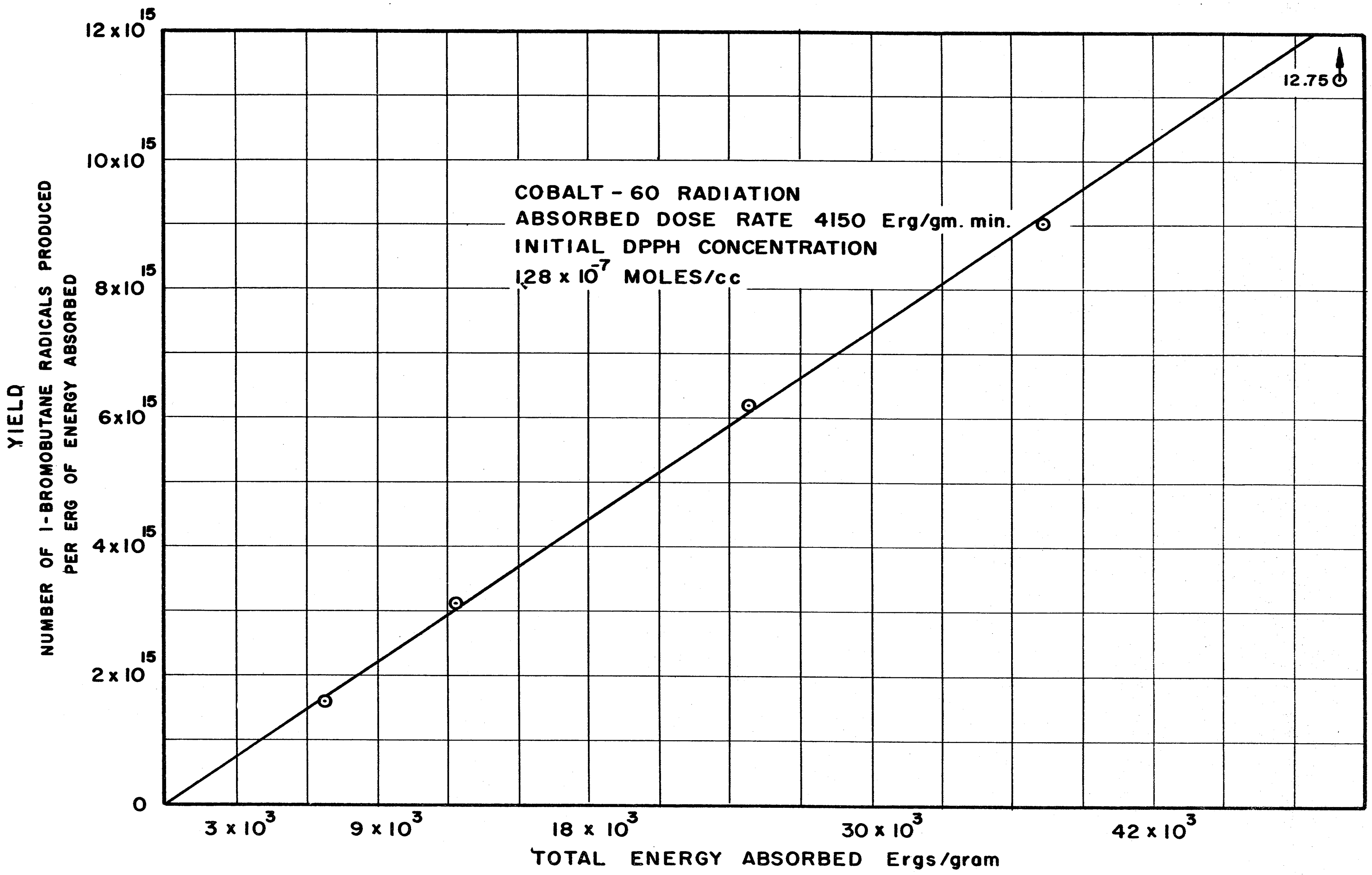


Figure 33. Linearity of Free Radical Yield with Total Absorbed Dose--Cobalt γ-Radiation.

the yield should be proportional to the first power of the dose rate and to the square root of the DPPH concentration. No such dependencies were noted with 1-bromobutane within the limits of the variables studied in this test series.

The absence of a $\mathrm{DPPH}_{\mathrm{crit.}}$ concentration does not negate the applicability of the theoretical treatment of Chapiro to the system under study, rather it seems likely that the critical concentration for 1-bromobutane is lower than the concentrations used in this test series (and thus too low to be measured colorimetrically with available equipment). The radical yield for 1-bromobutane (expressed in G value units of molecules/100 ev of energy absorbed) determined in this test is 3.7 compared to Chapiro's value of 59.5 for chloroform(139). It would appear that the considerable difference between the radiation yields for the two compounds could account for the different DPPH critical concentrations (about 1×10^{-6} moles per cc for chloroform compared to a concentration of less than 4×10^{-8} moles per cc for 1-bromobutane). The determination of $\mathrm{DPPH}_{\mathrm{crit.}}$ would be of interest in order to relate this work more closely to the work of Chapiro, but the basic purpose of the cobalt irradiations was to show that the scavenging action of DPPH was essentially complete and independent of dose rate and DPPH concentration, for a range of conditions surrounding those to be encountered in the x-ray studies. The results show that the use of DPPH under the conditions studied should be satisfactory.

Sample calculations for the cobalt irradiations are given in Appendix A.

B. Irradiations with Monochromatic X-Rays

This section contains a discussion of the results of the preliminary x-ray tests to determine usefulness of DPPH as a scavenging agent for 1-bromobutane radicals produced by irradiation and the results of the final x-ray tests to determine whether the radical yield of irradiated 1-bromobutane was dependent on the photon energy of the radiation.

Preliminary Tests. The insensitivity of radical yield to changes in dose rate, DPPH concentration and the linearity of yield with total energy absorption were verified with x-radiation in tests which were similar to those discussed in the previous section using cobalt gamma radiation. All x-ray irradiations were made in the radiation cell as described in Section II D. Detailed procedures for the irradiations were developed to ensure that all irradiations were done in the same way. These procedures and some typical calculations are given in Appendix A. The preliminary test were conducted with several photon energies which bracketed the range of energies to be used in the final study to ensure that the DPPH concentrations used would be sufficient to effect complete scavenging at all energies and dose rates to be used in the final study.

The results of the preliminary tests are shown in Figures 34, 35 and 36. These test confirm the results obtained with cobalt radiation and show that the use of DPPH to determine radical yield within the range of conditions studied is justified. Figure 34 indicates that the variations of yield due to the differences in dose rate encountered in the final (unfiltered) tests of energy dependence should be less than 5%. The

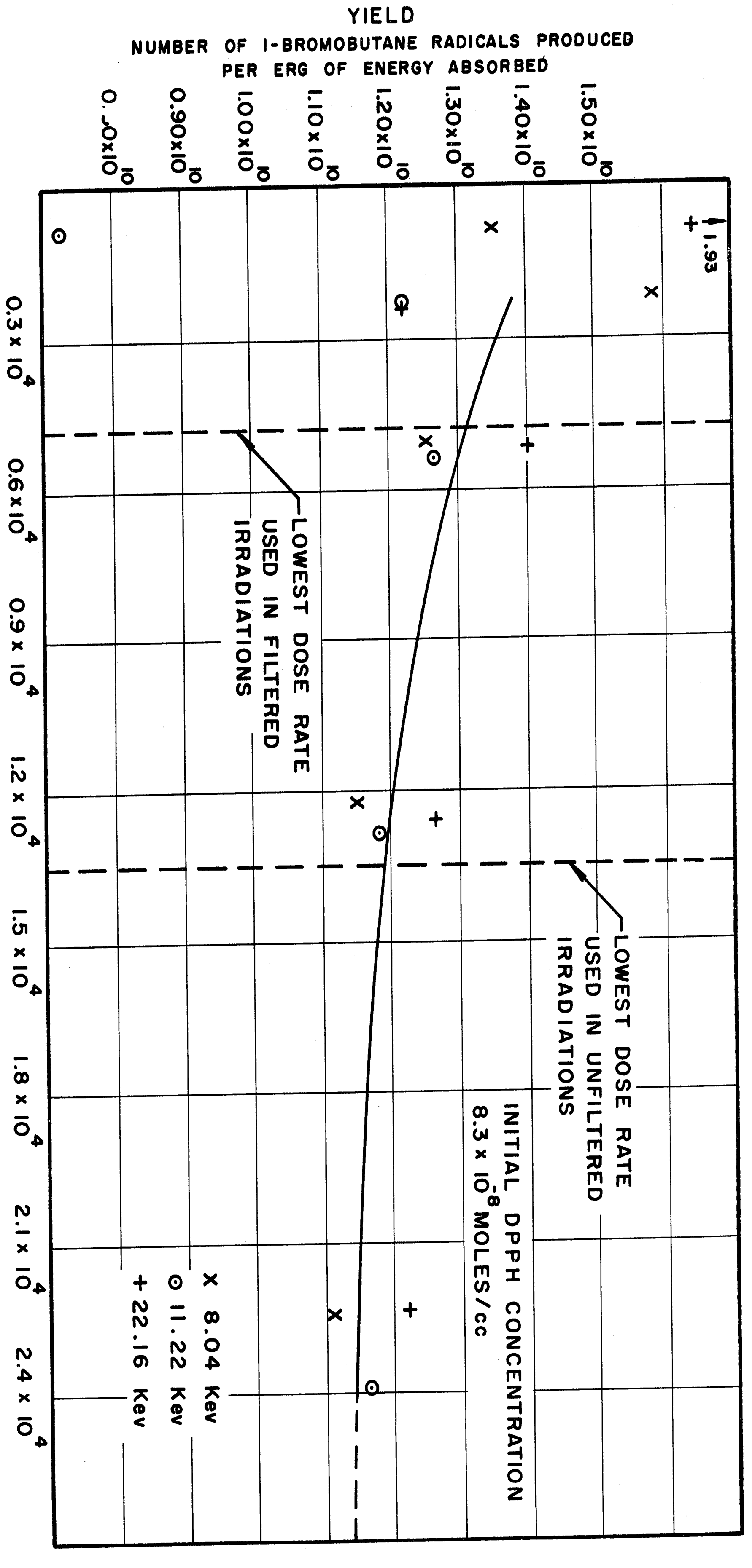


Figure 34. Effect of Dose Rate on Free Radical Yield--X-Radiation.

variations encountered in the filtered studies should be less than 13% due to dose rate differences. Variations in yield due to different initial and final DPPH concentrations should be limited to less than ± 10% for all final tests as shown in Figure 35. Most of the tests were confined to the more limited range shown in the figure. The differences due to concentration were further limited by using the same initial DPPH concentration for all irradiations in a series* and by varying irradiation times to maintain the observed change in DPPH concentration between 30% and 50%. The linearity of the yield with total absorbed dose is shown in Figure 36.

Final Results. The final results of the study are shown in Figures 37-41. These results show the energy dependence of the radiation yield of 1-bromobutane for x-ray photons of energies between 6.4 and 25.3 Kev. Figure 37 summarizes the results of eight test series and represents 250 samples. Average values of the radiation yield data are plotted for each photon energy used in the study. The confidence intervals shown correspond to 90% certainty and will be discussed in more detail in the next section. Since the radiation source for these radiations was unfiltered fluorescence radiation, two photon energies corresponding to the K_α and K_β energies of the radiator elements were actually used in each irradiation. The resulting yield per erg of total energy emitted from each radiator used in the study was plotted at the K_α energy.

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* A series is defined as a group of irradiations including at least one sample irradiated with each photon energy used in the study and done with experimental conditions maintained as consistently as possible.

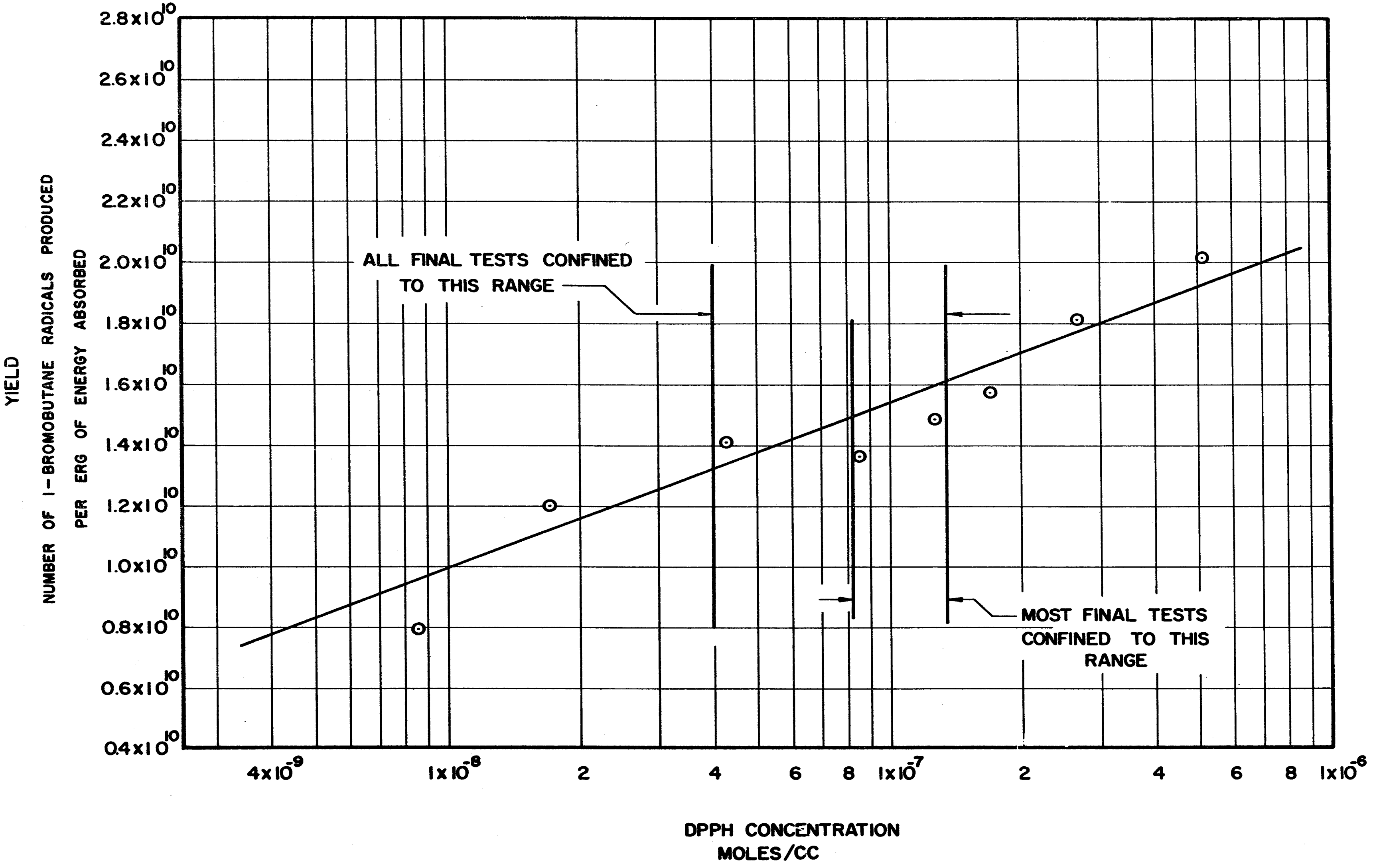


Figure 35. Effect of DPPH Concentration on Free Radical Yield--X-Radiation.

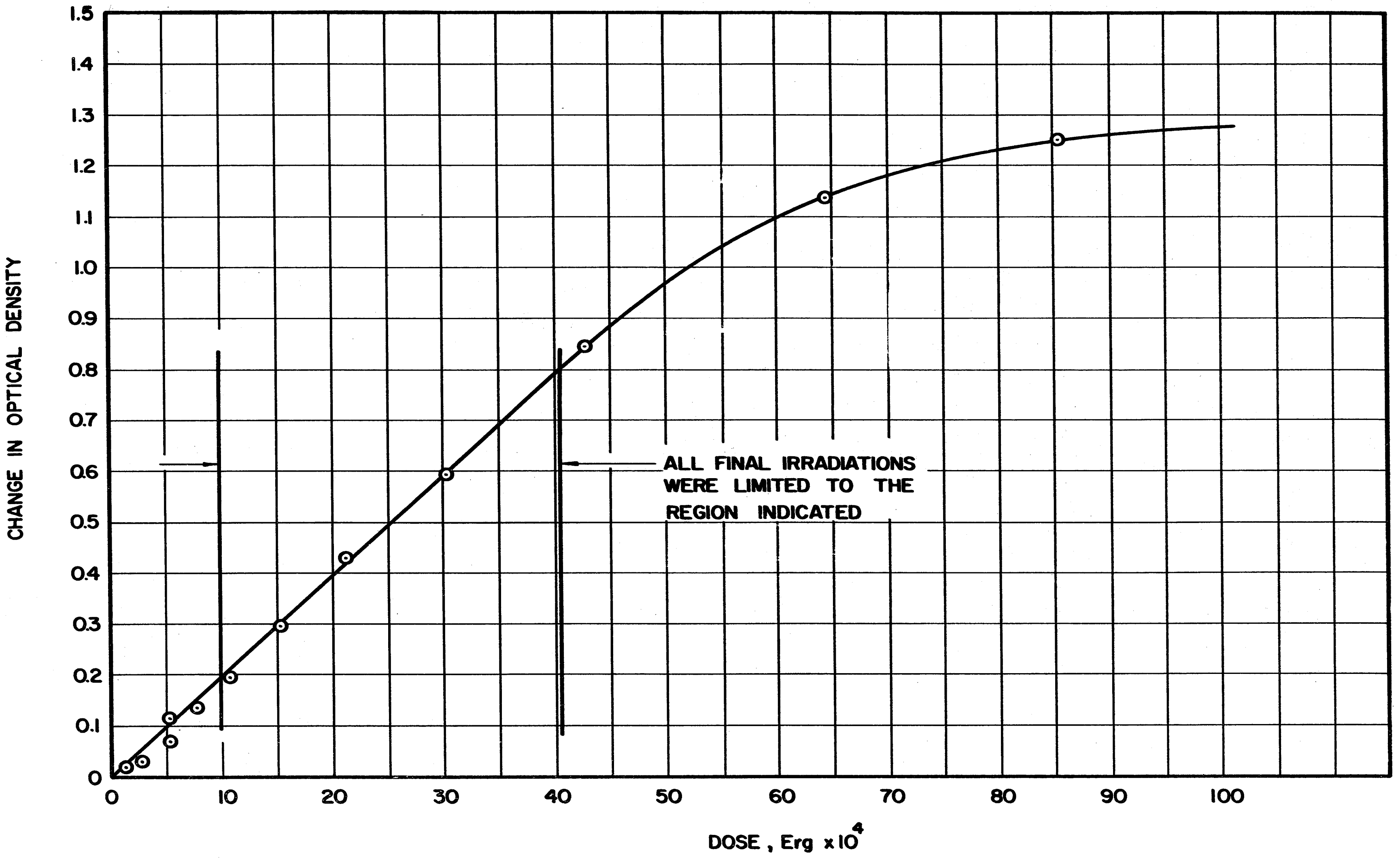


Figure 36. Linearity of Free Radical Yield with Total Absorbed Dose--X-Radiation.

It will be noticed in Figure 37 that a straight line has been drawn through the data points. Since the radiation used in this study is monochromatic and has very high energy resolution, the radiation yield determinations shown are, strictly speaking, valid only for the specific energies studied.

Apparent Loss of Fluorescence Energy. One of the significant features of Figure 37 is the sudden drop of radiation yield at the K edge of bromine. It should be noted that the data points in Figure 37 are plotted on the basis of the amount of energy initially absorbed. For photon energies greater than the K edge energy a significant fraction of the energy initially absorbed can be re-emitted as secondary radiation (bromine fluorescence radiation). This radiation can escape from the sample due to the lower absorption coefficient of the sample for secondary radiation compared to the coefficient for the incident radiation.

The escape of secondary radiation is not significant in most radiation effects studies since:

(1) The energy of the incoming radiation is most frequently considerably higher than the K edge energy. For photoelectric absorption the difference in incident energy and the absorption edge energy is given to the photoelectron which will dissipate the energy in a short distance compared to the mean free path of the incident photon. Although fluorescence radiation may escape from the sample its energy content will be small compared to the energy of the photoelectron which will be absorbed in the sample in most cases and little error will be introduced by neglecting fluorescence radiation escape.

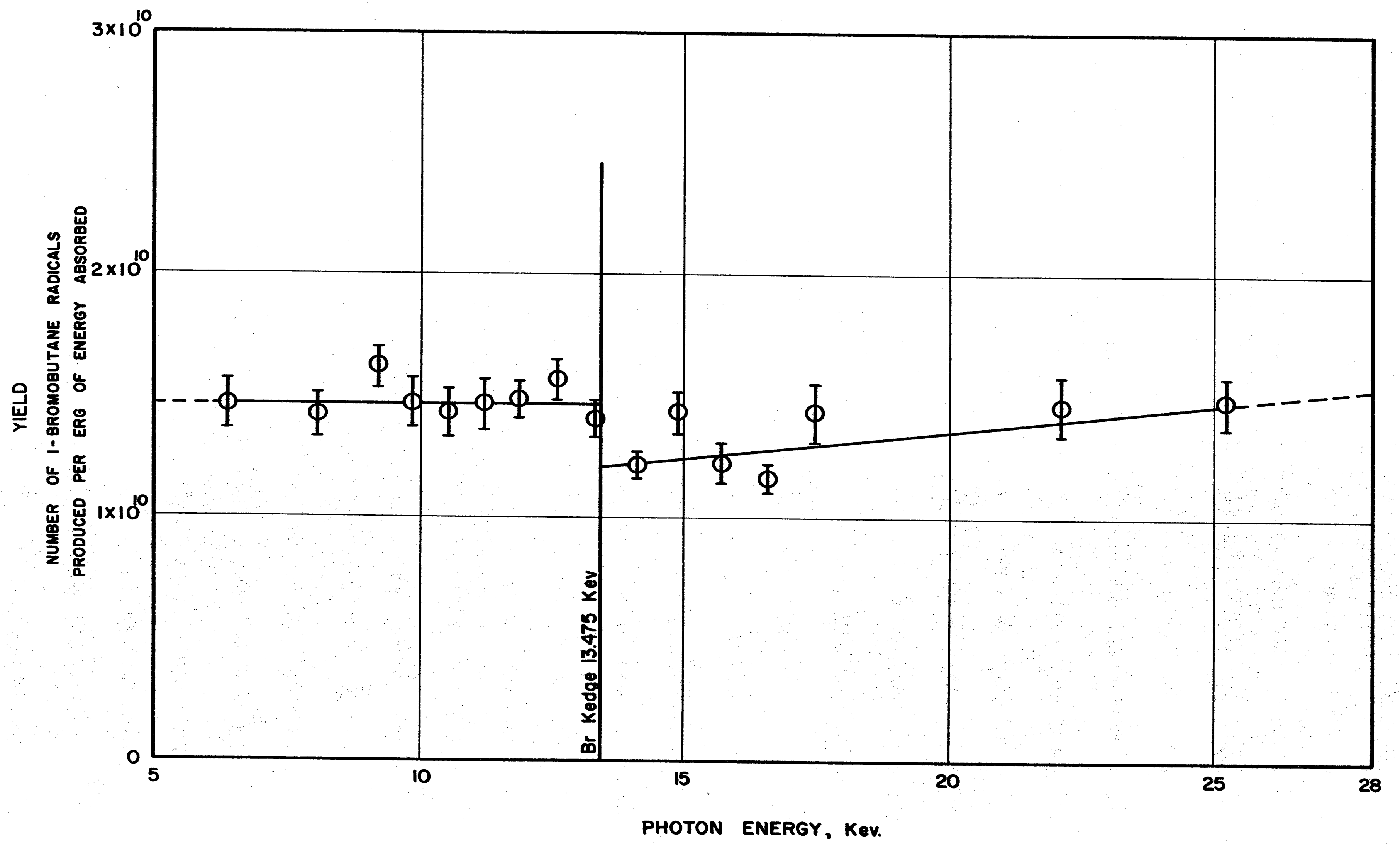


Figure 37. Free Radical Yield Produced in 1-Bromobutane as a Function of Photon Energy.

(2) For incident photon energies somewhat higher than the K edge energy of the sample but not so high that (1) applies, the absorption coefficient of the sample for the incoming radiation is likely to be of the same order as, or smaller than, the coefficient for the secondary radiation. Due to the smaller absorption coefficient for the incident radiation the sample will likely have larger dimensions (compared to a mean free path for the secondary radiation) than the sample used in these studies. As a result secondary radiation will be produced at a greater depth in the sample and will have to escape through longer distances in the sample, resulting in less escape of secondary radiation.

The escape of fluorescence radiation is thus of little consequence in most tests unless the experiment is specially designed to maximize the effect (in a test to determine the fluorescence yield of an element, for example) or if the experimental conditions require thin samples and incident radiation with energy just exceeding the K absorption edge of the sample.

The discussion above has been directed more specifically to K fluorescence since in the case at hand L fluorescence will in all cases be almost totally absorbed in the sample and may be neglected.

Calculation of Loss of Fluorescence Energy. Several approximate calculations of the energy loss by fluorescence from ionization chambers have been reported in the literature(18,261,264). No rigorous solution was found: all of the analyses found in the literature assumed that most of the fluorescence could escape through the sides of the chamber volume; thus integration of all possible exponentially attenuated escape paths $[\int_{\vec{r}} e^{-\mu\bar{r}}(\text{Source})dr]$ could be replaced by $[e^{-\mu\bar{r}}(\text{Source})]$ where $\bar{r}$ is some linear average escape path length. A closed-form solution to the actual geometry used in this study would be rather difficult (if possible at all) and somewhat unnecessary, considering the degree of uncertainty of the experimental data. A qualitative answer can be easily obtained representing the physical situation to the least as good accuracy as the experimental data.

The following assumptions are made:

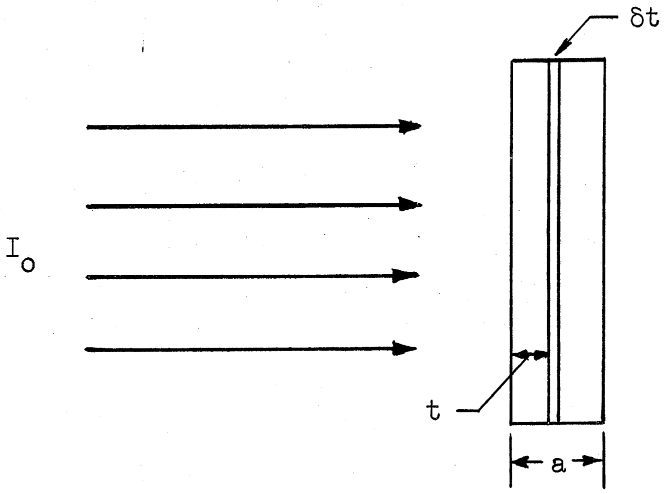
(1) A one dimensional model will be adopted; re-emission of secondary radiation will either be in line with the incoming radiation or in the opposite direction (with equal probability), thus all radiation will be incident, or leave, only the front and rear of the sample.

(2) All fluorescence radiation will be assumed to be K shell radiation for simplicity.

(3) The radiation beam intensity is uniform. (Film irradiations have shown that the beam intensity is uniform.)

The validity of the assumptions can be inferred qualitatively as follows. One dimensional escape of radiation through the front face gives a shorter average escape path than is actually experienced; thus, this assumption provides for too much leakage. Since the incoming photon beam cross-sectional area is equal to the area of the cell face, some of the secondary radiation will be formed near the sides of the cell and can leak out the sides. The latter error will tend to offset the former error and both are minimized by the fact that the dimensions of the cell are large compared to the mean free path of both the incident and fluorescent radiation.

The maximum and minimum limits for fluorescence escape are 28% and 0% respectively. The upper limit corresponds to total absorption of all the incident radiation on the front surface of the sample. One-half of the fluorescence radiation can escape out the front face while (effectively) all of the fluorescence radiation entering the sample will be absorbed:



Let C = the fraction of energy initially absorbed which escapes from the sample.

The source intensity for secondary emission from the thin slab δt can be written as

$$S = f\mu_1 I_o e^{-\mu_1 t}\delta t$$

f is the fluorescence yield of the target atom (0.56 for bromine)

μ_1 is the linear absorption coefficient for the incident radiation of energy K_{α_1}

I_o is the intensity of the incident K_{α_1} photons in units of photons/cm^{2}sec.

a is the thickness of the radiation cell

subscript 2 indicates secondary radiation.

The escape probability through the front face for the fluorescence radiation of photon energy K_{α_2} is $e^{-\mu_2 t}$ and through the rear face $e^{-\mu_2(a-t)}$.

Thus C =

$$\frac{K_{\alpha 2}}{K_{\alpha_1}}\,\frac{f}{2}\,\left[\int_0^a \mu_1\, e^{-\mu_1 t}\, e^{-\mu_2 t}\, dt + \int_0^a \mu_1\, e^{-\mu_1 t}\, e^{-\mu_2(a-t)}\, dt\right] .$$

Integration yields

$$C = \frac{K_{\alpha 2}}{K_{\alpha_1}}\,\frac{f}{2}\left(\frac{\mu_1}{\mu_1+\mu_2}\right)\left[\left(1 - e^{-(\mu_1+\mu_2)a}\right)\left(1 + e^{-\mu_1 a}\right)\right].$$

For all photon energies used in this study the thickness a of the cell was chosen to give 97% or greater absorption of the incident radiation. Thus for all incident photon energies used in the study

$$1 - e^{-\mu_1 a} \approx 1$$

and c reduces to

$$\frac{K_{\alpha 2}}{K_{\alpha_1}}\,\frac{f}{2}\,\frac{\mu_1}{\mu_1 + \mu_2}$$

Two cases are of interest: (1) $K\alpha_1$ energy only slightly greater than the K edge energy and (2) for $K\alpha_1$ energy somewhat removed from the K edge energy.

TABLE II

Fluorescence Escape Correction Factor

Radiator	$K\alpha_1$ Energy in Kev	$K\alpha_2(BrK_\alpha)$ in Kev	$\mu_1{}^*/\rho$ BuBr in cm^2/gm	$\mu_2{}^*/\rho$ BuBr in cm^2/gm	C	$CF=\frac{1}{1-C}$
Sr	14.164	11.923	138	24	.201	1.25
Ag	22.162	11.923	138	39.5	.117	1.13

Final Results Corrected for Fluorescence Energy Escape. The results obtained by applying this correction factor to the data in Figure 37 are shown in Figure 38.

It should be noticed that Figure 38 is also corrected for the absorption of DPPH products as discussed in Section II D (a factor of 1.19 is used to convert the relative yield data reported thus far into absolute yields). The yield is also reported in G units (number of radical pairs produced per 100 ev of energy absorbed) to assist the comparison of this data with other values in the literature.

Temperature Sensitivity of the Irradiation Yield. Late in the course of the test series shown in Figure 37 it was discovered that the radiation yield was somewhat sensitive to the temperature of the sample during irradiation. This results was unexpected from the preliminary studies since the background reactions did not appear to be temperature sensitive. The presence of a temperature effect on the yield is not understood from the kinetic equations in Section II D. The occurrence

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* See Figure 2.

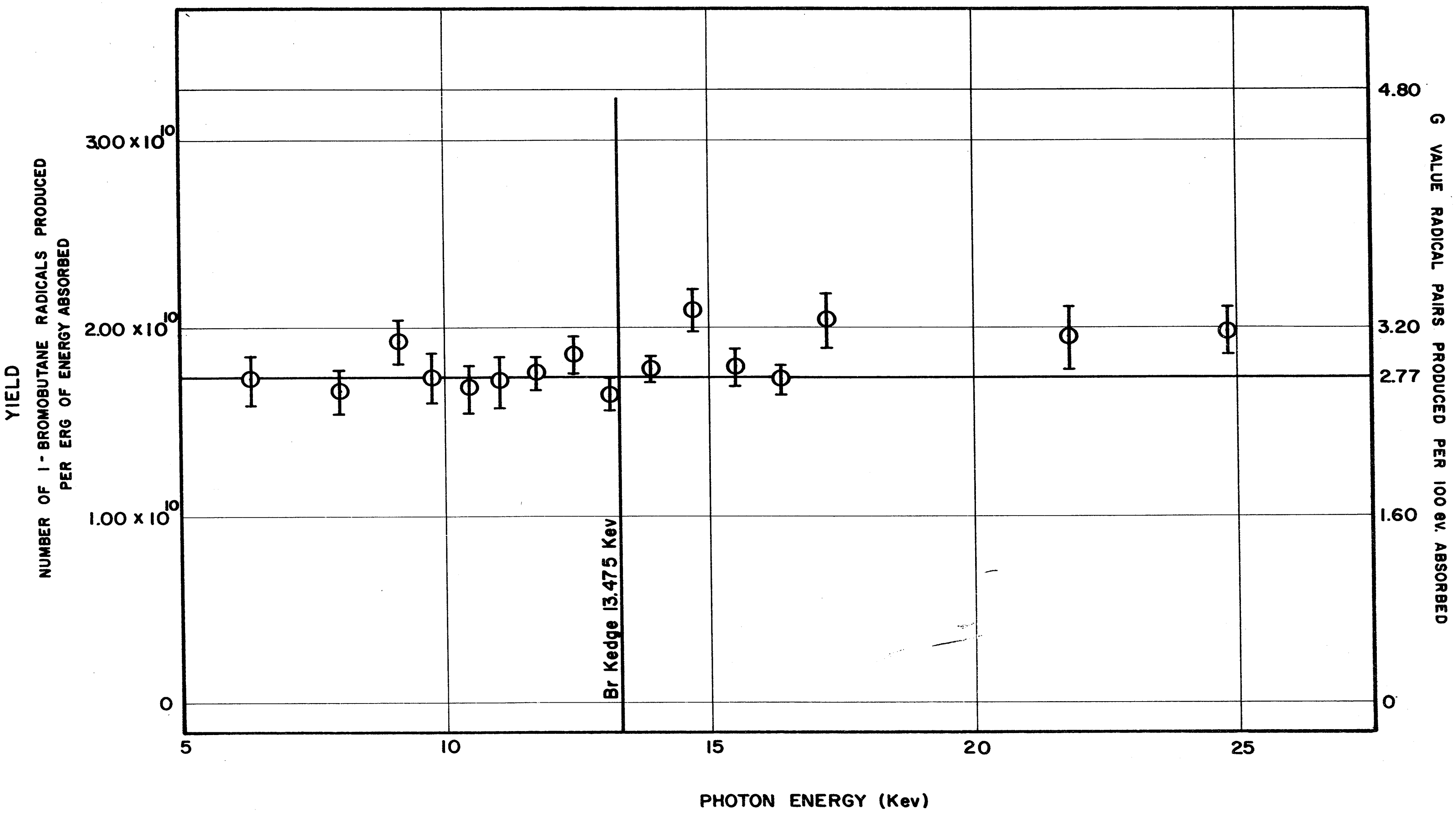

Figure 38. Free Radical Yield Produced in 1-Bromobutane per Unit of Energy Absorbed as a Function of Photon Energy.

of temperature effects for solutions with lower than $DPPH_{crit.}$ concentrations would be expected; however, results from the preliminary tests with cobalt and x-radiation indicates that the concentrations of DPPH used in this study were considerably greater than $DPPH_{crit.}$. The possibility that the actual radiation yield may change with temperature cannot be excluded.

Figure 39 shows a very approximate temperature-yield curve resulting from a test which was made in an attempt to determine if temperature effects could account for some of the scatter of data observed in earlier experimental results. As the figure shows, the yield of the reaction appears to be sensitive to temperature; however, the temperature sensitivity does not appear to be very large in the range of temperature used in the study. As shown, the errors introduced in the initial tests due to temperature changes should have been less than 10%.

Test Series Conducted with Temperature Control. Subsequent to the determination of the temperature sensitivity an additional three test series were made to verify that no systematic errors were introduced into the earlier study due to temperature effects. The results of these runs are plotted point by point and are shown in Figure 40. As is apparent from Figure 40 no significant changes were observed in this data compared to the earlier work. The statistical spread of data is significantly improved over the earlier data. Some minor deviations of this curve from the earlier results shown in Figure 37 will be discussed in the next section.

Filtered Irradiations. One of the most significant results of the temperature sensitivity of the radiation yield was that earlier results with filtered radiation gave consistently higher yield values than the

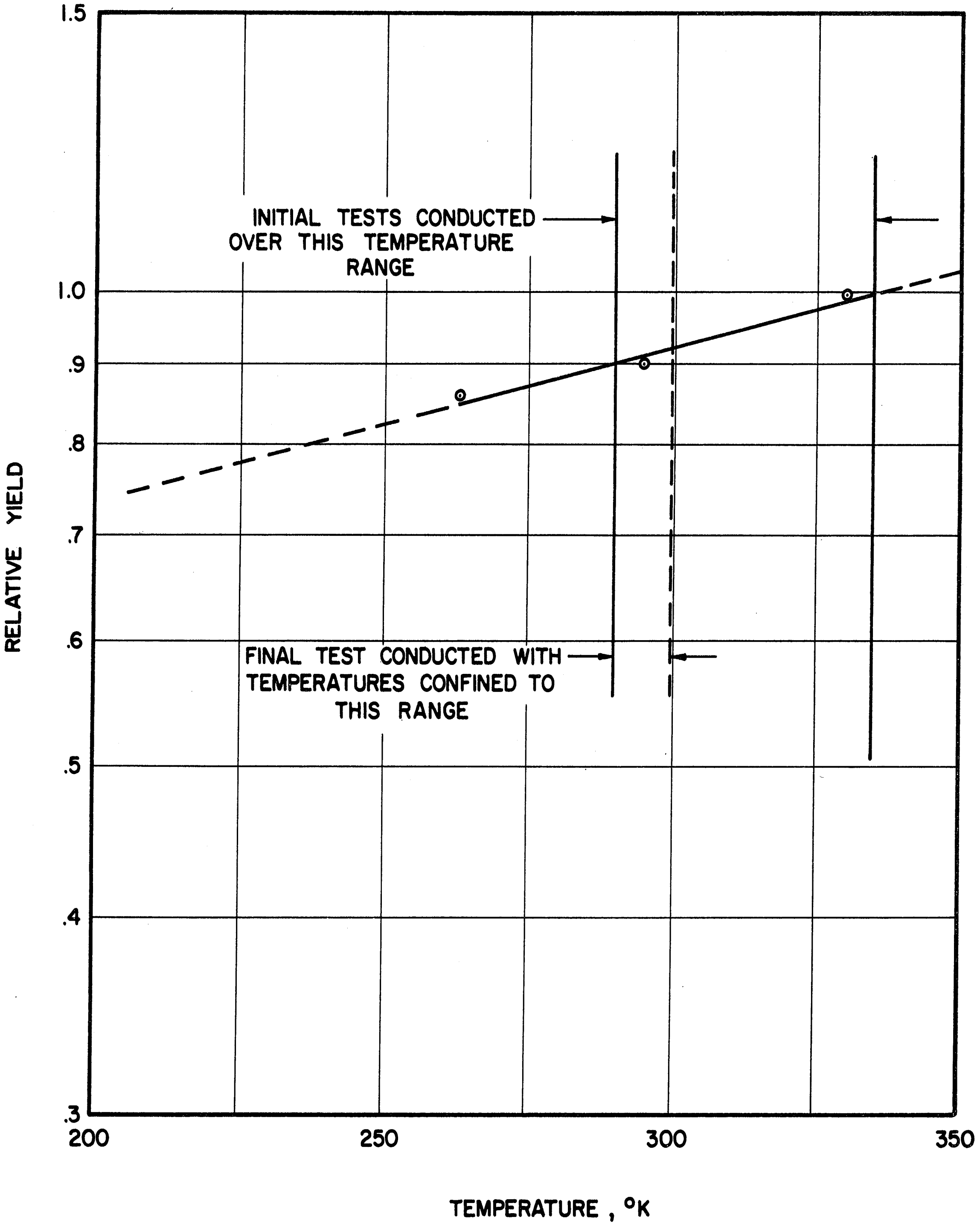

Figure 39. Effect of Temperature on Free Radical Yield.

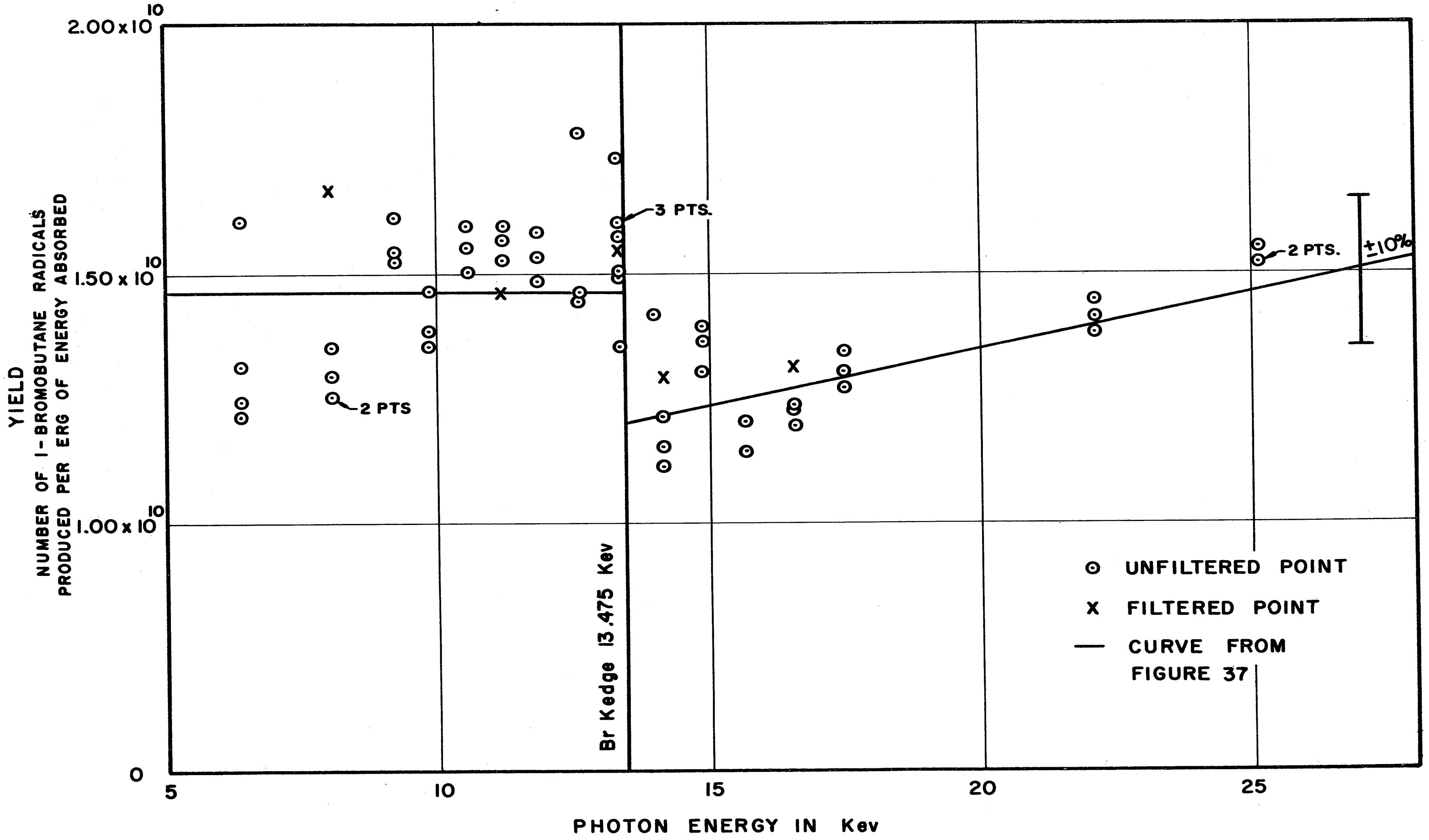

Figure 40. Free Radical Yield Produced in 1-Bromobutane as a Function of Photon Energy--Temperature Controlled During Irradiation.

unfiltered irradiations. Due to the lower dose rates attainable with filtered radiation those irradiation periods were always longer than the unfiltered irradiations by a factor of three or so. Although the x-ray tube is cooled by forced circulation, the recirculation system, fluorescence box and associated equipment have an appreciable heat capacity; consequently the entire system did not reach equilibrium for 30 minutes or so after the x-ray tube current was turned on. This period was of the same order of time as the unfiltered irradiations; thus the filtered irradiations were conducted usually at an appreciably higher temperature than most of the unfiltered irradiations.

The results of the earlier filtered irradiations are shown in Figure 41. For the final three series of the study the heat exchanger which cools the fluorescence box (and therefore determines the temperature of the sample) was connected to an external cold water supply. As a consequence all of the irradiations in the final test were conducted at room temperature ± 5°. The filtered results in the final test were undistinguishable from the unfiltered results as shown in Figure 40.

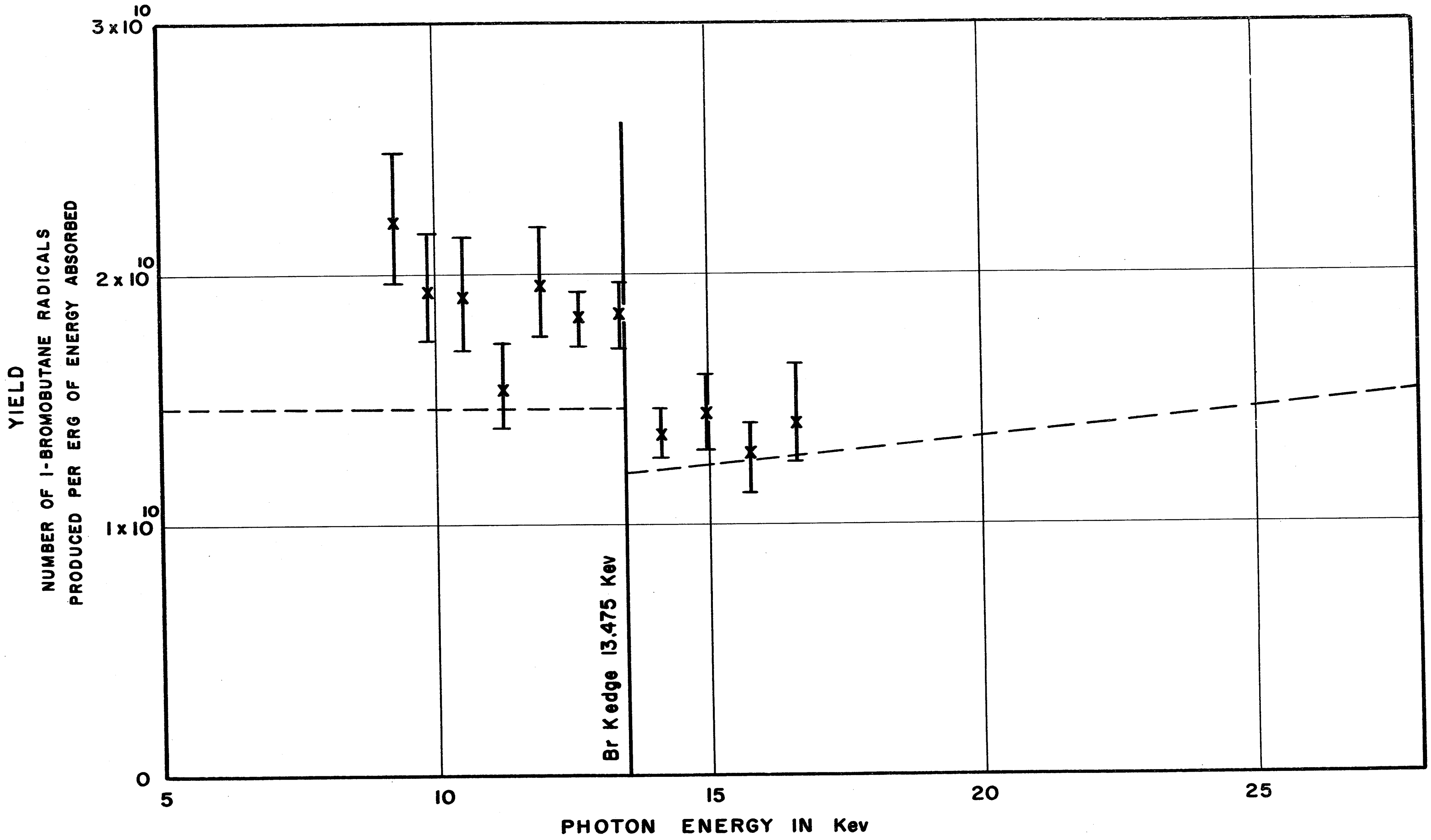

Figure 41. Yield vs Photon Energy-Filtered Data

C. Consideration of Errors

From the onset one of the objectives of the study was to obtain radiation-yield results with a relative accuracy of ± 20% or better in order to state with some confidence whether there was any dependence of the radical yield on photon energy. This accuracy goal was set as a sufficiently narrow limit to detect readily changes in yield of the order of magnitude which were observed by Garsou and Emmons(3,1). On the other hand such a limit was sufficiently large that the rather considerable problems of point by point dosimetry for differing photon energies, and the problems of obtaining reproducible radiation yields from a chemical system which was altered less than 1 part per million, could be realistically confined to the limits set. It would appear from the analysis to follow that these objectives have been met.

Experimental errors were divided into two groups depending on whether the errors arose from measurements of the source intensity or from measurements of the radiation yield. For the purpose of this analysis errors will be classified as systematic or random depending on the source. Systematic errors will include all errors which would tend to introduce a constant or known deviation into the data. Random errors will include statistical variations and errors arising from unknown sources. The former would include, for example, geometry errors and variations due to air and window absorption encountered in the calibration of the calorimeter. Errors of the latter type would include statistical errors in counting radiation and the spread in data caused by temperature variations in the earlier work which was completed before the effects of temperature on the radiation yield were recognized.

1. Errors in X-Ray Intensity Measurements

A detailed analysis of the errors incurred in the calibration of the radiation source is included in Reference (5); the major points only will be reviewed here.

Calorimeter Calibration. The systematic errors which were considered in the calibration of the calorimetric dosimeter included: (1) The errors related to the geometry of aligning the radiation beam and the receiver plate in order to effect total absorption of the radiation in the receiver plate of the calorimeter. (2) Possible errors in the calculation of the correction factors for x-ray absorption in the calorimeter window and in the heat shields between the radiator and the calorimeter. (3) Errors related to radiation scattered from, or fluorescence radiation leaving, the receiver plate should be small, but must be considered. (4) Errors related to the heater calibration of the calorimeter receiver include the measurement of actual power consumption of the heater exclusive of the leads and the loss of heat directly to the heater leads.

Random errors which occurred during the calibration of the calorimeter included: (1) The statistical fluctuations of the measurements of the heater calibration. (2) The statistical fluctuations of the measurement of the heating of the receiver plate by the x-ray beam. (3) An important part of the errors of (1) and (2) above were the errors incurred in determining the slope of $d\Omega/dt$ (the output signal of the thermistor was in the form of resistance which changed with the temperature of the receiver plate) from the recorder output. (4) Since no independent measurement of x-ray output intensity could be made during the calorimeter calibration any variations of output from the x-ray machine or changes in the fluorescence radiators which occurred during the calibration would appear as random errors.

The random errors associated with heater calibration were estimated by statistical analysis as ± 5% (standard deviation). The random errors from the x-ray power measurement were estimated by the same technique as ± 10%. The overall absolute errors associated with the calibration of the calorimeter were estimated as ± 20%.

The calibration of the calorimeter was checked by three other independent dosimetric methods. The general agreement of the four measurements reduced the possibility of a large systematic error considerably. The analysis of these measurements is discussed in detail in Reference (5).

2. Errors in the X-Ray Irradiations

The systematic errors related to the sample irradiation and yield determination have been divided into two groups: Those systematic errors which will be observed by the system in general and are independent of the photon energy used in the irradiation will be termed general errors. Those errors which will affect the relative yield of the sample due to possible energy dependence will be termed relative errors. Since the primary purpose of this study has been to determine the energy response of the irradiation system, relative errors are considerably more important than general errors.

Efficiency of DPPH as a Scavenger. A basic source of general systematic errors in the system studied is the efficiency of DPPH to count all radiation produced radicals (and nothing else). The primary results of the preliminary studies of the effects of dose rate and DPPH concentration on the reaction yield established conclusively that no variation of scavenging efficiency would occur as a function of the photon energy. The complete effectiveness of the scavenger to react with the radicals produced by radiation on an absolute basis is inferred by the fact that the yield is (effectively) independent of dose rate and DPPH concentration as predicted by theory(4). Previous work by Chapiro has confirmed the use of DPPH (with other similar organic materials but not specifically with 1-bromobutane) as a radical counter by comparison of yields with values obtained by polymerization initiation. Many of these values were also confirmed by yields obtained with other scavenger materials and by total decomposition yields(4,139). Since the use of DPPH in this study has been similar to its use in earlier studies and since similar characteristics and results have been obtained in this study the effectiveness of DPPH in this study is believed to be no different than experienced in earlier work by others in the field.

One possible exception to the conclusion above is the observed temperature sensitivity of the system studied. Temperature effects were restricted sufficiently so that satisfactory relative yields with energy could be obtained; no critical evaluations of the effects of temperature on the absolute yield of the reaction were made as this information was not felt to be of direct interest to the original purpose of the work.

Radical Yield vs. Decomposition Yield. The exact relationship between the radical yield reported here (really the radical pair yield since the expenditure of two DPPH radicals per 1-bromobutane molecule initially disrupted was assumed) and the decomposition yields reported by Wilcox(71) is not known. Since the experimental value obtained here with cobalt radiation compares favorably with the value obtained by Wilcox based on decomposition (3.7 compared to 3.6) it would appear that the radical yield as determined by DPPH is equal to the total decomposition of the compound.

Other General Errors. The effects of the absorption coefficient of DPPH reaction products for the 520 millimicron wavelength light used to measure DPPH concentration were discussed in Section I D. Errors due to the absorptivity of DPPH products will affect the absolute yield but should not affect the relative yield as a function of energy. No special effort was made to determine this factor accurately; a rough estimate from several samples verified the results obtained by Chapiro(149).

Other general systematic errors which might occur are due to geometric measurements and the possible effects of impurities (particularly air). Measurements of the cell volume and geometrical alignment of the cell with the radiation beam should be better than 3%. The effect of impurities was not studied extensively. It is believed that some of the random variations of the study are probably due to impurities. The effectiveness of small quantities of impurities is enhanced since such small concentrations of scavenger and radiation products are present in the sample. This possibility was suggested by Wilcox following his work with butyl bromides(71), although he found no gross effects of oxygen or the impurities contained in the Eastman White Label product as-received on the yields of samples subjected to gross radiation damage. It would appear that no significant systematic errors were caused by impurities.

Random Errors. The random errors which contributed to the variations in yield include the following: (1) Measurements of the original and final optical density of the sample. (2) Measurements of the sample volume. (3) The reproducibility of sample placement. (4) The effects of temperature in the earlier study, before temperature control was initiated and (5) Variations in the yields due to unknown causes.

(1) Optical Density Measurements

Measurements of sample optical density were quite accurate, particularly in view of the small volumes of sample which were used. Table III lists the observed optical densities for the control solution during a particular run. The percentage deviation (standard deviation) of 0.44% is small; however, the actual error which is introduced by the difference of the initial and final OD measurements is dependent on the magnitude of the change in OD as follows:

$$OD_1 = A_1 \pm S_1$$

$$OD_2 = A_2 \pm S_2$$

Experience has shown that S/A, the percentage standard deviation (for a finite number of samples), is constant for OD measurements between 0.500 and 1.600 (which includes most of the measurements made in this study). Below 0.500 S is a constant and S/A increases.

The worst errors then would arise for the smaller percentage changes in OD. The smallest $\Delta\ OD/OD_1$ used in the study were greater than 30%.

Then $$\Delta\ OD = OD_1 - OD_2 = A_1 \pm S_1 - A_2 \mp S_2 .$$

TABLE III

STATISTICAL VARIATION OF THE OPTICAL DENSITY MEASUREMENT OF SEVEN CONTROL SAMPLES

Optical Density	Square of Variance
1.568	4×10^{-6}
1.573	9×10^{-6}
1.570	0
1.565	25×10^{-6}
1.570	0
1.567	9×10^{-6}
1.575	25×10^{-6}

Average value 1.570

$$\text{Variance S} = \sqrt{\frac{\Sigma(X-\bar{X})^2}{6}} = 3.46 \times 10^{-3}$$

$$\text{Fractional Error} = \frac{3.46 \times 10^{-3}}{1.570} = 0.22\%$$

Since only a limited number of samples were considered, the variance of the finite number of samples will differ statistically from the standard deviation of the sample universe. The standard deviation is obtained from the variance by using the t distribution(513). Based on a 90% confidence level and 6 degrees of freedom (number of samples - 1) $t_{.90}(6) = 2.01$. Therefore the average percentage error (90% confidence) for an optical density measurement is ± 0.44%. This analysis assumes that the sampling errors are distributed normally.

TABLE IV

STATISTICAL VARIATION OF ENTIRE OPTICAL DENSITY MEASUREMENT PROCEDURE

Sample Weight (μgm)/cc.	Optical Density		Square of Percentage Error ($\times 10^6$)
	measured	calculated*	
53.8	1.625	1.602	206
33.325	0.996	0.993	16
27.5	0.822	0.818	24
39.4	1.179	1.172	35.5
50.9	1.512	1.516	7
34.04	1.004	1.013	79
17.0	0.509	0.506	35.5
131.2	3.894	3.918	37.8
531.0	15.68	15.80	58

$$\text{Variance S} = \sqrt{\frac{500}{8}} = 7.9\text{x}10^{-3} = 0.79\% \quad t_{.90}(8)=1.86$$

Thus Error = ± 1.5%.

---

* Based on the straight line average of 33.6_{μ} gm/cc = 1.000 O. D.

Since the errors S_1 and S_2 are independent, the summation of errors is performed as the square root of the sum of the squares or

$$\Delta \text{ OD} = A_1 - A_2 \pm \sqrt{S_1^2 + S_2^2}$$

but

$$\frac{S_1}{A_1} \approx \frac{S_2}{A_2} \text{ and } A_2 = 0.7A. \quad \text{then } S_2 \approx 0.7S_1$$

$$\Delta \text{ OD} = 0.3A_1 \pm S_1 \sqrt{1+(0.7)^2} = 0.3A_1 \pm 1.225,$$

since

$$\frac{S_1}{A_1} = 0.44\%$$

the error of

$$\Delta \text{ OD} = \pm \frac{1.22S_1}{0.3A_1} = \pm \frac{1.22}{0.3} \times 0.44\%$$

$$= \pm 1.8\% \text{ (for 90\% confidence level).}$$

This error, although somewhat larger than desired, is sufficiently small so that compared to other errors the techniques are considered as adequate. Considerable improvement is achieved by allowing the DPPH concentration to decrease by 50%, as was done in many samples.

The error associated with the determination of the extinction coefficient of DPPH in 1-bromobutane was estimated. Table IV lists the results of 9 measurements of the OD produced by different DPPH concentrations. The percentage error (90% confidence level) of 1.5% will be a general systematic error since only the Δ OD values are used in calculating yields. This error includes the total contribution of errors in weighing, mixing, dilution and optical determination of DPPH dissolved in 1-bromobutane.

(2) Total Random Errors for Entire Irradiation Procedure

The statistical distribution of results of eight identical irradiations at a representative energy value are given in Figure 42. The

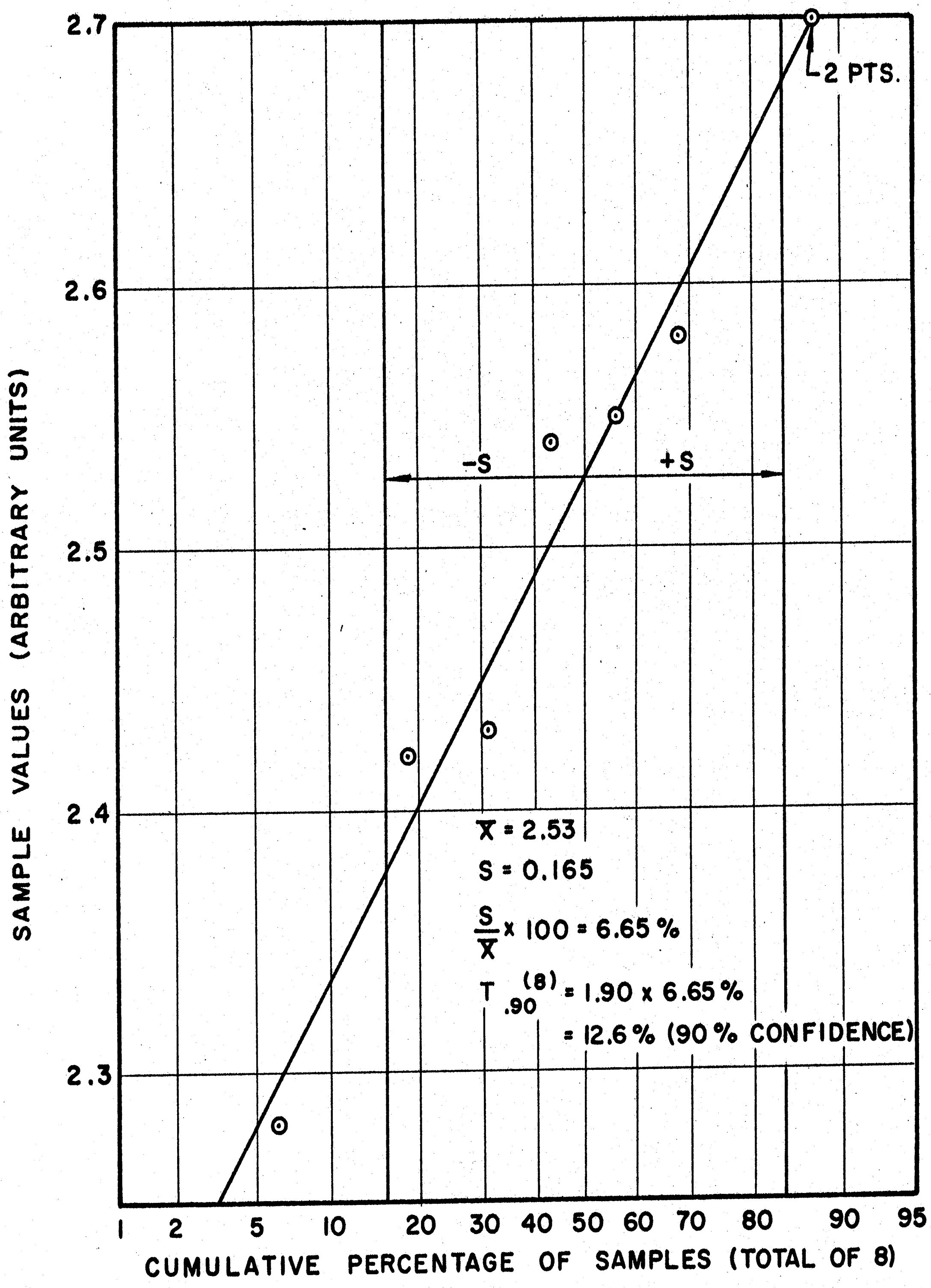

Figure 42. Data Reproducibility of Representative Raw Data Values from X-Irradiation Run

yield (in arbitrary units) is plotted versus the cumulative percentage of samples on normal distribution probability paper. The relatively good adherence of the data points to a straight line distribution indicates that the data are probably distributed normally. These data were taken before temperature control was initiated and were used to determine the variance for computation of the confidence limits of all the data points shown in Figure 37. This error analysis represents the total of all the random errors; thus the confidence intervals (90% confidence limit) for each energy point is given as $\pm t_{.90}(8)\frac{S}{\sqrt{N}}$ and is shown for each energy value in Figure 37.

Examination of Agreement of Final Data. An examination of the data in Figures 37 and 40 point by point shows good agreement among the data with the line of constant yield within statistical variation for all but a few points. The values for 6.4 Kev (iron radiator) and 8.05 Kev (copper radiator) in Figure 40 appear to be at variance with the values for the same energies in Figure 37. The exact cause of this variation could not be determined. The deviation of these points from the line of constant yield was not believed to be significant because: (1) The possibility of an error in the calibration of the source intensity is highest for the low energy region since the largest corrections in the calorimeter data (for window absorption, etc.) were made in this region. If the actual source intensity were lower by 10-20% (i.e., in agreement with the R-meter and Fricke dosimeter values in Figure 19) the agreement of these points (and those of iron and copper in Figure 37) would be in satisfactory agreement with the line of constant yield. (2) If the source intensity is correct as it stands, the average value for the iron and copper points from both Figures 37 and 40 will not deviate significantly from the constant yield line.

The yield values for ytterium K_α radiation (14.957 Kev) were consistently high in all of the runs. Additional samples were run, the fluorescence spectrum of ytterium was re-examined for contaminants and the source intensity from this radiator was rechecked. No explanation for the deviation of the yield values from the constant yield line could be found.

In view of the general agreement of all other points with a constant yield value, the deviation of this one point is not believed to be significant.

The difference in G value yield for the x-ray studies (2.8) and the yield for the cobalt studies (3.7) is not large (30%). It is felt that no significance should be attached to the difference unless yield values could be obtained for some of the intermediate energies between the two current measurements (6-27 Kev and 1.25 Mev, respectively).

IV CONCLUSIONS AND DISCUSSION

Summary of Results

Purified 1-bromobutane was irradiated with monochromatic x-rays of differing photon energies and the free radical yield was determined for each energy. About 250 different samples were irradiated during the study. At least 8 irradiations were made at each of 16 photon energies (6-27 Kev) in the region of the K absorption edge of bromine (13.475 Kev). The radiation source used was the characteristic K_α and K_β fluorescence radiation obtained by exciting different radiator elements.

Most of the irradiations were made using unfiltered K_α and K_β radiation. The K_β intensity in the mixed beam is low (about 16% of the total beam intensity. In order to evaluate the possible effects of the K_β contamination of the radiation beam, filter elements were used to selectively attenuate the K_β radiation to 5% or less of the total beam intensity for certain irradiations. Within experimental error no differences in free radical yield were observed between the filtered and unfiltered irradiations.

The yield per unit of energy absorbed was found to be independent of energy within ± 10% for all photon energies used in the study. These results are shown in Figure 38.

Conclusions

Within experimental error, the free radical yield of 1-bromobutane per unit of energy absorbed is independent of energy for the 16 K emission energies used in this study.

This result is in contrast to the results of Emmons(1) and Garsou(3) who found regions of high radiation yield (resonances) for photon energies slightly greater than the K absorption edge energy of target atoms in the molecular system irradiated.

The absence of photon energy dependence of the radiation yield of 1-bromobutane observed in the present study is consistent with the conclusions of the analysis of radiation effects presented in Section I D.

Discussion

The radiation effects yield produced in 1-bromobutane by the low energy x-rays used in the present study as measured by the free-radical-pair yield is close to the decomposition yield measured by Wilcox(71) using cobalt γ-rays with much higher photon energies.

The results of the present study are in agreement with the results of a concurrent study by Atkins(2) of the energy dependence of release of mercury from an organic mercury compound irradiated with monochromatic x-radiation.

The author is unable to reconcile the differences in results between the present study and the earlier studies by Garsou and Emmons. While the irradiation and dosimetric techniques used in the earlier studies were not identical to the present study, no differences in techniques were found which would explain the differences in results.

Both Emmons and Garsou were unable to devise a satisfactory model to explain the resonance effects which they observed for certain photon energies. No previous radiation effects studies using monochromatic radiation were found in the literature. Thus there is no other experimental evidence to support or discount the existence of these resonance effects.

The present study was carried out with the hope of learning more about the resonance effects observed in the earlier studies. The present system was chosen to be similar to, but less complex than, the alkyl halide-dye system studied by Garsou and the catalase system studied by Emmons.

The 1-bromobutane-DPPH system is similar to the systems studied by Garsou and Emmons since in each case the target molecule contains a high atomic-number target atom which is surrounded by low atomic-number atoms. The major differences between the present study and the previous studies are believed to be:

(1) The compounds used by Garsou and Emmons contained molecules which were considerably larger and more complex than 1-bromobutane.

(2) The detection methods used by Garsou and Emmons for determining the quantity of radiation effects produced were different from the method used in the present study.

The failure of the present study to show the resonance effects does not contradict the results obtained by Garsou and Emmons. If the existence of resonance effects can be verified, further investigations should be initiated to determine the specific characteristics of a molecular system which will display resonance effects.

Suggestions for Future Studies

Future studies with monochromatic x-radiation using the same irradiation and dosimetric techniques developed in this study to investigate other compounds would certainly be of interest. It is hoped that the work of Emmons and Garsou can be repeated using the same techniques.

Two particularly interesting materials for further study would be a high molecular weight mono-bromo-substituted paraffin (such as 1-bromoctadecane) and a tetra-organic-metal compound (such as tetraethylgermanium). These materials are similar to the one already studied and are also similar to the materials studied by Emmons and Garsou.

APPENDIX A

SAMPLE CALCULATIONS AND IRRADIATION PROCEDURES

A. Sample Calculations for X-Irradiations

Typical Information from data book:

Sample #	500	Final OD	0.993
Radiator	Nb K_α and K_β	ΔOD	0.527
Filter	none	Volume	0.41cc
Time	20 min	Observed Count Rate	7936 cps
Initial Optical Density	1.520	Transmitted Count Rate	89 cps

Calculation of Incident Dose Rate

1) Actual Count Rate

Observed count rate X coincidence correction factor = actual count rate

7936 X 1.015 (correction factor for 8,000 cps) = 8,090 cps

2) Incident Dose Rate

$$\text{Actual Count Rate} \times \left[\begin{array}{c}\text{correction factor obtained}\\ \text{by calibrating SPG-1 counter}\\ \text{with \#1 pinhole}\\ \text{against the calorimeter}\end{array}\right] \times \begin{array}{c}\text{air}\\ \text{absorption}\\ \text{factor}\end{array}$$

$$\times \text{ window absorption factor} = \text{incident dose rate}$$

$$8090 \text{ cps} \times \frac{2.80 \times 10^4 \text{ ergs/min}}{9830 \text{ cps}} \times 1.015 \times 1.00 = 2.33 \times 10^4 \text{ ergs/min}$$

3) Absorbed Dose Rate

$$\text{Incident dose rate} \times \left(\begin{array}{c}\text{fraction of incident dose}\\ \text{absorbed in the sample}\end{array}\right) = \text{absorbed dose rate}$$

$$2.33 \times 10^4 \text{ ergs/min} \times \frac{7936 - 89}{7936} = 2.31 \times 10^4 \text{ ergs/min}$$

4) Yield

$$\frac{\text{Change in optical density}}{\text{time}} \times \begin{matrix}\text{Volume}\\ \text{of sample}\end{matrix} \times \frac{\begin{matrix}\text{number of DPPH}\\ \text{molecules/cc}\end{matrix}}{\text{optical density}} \times 2$$

$$= \frac{\text{number of radical pairs produced}}{\text{time}}$$

$$\frac{0.527}{20 \text{ min}} \times 0.41\text{cc} \times \frac{2.56 \times 10^{16} \text{ free radical pairs/cc}}{}$$

$$= 2.77 \times 10^{14} \text{ free radical pairs per min}$$

5) Yield/Absorbed Dose

$$\frac{2.77 \times 10^{14}}{2.31 \times 10^{4}} = 1.20 \times 10^{10} \text{ free radical pairs produced/erg absorbed}$$

B. Sample Calculations for Cobalt γ-Irradiations

Typical data from data book:

Sample #	Dose Rate	Time	Volume	Initial OD	Final OD	ΔOD
101	250 r/min	10 min	2cc	0.509	0.245	0.264

1) Yield - Calculated as Before

$$\frac{0.264}{10} \times 2\text{cc} \times \frac{2.56 \times 10^{16} \text{ 1cc}}{\text{1 OD unit}} = 1.35 \times 10^{15}/\text{min.}$$

2) Absorbed Dose

$$\text{Dose rate in rep} \times \frac{83.8 \text{ erg/gm}}{1 \text{ rep}} \text{ dose absorbed in air } \times$$

$$\frac{\left\{\begin{matrix}\text{energy absorption coefficient} \\ \text{of 1-bromobutane}\end{matrix}\right\}}{\left\{\begin{matrix}\text{energy absorption coefficient} \\ \text{for air (for 1.25 Mev } \gamma\text{-ray)}\end{matrix}\right\}} \times \text{Volume} \times \begin{matrix}\text{density} \\ \text{of 1-bromotuane}\end{matrix} = \begin{matrix}\text{absorbed} \\ \text{dose rate}\end{matrix}$$

$$250 \text{ r/min} \times \frac{83.8}{1} \times 1.05 \times 1.299 \text{ gm/cc} \times 2\text{cc} = 5.70 \times 10^4 \text{ erg/min}$$

3) Yield/Absorbed Dose

$$\frac{1.35 \times 10^{15} \text{ free radical pairs produced/min}}{5.70 \times 10^4 \text{ erg absorbed/ min}}$$

$$= \frac{2.37 \text{ free radical pairs produced}}{\text{erg absorbed}}$$

C. Irradiation Check List

1) On first run each day and after every four or five runs take a 100 second count of the radioactive standard.

2) With the x-ray machine set at 50 kv and 50 ma, take a standard count of the radiator intensity with the radiator and standard pinhole # 1 in place.

3) If a filter is to be used, also count the filtered intensity. For good statistics, the total number of counts should be at least 5,000. If 10 seconds will result in insufficient counts, use a 100 second count period. Also note that a count of greater than 15,000 per second will required an excessive coincidence

correction and should be avoided. In this case take a count at both 10 and 50 ma. The filter spacer should be used when no filter is indicated.

4) Insert the sample and then remove the standard pinhole. Insert the #2 pinhole.

5) Reset the clock and simultaneously push in the radiator box and start the timer.

6) Take a 10-second count of the transmitted counts and then set the scaler to 100 seconds for a 15-minute run or to 200 seconds for a longer run.

7) When the irradiation has been completed repeat the above steps in reverse, i.e., take a filtered count, unfiltered count, and, if necessary, a 10 ma count.

D. Irradiation Cell Loading and Unloading Technique

NOTE: The following procedures may seem somewhat lengthy and cumbersome and some of the steps may be unnecessary but so far they have yielded good results and thus are probably worth continuing. Four small (0.25, 0.5 and 1 cc) hypodermic syringes and two polyethylene squeeze bottles were used for convenience and to avoid contamination of the sample.

1) The pure 1-bromobutane (BB) solution will be called the blank, the unirradiated BB solution with DPPH added, the control and the irradiated solution the sample. Exercise extreme caution at all times to avoid contamination of the control solution. Whenever some control solution must be removed from its container always use the proper syringe and keep it in a clean place so that it cannot get dirty. Due to the high sensitivity of DPPH, extremely small additions of contaminants (ethyl alcohol for example) can react with the DPPH in a control solution.

2) At all times the Beckman cells should be loaded and read in the following order: blank, new control, sample, sample. The evaporation rate is low enough that the blank can be left undisturbed for several hours. More blank should be added as necessary.

3) Load the irradiation cell as follows. Take the fill syringe with a coarse needle and insert into the control bottle. Withdraw about 400 to 500 lambda of solution. Add about 100 lambda of the control solution to #2 Beckman cell, remove the needle and insert the remainder of the solution into the irradiation cell, swishing it in and out several times in order to wash the cell thoroughly; suck out the wash solution and flush it into the reprocess drain. Again fill the fill syringe to at least 500-600 lambda and again fill the irradiation cell. Care will be needed to avoid a large bubble remaining in the cell. By holding the cell at an inclining angle most of the air can be forced out of the upper needle while the solution is being inserted into the other needle. After the cell is filled and some liquid is visible in the exit needle reverse the incline so that any air bubbles remaining will float up to the inlet needle. Suck out a small amount of solution in order to void the cell of air, yet not enough to suck air through the other needle. This step may need to be repeated several times until all of the air is exhausted from the cell. The final step should always be to force more solution into the inlet needle until some is forced out the exit needle indicating a positive pressure in the cell. All of this is necessary to ensure that the cell is always full since the Mylar windows can expand or contract depending on the pressure in the cell. The cell can then be placed in the "irradiate" position.

4) After irradiation the volume of solution contained in the cell must be determined. The <u>measure</u> syringe is used to exhaust the cell. Be sure that all of the solution is evacuated from the cell. Next measure carefully the volume by means of the graduations on the syringe after pushing the plunger up until the liquid level is even with the top of the syringe.

5) Put a clean needle on the <u>measure</u> syringe and insert about 100-150 lambda of sample solution into cells 3 and 4. Enough sample should remain to run one more Beckman test if the first two values do not agree.

6) The Beckman measurement techniques are similar to other Beckman measurements except that more care will be needed in order to get good results due to the use of the small cells.

7) The optical density of the cells should be measured at 520 millimicrons with a slit width of less than 0.1 mm.

8) After reading, the cells and measure syringe must be thoroughly cleaned as follows: exhaust the control and sample solutions from the cells with the <u>drain</u> syringe, flush the cells with the BB from the squeeze bottle, exhaust the last remaining liquid with the <u>pure</u> syringe and dry the cells with air from the empty squeeze bottle. The syringe should be emptied into the drain and pure BB from the beaker swished in and out several times. Disconnect the needle and wash it out, then dry both needle and syringe with the <u>dry</u> squeeze bottle.

9) The cells should always be stored in the Beckman while not in use, and the syringe and needles can be left on the table (needles can be rotated to ensure that the one to be used will be absolutely dry).

APPENDIX B

STUDIES WITH THE METHYL BROMIDE IONIZATION CHAMBER

The importance of ionization chamber measurements and the significance of w, the average energy required to produce one ion pair were discussed in Section I D.

A short study of the w value for methyl bromide determined as a function of the photon energy of a monochromatic beam of x-rays was initiated for two reasons: (1) Very little information is available regarding the dependence of w on photon energy for molecular gases. Current theories(214) and available data indicate that w should be independent of energy. Some early work was done with methyl bromide,(19,22) however only a few photon energies were studied and the x-ray beam was not monochromatic (direct-beam radiation with filtration to remove the K_β and short energy continuous spectra was used).(19) (2) Since methyl bromide is similar to butyl bromide it seemed desirable to use the methyl bromide ionization chamber as a secondary dosimeter by assuming the value of w was independent of energy; thus, the energy content of the beam could be determined by the ionization current produced by the absorption of the radiation beam in methyl bromide. Extreme precision was not demanded in this test series since the purpose of the test was to obtain order-of-magnitude checks of the values obtained in the main study.

The chamber used in this study was a rectangular box measuring 5 x 5 x 7.5 cm. and constructed of lucite. The ends were covered with $\frac{1}{2}$ mil Mylar sheet for maximum x-ray transmission. The methyl bromide gas was introduced through a small tube in the side of the chamber and was ejected at the opposite end of the chamber on the other side from the entrance. The conductive surfaces were made by application of a thin layer of collodial carbon (applied as a suspension in an organic solvent and cement - General Cement Mfg. Co. Television Tube Coat No. 49-2) with suitable leads painted to the outer surface where electrical contact was made with copper wires. The outer surface of the chamber was coated with carbon and grounded to provide shielding to avoid stray capacitance effects.

The design of the chamber was modeled after designs of free air chambers as discussed in References [353] and [364]. The minimum radius of 2 cm. was designed to provide complete collection of the photoelectrons produced in the photoelectric absorption of the incident X-rays. The selection of 2 cm. was based on a parametric curve of percentage of electron loss versus chamber radius as a function of the maximum X-ray energy to be used as shown in Reference [353]. Less than 0.2% of the electrons will be lost with a minimum radius of 2 cm. for X-ray energies less than 60 Kev. The X-ray beam was masked down to a pencil beam with a lead sheet pierced with a pinhole. The entire radius of the chamber is effective for stopping electrons since the X-ray beam dimensions are small compared to the chamber dimensions.

The chamber and associated equipment were arranged as shown in Figure 43 . The battery power supply is shown in the foreground and the Hewlett Packard Model 425 A DC Micro Volt Ammeter which was used for current measurements is shown on the right. Saturation voltage was determined by increasing the chamber voltage until further increase produced no increase in current and was checked by testing for linearity of current with X-ray current input. Irradiations were all performed at 1 ma X-ray

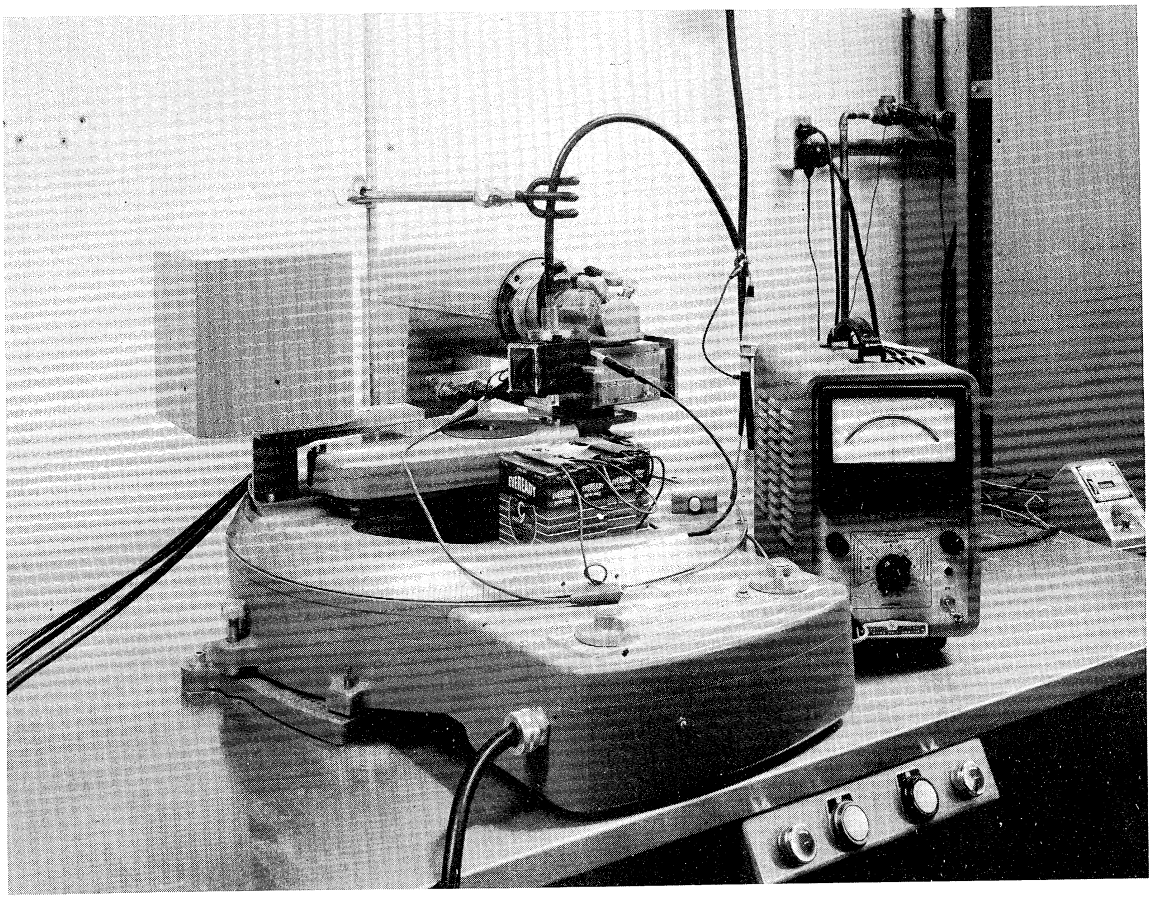

Figure 43. Ionization Chamber and Associated Equipment Used in the Methyl Bromide Studies.

tube current. Ionization current linearity was observed up to 10-20 ma. Saturation voltage was determined as 360 volts subject to the above requirements. The resulting voltage gradient of 90 volts per cm. is consistent with those used in earlier studies with methyl bromide (22,261).

Figure 44 gives the results obtained using fluorescence x-radiation as the source. The ordinate gives the number of ion pairs formed per 100 ev of energy absorbed in the sample (expressed as the G value). Similar results were obtained with the crystal spectrometer using the highest resolution alignment of the XRD-5 unit. Figure 44 is similar to Figure 37, in that the data are presented without corrections for reemission of radiation. The overall appearance of the data from the two curves is similar.

Correction of the data in Figure 45 for fluorescence radiation escape has been calculated in much the same manner as was done earlier (page 88).

The fraction of the energy initially absorbed which escapes is given as:

$$C = \frac{K\alpha_2}{K\alpha_1} \frac{f}{2} \left(\frac{\mu_1}{\mu_1 + \mu_2} \right) \left[(1 - e^{-(\mu_1+\mu_2)a})(1 + e^{-\mu_1 a}) \right]$$

In this case, since the chamber was not totally absorbing, the exponential terms also contribute to the final value of C.

From absorption measurements the thickness of the chamber was determined as

$$1.09 \times 10^{-2} \text{ gms/cm}^2 .$$

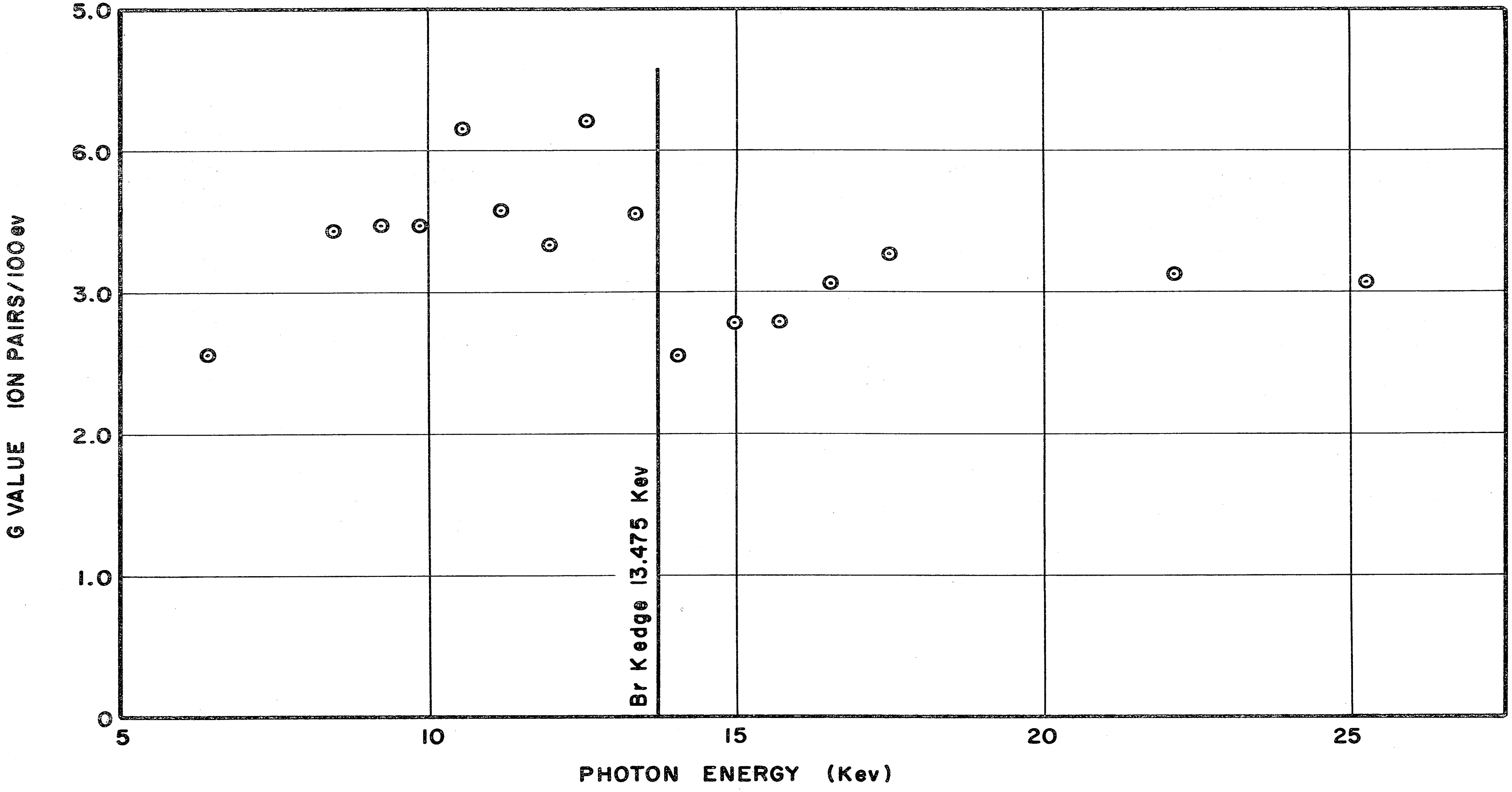

Figure 44. Ionization Yield of Methyl Bromide vs Photon Energy

Thus, using the previous values for

$$\frac{K\alpha_2}{K\alpha_1} \quad \frac{f}{2} \quad \frac{\mu 1}{\mu_1 + \mu_2}$$

$$C_{Sr} = 0.201 \left[(1 - e^{-(162)(.0109)}(1 + e^{-(138)(.0109)})\right] = 0.20$$

similarly

$$C_{Ag} = 0.15 \ .$$

The above approximation is not as good for the ionization chamber analysis as for the liquid cell, however this approximation should be satisfactory since a pencil beam was used and much of the fluorescent escape is probably still through the ends of the chamber. Other analyses of the radiation escape from a weekly absorbing chamber have been made in the literature(18,261,264). The assumptions which are used in the literature studies are not any more applicable to the present case than the analysis just performed, thus no attempts were made to compare the different methods.

Figure shows the final data corrected for total energy absorption. The constant yield as shown gives a G value of 3.6 which is independent of energy of photons of energies between 6.4 and 25.3 Kev. This G value corresponds to a value of w equal to 27.8 ev per ion pair. This value of w agrees well with the previous value of 28.7 obtained by Gaertner(22) for continuous X-rays with an average photon energy of 9 Kev.

The results of this test indicate that the value of w remains constant over the range of energies studied. As a consequence of the

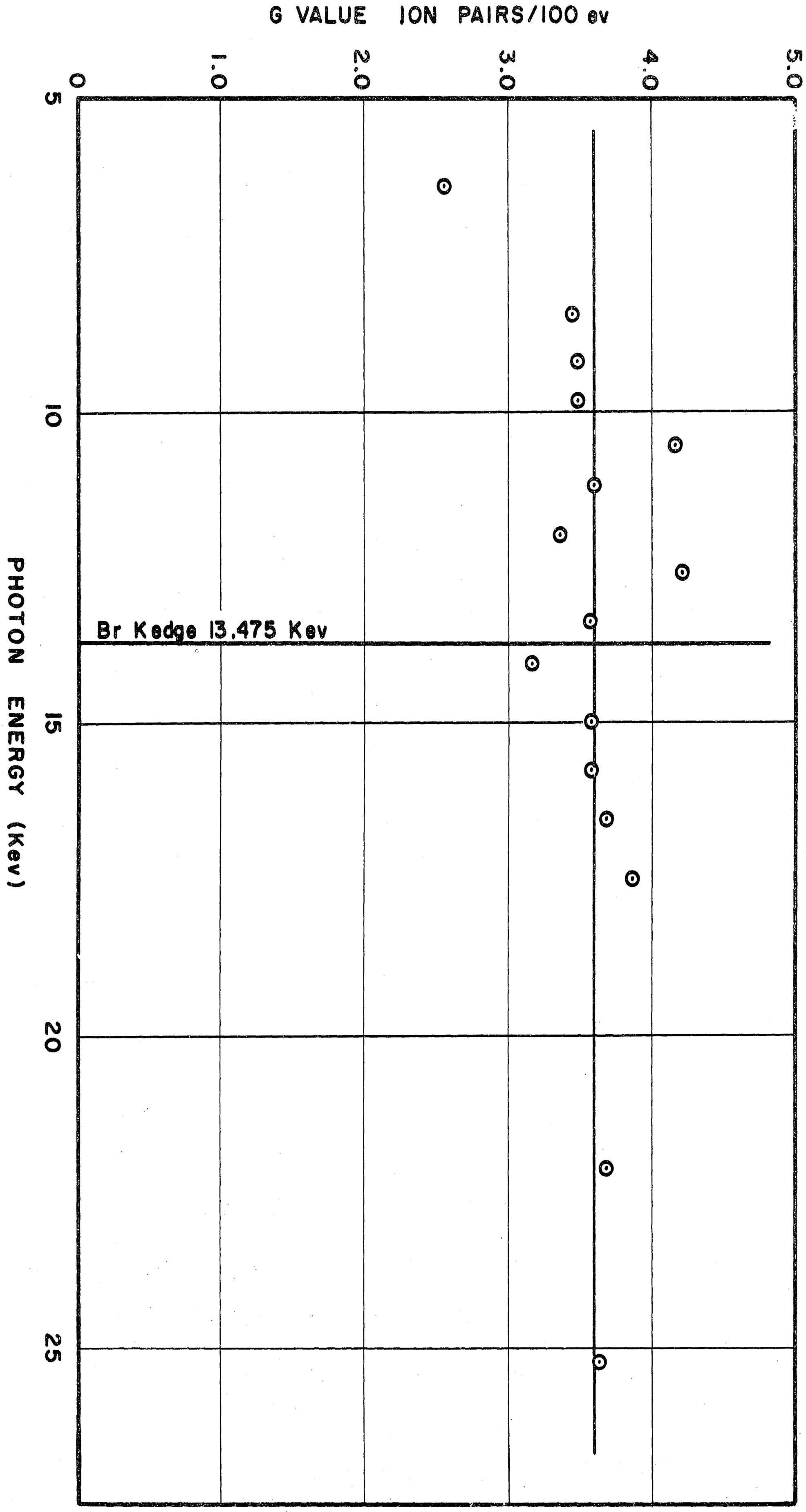

Figure 45. Ionization Yield of Methyl Bromide vs Photon Energy (Corrected for Fluorescence Escape)

constancy of w the quantity of energy initially absorbed to produce excited states in the molecules will also have to remain constant with photon energy. It would appear that if 1-bromobutane reacts in a manner similar to methyl bromide the relative yield of ionized species formed initially compared to the yield of excited species formed initially would have to be a constant and independent of energy. The occurrance of energy dependent reactions would then depend on the formation of different ionized and/or excited species for different photon energies which were more or less stable than those species formed at other energies. No such mechanisms were found in the literature. Thus the constancy of w would seem to eliminate the possibility of a shift of energy absorption in either ionized states or excited states to the other form as a function of energy. The presence of species initially formed from the radiation reaction which were composed predominately of one or the other of the possible states for certain photon energies might well produce final radiation effects which would thus be dependent on the photon energy.

Numerous experiments have shown that w for air is independent of energy but no such data could be found in the literature for methyl bromide (or any other poly-atomic compound). In particular no observations with monochromatic radiation are believed to exist. Thus the present work would tend to confirm existing theory that w should be independent of energy even for poly-atomic materials.

APPENDIX C

SUMMARY OF WORK ON CHEMILUMINESCENT SYSTEMS FOR RADIATION EFFECTS STUDIES

The initial effort of this study was directed toward producing a chemiluminescent detector for determining the quantity of radiation products being produced in an alkyl halide by the absorption of monochromatic x-radiation. It was hoped that the chemiluminescing solution would emit photons due to the reaction between the active luminescing agent and the free radicals produced by irradiation of the alkyl halide, or that the excited states of the alkyl halide produced by the degraded radiation would produce luminescence by energy transfer to the active luminescing agent. The luminescence of the solution would provide a convenient indication of radiation yield and the arrangement of radiation source and detection system could be made to permit continuous measurement of the effect. Thus, the use of such a system with a crystal spectrometer would produce a continuous record of radiation effect versus photon energy.

Three different chemiluminescent agents were used, but no detectable luminescence produced by irradiation was observed with direct beam intensities (50 milliamperes at 50 kilovolt tube potential).

Since this work was only a preliminary study, the data obtained were mostly qualitative; however, it is felt that some of the information might be of use in future studies.

Three chemiluminescent agents were used in the study: (1) luminol (3-aminophthalhydrazide, purchased from Eastman Kodak as #3606); (2) luzigenin (N,N dimethyldiacrylium nitrate, prepared according to the method of Decker,(471) and later purchased from Light's, Colnbrook, Bucks, England in somewhat impure form) and (3) siloxene $(Si_6H_6O_3)_n$ prepared according to the method described by Kenny and Kurtz (469).

The basic reaction mechanisms of these materials are not completely known. Considerable study has been made of the reaction mechanism of luminol(467,472). Luminol and luzigenin will chemiluminesce only in alkaline solutions while siloxene requires slightly acidic solutions. The literature references generally state that oxidizing agents are required for the reaction although some of the references indicate that oxygen (usually in the form of perozide) is specifically required. Siloxene is known to react with many strong oxidizing agents (including chromic acid, potassium permanganate, nitric acid, ceric solutions, and per-compounds. Siloxene was observed to glow dimly (even in the solid state) when air was admitted into the container. No specific references to reactions with free radicals or ionic states (such as Br^+) were found in the literature. Alkyl halides have been observed to quench some of the luminol reactions.

An interesting property of all three agents which has been observed previously for I and III is the ability of the chemiluminescing agent to transfer its energy to other fluorescent materials which can emit their own characteristic fluorescence. The brightest reaction of I was observed in the reaction originally proposed by Geiduschek(468) which involved the oxidation of I by dissolved oxygen in a strongly alkaline solution of KOH in dimethyl sulfoxide. Additions of fluorescein to the blue-glowing solution produced orange to yellow light. A similar reaction was observed with fluorescein added to a chemiluminescing reaction of III. Blue, yellow, and red light were produced by additions of anthracene, fluorescein, and neutral red dye to a solution of II dissolved in a slightly alkaline, acetone-water solution to which dilute hydrogen peroxide was added. These phenomena would tend to indicate that the species producing the energy for chemiluminescence are not necessarily the same species which luminesce, i.e., excitation energy can be transferred to other species which can luminesce.

After the preliminary work of optimizing pH and concentrations was completed to determine whether the agents would luminesce they were exposed to X-radiation in various states (dry, dissolved in organic solvents and suspended in water, with and without additions of acid, base or catalyst as required). Observations for luminescence were made with a 1P21 phototube and with dark-adapted natural eyesight. Dark-adapted eyesight was as least as sensitive for these observations as the phototube. No luminescence was observed with II, but dim light was observed with I in aqueous solutions (apparently due to peroxide formation by the radiation) and III glowed dimly in air saturated solutions. The luminescence of air and the Mylar sheet used to support the solutions were dimly visible in the radiation beam.

Several target materials were each tested with the above mixture to determine whether any luminescence could be produced by the free radical and excited species produced by irradiation. The target materials used included KBr, $KBrO_3$, LiBr, CBr_4 and CBr_3H. None of the materials tested produced a significant amount of luminescence (compared to the blank solution which luminesced dimly in some cases). Since the most intense monochromatic radiation which could be obtained was less intense by several orders of magnitude than the radiation used in the preliminary study it cas concluded that none of the reactions studied would produce a satisfactory signal with monochromatic radiation. Further work was not attempted since the DPPH system appeared more feasible. It is felt, however, that more extensive and thorough study might produce some very interesting results with systems of this type.

One interesting by-product of this investigation was the observation that additions of DPPH to any of the three systems while luminescing did not quench the reaction. This result would seem to indicate that the reaction between DPPH and excited states (proposed by Griffith(307)) was not significant in these systems since any appreciable reaction with excited species would be expected to reduce the light emission of the reaction. Another implication of this result is that apparently the light-producing reaction does not involve free radical intermediates since DPPH did not quench the reaction. Previous studies(467,468,472) have all postulated the existence of free radical intermediates in the reaction. The observation of the capability of hydroquinone to quench luminol reactions indicates that the reaction may be more complex than originally postulated.

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NOTE: Some of the references included in this bibliography were not related directly to the experimental program outlined in this thesis. They are included, however, in the hope that they could be of use to future investigators. The organization of the bibliography is discussed in Section I-C (pages 5-23).