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ABSTRACT

A cooled liquid scintillation system with single-photon-resolution photomultiplier tubes was employed to increase the sensitivity of luminol-enhanced lyoluminescence (LL). The problems of reagent purity and mechanical mixing were studied. For the disaccharide trehalose, the lowest dose significantly different from background was at the 1.2-rad level for ^{60}Co gamma rays, with a relative standard deviation of 33 percent. The system suffers from poor reproducibility in the mixing of the disaccharide with the solvent, and recommendations are made for improvements. Detector compounds of different hydrogen content were studied for possible application in neutron dosimetry and for their ability to retard free-radical recombination. The results were not conclusive. Enhancement of the LL effect was accomplished by radiation sensitization of solutions of trehalose with irradiations between 30 and 300 krad to water. The disaccharide was then recrystallized from solution, along with associated radiolysis products and, in some instances, with separately added chemical dopants. Preliminary intercomparison of these doped sugars with untreated materials at doses of 1, 5, and 10 rads indicates that they give a better signal-to-background ratio than the untreated disaccharide. A promising reaction model was postulated which assumed a two-component exponential decay of light, multiplied by a first-order buildup term for the dissolving factor. The model seems to fit both the ordinary and luminol-enhanced LL glow-curves.

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*NRC-NAS Postdoctoral Research Associate, 1980-1982.

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1. INTRODUCTION

1.1 Brief Overview and Goals

There is a strong need to search for materials that exhibit phenomena that would be applicable to fast-neutron dosimetry. For accurate fast-neutron dosimetry, a dosimeter must respond over a range of nine decades in energy and, over this energy range, its response must parallel the fluence-to-dose-equivalent conversion factor (ICRP-71). An equally important property for a fast-neutron dosimeter is the capability of detecting a neutron absorbed dose in mixed radiation fields having gamma-ray-to-neutron-dose ratios greater than ten. The dosimeter should also be able to detect a fast-neutron dose equivalent as small as $\sim$10 mrem and have good signal stability. Other considerations are that it should be non-toxic and cost effective for the nuclear industry.

There are no currently-available personnel neutron dosimeters that meet all of the above criteria, and specifically, there appear to be no effective neutron dosimeters for the energy range of 20 keV to 1 MeV.* Lyoluminescence dosimetry (LLD), however, may have the potential to meet many of the above criteria.

LLD is the evaluation of lyoluminescence in terms of absorbed dose to the material of interest. Lyoluminescence is the emission of light accompanying the dissolution in water of certain previously-irradiated solids. Examples of lyoluminescent materials are alkali halides (including LiF commonly used in thermoluminescence dosimetry) and saccharides. The energy dependence of the response of the saccharides is particularly attractive because saccharides are nearly tissue equivalent for both neutron and gamma radiation. The mechanism of light emission for alkali halides has been postulated as being both the recombination of hydrated electron-hole pairs and the recombination of trapped free radicals, both

*Robert Schwartz, National Bureau of Standards (private communications).

entities being radiation induced. The latter mechanism is also used to explain the response of saccharides. To improve the radiation sensitivity of saccharides, a sensitizer such as the chemiluminescent compound luminol is added to the solution. Upon dissolution of the irradiated solid saccharides, the luminol is oxidized by the radiation-induced free radicals that are trapped in the matrix of the solid.

The goal of this research is to improve the sensitivity and reproducibility of lyoluminescence by using different instrumentation, using purer reagents and sensitizing agents, and using new and doped phosphors. Also modeling for the light output vs time may help in evaluating future spectral and kinetic data.

1.2 Brief Summary of the Light Emission Process in Lyoluminescence

For a complete understanding of the mechanism of lyoluminescence (LL) it appears that more precise spectral and kinetic data are needed. The character of the observed light may depend on several competing mechanisms and on conditions of dissolution, type and nature of radiation dose and, of course, on the type of phosphor.

For alkali halides or other inorganic materials, LL is believed to be caused by electrons freed from F centers (Ah-66). It is postulated that dissolution in water results in the hydration of the electron-hole pairs created by radiation, and in turn these pairs recombine with the emission of light.

It has been shown (Lo-61) that in organic materials such as saccharides, trapped free radicals are involved in the LL process in a manner analogous to the reactions of the trapped electrons from the F centers in the alkali halides. According to Atari and Ettinger (At-73b) when solid saccharides are irradiated, some of the energy is stored in the form of stable free radicals. When the material is dissolved, the free radicals can react freely in the solvent. Possible reactions may

include recombinations of free radicals, reactions with dissolved oxygen, or reactions with the solvent resulting in the emission of luminescence. For example, Ettinger (Et-82a) has speculated on a reaction mechanism he labels the Russell-Vassiliev scheme. Once an alkyl radical has been generated by ionizing radiation the following is one of the reactions that take place:

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \ .$$

And out of many possible reactions,

$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow \text{non-radical products}$$

is one of a small minority during which light is emitted.

Other mechanisms for LL involve the generation of singlet oxygen or perhaps decomposition of hydroperoxide. Reactions that may compete with the ones mentioned above involve perhydroxyl ($HO_2^{\bullet}$) and superoxide anion ($O_2^{\bullet -}$) mechanisms. For details see Ettinger (Et-82a) and the references listed there. Mechanisms involving luminol have been discussed in the literature (Wh-63a, Wh-63b, Bo-75, Ma-73, Bo-68, Sc-76, He-70).

1.3 Radiometric Characteristics of Lyoluminescence Dosimeters

The materials whose LL response have been studied by various investigators are briefly summarized in Table 1 (pages 35 through 40). The dose range over which the response was studied as well as the range of linearity of dose and response are included whenever such information was provided. The gamma-ray energy dependence has been studied in only a few cases (Pu-77 and Et-77a).

It is not clear in most of the cases cited whether or not the low value of the range studied is a detection limit. For many of the studies cited, the dose rates were not specified. The LL response may be dose-

rate dependent, although Ettinger and his coworkers (Et-77a) found no dose-rate dependence for saccharides in the range of 3 rad/min to 18.5 krad/min.

It appears that the radiometric properties of LL dosimeters may be altered by the method of readout. Avotinsh and his coworkers (AV-81) have extended the linear range of LiF LL by using a rotating disc method and slow dissolution in sulfuric acid.

Although most of the studies on LL dosimetry have involved the use of gamma radiation (usually ^{60}Co or ^{137}Cs sources), it would appear that the most important use of LL would be in neutron personnel dosimetry. Ettinger et al. (Et-77a) have pointed out that saccharides, because of their atomic composition, approximate soft tissue for neutrons and mesons. Saccharides are somewhat deficient in hydrogen, however (a content of about 7% vs 10% for tissue), which may be of concern in the 100-eV to 10-MeV range. On the other hand, the amino acid valine, with a hydrogen content of 9.4 percent, may be very suitable for neutron dosimetry. Ideally, a suitable compound should have 10 percent hydrogen, be a solid that is not deliquescent and be soluble in water or other solvents to which sensitizers may be added. A compound that seems to meet all these requirements is diethyldithiocarbamic acid diethylammonium salt. The author has tried this compound in luminol solutions and unfortunately there was no response at a gamma-ray exposure level of 1 rad. Some aspects of sensitivity will be mentioned later.

Although amino acids appear to be less sensitive than saccharides, Ettinger's group has investigated the neutron response of valine relative to its ^{60}Co gamma-radiation response for 2.5-MeV, 7.5-MeV, and 14-MeV neutrons. They found a relative response of 0.8 in the 7.5- and 14-MeV range, and a relative response of 0.5 at 2.5 MeV. These data appear to be more reliable than the data by Ahnstrom and Ehrenstein (Ah-59) who observed that the neutron response of crystalline glucose relative to its ^{60}Co gamma response produced 5 to 7 times more luminescence.

Puite (Pu-77) studied the neutron response for mannose. He found that the LL per rad relative to ^{60}Co gamma rays was 0.24 for neutrons in a degraded fission spectrum, 0.45 for 5.3 MeV neutrons and 0.60 for 15 MeV neutrons. See also Si-76.

For a more complete discussion of energy dependence see the review articles by Ettinger and Puite (Et-82a, Pu-82) and the papers by Bartlett (Bar-81, Bar-80).

1.4 Factors Affecting Lyoluminescence Response

In conducting LL research or in using LL for practical dosimetry, attention must be given to controlling a number of factors which may affect the light output from the sample. Based on the available literature, a summary of these factors is given in Table 2 (page 41). The table includes only those factors associated with sample treatment and readout, and does not include dose, dose rate, energy or LET factors which must also be considered as for any dosimeter system. A brief discussion of the factors applicable to practical dosimetry listed in the table is given here. For details, the reader should consult the reference listed.

1.4.1 Solvent Factors. In studies on the alkali halides, Atari and Ettinger (At-73a, At-74a, At-57) used distilled water and TlCl solutions as solvents. Compared to water, the fluorescent TlCl solution enhanced the light yield 200 times for a 500-krad dose. The degree of enhancement decreased with decreasing dose, dropping off linearly from 10^3 krad down to 1 krad, and fading to zero enhancement below 1 rad.

Ettinger (Et-82b) has achieved LL enhancement from the amino acids glutamine, threoine and serine, in solutions containing Tb^{3+} ions at a pH of 2. The increases after phototube spectral-response corrections were 700, 330, and 245, respectively, for these amino acids. For saccharides, only glucose showed a slight enhancement using the above solu-

tions. Thwaites and co-workers (Th-76) indicate that, for irradiated amino acids, the light yield can be extended by using a solution of NaOH instead of distilled water. This enhancement is probably related to the pH of the solutions.

Laflin and Baugh (La-79) have observed LL in an aqueous solution of micelles containing diphenylisobenzofuran (DPBF) at a concentration of 10^{-5} mole/liter with an enhancement for irradiated carbohydrates of 10 as compared to pure water.

Some of the problems of reproducibility of LL may have been solved by Avotinsh and co-workers in the case of LiF (Av-81). They use a rotating disc made of a single crystal of LiF which, after irradiation, is dissolved in concentrated sulfuric acid. The dissolution time is very slow and is a function of angular velocity of the disc. In the Mrad range, after initial start up, the light output is constant in time.

The pH of the solvent affects the dose-response relationship by influencing the yields of reactive products that cause luminescence. Ettinger et al. (Et-77a) indicate that small variations in pH, not exceeding 0.2, do not change the yield by more than 1 to 2 percent. Atari and Ettinger (At-74a) showed that the slope of the dose-response curve is dependent on the pH of the trehalose dihydrate phosphor solution. In the studies on glucose by Ahnstrom and Ehrenstein (Ah-59) it was found that the intensity of luminescence was a function of the pH of the solution. These investigators found a twenty-fold increase in intensity after alkalinization of their aqueous solutions with NaOH. Similar results were reported by Buchan and Ettinger (Bu-75) who found that all the carbohydrates studied showed enhancement of light output in alkaline solutions. Glucose monohydrate was found to be the most sensitive to pH changes. There are also other earlier results reported by Klimentov (Kl-73) on solid polyhydroxy compounds (mannitol, saccharose, raffinose, etriol, xylitol) which confirm the above general trends with pH.

Ettinger (Et-82a) has concluded that due to significant lack of reproducibility with alkaline solvents, neutral or slightly acidic solutions should be used in practical LL dosimetry; also, that the selection of buffers should be done with care, for the gain in stabilization with respect to the influence of pH may be accompanied by a loss of sensitivity due to LL quenching by foreign ions and molecules introduced into the solvent. For pH profiles of LL and a more complete discussion, see Ettinger (Et-82a).

With respect to oxygen concentration in the solvent, Ettinger et al. (Et-77a) indicate in their studies with saccharides, that variations in the oxygen concentration close to the value of equilibrium with air have no observable effect on the light yield. In a related study, Atari and Ettinger (At-73b) compared the effect of oxygen or nitrogen dissolved in water with freshly-distilled water. They found that water saturated with nitrogen had a quenching effect in some cases but not in others, while water saturated with oxygen has an enhancing effect in some cases and a quenching effect in others. The details on material and radiation dose can be found in the references cited in Table 2.

The oxygen effect has also been studied by Baugh and Laflin (Ba-80). By using acetone and water solutions, they slowed down the dissolving processes, thereby keeping oxygen in equilibrium, and found that the abundance of oxygen determines the shape of the dose-response curve. Briefly summarizing their conclusions, it can be said that the primary alkyl radicals need sufficient amounts of oxygen in order to be converted to peroxy free radicals which are the ones that produce the light yield upon recombination at or near the solid-liquid interface during dissolution.

1.4.2 Sensitizer Factors. A number of investigators have shown that significant enhancement of light yield can be obtained through the use of sensitizers. Atari and Ettinger (At-74a, At-74b) sensitized their solutions using luminol (5-amino-2,3 dihydrophthalazine-1,4 dione) plus

Na_2CO_3 and chlorohemin dissolved in water. With this solution, they found an increase in the LL response by a factor of 10^6 for glucose and a factor of 20 for trehalose dihydrate. The author has found a luminol enhancement of trehalose dihydrate LL by a factor of 100 over pure buffer solution.

A major problem using luminol is the presence of self-glow or chemiluminescence associated with the dissolved oxygen and impurities such as ions of iron, cobalt and nickel. The self-glow increases sharply with the temperature. The author has found that purifying the luminol solutions with Chelex 100, a chelating resin, decreased the self-glow by 25 percent. Also, lowering the temperature from ambient to 6°C decreases the self-glow by a factor of 10.

Klimentov (Kl-73) has found a steady increase in light yield with dissolved oxygen in a luminol-solid polyhydroxy compound system, with a saturation value of approximately 2.3 mg/100 ml.

In considering the signal-to-"chemical noise" ratio, Chang and Patterson (Cha-80) have found halide ion enhancement of chemiluminescence of trace metal ion catalyzed by luminol oxidized by hydrogen peroxide. Their technique should be looked into in reference to improvement of luminol-enhanced LL, in order to determine whether the halides will act in conjunction with other impurities to worsen the system or perhaps will work alone to enhance the light output.

In another study Ettinger et al. (Et-77c) indicated that lucigenin (N,N-dimethyl-9, 9-biacridinium dinitrate) is a sensitizer with properties similar to luminol. They also found that the light yield is dependent on the concentration of the lucigenin, with the light enhancement increased by a factor of about 10^4 at a concentration of 10^{-8} mole/ml, but then decreased as the concentration was increased further. For details see reference (Et-82a).

Both lucigenin and luminol have the problem of self-glow and of decreasing LL reproducibility, which may indicate the need for a low-pH system for good reproducibility with sensitizer-enhanced LL. A chemiluminescence system using bis-(2,4,6-trichlorophenyl) oxalate (TCPO) has been evaluated by Williams et al. (Wi-76). This system can operate at a pH of 4 and should be investigated as an enhancement technique for LL.

Sensitization can also be achieved by the addition of certain impurities to the solution. Ahnstrom and Ehrenstein (Ah-59) found that light intensity could be increased by the addition of peroxides to the solutions, such as hydrogen peroxide, benzoylperoxide, or the ether dioxane. They observed a ten-fold increase in luminescence intensity by this method.

1.4.3 Sample Factors. In the study on alkali halides (At-75) the LL properties of different NaCl samples appear to depend on the origin of the samples. For six samples of NaCl of different origin, light yields differed by factors of up to five for a 100-rad dose. These differences were attributed to differing amounts of impurities and differing heat treatment histories. It was observed that pre-irradiation annealing (600°C for 5 hours) or crushing enhanced the response. A study of pre-irradiation annealing of NaCl showed that although higher temperatures improve sensitivity, they also result in increased fading of the luminescence.

Klimentov (Kl-73) has measured light output vs. annealing temperature for various solid polyhydroxy compounds. His curves, which are in terms of percent maximum light yield vs. the ratio of annealing temperature to the melting point of the hydroxy compound, show plateaus that rapidly decrease to zero light yield within 15 percent of some critical temperature ratio that is different for each compound used.

The response of monosaccharides has been found to remain stable for a period of seven months when the samples were stored at room temperature. Samples of trehalose heated to 80°C for two hours after irradiation dis-

played no change in light output, and heating to 60°C for 60 hours gave a decrease of only 18 percent (At-74b). On the other hand, in the amino acid study (Et-77b), valine, typical of the amino acid group, was found to have lost 20 percent of its response over a one-year period when stored in a desiccator at room temperature. Bartlett (Ba-79) has found that for the mannose-water system there is a loss of light yield of 10 percent for the first six hours; thereafter the decay is slower, the response decreasing from 90 to 60 percent of the initial response in the ensuing 240 days. These results were for doses around 4000 rad; however, Bartlett has found that there is an enhancement of the response upon storage for doses greater than the saturation dose (10^5 rads)--a fact that is of theoretical importance. Since there were no corresponding changes in electron spin resonance (ESR) absorption, Bartlett postulated that the local concentration of oxygen near the free radical sites in the irradiated mannose is a determining factor in the LL response.

Atari et al. (At-73a) have indicated that particle size is an important factor affecting LL output for NaCl. In their work, they controlled particle size by sieving, although the actual sizes they used are not indicated. Buchan and Ettinger (Bu-75) have shown a dependence of light yield on the particle size for LL of xylose in water. Samples studied ranged from about 50 to 350 μm in size, with light yields being greatest for the larger particles. Bartlett (Ba-79), however, using a mannose-water system, displays curves for two different particle sizes with median diameters of 68 and 120 μm which indicate that the smaller size produces higher photon yield. Kannan (Ka-79), who used a mannose-water system and covered a dose range of 4×10^2 to 7×10^4 rads, found improved reproducibility of LL output by using grain sizes from 75 to 180 μm and pre-irradiation annealing at 45°C. In this experiment there was no significant fading of the LL signal for mannose in 72 hours, but for a similar glucose-water system a 41-percent fading occurred in 25 hours. The mannose response faded by 13 percent after 213 hours.

Humidity is an important factor when the materials are hygroscopic. Atari and Ettinger (At-73b) found that samples of glucose, xylose, and mannose stored 16 hours in a relative humidity of 60 percent, lost 20 percent, 40 percent, and 50 percent, respectively, of their luminescence.

For most saccharides, exposure to daylight for 48 hours, or to a tungsten lamp, had no effect on the response (At-73b). For trehalose dihydrate, exposure to direct sunlight for a period of 5 hours produced a loss of 10 percent in light yield. Exposure to UV gave an increase in LL output for the saccharides (At-73b). A similar situation was observed by Ettinger et al. (Et-77b) for proteins and nucleic acids. When these materials were exposed to a broad spectrum of UV radiation in the range of 180 to 370 nm, the light emitted on dissolution was found to be proportional to the energy fluence of the UV. Proteins are also reported to be sensitive to the UV component of daylight. Bleaching by visible light was observed in pepsin but not in trypsin.

The temperature at which dissolution takes place is reported by Atari et al. (At-73b; Et-77a; Et-77c) to have a marked effect on the light yield. The decrease in yield is of the order of 2 to 4 percent per °C in the temperature range from 6°C to 60°C.

The fact that impurities in the sample can affect light emission during dissolution was considered by Atari and Ettinger (At-75). In their studies with alkali halides they found large differences in light yields due to the effect of impurities. They indicate that the most common impurities for the alkali halides are OH^-, Cu^+ and O_2^- ions. Of these, they found the Cu^+ ion to have the greatest effect, with light emission enhancement of more than one order of magnitude resulting from dissolving the NaCl powder in water containing a 10^{-4} M concentration of Cu^+. Klimentov (Kl-73) has measured various LL responses in the presence of free radical scavengers. The most notable results are that the hydroxy compounds-luminol system is unaffected by the presence of transition-metal salts (Cu^{+2}, Ni^{+2}, Fe^{+3}), whereas β-naphthol, hydro-

quinone, sodium iodide, sodium sulfite and sodium nitrite all reduce the light yield of the following compounds: etriol, pentaerythritol and xylitol.

In reference to impurities of sugars, the author was able to purchase from Baker Chemical Co. sucrose and lactose that had an order of magnitude less trace metal impurities than reagent-grade chemicals, and attempted a LL study coupling these with luminol passed through a chelating resin. These substances produced unaccountably high backgrounds for the low doses ($\sim$1 rad) that are of greatest interest. Takovar obtained a similar result for reducing sugars and pure water (see Et-82a). The most successful combination appears to be the non-reducing sugar trehalose and luminol, which can be read out at the 1-rad level. However, "trehalose ultrapure" is not available commercially.

1.5 Luminol Chemiluminescence Assays and the Application to Lyoluminescence

There are well-established procedures (Mc-73, Bo-75, Sh-77) to handle the luminol-generated chemiluminescence assays of trace metals (Co(II), Cu(II), Fe(II)) and of compounds such as hemin and vitamin B_{12} containing iron and cobalt, respectively, as the central atoms. Trace analysis using the metal-luminol system is based on the metal ions' ability to promote the hydrogen peroxide oxidation of luminol in basic aqueous solution to produce chemiluminescence (CL). In the presence of excess luminol and hydrogen peroxide, CL intensity is proportional to the limiting concentration of the metal ion present. Usually the metal ion will possess oxidation states requiring a one-electron transfer that aids in the peroxide reaction with luminol to form an excited aminophthalate anion, which then returns to the ground state emitting a photon (Bo-75). Luminol has also been used to measure the production of H_2O_2 which specifically assays the concentration of blood glucose when it is enzymatically oxidized (Bo-75, Se-78). Other known luminol reactions are the hydrogen peroxide enhancement of the oxidation of luminol by the

superoxide radical ($O_2^{\cdot}$) (Sc-76) and the luminol enhancement of LL in saccharides. These may be related since there is evidence that superoxide radicals are generated when dry saccharides are irradiated (At-74b).

There are several mechanisms proposed for the LL effect in saccharides (Et-82); the correct one must enable one to explain both LL as such and its enhancement by luminol, i.e., the activation of luminol chemiluminescence by the radiolytically-produced and subsequently trapped free radicals stemming from the saccharides. Baxendale (Ba-73) has proposed a mechanism for luminol interacting with free radicals formed in aqueous solution during pulse radiolysis. For the luminol-amplified LL, the mechanism would probably involve decomposition of hydroperoxides which could provide the hydroxyl radicals needed in Baxendale's mechanism.

Ettinger and co-workers (Et-77c) used luminol to increase the sensitivity of their LL system. It would appear that luminol-enhanced LL is based on the presence in the solvent of excesses of luminol and dissolved oxygen as compared to the limited number of free radicals liberated upon dissolution of the organic solid under investigation. The resulting CL intensity should be proportional to the concentration of free radicals trapped in the organic solid irradiated. The limiting aspects to this system will be the amount of trace metal impurities in the reagents and the autoxidation which causes free radicals to be formed in the organic solids used, even in the absence of ionizing radiation.

1.6 Lyoluminescence Readers

LL can be quantitated using a photomultiplier (PM) tube and the associated electronics for the luminescence readout. The LL detection method used by the British researchers (At-73a) is a relatively simple one. A borosilicate glass cell containing the solvent is placed above the window of a PM tube inside a light-tight box. The irradiated samples are added to the cell by remote control and stirred automatically. The signal from the PM tube is fed to a DC amplifier and from there to a

voltage-to-frequency converter and scaler. The light yields are recorded as number of counts per unit sample weight. The amount of sample used varied between 2 and 15 mg depending on the sample material; when water was the solvent, the volume used was 5 ml.

The shape of the light decay curve indicates the presence of two or more diffusion controlled LL reactions differ in time scale. Because of its greater intensity and direct relation to dose, only the short-lived peak, which appears to have two components, was measured. The light intensity was found to peak in approximately 0.1 second and then to die off, at first quickly and then more gradually. For this reason the light output was integrated over a 3-second period (At-73a; At-74a).

In an alternate readout method used by Puite (Pu-77; Pu-82), a glass cup covered with a light-tight rubber membrane and containing 15 mg of the sample was placed above the closed shutter of a PM tube. After the shutter was opened, 4 ml of distilled water were injected through the membrane. In this method the light output was integrated over 10 seconds.

An improvement in the sensitivity of the readout system is possible by the use of a liquid scintillation counter (LSC) which has two PM tubes, and therefore, an almost 4-π counting geometry, and automatic temperature control, down to 6°C for the Packard Model 3320 "Tricarb", Packard Instrument Co., Downers Grove, IL* (Zi-78; Ha-80). The temperature control is useful in stabilizing (and at low temperature reducing) the "self-glow" or chemical background of the luminol (Et-82).

There are well established procedures (St-69; Sc-70; Go-79) to handle the luciferin-luciferase-generated chemiluminescent assay of

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*Throughout this paper, commercial product identification does not imply a recommendation or endorsement by the authors or their institutions, nor does it imply that they consider the identified product to be the best available for the purpose.

adenosine triphosphate (ATP) using a liquid scintillation counter as a single-photon counter. Also, there is wide use of LSC in health physics establishments and the conversion of one to an LL reader (if the system becomes sensitive enough for personnel dosimetry) may be far cheaper than building or buying an ATP photometer.

It should also be noted that (1) the author has compared SAI Technology ATP Photometer Model 3000 with a Packard LSC Model 2002 and found preliminary results indicating that for a tritium check source, the LSC gave one hundred times the counts for a number of one-minute counts; and that (2) Ettinger (private communication) has stated that Packard appears to make the most sensitive chemiluminescence photometer.

2. SYSTEM AND PROCEDURES CHOSEN FOR THIS WORK

2.1 System Chosen

The system chosen for this work was similar to that used earlier by the author (Ha-80). It consisted of an LSC at an operating temperature of 6°C, counting electronics, and a pre-cooled sample-delivery assembly, in which capsules filled with about 10 mg of the sugar under investigation were emptied into modified LSC vials, each containing 2 ml of an aqueous luminol solution of suitable concentration. The Packard LSC has a six-second delay in counting, for moving the sample-delivery assembly down a shaft and placing it into a shielded counting chamber. In order to allow for this delay and to be able to record the entire LL emission, the sample-delivery assembly incorporated a small modified timer system (Tatone "1/2 A Tick Off" model airplane fuel shut-off timer, Tatone Products, San Francisco, CA) which supported the sample capsule and dumped its contents after the assembly had entered the counting chamber. Figure 1 shows the assembly in the chamber.

All the counting electronics used in the present application were external to the LSC (see the block diagram, Figure 2). However, an NBS-

constructed electronic splitter (not shown in Figure 2) enabled a user to switch easily back to normal instrument operation.

Single-photon-resolution RCA 8850 PM tubes were employed, operating at a nominal 2650 V, with a maximum response at λ = 390 nm, which is well within the range of the luminol-amplified LL response of λ = 424 nm.

2.2 System Setup and Calibration

Throughout any given experiment, a scintillator source of ^{3}H in PPO-toluene was used to calibrate the system and select a discriminator level suited for luminol-sensitized LL readout. A pulse-height spectrum was taken for ^{3}H (Figure 3a) and was visually compared with a published pulse-height distribution of a ^{55}Fe nearly-monoenergetic electron and photon source (Ho-73), in order to check out the system. Figure 3b is a ^{3}H pulse-height distribution obtained with both PM tubes, after they had been brought in "register", i.e., after their individual amplifier and voltage settings ($\approx$ 2650 V) had been adjusted to line up the various ^{3}H spectrum peaks in order to make the discriminator level the same for both tubes.

The reason for the choice of ^{3}H in PPO-toluene for calibration purposes lies in the similarity of the pulse-height spectra of ^{3}H in PPO-toluene and luminol. Figure 4 shows a comparison between these pulse-height spectra (luminol light emission in the steady state). Luminol, in reasonable concentrations (10^{-3} M), is a single-photon emitter with respect to the resolving time of the system and, as such, produces a single photon peak. For very high light outputs which might result from luminol-enhanced LL, distortions in the pulse-height spectrum due to pulse pile-up would cause multiple peaks, just as those shown in Figure 3 for the beta-emitting ^{3}H in the liquid scintillator, in which bursts of photons resulting from beta-particle absorption in the scintillator causes double and higher-order photopeaks. While, in principle, it is possible to correct for spectral distortion (He-65, Ha-80), it is preferable to avoid pulse pile-up altogether when one desires to obtain light

intensity as a function of time. In the experiments described in this paper, counting rates as a rule were kept below 80,000/s.* The last part of the calibration was concerned with setting the discriminator level just below the ^3H single-photon peak. Once that level was chosen, it was kept through all experiments. Each time the system was used, the first non-zero channel and the ^3H single-photon peak height were checked. Also measured was the signal-to-noise ratio in the single-photon peak of ^3H in the liquid scintillator; this ratio was found to be 10 to 1 and was expected to be at least as high for the luminol-enhanced LL.

It should be noted that a considerable improvement in geometry could still be made by introducing aluminum reflectors about the sample. In the present geometry (Figure 5a) the counting efficiency for a quenched ^3H source**, which fairly well resembles a chemiluminescent source, was measured to be 11.5 percent, whereas the geometry in Figure 5b from an identical LSC setup with photomultipliers of almost identical characteristics produced a 19.4-percent efficiency.

2.3 Preparation of Readout Solutions and Samples

All glassware and plastic items are acid-washed (10% nitric acid) and rinsed with deionized water (purified using a Millipore system). Luminol (Eastman Kodak) solutions are prepared in 0.1 N Na_2CO_3 (Baker) at a pH of 11. This is close to the optimum pH (Et-82a). The concentration of the luminol is adjusted based on the dose to be administered

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*Measurements with pulses from a pulse generator, shaped similarly to the pulses from luminol (total pulse width of 2 μs, equal rise and fall times of 0.5 μs) established that at a counting rate of 500,000/s the system exhibited a 4-percent counting loss. Taking into account that the pulses from the luminol would be random, it was decided to reject measurements resulting in a counting rate higher than one-third of this rate, in order to allow for pulse sorting. As a rule, the counting rate, in fact, was kept to within one-sixth this number, i.e., to within ∿80,000/s.

**The ^3H source in PPO-toluene used as a check source during the experiments had no additional quencher added. It was counted with a 73.3-percent efficiency (summing the response of the PM tubes).

to the sample in order to avoid saturation of the electronics. For doses less than or approximately equal to 1 rad, 5 rads and 10 rads from a ^{60}Co γ-ray source, concentrations of $3.6 \times 10^{-4}M$, $1.8 \times 10^{-4}M$, and $9 \times 10^{-5}M$, respectively, are used. Two milliliters of the solution are pipetted into the liquid-scintillation vials, sealed and refrigerated at 6°C for at least two days to allow them to come to equilbrium. The temperature was selected to lower the "self-glow" of the luminol when it is used in the LSC which is also at 6°C.

Acid-washed glass beads ($\approx$ 500 μm in diameter) are placed at the bottom, and then a weighed sample ($\approx$ 10 mg) is placed on top of the beads inside the capsule and stoppered (see Fig. 1). The glass beads are used to help disperse the sample as it contacts the solution.

The capsules are given the appropriate radiation doses. (Some are left unirradiated and used as controls.) Each capsule is then opened, placed into its individual small plastic container with a dessicant, and left over night. Subsequently, the capsules are refrigerated to 6°C.

The readout of the samples is performed with dark-room illumination to avoid large self-glow of the luminol solutions as each vial is transferred from the refrigerator to the LSC and its contents poured one at a time into one of the LSC vials containing the luminol solution, using the timer-dumper (see Fig. 1). Readout of the LL is accomplished using the LSC in the manual mode. Prior to each readout, the system is checked with a ^{3}H source and then the multichannel analyzer (MCA) is set at 0.1 s/channel. A typical LL "glow-curve" (counts vs. time) is shown in Fig. 6. A fixed number of channels is summed and used throughout the experiment to represent the response corresponding to a certain dose. Some of the curves are found to have more than one peak, probably due to mixing problems; in this case, suitable alternate starting and stopping points are chosen for obtaining the sum of the region of interest for all curves of the particular experiment.

3. BRIEF SUMMARY OF EXPERIMENTS PERFORMED

The following is a brief summary of the experiments performed and, where appropriate, mention is made of any difference in the procedure from that stated in Section 2.

3.1. Advantages and Disadvantages of Using Low-Temperature Readout

The self-glow of luminol was measured at room temperature and at 6°C. At the lower temperature, the self-glow was lower by a factor of 10 than at room temperature. This means that the luminescence peak rides on a much lower baseline and increases the range of doses that can be assayed at a given luminol concentration; also, the larger signal-to-noise (self-glow) ratio that ensues makes noise subtraction less of an influence on accuracy. However, the lower temperature seems to cause more samples to lose their signal (fade). This may be due to high humidity conditions at readout, even though the samples are initially dessicated. It takes about 25 seconds to transfer the sample from the refrigerator to the timer-dumper and then into the LSC; during this time water condensation may occur. An exhaustive set of tests would have to be performed to determine the cause of fading.

3.2. Effect of Luminol

The sensitivity of the system without luminol was measured. ^{60}Co γ-ray doses of 50, 150, 450 and 1350 rads were given to samples of trehalose dihydrate. The solution was 0.1 N Na_2CO_3. If other buffers are used, it should be made certain that they are not free-radical scavengers. Figure 7 is a curve of response-vs-absorbed dose to water (briefly referred to as dose) for this experiment. There are three replicates for each point showing relative standard deviations of up to 25 percent from the mean. The lowest dose administered (50 rad) was seen not to produce a response significantly different from background.

The system was then used with luminol at a concentration of 4.0 x 10^{-4}M, a pH of 10.88, a temperature of 4°C, and a sample weight of approximately 14 mg. The doses to trehalose samples were 0.15, 0.30, 0.60 and 1.20 rads of ^{60}Co γ-rays. Figure 8 shows the corresponding response-vs-dose curve. There were three replicates per point and the average relative standard deviation from the mean was 35 percent. The three lowest doses were not significantly different from background. The luminol improved the sensitivity by a factor of 100; however, the reproducibility was poorer. In this experiment, purified luminol was used (see discussion in the next section). Whether the luminol was purified or not made no difference in reproducibility. EDTA, a chelating agent for trace metals, was also used; it had no effect.

3.3 Influences of Increased Reagent Purity

Luminol was passed through a column containing Chelex 100 (BioRad) (mesh 200-400 sodium form), at a pH of 8 in order to take out trace metals that might contribute to self-glow. The pH was adjusted back to 11 with Na_2CO_3 (Baker-Ultrex grade). The concentration of luminol was measured on a Cary spectrophotometer (λ = 347 μm, ε = 7680M^{-1}), and adjusted to 4.0 x 10^{-4}M. The process lowered the self-glow by 25 percent. Compared to the temperature effect and labor involved, it was deemed unnecessary to repeat the luminol purification process for each experiment. However, an experiment was designed to use very pure sugar samples with the purified luminol. J. T. Baker Chemical Company produces a grade of reagents called Ultrex, having one-tenth the amount of trace metals such as Ni, Co, Fe, as compared to "reagent grade" chemicals. The trace metals could be one reason for high background. The only disaccharides that can be purchased at this purity were lactose and sucrose. Unfortunately, they produced a background that was very much higher than that of trehalose (non-reagent grade purity). The high background does not seem to depend on whether the sugar is a reducing sugar or non-reducing one. (Lactose is a reducing sugar and trehalose and sucrose are not.)

3.4. Baseline Data for Different Detector Compounds

A number of compounds other than disaccharide were tried. A carbonic acid derivative mentioned earlier and NH_4Cl were chosen for their hydrogen content, which could be useful for neutron dosimetry. They gave no meaningful response. Stearic acid was assayed, because it was thought that perhaps a long-chain molecule might hold trapped free radicals further apart as compared to other compounds and retard free-radical recombination. It produced a signal-to-background ratio of 2:1 at the 0.1-rad level in an aqueous solution of luminol and 10 percent alcohol. The relative standard deviation from the mean of the signal for identically exposed samples was 85 percent. The mixture of water and alcohol leaves the measurement of pH somewhat ambiguous. Also there may have been age problems associated with the luminol. This experiment needs to be repeated.

Deoxy-D-ribose was tried as a lyoluminescence phosphor because it has a G-value of 650 per 100 eV (So-74). The relationship between G-value and lyoluminescence is one that should be explored. The doses were 0.15, 0.30, 0.60, and 1.20 rad. For this compound no meaningful area of the glow curve could be defined; the light output reached a peak that was maintained for over twenty-four seconds. Figure 9 is a response-vs-dose curve for the area in the vicinity of maximum peak height. The electronics of the system was very close to saturation for the last three doses. The 0.3-rad level is significantly above background; however, the 0.15-rad level is not. There are three replicates per point, and the experimental parameters are the same as described for the trehalose-luminol experiment.

The last set of compounds examined, mainly for future experiments involving dopants, were dextrose, fructose and vitamin C (which has a structure similar to a monosaccharide). Dextrose produced a high background and fructose gave poor reproducibility (relative standard deviation of 60% at a 1.2-rad level). Figure 10 is a response-vs-dose curve

for vitamin C in luminol. The largest relative standard deviation is 25 percent, but only the 1.2-rad dose produced a response significantly above background. There are three replicates per point, and the experimental parameters are the same as described for the trehalose-luminol experiment.

3.5. Attempts to Improve Reproducibility

These experiments involved mechanical mixing, and sample-mass and baseline corrections to the observed response. The MCA was interfaced to a Tektronix microcomputer, Model 4051. Sample-mass and luminol-baseline (self-glow) corrections could be made to the peak areas. Four treatments were tried: no mixing (the standard method described earlier), mixing with a paddle hooked onto the timer-dumper, pre-stirring of the luminol for aeration, and pre-stirring and mixing. Unfortunately the mixing with a paddle was mechanically unreliable (it would not always start) but there were strong trends toward improved signal-to-background ratio. The analysis is complicated because there are four treatments and two corrections (mass and baseline subtraction). For the "no mixing" case, mass and baseline corrections optimized the combination of signal-to-background ratio and reproducibility. For all other cases, some sort of mechanical mixing improved the signal-to-background ratio as compared to "no mixing" by 20 to 400 percent. However, after corrections were made, no treatment had necessarily any clear-cut better reproducibility. Baugh et al. (Ba-77) point out that, in mannose, lyoluminescence (per mg) increased non-linearly with mass of the irradiated sample up to 13 mg and then increased more gradually up to 18 mg. It can be postulated that just weighing the samples is not enough; the range of masses must be kept very small. This will need further verification. To implement some of the trends found in the mixing experiments would call for a major modification or a completely new system. This point will be addressed later.

3.6. Use of Dopants

The sensitivity of lyoluminescence is dependent on the number of free radicals trapped in the matrix of the solid. The problem of enhancement of LL has been addressed by a number of authors (Bu-77, Ch-79, Bar-79, Et-81). In the present study, a different approach was used. The author investigated a solid's ability to trap radiolytically-produced free radicals by increasing the number of lattice defects in the material. A simple method of introducing suitable dopants to the material (in this case, trehalose) was to prepare solutions that were subjected to large doses of radiation, then to recrystalize the material containing the radiation products as the dopants; and finally to isolate the product which might be responsible for any enhancement effect. In spite of poor reproducibility, a definite trend towards enhancement can be reported. Since the poor reproducibility may be due mainly to inadequate mechanical interfacing, this method should be pursued.

Sample preparation involved irradiating three 1-M solutions of trehalose with ^{60}Co γ-radiation at a dose rate of $\sim$13 krads/min to levels of 32, 96, and 288 krads, respectively. (A fourth solution remained unirradiated for use as a control.) The major irradiation product is glucose and, although the conditions of irradiation (concentration and ambient atmosphere) were different from the work of Adam (Ad-77), his value for glucose formation from trehalose (G = 2.3/100 eV) was used. Using this value in the formula (Dr-71):

$$\text{Concentration (moles/liter)} = G \cdot D(\text{rads}) \cdot 1.037 \times 10^{-9} ,$$

with the above doses, gives 78, 234, and 702 parts per million (ppm) of glucose formed. Solutions of trehalose doped with 235 and 700 ppm glucose were prepared; also, for comparison with an inorganic dopant, solutions of trehalose were doped with NaCl to the same levels as above. All samples were kept in an oven at 45°C for four days, then placed in a refrigerator at 6°C until they crystallized. Of the samples irradiated

in the kilorad range (doped by radiation), those given higher doses crystallized first, whereas the opposite was true for the chemically-doped solutions. All samples were chopped up, dried at 45°C for one hour, and sifted to a particle size of less than 250 μm in an acid-washed plastic sieve (Nalgene). (The plastic sieve is used to avoid metal contamination to the luminol solutions.) The samples were irradiated with ^{60}Co γ-radiation at levels of 1, 5, or 10 rads at a rate of ∿68 rad/h. The luminol concentration was 9.0×10^{-5} M in 0.1 N Na_2CO_3. The MCA was set at 0.1 s/channel.

Figure 11 is a graph of enhancement factor versus sensitizing dose. The enhancement factor can be defined for a fixed concentration of luminol as the ratio of signal-to-background of the sensitized sample divided by the ratio of signal-to-background of the unsensitized sample. (Background here is defined as the signal of the undosed sample.) The concentration of luminol was chosen so that the signal from an unsensitized sample exposed to 10 rad would be different from its background signal; in this case, the signal-to-background ratio for the unsensitized sample was 1.2.

Figure 12 is a graph of the enhancement factor versus dopant concentration, with the 5-rad curve of Fig. 11 being repeated for comparison. The concentration of glucose is approximately equal to the amount that is created by the sensitizing radiation. For a comparison of the action of organic and inorganic dopants, the NaCl concentration was chosen equal to the glucose concentration. In both figures, there are four replicates per point, with the other experimental parameters being the same as in Section 3.4. The relative standard deviation of the un-normalized data is between 20 and 50 percent. The exact shapes of the curves can only be estimated.

The sensitizing radiation appears to increase the signal considerably, while only slightly increasing the background. However, whereas the enhancement due to the chemical dopants appears to lower the background considerably, the signal remains essentially the same. Therefore, it would appear that some product other than glucose in the radiation sensi-

tization process is causing the enhancement. The next logical step would be to try chemical dopants in the sample or the trace chemicals mixed with the luminol, in order to lower the background, and to try radiation sensitization of the sample in order to increase the signal.

4. REACTION MODEL

Finally, it should be noted that a glow-curve fit was accomplished for LL without enhancement using Marquardt's nonlinear least-square technique (Be-69). The curve-fit assumes a two-component (fast and slow) exponential decay of light multiplied by a first-order buildup term for the dissolving factor, in the form of

$$\text{counts/channel} = C_1 \left[e^{-C_2 t} + C_3 e^{-C_4 t}\right]\left[1 - e^{-C_5 t}\right]^3, \; C_2 > C_4.$$

By neglecting the very first point in the curve (the 100-ms flash of light mentioned earlier) and cubing the buildup factor term, it was possible to achieve a chi square of $\sim$2. For six spectra (three dosed to a 1-rad level and three unirradiated), all constants except C_3 agreed to within 20 percent, C_3 being the ratio of the slow component to the fast component at $t = 0$. C_3 decreases with an increase in dose, but at the 1-rad level this trend is not significant. C_2 and C_4 may be related to the kinetics of the system, however, a diffusion model and the work of Baxendale (Ba-73) should be taken into consideration for a complete understanding of the system. In this particular case, values of $C_2/C_4 \approx 10$ and $C_5/C_2 \approx 3.5$ were obtained. For the case of no luminol (just LL), the values were $C_2/C_4 \approx 60$ and $C_5/C_2 \approx 7.5$. It appears that, since the curve fits simultaneously two processes (irradiated and unirradiated luminol-enhanced LL) with five constants, there are only three degrees of freedom. Curve-fitting was also planned for the data from the enhancement experiments to see if there were any shape changes due to added dopants; however, lack of reproducibility in the shape of the glow curve due to mixing problems made this unattainable.

5. CONCLUSIONS AND RECOMMENDATIONS

Radiation sensitization and the use of dopants seem to improve the sensitivity of lyoluminescence in the presence of luminol. It also appears that solutions ought to be well aerated, in order to eliminate oxygen mixing effects that take place at the liquid-solid interface and lead to high backgrounds and poor reproducibility. The two effects (mixing and sensitization) are independent in their increase of signal-to-background ratios (a factor of 4 for mixing and a factor of 8 for sensitization), and could combine to produce an overall increase of signal-to-background ratio by a factor of 32 at the 10 rad level. This means that even without optimizing the conditions, doses as low as 0.31 rad could be measured.

Reproducibility of the results, to date, has been poor. However, higher signal-to-background ratios and improved reproducibility may be achieved with a new readout system. The author proposes one in which the sugar is kept in a suspension of acetone which will not dissolve the sugar. Then, as the suspension is mixed, a well-aerated low-temperature aqueous luminol solution is infused into the system. The dissolution would be slowed down, and perhaps made more reproducible. In a continuous flow system the possibility exists for using much larger samples, and this would increase the sensitivity of the method.

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Table 1

Summary of the Properties of Lyoluminescence Materials Used in Studies Appearing in the Literature

Reference	Material	Solvent System	Dose Range Studied (photons-γ; or neutrons-η) rad	Saturation Dose* rad	Notes-
	Alkali Halides:				
Ah-65	Sodium chloride	Water	1 to 10^6 (γ)	10^5	Linear to 30 rads; response proportional to square of dose between 30 and 10^3 rad, logarithmic above 10^3 rad
We-60	Sodium chloride	Water, PPO, thallium chloride	up to 2×10^8 (γ)		KI also studied
At-73a	Sodium chloride	Water	1 to 10^7 (γ)		Sublinear
At-80	Sodium chloride	Water	10^5 to 6×10^5 (γ)		Spectra presented; NaBr, KCl, KBr, CsCl, CsBr also studied
We-60	Lithium fluoride	Water	up to 2×10^8 (γ)		

*Saturation dose indicates the dose for which response is a maximum, with subsequent decrease in light yield at higher doses.

Table 1
(Continued)

Reference	Material	Solvent System	Dose Range Studied (photons-γ; or neutrons-η) rad	Saturation Dose* rad	Notes
Av-81	Lithium fluoride	Sulfuric acid	10^5 to 10^9 (γ)		Linear from 10^6 to 10^9 rads; studied by rotating disc method; variable dissolution rates
	Amino Acids:				
Th-76	Valine	Water	10^3 to 10^6 (γ)		Approx. linear
Et-77a	Valine	Water	10 to 10^6 (γ)	>6 x 10^5	Linear below 10^3 rads
Et-77b	Valine	Water	10^3 to 10^6 (γ)		Approx. linear
	Glutamic acid	Water	10^3 to 10^6 (γ)		Approx. linear
Th-76	Phenylalanine	Water	10^3 to 10^6 (γ)		Approx. linear
Th-76	Threnine	Water	10^3 to 10^6 (γ)		Approx. linear
Th-76	Glutamine	Water	10^3 to 10^6 (γ)		Approx. linear
Et-80	Glutamine	Water	10^2 to 3 x 10^4 (η)	8 x 10^6 rads	Approx. linear; LET dependence also studied
Et-82b	Glutamine	Aqueous terbium nitrate	30 to 10^4 (γ)		Linear; threonine also studied; enhancement factor over aqueous solution: 200

*Saturation dose indicates the dose for which response is a maximum, with subsequent decrease in light yield at higher doses.

Table 1
(Continued)

Reference	Material	Solvent System	Dose Range Studied (photons-γ; or neutrons-η) rad	Saturation Dose* rad	Notes
	Antibiotics:				
Et-77b	Streptomycin	Water	10^3 to 10^6 (γ)		
Et-77b	Gentomycin	Water	10^3 to 10^6 (γ)		
Et-77b	Oxytetracycline	Water	10^3 to 10^6 (γ)		
	Enzymes:				
Et-77b	Lysozyme	Water	10^3 to 10^6 (γ)		
Et-77b	Alkaline phosphatase	Water	10^3 to 10^6 (γ)		
Et-77b	Trypsin	Water	10^3 to 10^6 (γ)		Linear to 2 x 10^5 rads
Et-77b	Pepsin	Water	10^3 to 10^6 (γ)		
Et-77b	Nucleic acids	Water	10^3 to 10^6 (γ)		Linear to 4 x 10^5 rads
	Saccharides:				
Et-77a	Sucrose	Water	10 to 10^6 (γ)	9 x 10^4	Linear below 10^3 rads
We-60	Alginic acid	Water	up to 2 x 10^8 (γ)		
At-74a	Trehalose	Water	1 to 10^6 (γ)	10^5	Linear to 10^5 rads

*Saturation dose indicates the dose for which response is a maximum, with subsequent decrease in light yield at higher doses.

Table 1
(Continued)

Reference	Material	Solvent System	Dose Range Studied (photons-γ; or neutrons-η) rad	Saturation Dose* rad	Notes
At-74a	Trehalose	Aqueous luminol	1 to 10^6 (γ)		Approx. linear
Et-77c	Trehalose	Lucigenin	10 to 10^6 (γ)	10^5	Approx. linear to 10^5 rads
Zi-78	Trehalose	Luminol	0.5 to 30 (γ)		Linear; vitamin C also studied; liquid scintillation counter as readout system
At-73b	Xylose	Water	500 to 5 x 10^6 (γ)	10^5	Approx. linear to 10^5 rads
Et-77a	Trehalose $\cdot 2H_2O$	Water	10 to 10^6 (γ)	10^5	Linear below 10^3 rads
Ah-59	Glucose	Aqueous alkaline solution	60 to 1.7 x 10^7 (γ)		Luminescence intensity directly proportional to dose
We-60	Glucose	Water	up to 2 x 10^8 (γ)		
Ch-79	Glucose	Water	200 to 3 x 10^4 (γ)		Glucose crystallized with luminol

*Saturation dose indicates the dose for which response is a maximum, with subsequent decrease in light yield at higher doses.

Table 1
(Continued)

Reference	Material	Solvent System	Dose Range Studied (photons-γ; or neutrons-η) rad	Saturation Dose* rad	Notes
Bar-80	Glucose monohydrate	Water			The relative effectiveness of 10 MeV protons, 30 MeV ^{3}He, 9.7 MeV and 2.4 MeV alpha particles was studied
At-73b	Mannose	Water	500 to 5 x 10^6 (γ)	10^5	Approx. linear to 10^5 rads
Et-77a	Mannose	Water	10 to 10^6 (γ)	8 x 10^4	Linear below 10^3 rads
Pu-77	Mannose	Water	5 to 10^5 (γ)	10^5	Linear to 300 rad; supra-linear above 300 rad
			10^2 to 2 x 10^3 (η)		Linear to 300 rad; supra-linear above 300 rad
Et-80a	^{6}Li pyrinate	Water	10^3 to 10^5 (γ)		Linear

*Saturation dose indicates the dose for which response is a maximum, with subsequent decrease in light yield at higher doses.

Table 1
(Continued)

Reference	Material	Solvent System	Dose Range Studied (photons-γ; or neutrons-η) rad	Saturation Dose* rad	Notes
Et-80b	^{6}Li pyrinate	Water	Thermal neutron fluence: 10^{-15} to 10^{-13} n/cm^2	1×10^{-13} n/cm^2	Approx. linear to 5×10^{-13} n/cm^2 of thermal neutron fluence

*Saturation dose indicates the dose for which response is a maximum, with subsequent decrease in light yield at higher doses.

Table 2

Factors Affecting Lyoluminescence Response

Solvent Factors	References
Type	At-73a, At-74a, At-75, Av-81, Et-82, La-79
pH	Ah-59, At-74a, Et-77a, Bu-75, Ka-79, Kl-73
Dissolved oxygen concentration	At-73b, Ba-80, Er-62, Et-77a, Kl-73
Volume	Et-77a, Et-82
Impurities	At-74b, Ka-79, Kl-73
Sensitizer Factors	
Type	At-74a, At-74b, Bu-77, Ch-79, Et-77c, Et-82b
Concentration	Et-77c, Kl-73
Impurities	Ah-59
Particle size	Ba-79, Bu-75, Ka-79
Sample Factors	
Purity	At-75
Heat treatment history	At-75, Kl-73
Storage temperature	At-74b, Et-77b, Ka-79
Storage time after exposure	At-74b, At-74b, Ba-79, Ka-79, Pu-77
Exposure to light	At-73b, Et-77b
Exposure to humidity	At-73b
Temperature at dissolution	At-73b, Et-77a, Et-82

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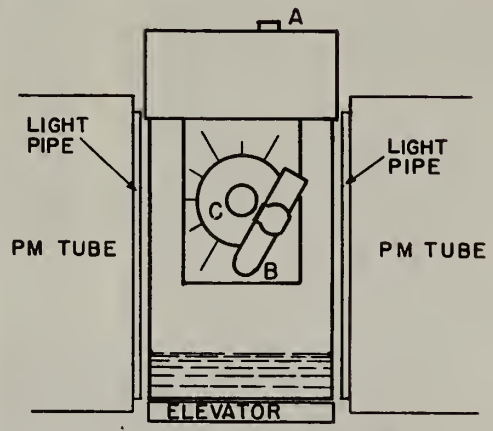

FIGURE 1. TIMER-DUMPER. THE SUGAR SAMPLE (~10 MG) IS INSIDE THE DETACHABLE HOLLOW ROD (B) CONNECTED TO THE WHEEL (C). THE WHEEL SPINS AND POURS THE SUGAR INTO THE SOLUTION. THE TIME SPAN FROM TURNING THE SWITCH (A) TO "ON" TO POURING THE SUGAR IS TEN SECONDS. THE VIAL IS A LIQUID SCINTILLATION VIAL WITH THE TOP CUT OFF AND REPLACED WITH A PLASTIC HOLDER FOR THE TIMER-DUMPER.

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Fig. 1 NBSIR 83-2794

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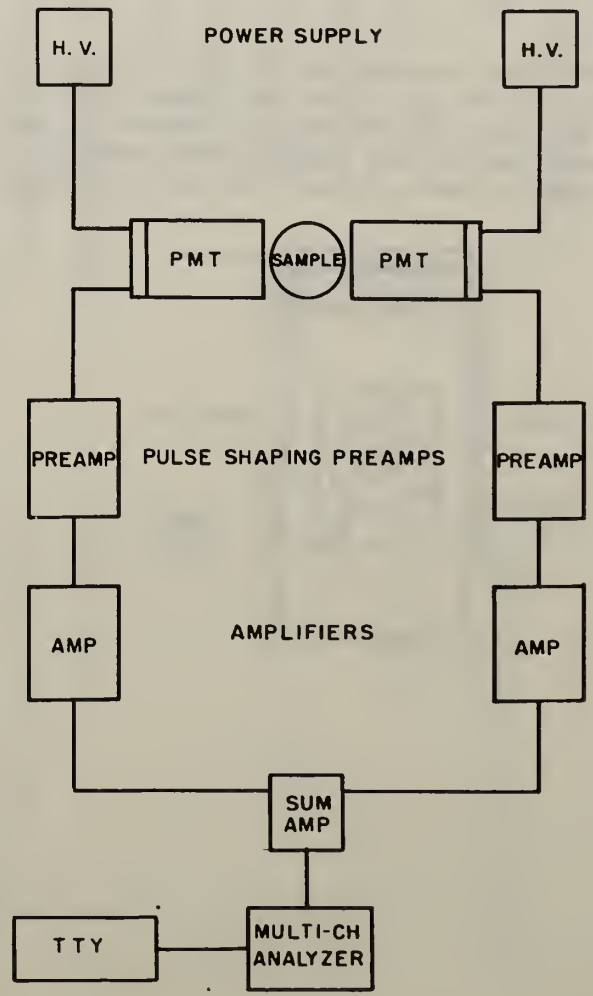

FIGURE 2. BLOCK DIAGRAM OF LL READER USING THE HOUSING OF A LSC.

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Fig. 2 NASIN 77-2734

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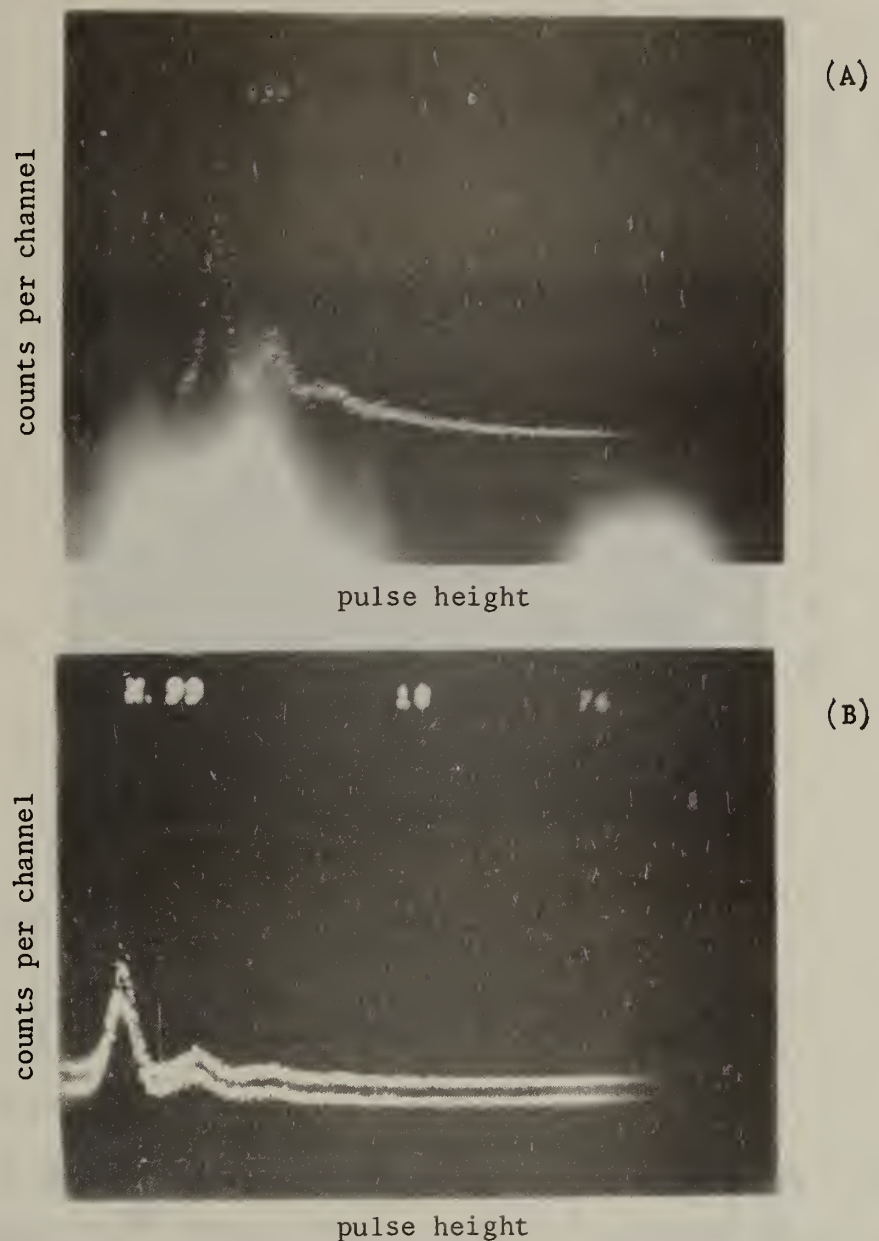


FIGURE 3. ^{3}H PULSE HEIGHT SPECTRA (LINEAR SCALE) TAKEN WITH RCA 8850 PHOTOMULTIPLIER TUBES, SHOWING THE SINGLE, DOUBLE, AND TRIPLE PHOTOPEAKS. (A) SPECTRUM TAKEN WITH A SINGLE TUBE. (B) SPECTRA TAKEN WITH TWO TUBES BROUGHT INTO "REGISTER", SO THE PEAKS LINE UP; THE DISTRIBUTION FROM ONE OF THE TUBES IS VISUALLY RAISED FOR CLARIFICATION.

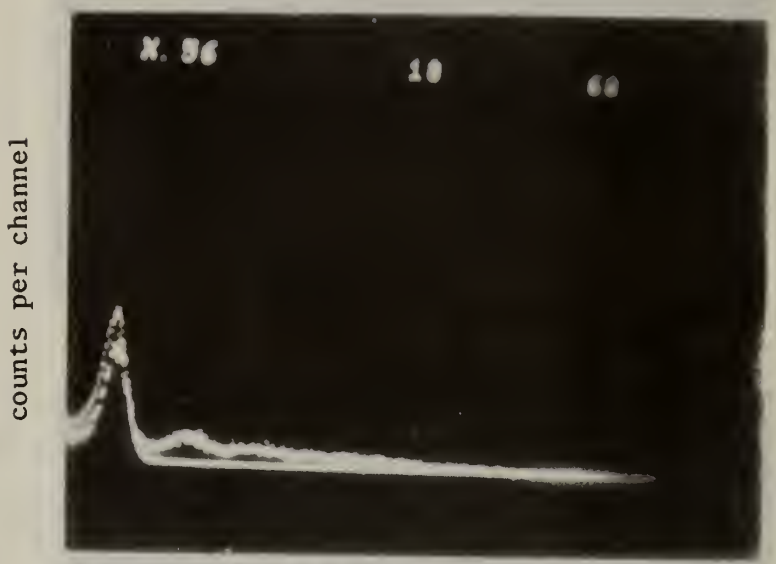
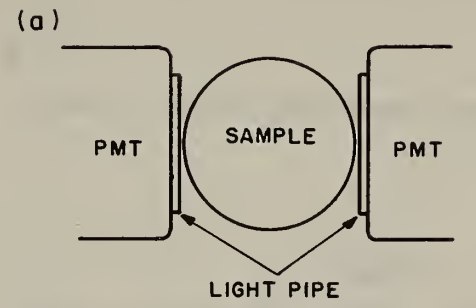


FIGURE 4. COMPARISON OF THE PULSE HEIGHT SPECTRUM OF ^{3}H AND OF LUMINOL. IN THE SCINTILLATOR PPO-TOLUENE, ^{3}H PRODUCES A BURST OF PHOTONS, CREATING THE ADDITIONAL PEAKS WITH GREATER PULSE HEIGHTS, WHEREAS LUMINOL IN REASONABLE CONCENTRATION IS A SINGLE-PHOTON EMITTER AND PRODUCES ONLY A SINGLE PEAK. THE SPECTRA ARE VISUALLY OFFSET FOR CLARIFICATION.



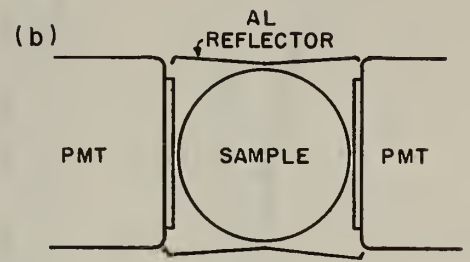


FIGURE 5. IMPROVEMENT IN COUNTING GEOMETRY. (A) PRESENT GEOMETRY. (B) AL REFLECTORS ADDED.

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Fig. 5 NBSIR 83-2734

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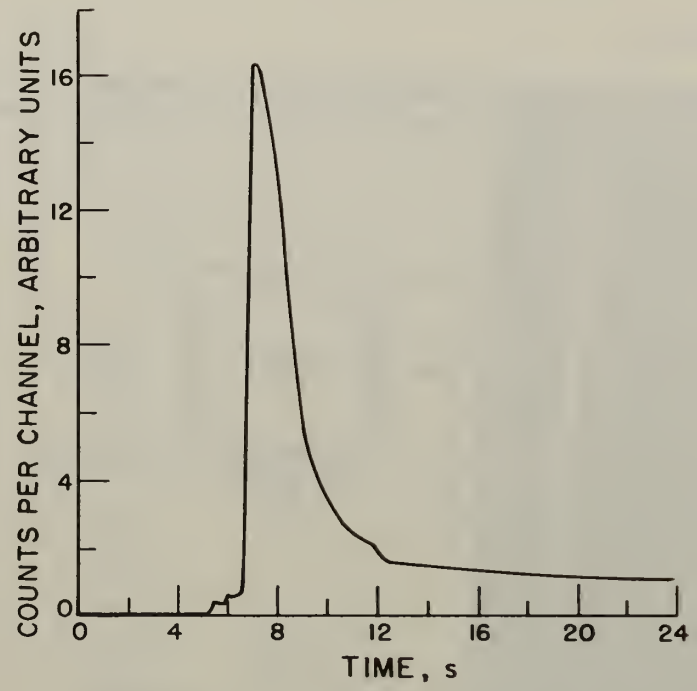

FIGURE 6. TYPICAL LYOLUMINESCENCE "GLOW CURVE".

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Fig. 6 NBSIR 83-2734

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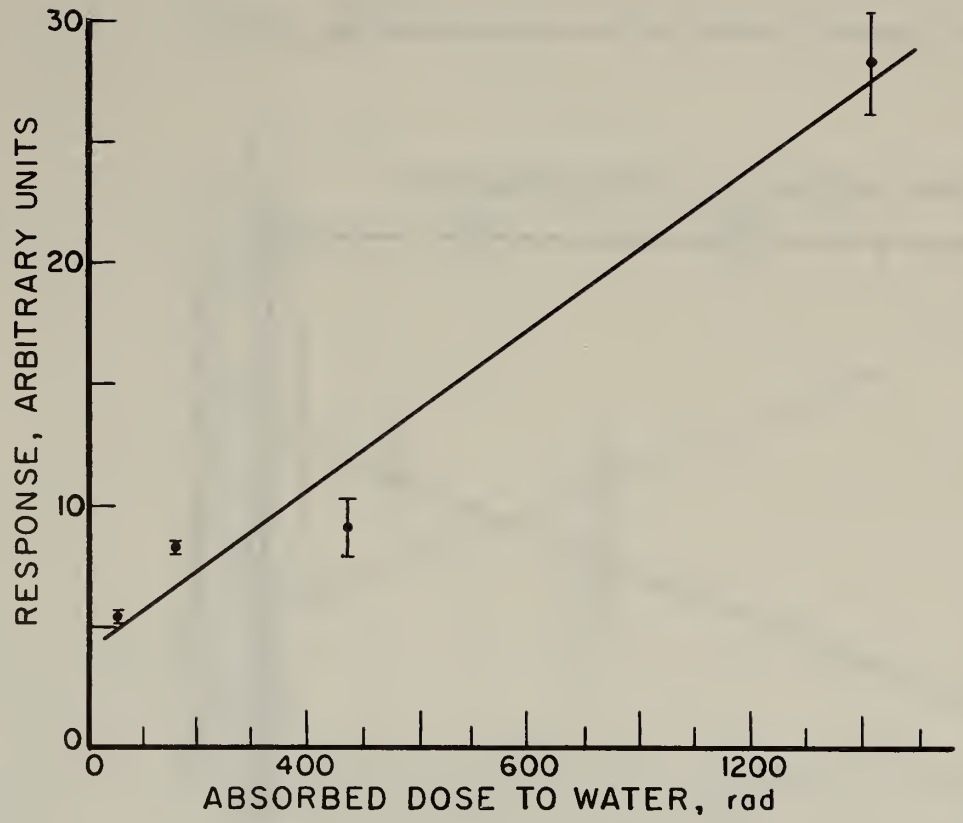

FIGURE 7. RELATIVE RESPONSE-VS-DOSE FOR TREHALOSE, DISSOLVED IN 0.1 N Na_2CO_3 FOR LL READOUT.

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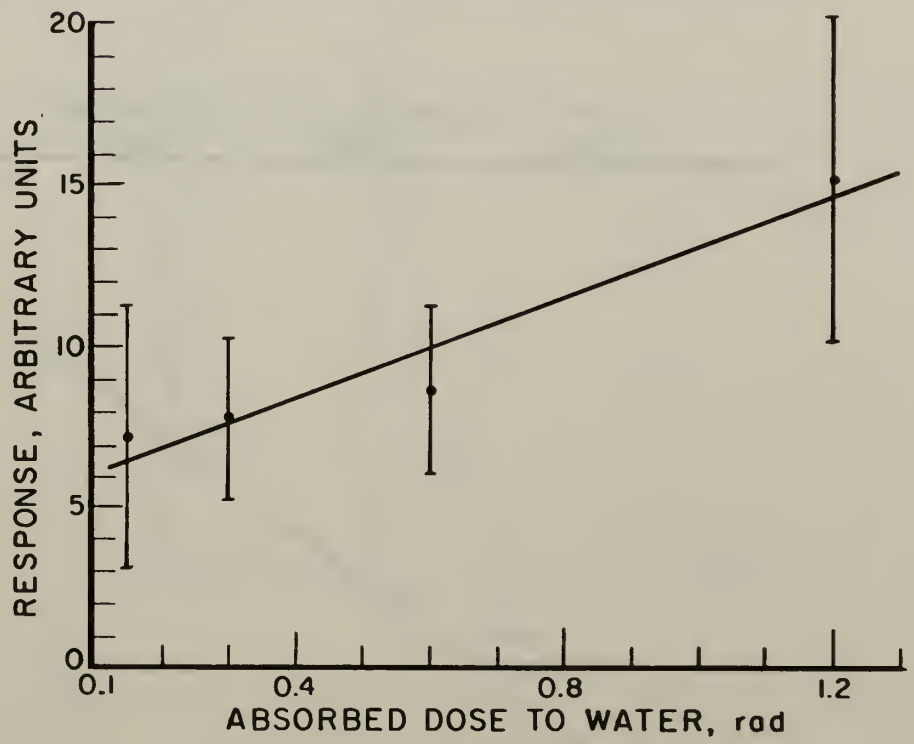

FIGURE 8. RELATIVE RESPONSE-VS-DOSE FOR TREHALOSE, DISSOLVED IN LUMINOL FOR LL READOUT.

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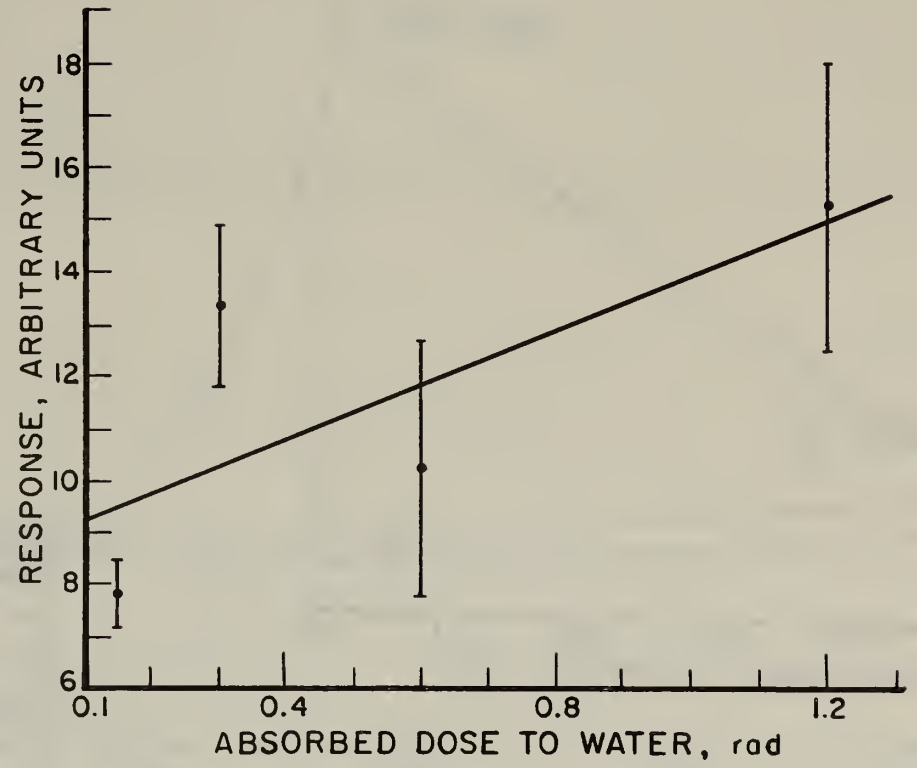

FIGURE 9. RELATIVE RESPONSE-VS-DOSE FOR 2-DEOXY-D-RIBOSE, DISSOLVED IN LUMINOL FOR LL READOUT.

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Fig. 9 NBS IR 83-2734		
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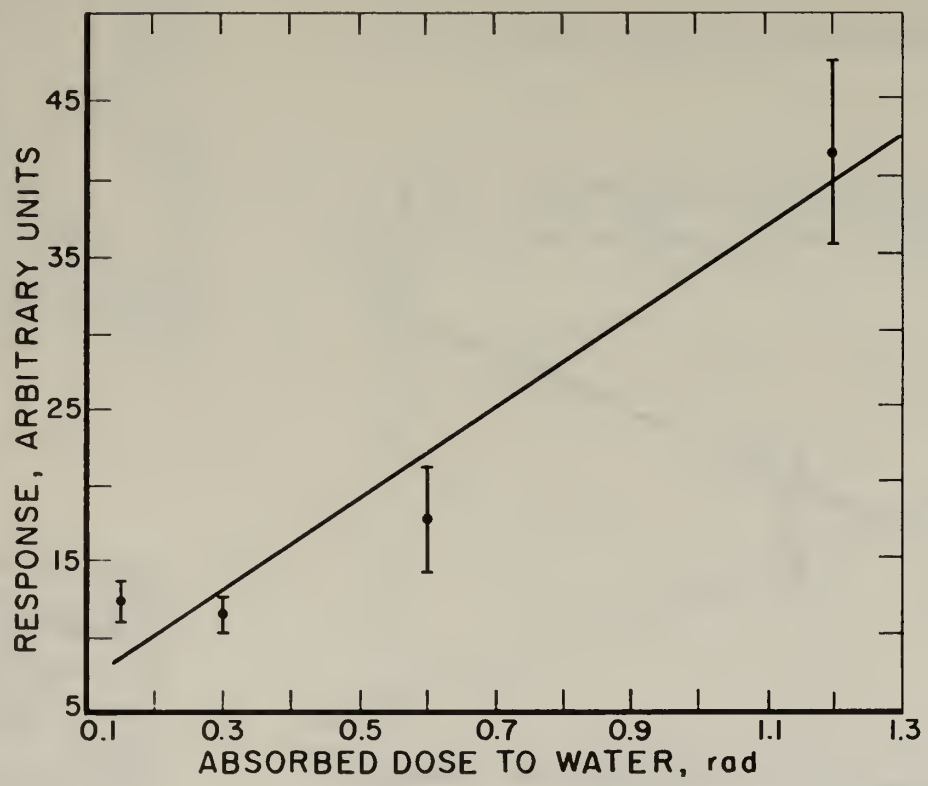

FIGURE 10. RELATIVE RESPONSE-VS-DOSE FOR VITAMIN C, DISSOLVED IN LUMINOL FOR LL READOUT.

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Fig. 10 NBSIR 83-2734

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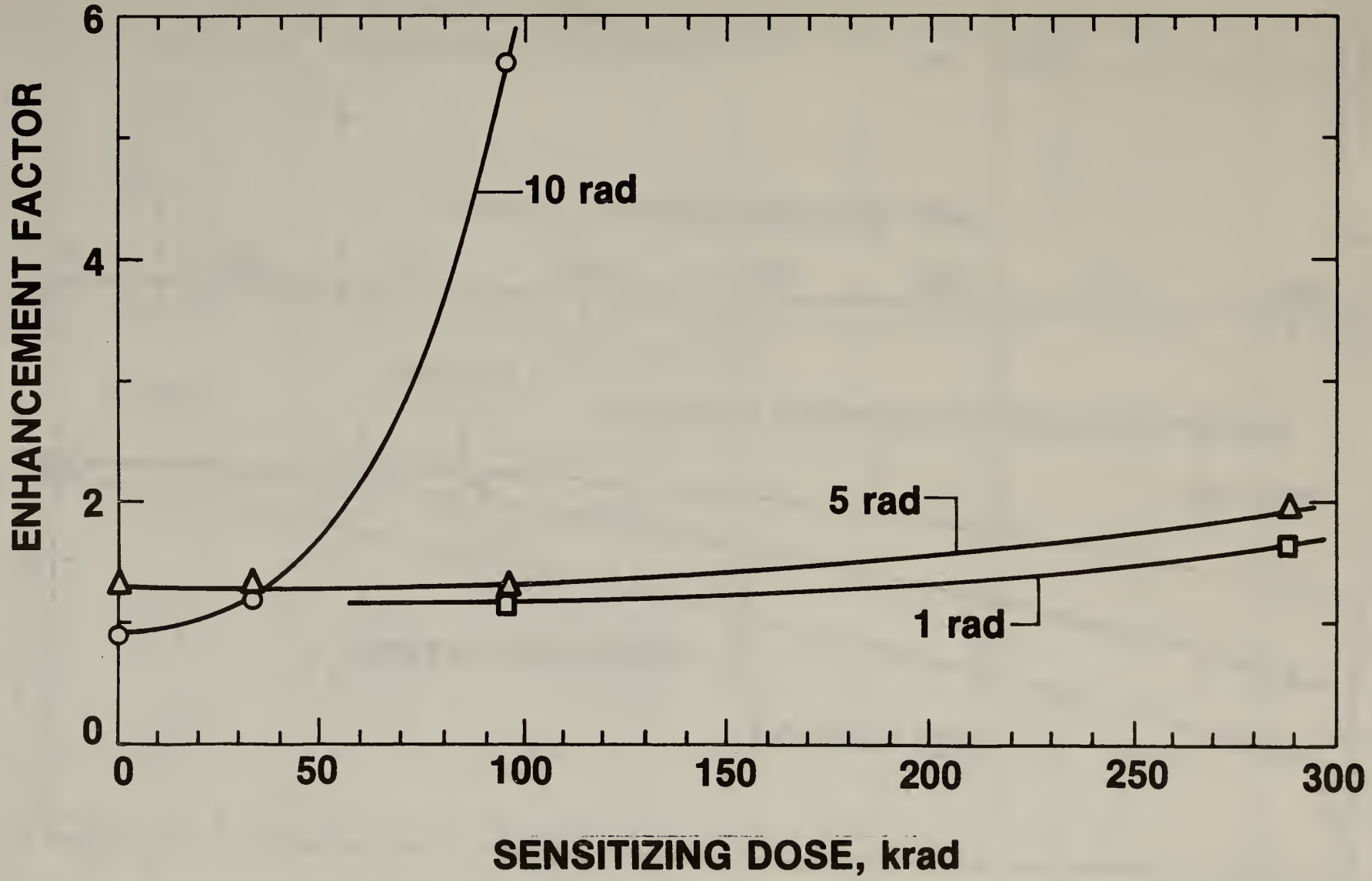

FIGURE 11. ENHANCEMENT FACTOR-VS-SENSITIZING DOSE (^{60}Co GAMMA RADIATION) FOR TREHALOSE, DISSOLVED IN LUMINOL FOR LL READOUT. THREE LEVELS OF ^{60}Co GAMMA-RAY TEST EXPOSURES WERE GIVEN TO THE SOLID TREHALOSE. THESE ARE PRELIMINARY DATA WITH A RELATIVE STANDARD DEVIATION BETWEEN 20 AND 50 PERCENT BEFORE NORMALIZATION.

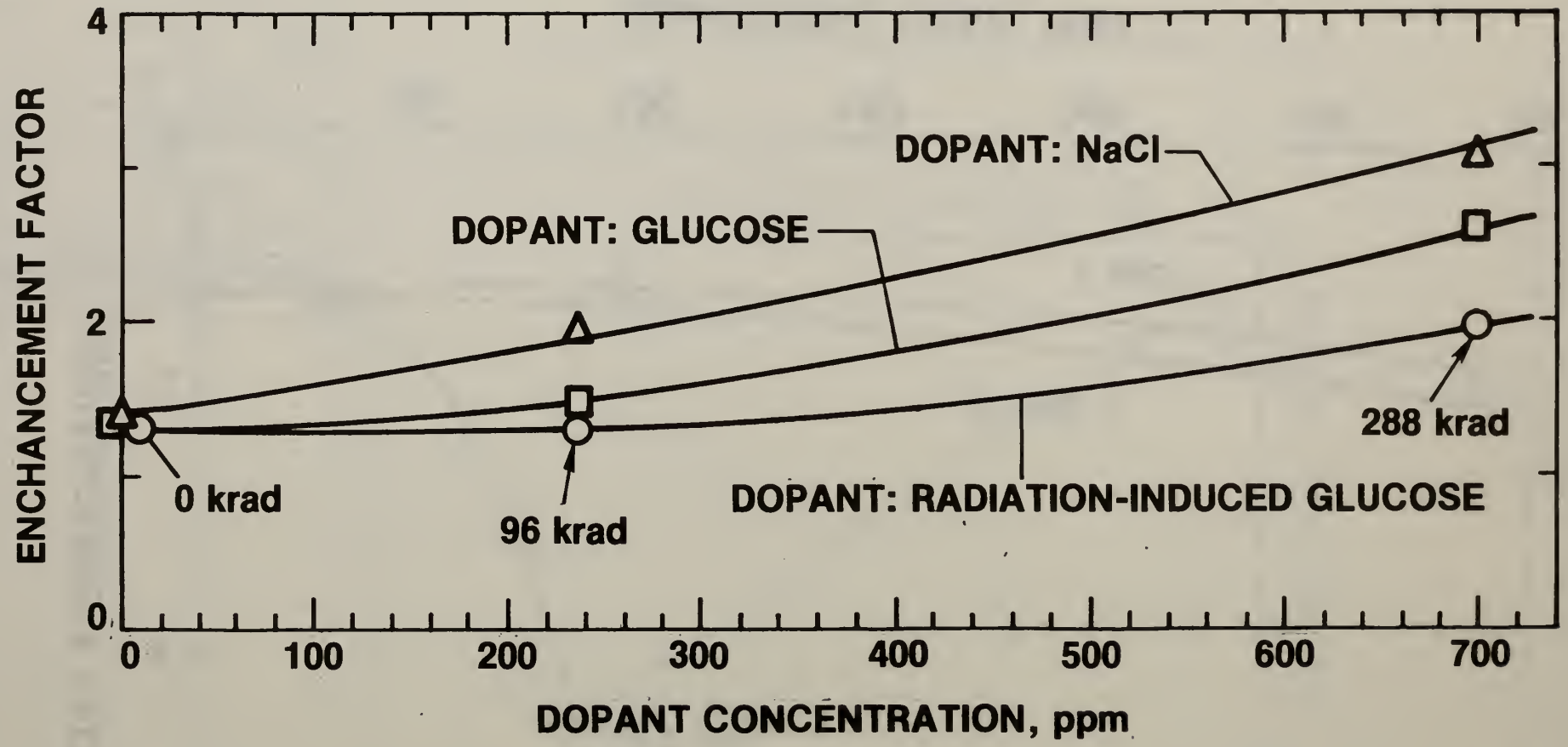

FIGURE 12. ENHANCEMENT FACTOR-VS-DOPANT CONCENTRATION FOR THREE DOPANT MODES OF TREHALOSE, DISSOLVED IN LUMINOL FOR LL READOUT. IDENTICAL TEST EXPOSURES (5 RAD OF ^{60}Co GAMMA RADIATION) WERE GIVEN TO THE SOLID TREHALOSE.

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5. AUTHOR(S)

Dr. Richard Hanig

6. PERFORMING ORGANIZATION (If joint or other than NBS, see instructions)

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☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

A cooled liquid scintillation system with single-photon counting photomultiplier tubes was employed to increase the sensitivity of luminol-enhanced lyoluminescence (LL). The problems of reagent purity and mechanical mixing were studied. For the disaccharide trehalose, the lowest dose significantly different from background was at the 1.2-rad level for ^{60}Co gamma rays, with a standard deviation of 33 percent. The system suffers from poor reproducibility in the mixing of the disaccharide with its solvent, and recommendations are made for improvements. Detector compounds of different hydrogen content were studied for possible application in neutron dosimetry and for their ability to retard free-radical recombination. The results were not conclusive. Enhancement of the LL effect was accomplished by radiation sensitization of solutions of trehalose with between 30 and 300 krad to water. The disaccharide was then recrystallized from solution, along with associated radiolysis products and, in some instances, with separately added chemical dopants. Preliminary intercomparison of these doped sugars with untreated materials at doses of 1, 5, and 10 rads indicates that they give a better signal-to-background ratio than the untreated disaccharide. A promising reaction model was tried which assumed a two-component exponential decay of light, multiplied by a first-order buildup term for the dissolving factor. The model seems to fit both the ordinary and luminol-enhanced LL glow-curves.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

chemiluminescence; liquid scintillation counter; luminol; lyoluminescence; lyoluminescence enhancement by radiation sensitization; lyoluminescence glow curve fitting; saccharides

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