



## On a radiochromic dye dosemeter

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*Publication date:*  
1980

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Miller, A., & McLaughlin, W. L. (1980). *On a radiochromic dye dosemeter*. Risø National Laboratory. Risø-M No. 2254

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ON A RADIOCHROMIC DYE DOSE METER

Arne Miller and William L. McLaughlin

Abstract. Radiochromic dye dose meters made of polyvinyl butyral (PVB) with hexa(hydroxyethyl)pararosaniline cyanide (HPR-CN) as the radiation-sensitive element are being developed and investigated at Risø. This report summarizes the present results and outlines plans for further research on this dose meter. Currently the response is found to be almost stable after irradiation, but recalibration of a given batch is needed every 3-6 months because of changes in response characteristics with age. Under typical laboratory conditions, the temperature coefficient is found to be about +1% per degree Celcius and the relative humidity coefficient +(0.4-0.5)% per percent change in relative humidity. The response drops ~ 15% when the dose rate is lowered from 1.1 Gy/sec to 0.2 Gy/sec.

This research is supported by IAEA through research contract No. 2051/RB, and this report constitutes the progress report for the period November 1979 - October 1980.

INIS-descriptors: COLORIMETRIC DOSEMETERS, CYANIDES, DOSE RATES, DOSE-RESPONSE RELATIONSHIPS, DYES, HUMIDITY, IONIZING RADIATIONS, RADIATION DETECTORS, SPECTROPHOTOMETRY, STABILITY, TEMPERATURE DEPENDENCE, TRIPHENYLMETHANE DYES.

UDC 539.12.074

December 1980

Risø National Laboratory, DK 4000 Roskilde, Denmark

ISBN 87-550-0737-6

ISSN 0418-6435

Risø Repro 1980

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## 1. INTRODUCTION

Plastic dose meters are the most commonly used indicators of absorbed dose in radiation processing as well as in research<sup>(1)</sup>. In gamma facilities clear and red Perspex specially prepared for radiation dosimetry<sup>(2-3)</sup> are widely used, while for electron beam facilities with electron energies in the range of less than 200 keV to 10 MeV, thinner plastic films are preferred, so as to produce a more homogeneous dose distribution in the dose meter. Some commonly used plastic film dose meters having thicknesses ranging from 20  $\mu\text{m}$  to 200  $\mu\text{m}$  include polyvinyl chloride<sup>(4)</sup>, dyed (blue) cellophane<sup>(5)</sup> and cellulose triacetate<sup>(6)</sup>, but several others have also been suggested and used<sup>(1)</sup>.

These plastic film dose meters suffer from different drawbacks like nonlinearity, dose rate dependence, oxygen dependence, etc.<sup>(1)</sup>, and the user depends on the ability of the producer to make batches with uniform and constant absorbed dose characteristics. That has proved difficult since most of the plastics used for dosimetry have not been designed for this purpose.

During the last decade different types of plastic film dose meters have been developed in attempt to overcome some of these difficulties. These dose meters consist of certain types of radiochromic dyes dissolved in their leuco form in various plastics<sup>(7,8)</sup>. The plastics can be chosen with radiation absorbing characteristics matching those of materials to be irradiated in radiation processing or radiation therapy.

The colourless dye precursor used in the dose meters is shown in its basic form in Table 1. Upon irradiation the  $\equiv\text{C}-\text{CN}$  bond is broken thereby creating a negative CN-ion and a positive carbonium ion, which by rearrangement of bonding and charge becomes coloured. Table 1 also lists several dye precursors which are based upon the general structure, but with various chemical groups substituted at different positions of the benzene rings.

Table 1. Structure of Several Radiochromic Dyes

| Name of parent dye                 |  |                 |  |                 |  |                 |                |
|------------------------------------|--|-----------------|--|-----------------|--|-----------------|----------------|
|                                    | R <sub>1</sub>   | R <sub>2</sub>  | R <sub>3</sub>                                   | R <sub>4</sub>  | R <sub>5</sub>   | R <sub>6</sub>  | R <sub>7</sub> |
| Pararosaniline                     | NH <sub>2</sub>  | H               | NH <sub>2</sub>                                  | H               | NH <sub>2</sub>  | H               | H              |
| Hexa (hydroxyethyl) pararosaniline | N(C <sub>2</sub> H <sub>4</sub> OH) <sub>2</sub>                 | H               | N(C <sub>2</sub> H <sub>4</sub> OH) <sub>2</sub> | H               | N(C <sub>2</sub> H <sub>4</sub> OH) <sub>2</sub>                 | H               | H              |
| Malachite green                    | N(CH <sub>3</sub> ) <sub>2</sub>                                 | H               | H  | H               | N(CH <sub>3</sub> ) <sub>2</sub>                                 | H               | H              |
| New fuchsin                        | NH <sub>2</sub>  | CH <sub>3</sub> | NH <sub>2</sub>                                  | CH <sub>3</sub> | NH <sub>2</sub>  | CH <sub>3</sub> | H              |
| Formyl violet                      | N-C <sub>2</sub> H <sub>5</sub><br> <br>CH <sub>2</sub><br> <br> | H               | N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>   | H               | N-C <sub>2</sub> H <sub>5</sub><br> <br>CH <sub>2</sub><br> <br> | H               | H              |
| Helvetia green                     | N(CH <sub>3</sub> ) <sub>2</sub>                                 | H               | SO <sub>3</sub> Na                               | H               | N(CH <sub>3</sub> ) <sub>2</sub>                                 | H               | H              |
| Setoglaucine                       | N(CH <sub>3</sub> ) <sub>2</sub>                                 | H               | H  | H               | N(CH <sub>3</sub> ) <sub>2</sub>                                 | H               | Cl             |

Several papers describe dosimetry research with these dyes in liquid and solid phase<sup>(9-18)</sup>, but the first commercially available dose meters based on these dyes were made by EG&G. They consisted of free-standing poly(halo)styrene doped with malachite green, about 3% by weight and similar weight percent of new fuchsin cyanide in gelatin thinly coated on polyester film base. Although these films showed excellent characteristics<sup>(19-22)</sup>, they had limitations. The radiation induced colour of the poly(halo)styrene film was unstable after irradiation increasing slightly during storage, and the films were rather brittle. Research work was initiated at Risø in order to make dose meter films with better mechanical and radiation absorption properties, and we also wanted to make dose meters from various plastics in order to study radiation absorption distributions in different materials, at interfaces, and in assorted geometrical configurations.

Table 2 lists the thin film dose meters that were made in our Department<sup>(7)</sup>. Various dyes were chosen with the different plastics in order to obtain good compatibility between dye precursors and plastic host material. Such choices were based in part on previous experience and in part on the results of laboratory tests.

The dose meter films were cast from mixtures of solutions of the given polymer and the leuco-cyanide of the dye. In some instances plasticizers and other additives were required to achieve good optical and mechanical properties. It was also found that a combination of proper solvents was needed in each case to dissolve both polymer and radiochromic dye. The films were cast on an optically flat glass cylinder with a diameter of about 25 cm, and were then stripped from this block at a proper time and dried before being used.

We found that these dose meter films could be made strong, flexible and of good optical quality, but we also found various degrees of instability of the radiation-induced colour, involving both pre- and post-irradiation effect. The instability extent depended largely on formulation. Therefore we decided to



Table 2. New Dyed Plastic Thin Film Dosimeters and Imaging Systems

| Plastic Host               | Approx. Formula   | Approx. Density<br>(g cm <sup>-3</sup> ) | Radiochromic Dye Used                    |
|----------------------------|---|--|--|
| 1. cellulose acetate       | (C <sub>12</sub> H <sub>20</sub> O <sub>10</sub> ) <sub>n</sub> | 1.3                                      | pararosaniline-CN                        |
| cellulose triacetate       | (C <sub>24</sub> H <sub>32</sub> O <sub>16</sub> ) <sub>n</sub> | 1.4                                      |  |
| 2. polyvinyl acetate       | (C <sub>8</sub> H <sub>12</sub> O <sub>4</sub> ) <sub>n</sub>   | 1.1                                      | new fuchsin-CN                           |
| 3. polyvinyl butyral       | (C <sub>8</sub> H <sub>13</sub> O <sub>2</sub> ) <sub>n</sub>   | 1.1                                      | hexa(hydroxyethyl)<br>pararosaniline-CN  |
| 4. polyvinyl pyrrolidone   | (C <sub>5</sub> H <sub>9</sub> NO) <sub>n</sub>                 | 1.2                                      | formyl violet-CN or<br>helvetia green-CN |
| 5. polyvinyl chloride      | (C <sub>2</sub> H <sub>3</sub> Cl) <sub>n</sub>                 | 1.4                                      | malachite green-CN or<br>setoglaucine-CN |
| polyvinylidene<br>chloride | (C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> ) <sub>n</sub>   | 1.5                                      |  |

1  
∞  
1

investigate one of the dose meter types thoroughly in order to optimize the properties through changes in the formulation and in the dose meter casting procedure. We chose the dose meter made of polyvinyl butyral (PVB) with hexa(hydroxyethyl)para-rosaniline cyanide (HPR-CN) as the radiation-sensitive element, as one that has good sensitivity and a simple casting procedure. It is also the dose meter having density and radiation absorbing properties similar to those of water, among listed dose meters in Table 2. This research is being supported in part by the International Atomic Energy Agency through research contract No. 2051/RB.

## 2. DEVELOPMENT OF THE PVB RADIOCHROMIC DOSE METER

### 2.1. General

The reaction mechanism for the radiation-initiated colouration of the dye cyanides has been studied for one of the simplest forms of the parent dyes, namely pararosaniline, where an  $\text{NH}_2$  group is attached at the para position of each of the benzene rings (see Table 1)<sup>(18)</sup>, but these studies are not concluded. It is generally accepted that the reaction to produce the dye involves breaking of the  $\equiv\text{C}-\text{CN}$  bond followed by a rearrangement of the electronic charge of the positive carbonium ion to form the conjugated chromophore. This bond strength for pararosaniline cyanide is 3.8 eV, and the mean radiation threshold for cleavage of this bond is correspondingly in the ultraviolet at about 330 nm wavelength<sup>(18)</sup>. The ionization potential depends on the type of dye; for the hexa(hydroxyethyl)pararosaniline cyanide (HPR-CN) we have measured a threshold of about 370 nm<sup>(23)</sup>, but we believe the reaction mechanism for colouration to be similar to that for pararosaniline cyanide.

The absorption spectrum of HPR dye formed by radiation is in the visible region of the spectrum, with  $\lambda_{\text{max}}$  at 600 nm as

shown in Fig. 1. The dose is normally measured at this wavelength for doses up to 20 kGy and at 510 for higher doses, where the optical density may be too high for photometric analysis at 600 nm. An intermediate absorption band at 412 nm has also been observed for HPR dissolved in nylon, this band being more or less pronounced depending on the presence of water in the dose meter<sup>(24)</sup>. This band generally disappears within an hour or two after irradiation. This result indicates that complicated dye-forming reactions are taking place.

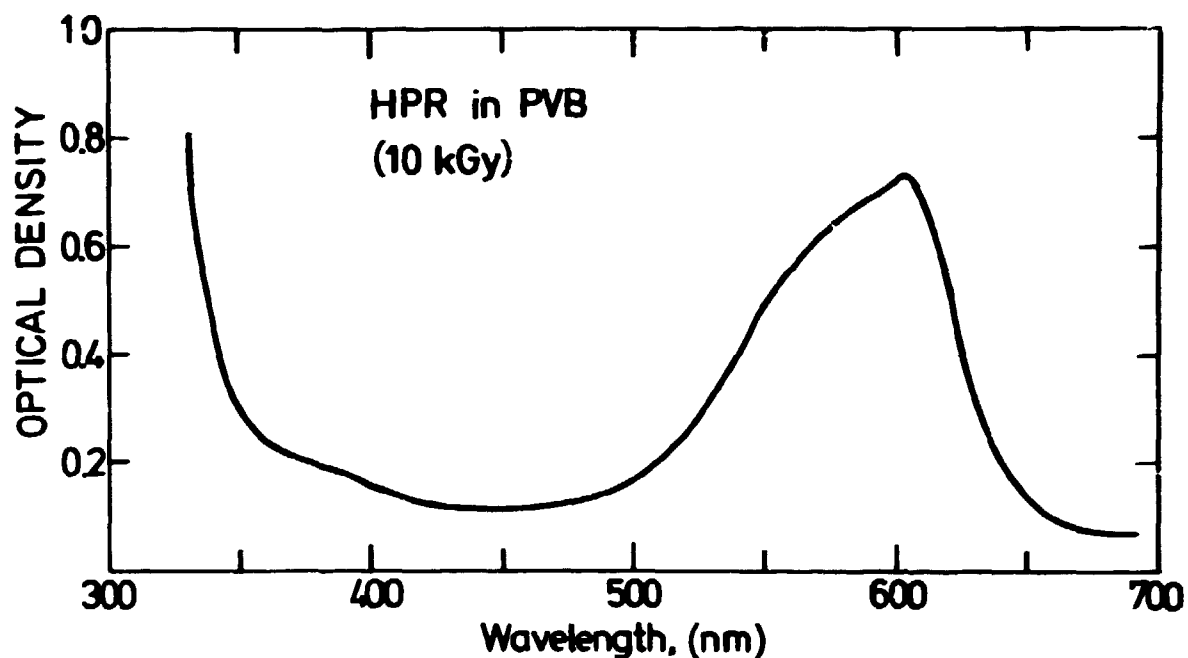


Fig. 1. Absorption spectrum for the radiochromic dye dose meter made of hexa(hydroxyethyl)pararosaniline cyanide (HPR-CN), dissolved in polyvinyl butyral (PVB). The dose meter was irradiated to an absorbed dose of 10 kGy with cobalt-60 gamma-rays.

For the dose meter with HPR dissolved in nylon, the response of colour formation in terms of change in optical density at 510 nm per unit thickness versus absorbed dose ( $\Delta OD/mm = f(D)$ ) has been shown to follow rather closely the expression

$$\text{Response} = 1 - e^{-D/D_{37}}$$

where D is the absorbed dose and  $D_{37}$  is that absorbed dose which gives 63% of the obtainable or saturation colouration<sup>(25)</sup>.  $D_{37}$  is found at 510 nm to be of the order of 200 kGy, and the dose response at doses up to 50 kGy is therefore almost linear, with less than 10% deviation.  $D_{37}$  at 600 nm cannot be measured with our instrumentation, because the optical density is too high ( $> 3$ ), but the response curves at 600 nm and 510 nm, plotted as the logarithm of the optical density change versus the logarithm of the absorbed dose, are parallel. This indicates that  $D_{37}$  may be of the same order of magnitude for 600 nm as for 510 nm. The dose range of linear response should therefore also be the same for the two wavelengths of analysis, and the dose measurement range is thus limited by the instrument capability and not by the dose meter itself. Exception to this would be in the case of very thin films, where maximum optical density at 600 nm might be readable. Figure 2 shows dose response curves at 600 and 510 nm for nylon dose meters on a linear scale.

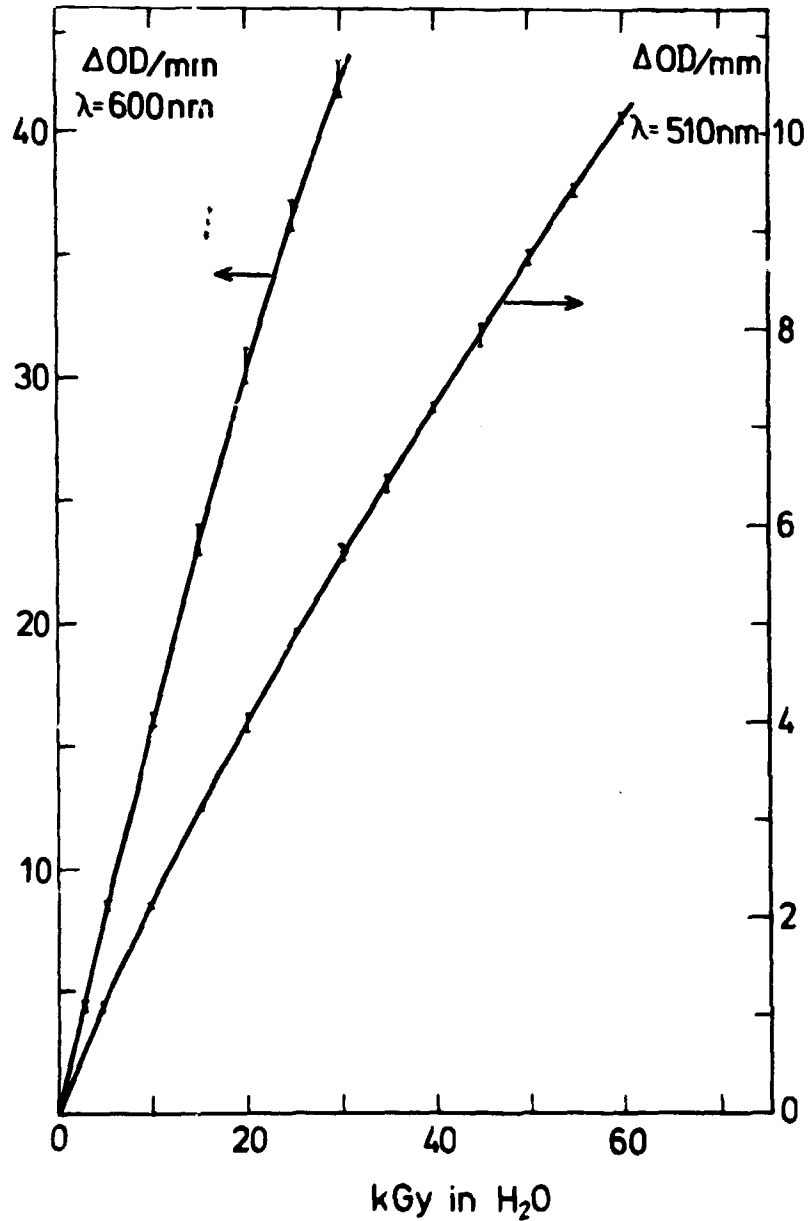


Fig. 2. Response curves for the radiochromic dye dose meter made of hexa(hydroxyethyl)pararosaniline cyanide (HPR-CN) dissolved in nylon and irradiated with cobalt-60 gamma-rays, with optical density per unit thickness made at two optical wavelengths.

## 2.2. Stability

The stability of the formed dye depends on its formulation and how the ingredients contribute to preventing back reactions between the cyanide and carbonium ions. Such stability is made possible by ensuring that the colour-forming reaction takes place in a weakly acid environment, but the dipole action of other molecules present may also be significant.

The formulation from which the PVB dose meter (see ref. (7)) was cast is as follows:

- 100 cm<sup>3</sup> 2-methoxy ethanol
- 40 cm<sup>3</sup> 2-butoxy ethanol
- 15 cm<sup>3</sup> 99% ethanol
- 20 cm<sup>3</sup> butanol
- 15 cm<sup>3</sup> N,N-dimethyl formamide
- 24 g polyvinyl butyral (containing various amounts of polyvinyl acetate and/or polyvinyl chloride)
- 0.75 cm<sup>3</sup> dioctyl phthalate
- 0.2 cm<sup>3</sup> glacial acetic acid
- 1.7 g hexa(hydroxyethyl)pararosaniline-CN

The glacial acetic acid ensures sufficient acidity for stability of colour. The amount of acid is important for the sensitivity<sup>(15)</sup> and 0.2 cm<sup>3</sup> was found to be optimum. The dioctyl phthalate is a suitable plasticizer; combination of 5 different solvents is also used. We arrived at this combination through a trial and error process, where the ultimate aim was to dissolve enough dye for a wide response and to cast a film with good optical and mechanical properties.

The dose meters made from this formulation were sensitive ( $\Delta OD/mm \sim 10$  for a 10 kGy dose) and homogeneous, but we found after irradiation that the colour intensity (i.e. optical density) for a given dose would increase by  $\sim 10\%$  during the next 10-20 days. Another problem was that the sensitivity of the dose meter continued to drop somewhat at repeated irradiations over several months<sup>(23)</sup>. We believed that both problems were

related to the content of acid, and since the glacial acetic acid has a rather high vapor pressure, it would be expected that the acid would continue to evaporate from the film thereby continuously changing the sensitivity and would therefore influence the stability of the colouration. We tried to stabilize the colouration of the dose meter after irradiation by exposing the irradiated dose meter to an accelerated aging process, i.e. a vacuum treatment for  $\sim 24$  hours at  $40^{\circ}\text{C}$ , and that did stabilize the response as shown in Fig. 3. The stability before irradiation was also affected when unirradiated dose meters were treated in the same way, but the sensitivity did not fully stabilize as can be seen in Fig. 4<sup>(26,27)</sup>. since we were not certain which factors influenced the response of the dose

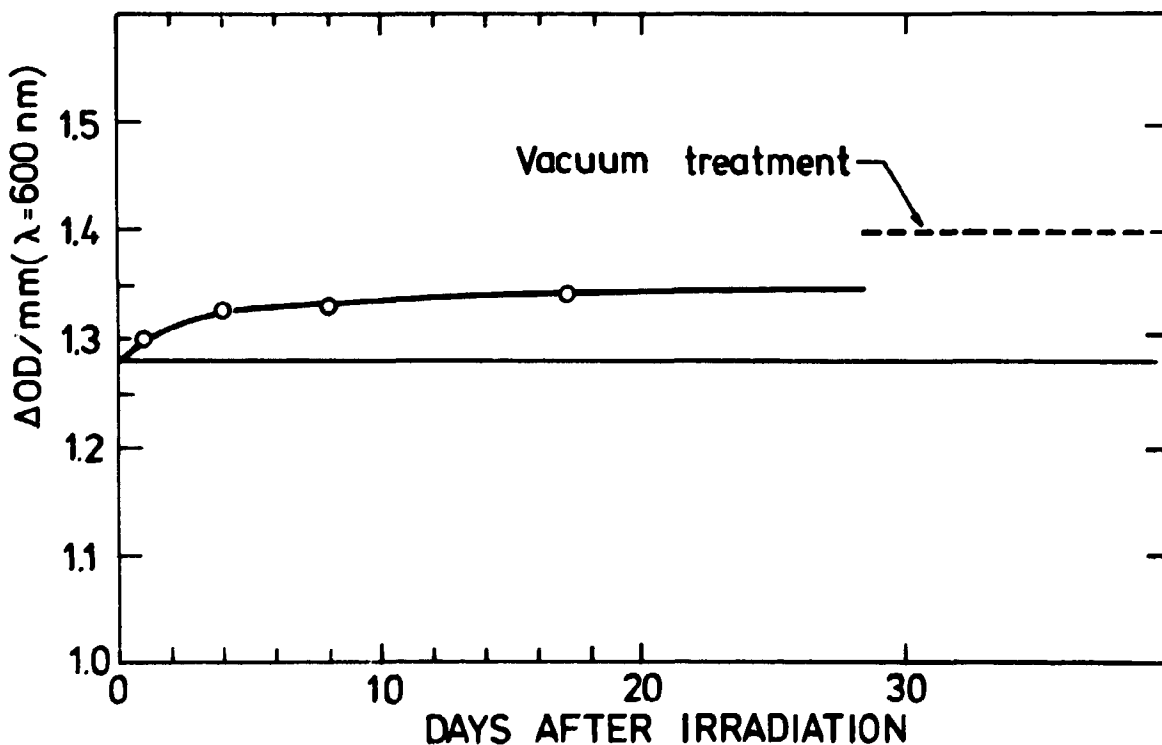


Fig. 3. Post-irradiation stability of PVB dose meter made with a combination of solvents and irradiated to 14 kGy with cobalt-60 gamma-rays. Storage under normal room temperature conditions.

meters, in further testing we decided not to rely on accelerated aging. Rather we let the films dry under atmospheric conditions at  $\sim 30^{\circ}\text{C}$  and at a relative humidity between 40 and 60% for prolonged periods of time. Measurements so far were made on dose meter films produced in 1977 and earlier. Laboratory rebuilding prevented film making for some time, and only in early 1979 have we been able to resume this activity.

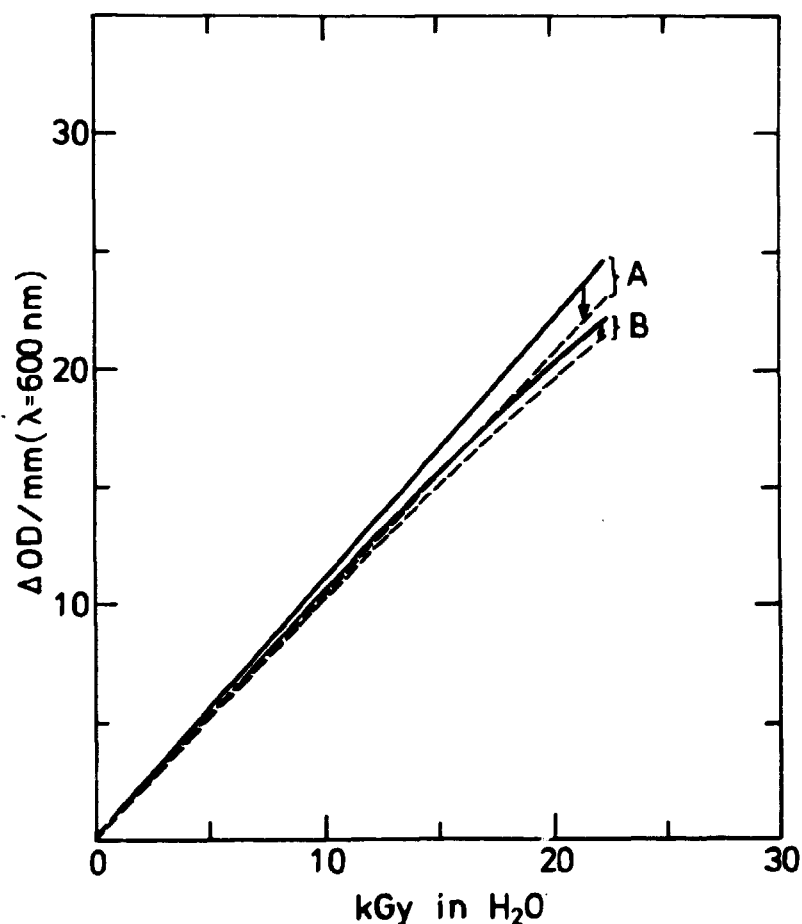


Fig. 4. Change in sensitivity with age for the same PVB dose meter as in Fig. 3. A was stored under vacuum for 48 hours prior to irradiation, B was not. A and B were irradiated simultaneously (— irradiation immediately after vacuum treatment, --- irradiation one month later).



The first step in solving instability problems was to use a different acid, namely citric acid, which in its pure form is a solid. We would therefore expect the acidity of the film dose meter to remain constant during aging, thereby improving the stability of response. Six dose meter films were cast with various combinations of glacial acetic acid and citric acid maintaining the same total acid strength. After a drying period of 5 weeks the colour intensity of each dose meter was monitored during storage after irradiation. The first results indicated that using pure citric acid produced the most stable dose meter, as we might expect. Therefore we proceeded making a batch of dose meter films with citric acid<sup>(26)</sup>.

As the responses of the dose meters were followed over longer periods of storage and as irradiations occasionally were repeated, other problems arose. None of the dose meters was found to be totally stable; generally the colour faded somewhat after irradiation, although some films with mixtures of glacial acetic acid and citric acid first undergo fading, followed by an increase in colouration. The sensitivity of the dose meters tended to decrease under repeated irradiations, but within a year after casting the sensitivity again increased.

It was difficult to see a definite trend in these results, although there was indication that some of the effects were due to residual solvent concentrations. In order to try to reduce these instability effects, we changed the formulation to only one solvent. We chose a solvent having high vapour pressure, so that it would evaporate rather quickly from the cast film. 2-methoxy ethanol was tried, but 2-ethoxy ethanol was found to be a better solvent for the dye.

Dose meter films were cast using this solvent and various combinations of acid, in order to determine optimum values empirically. The formulation was:

285 cm<sup>3</sup> 2-ethoxy ethanol  
0.4 cm<sup>3</sup> dioctyl phthalate  
25 g PVB  
1.5 g HPR  
various amounts of glacial acetic acid  
and citric acid.

In changing to this formulation, a different problem showed up. The finished dose meter film took on an orange-peel surface, consisting of rather regular polygons about 2 or 3 mm across. After irradiation it could be seen that the dye concentration was higher at the edges of these polygons. This effect is apparently caused by convection in the drying film solution. As 2-ethoxy ethanol evaporates, its temperature decreases, particularly the surface temperature. The resulting vertical temperature differential promotes convection. In ref. (28) is described how convection in thin layers tends to create polygons containing circulating liquid residues. Furthermore, it is shown that colour pigments, for example, tend to gather at the edges of the polygons. It is not certain if this also applies to the dissolved dye molecules in our case, but this seems to be so.

We corrected the problem by lowering the evaporation rate. This was accomplished by placing the film casting glass plane in a tight hood, containing saturated vapour from the solvent. That reduced the evaporation and gave smooth, clear films. After partial drying of the film, the evaporation rate can then be increased.

Because of uneven colour distribution in the first phase of dose meters made with one solvent, it was difficult to interpret the results. The colour was more stable after irradiation, but when the concentration of acid was changed, the sensitivity of the dose meter was changed accordingly, as was the long-term stability of sensitivity. The post-irradiation stability of the irradiated dose meter was not greatly influenced by the amount of acid. Figure 5 shows for repeated irradiations over 13 months how the sensitivity is affected by various amounts of acid (ratio of citric acid to glacial acetic acid was 3:1).

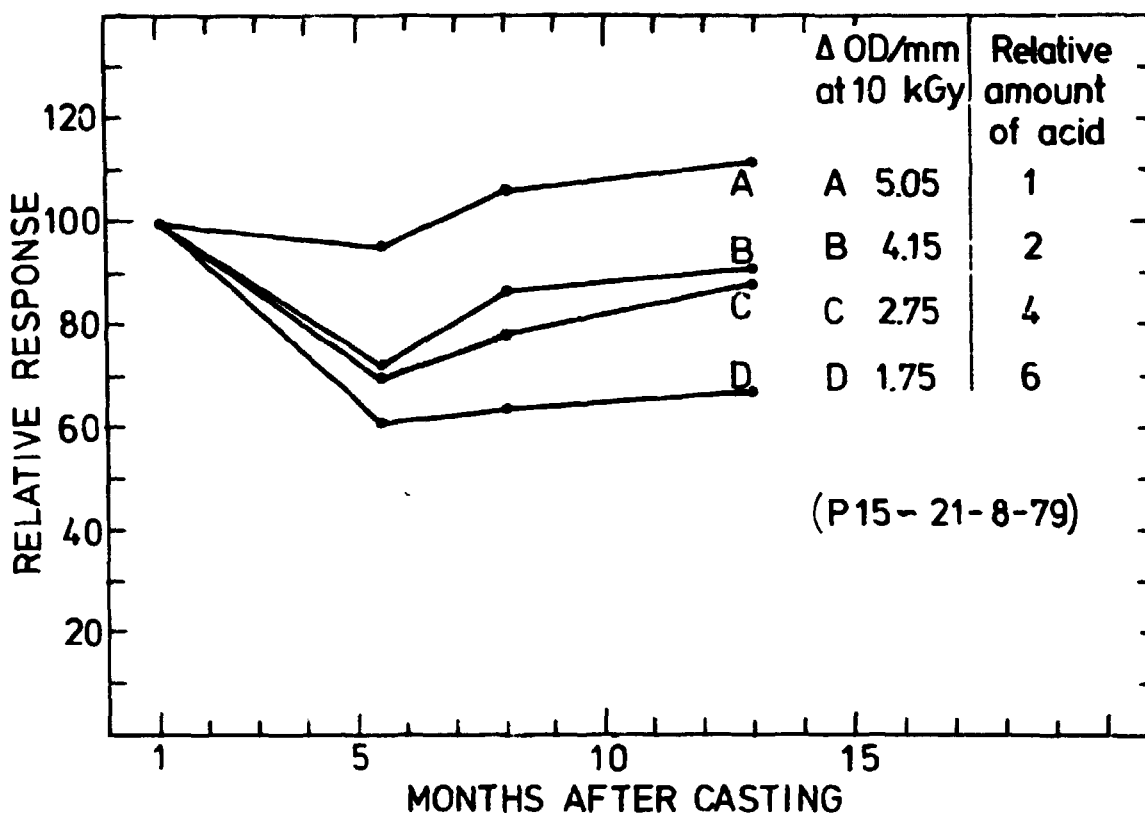


Fig. 5. Change in response for PVB dose meters containing various amounts of acid as indicated (for basic formulation see p. 17). The sensitivity as measured one month after casting of the dose meters is also indicated at the figure.

As less acid seemed to give the most stable and sensitive dose meters, we also made a dose meter without acid (P15, 5.10.79). The results proved the earlier contention that some acid is needed to ensure stability (see Fig. 6).

In order to determine the optimum concentration of acid for sensitivity and stability, a batch of dose meters with various amounts of acid were cast (P15, 30.11.79). We suspected that the behaviour shown in Fig. 5 was due to the presence of two acids, and therefore we chose to use only citric acid in this batch, with amounts ranging from 7% to 100% of the amount of acid used in the previous dose meters (100% corresponds to 2.4 g citric acid and the formulation was as on page 17). The results are shown in Fig. 7.

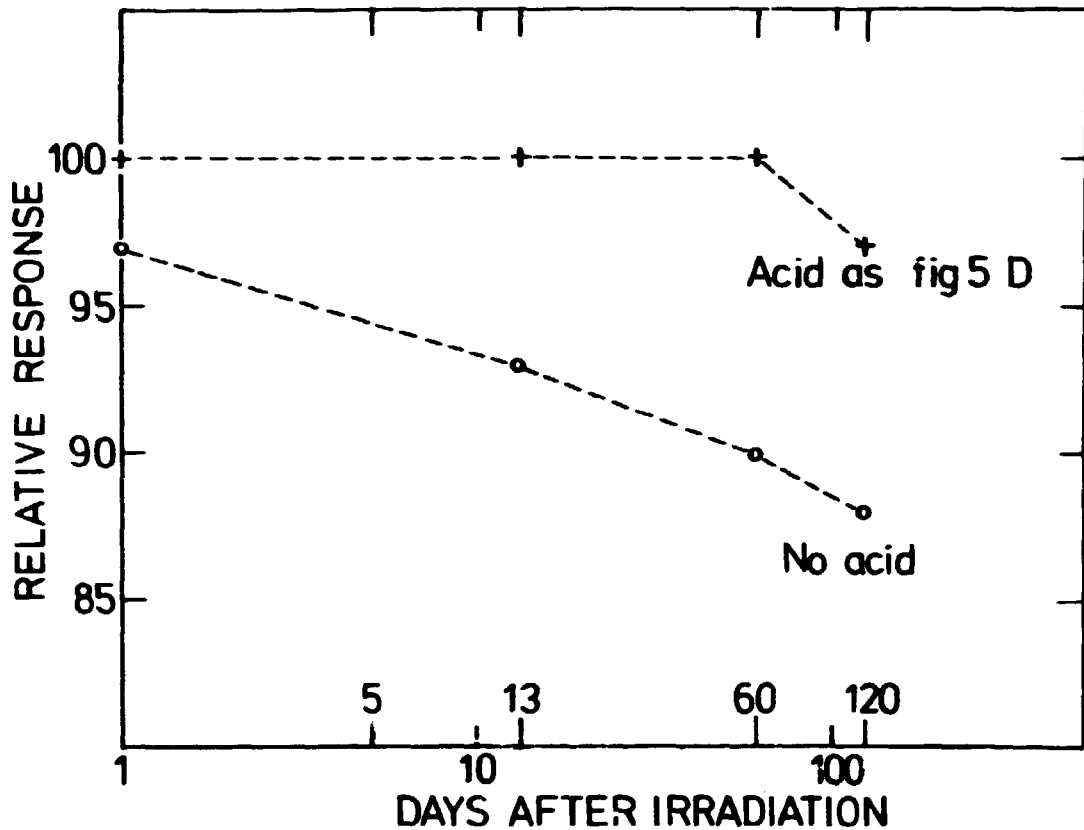


Fig. 6. Change in response for two PVB dose meters containing no acid and containing the same amount of acid as the dose meter marked "D" in Fig. 5.

All the dose meters were relatively stable after irradiation, the colour not changing more than  $\pm 3\%$  over 4 months for the type "C" (0.6 g acid) and even less for type "E" (2.5 g acid), but as the latter has a lower sensitivity, we have for the time being chosen type "C" as the basis for the next batch of dose meter films. Continued measurements will tell if this was the proper choice.

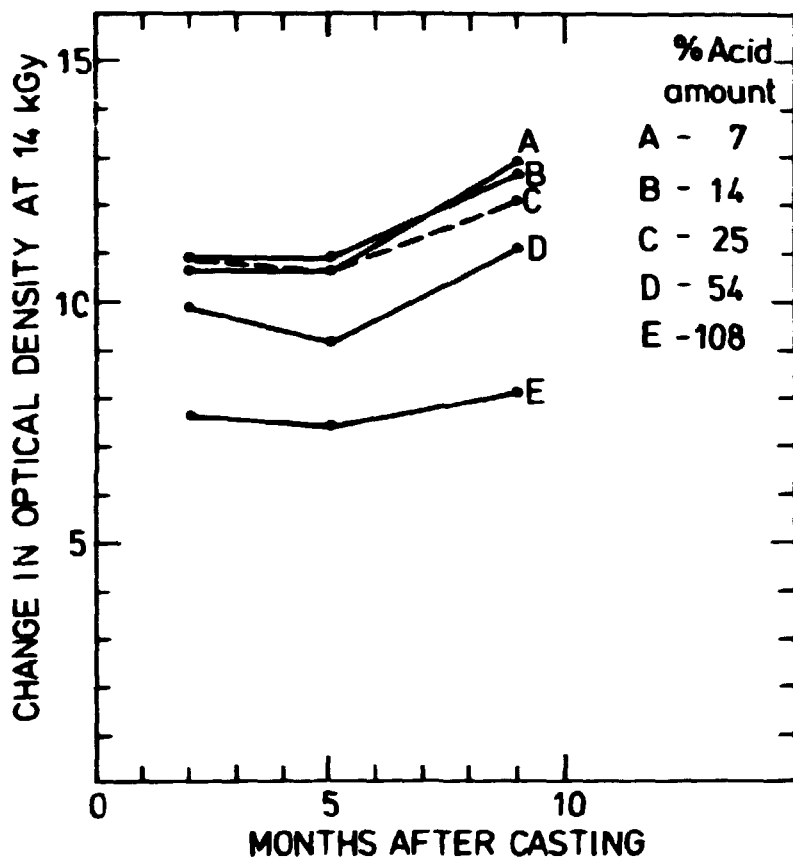


Fig. 7. Change in response for PVB dose meters made from one solvent and containing citric acid only, but with various amounts of acid as indicated. The percentage of acid is that corresponding to 2.4 g equal to 100%, for formulation shown on p. 17.

### 3. DEPENDENCE ON TEMPERATURE

As with other plastic dose meters the PVB film response depends on temperature during irradiation. This dependence has been tested so far only for older batches by irradiation with cobalt-60 gamma-rays to 1.5 Mrad at selected temperatures<sup>(29)</sup>. The dose meters were conditioned at a given temperature for about one hour before irradiation. The resultant temperature dependence curve is shown in Fig. 8, where 3 different batches were studied. As can be seen there are some difference between the batches, but the general trend is the same. At room temperature the temperature coefficient at 600 nm is about + 1% per degree Celcius, which is approximately double that of nylon-base films.

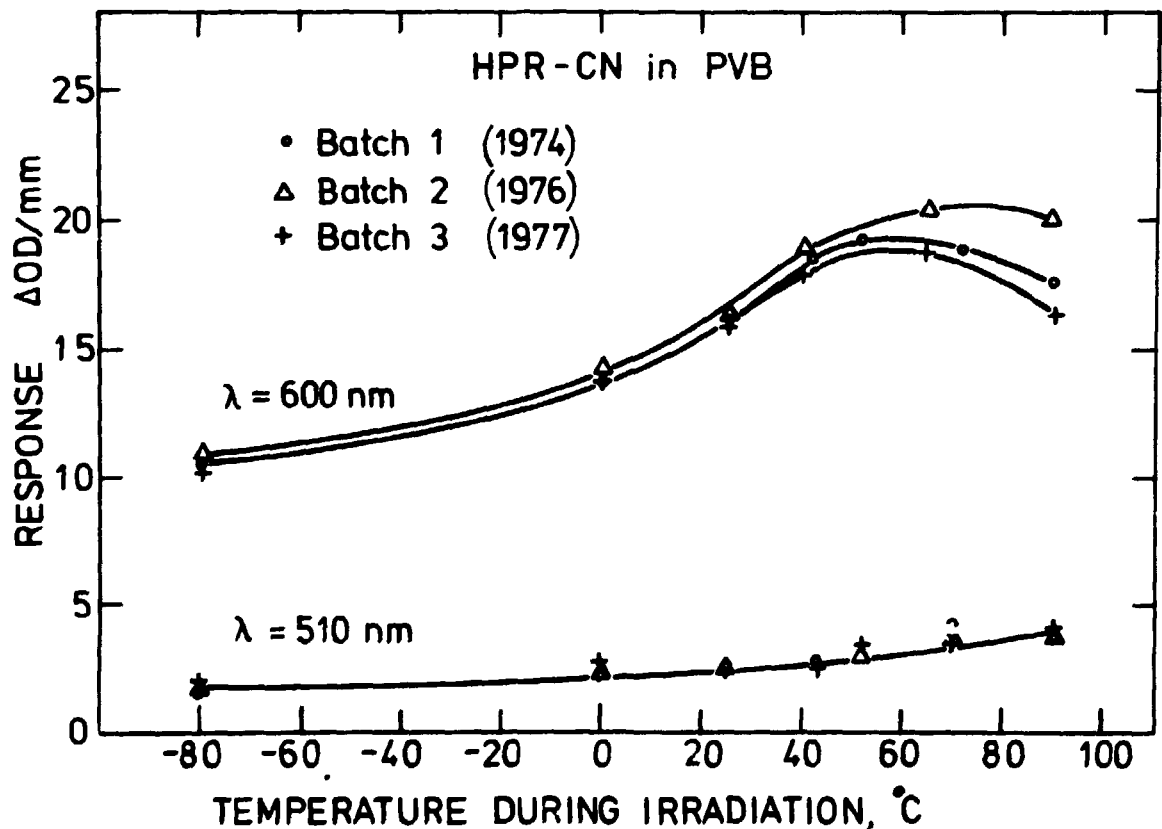


Fig. 8. Variation of response as a function of temperature for three batches of PVB dose meters containing HPR-CN, irradiated to 15 kGy with cobalt-60 gamma-rays.

Since the response is affected by pre- and post-irradiation storage time as shown in the previous section, it is expected that the response of the dose meter is affected by changes in storage temperature both before and after irradiation. This has not yet been thoroughly investigated, but will be as soon as we have chosen a final formulation for dose meter casting.

#### 4. DEPENDENCE ON RELATIVE HUMIDITY

The response of the dose meter may also depend on its water content. The dose meters mentioned earlier based on poly(halo)-styrene are rather ideal in this respect, in that this plastic absorbs very little water, and is reported essentially unaffected by moisture<sup>(20)</sup>.

The PVB dose meter on the other hand does readily absorb water, and the influence of relative humidity in the surroundings and in the dose meter itself has been studied.

Two different situations have been considered:

- A. The dose meter is stored for long times under relative humidity of 40-60% and then subjected to different relative humidities only one hour before irradiation and during irradiation, as might be the case, for example in very dry or damp irradiation rooms. The dose meter is in this case not completely in moisture equilibrium during irradiation, particularly under extreme conditions.
- B. The dose meter is stored for long periods (> 5 days) under the same relative humidity conditions as when irradiated; so that equilibrium moisture content in the dose meter is established before irradiation.

The results of study A are described in refs. (27) and (29),

where similar measurements were carried out for several plastic dose meters. The dose meters were suspended in a closed vial containing a small amount of saturated salt solutions to give different relative humidities in the air surrounding the dose meter<sup>(36)</sup>. After a period of about one hour, the dose meters were irradiated in the vial. After irradiation the dose meters were stored at 50% r.h. and read at different time intervals. Figure 9 shows that the response can vary as much as  $\pm 25\%$  when the relative humidity during irradiation is changed from 12% to 96%. In the range 20% - 80% r.h. the positive relative humidity coefficient is + 0.4% per percent r.h. change, but this factor may well depend on the conditioning time before irradiation.

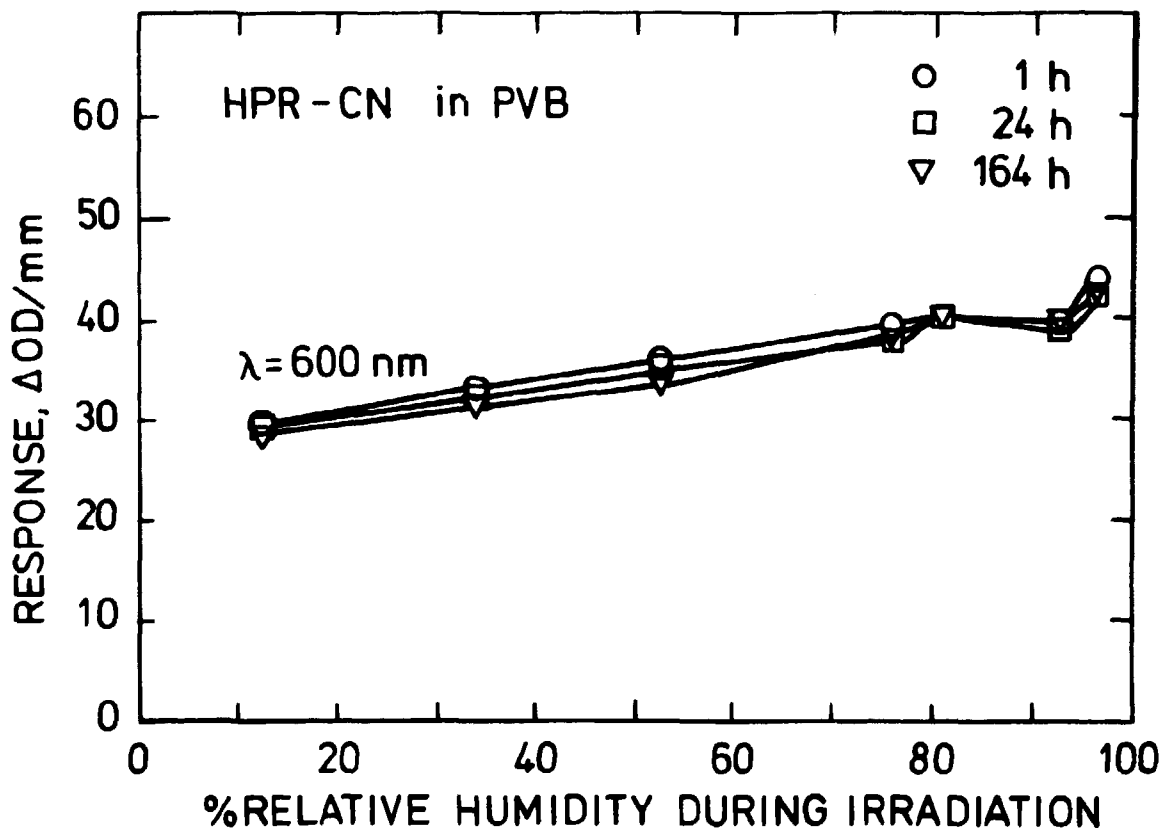


Fig. 9. Variation of gamma-ray response as a function of relative humidity during irradiation for a PVB dose meter with HPR-CN. The dose meters were exposed to the various humidities for about one hour prior to the irradiation to 35 kGy, and measured after different storage periods at 54% r.h. as indicated.



Study B deals with the situation where the conditioning time is sufficiently long (> 5 days) to establish relative humidity equilibrium in the dose meter before irradiation. The measurements were recently carried out here at Risø. In order to establish a common reference point the dose meters were desiccated for 5 days prior to exposure to the different relative humidities. The dose meters were stored for at least five days at the relative humidities chosen for the experiment. They were then irradiated at the same humidities, stored for about 24 hours still under the same conditions and finally measured. Three values of relative humidities were chosen for this experiment (12, 34 and 75%) and three types of PVB dose meters recently made at Risø were tested.

- 1: P15, 17.01.79 B (made from formulation with several solvents and glacial acetic acid).
- 2: P15, 11.07.79 F (made with one solvent and citric acid).
- 3: P15, 30.11.79 C (made with one solvent and citric acid, but less acid than above).

The measurements are shown in Fig. 10. The trend is the same as for shorter conditioning times, but the slope is greater, about + 0.5% per percent change in relative humidity. The difference in response between film types 2 and 3 may be due to the fact that these dose meters were aged for different periods of time (under normal atmospheric conditions) before being exposed to these different relative humidities. When measurements of OD were repeated after about 3 weeks, we saw that the colouration of all the dose meters had increased, except those irradiated at 75% r.h. which were almost constant. These effects will be studied further.

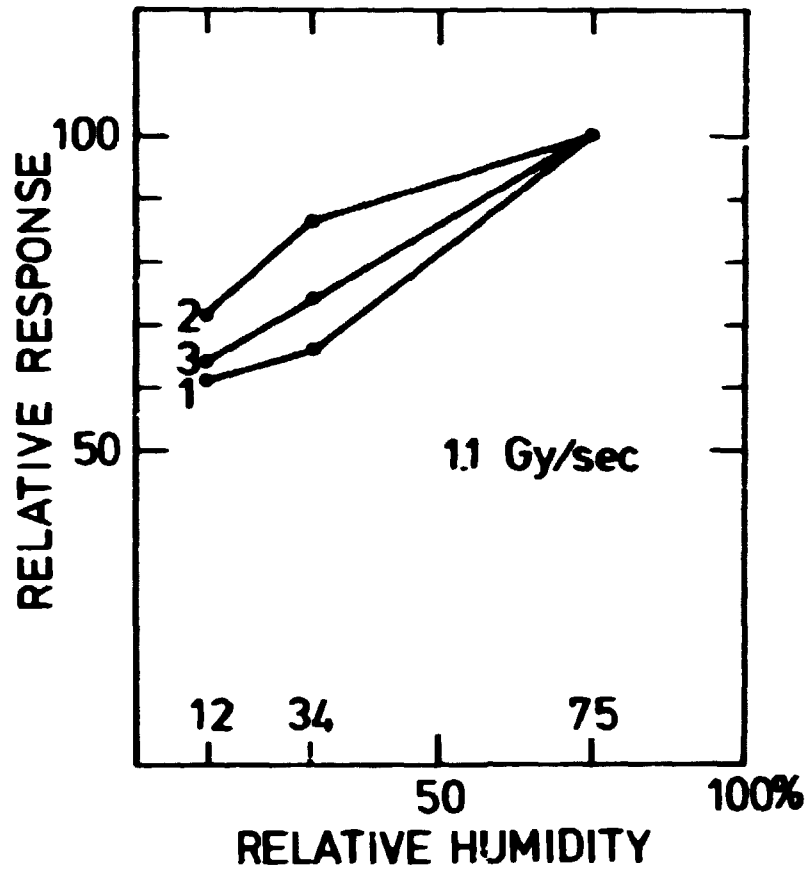


Fig. 10. Variation of gamma-ray response of PVB dose meters exposed to three different relative humidities prior to and during irradiation. Conditioning period was > 5 days.

1. PVB dose meter made from a combination of solvents and with glacial acetic acid.
2. PVB dose meter made from one solvent (2-ethoxy ethanol) and with citric acid.
3. PVB dose meter made from one solvent and with citric acid as in the case of No. 2, but cast 4 months later. The response is normalized with respect to response at 75% r.h.

## 5. DOSE RATE DEPENDENCE

Measurements made elsewhere on 50  $\mu\text{m}$  nylon-base radiochromic dose meters have indicated that the response might depend on gamma-ray dose rate<sup>(24)</sup>, when the dose was administered at rather low dose rates. A dose rate dependence in the response curve shape has been found at very high absorbed doses ( $> 100$  kGy)<sup>(25)</sup>. Previously it was reported that at dose rates from 1 Gy/sec and up, only a small decrease in response was found at higher dose rates<sup>(30,31)</sup>. In the previous reference (24), it was also found that radiochromic nylon dose meters would react differently to changes in relative humidity, if the dose rate was varied.

The measurements of relative humidity dependence mentioned in section 4 were carried out at 1.1 Gy/sec, but we also carried out experiments at 0.2 Gy/sec, changing the dose rate by using lead shields around the dose meters. The response of the same three dose meters irradiated with the same dose of 20 kGy became 15% lower when averaging all 9 measuring points (three relative humidities and three different dose meters). Moreover, the relative dependence on humidity was less, being approximately +0.4% per percent change of relative humidity, as shown in Fig. 11. Previous measurements did not reveal this apparent dose rate effect, but further preliminary experiments have indicated that it may vanish at higher dose rates<sup>(32)</sup> and at moderately high relative humidities, but this is a subject for further study.

It should be noted that in the process of finding the proper formulation for dose meter casting with respect to sensitivity and stability, it seems we may be approaching the optimum dose meter formulation with respect to dose rate dependence. The formulation with one solvent and citric acid has less rate dependence, particularly if properly aged after casting.

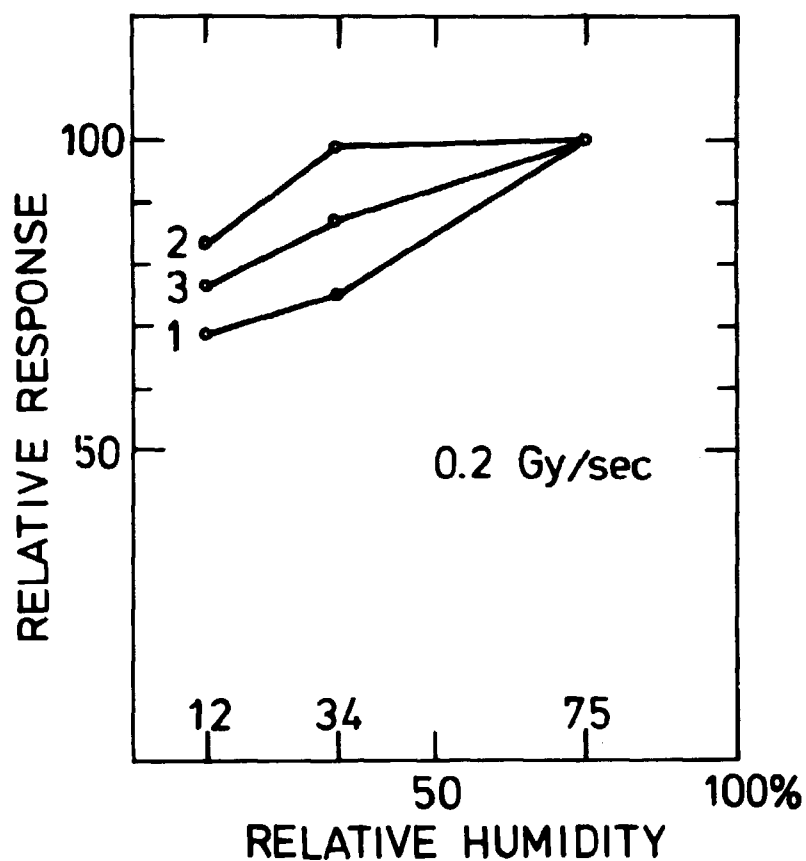


Fig. 11. Variation of response for the same PVB dose meters as in Fig. 10 and exposed under the same conditions, but irradiated at a smaller dose rate, as indicated. The response is normalized with respect to the response at 75% r.h.

$$\frac{\text{Response at 75\% r.h. and 1.1 Gy/sec}}{\text{Response at 75\% r.h. and 0.2 Gy/sec}} = 1.15$$

## 6. AMBIENT LIGHT

It was shown earlier<sup>(23)</sup> that the dose meters containing HPR as the radiation-sensitive element is coloured by ultraviolet radiation with wavelengths shorter than 370 nm. In daily use of the dose meters this can be a problem because daylight as well as incandescent or fluorescent lighting give appreciable illumination in this wavelength range.

Thus, when handling the dose meters, they should whenever possible be kept in light-tight envelopes, or windows and light fixtures should be covered with ultraviolet-absorbing filters. We found a plastic that is available under the name "Llumar"<sup>x)</sup> that shields the dose meters effectively. The absorption spectrum of this plastic is shown in Fig. 12 together with the response of the dose meters to ultraviolet irradiation of different wavelengths. Dose meters have been left in the laboratory for several days exposed to light through this plastic filter without colouration.

## 7. CONCLUSIONS

Dose meters made of hexa(hydroxyethyl)pararosaniline cyanide (HPR) dissolved in polyvinyl butyral (PVB) are being developed at the Accelerator Department at Risø National Laboratory. The dose meters are thin ( $\sim 0.05$  mm), strong, flexible and of good optical quality. The response of the dose meters at their present stage of development is linear within 10% from 100 Gy up to  $\sim 50$  kGy and the response (colouration) is stable within 3% for several months after irradiation, as long as optimum acidity is used. For the time being, the dose meters need recalibration every 3-6 months, because of differences of response with age after casting.

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<sup>x)</sup> Available from: Martin Processing Co. Inc., P.O. Box 726, Martinsville, Virginia, U.S.A.

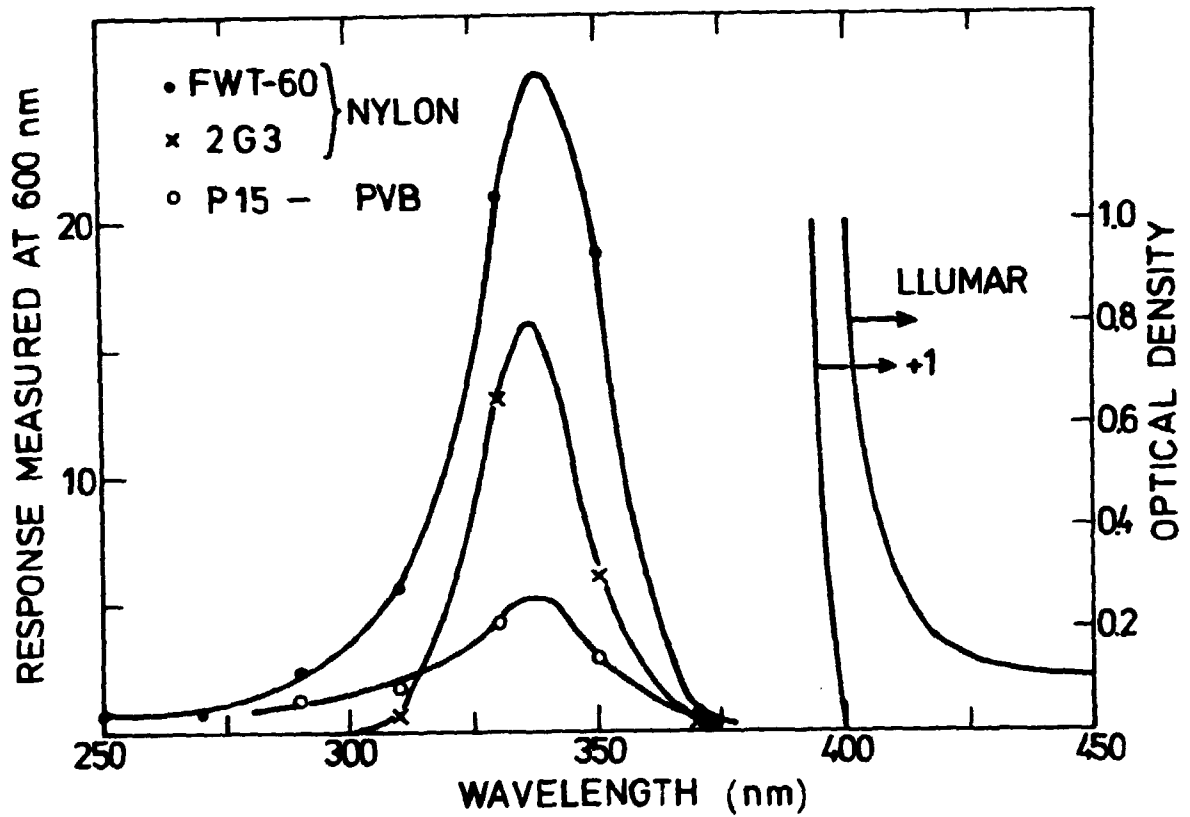


Fig. 12. The spectral response of different radiochromic dose meters to ultraviolet radiation. FWT-60 and 2G3 are nylon-base and P15 is PVB-base dose meters, all with HPR-CN. To the right is shown the absorption spectrum of the ultraviolet absorbing plastic Llummar film.

The work continues as follows:

- minor corrections of solution formulation from which the dose meters are cast in order to avoid recalibration from one batch to another, and from one time period to another.
- studies of the influence of storage period, dose rate, humidity, and different atmospheres, at different absorbed dose and optical density levels.
- testing of recent results<sup>(33)</sup> which indicate that it may be possible to stabilize the response after irradiation.
- testing of long term stability especially for high dose irradiations, where fading has been observed<sup>(34)</sup>.
- further tests of low-intensity rate dependence and possible bleaching effects<sup>(24,35)</sup>.
- further study of UV-light effect. This includes effects of Cerenkov and luminescence produced by irradiation.
- investigation of using PVP dose meters for very fast dosimetry for both spatial and time-resolved measurements down to the microsecond time scale.
- to investigate film types having least temperature dependence (cellulose acetate butyrate, methyl ethyl cellulose) and humidity dependence (PVC, halogenated styrenes).
- to find a light shielding coating material.

REFERENCES

1. McLaughlin, W.L., Solid-phase Chemical Dosimeters. In: Sterilization by Ionizing Radiation, edited by E.R.L. Gaughlin and A.J. Goudie. Multiscience Publication Ltd., 1974, 219-252.
2. Berry, R.J. and Marchall, C.H., Clear Perspex H.X. as a Reference Dose Meter for Electron and Gamma Radiation. Phys. Med. Biol., 1969, 14, No. 4, 585-596.
3. Whittaker, B., Red Perspex Dosimetry. In: Manual on Radiation Dosimetry, edited by N.W. Holm and R.J. Berry. Marcel Dekker, Inc., 1970, 363-369.
4. Ilić-Popović, J., The Use of Polyvinyl-Chloride Film for Electron Beam Dosimetry. Risø Report No. 141, Danish Atomic Energy Commission, Research Establishment Risø, Roskilde, Denmark, 1966.
5. Henley, E.J. and Richman, D., Cellophane Dye Dosimeter for  $10^5$  to  $10^7$  Roentgen Range. Anal. Chem., 1956, 28, 1580-1582.
6. Puig, J.R. and Laizier, J., Utilisation du Triacetate de Cellulose pour la Dosimetrie Megarad des Gammas et des Electrons. Paper No. 342-N/JL/JL, presented at Journées d'Information sur l'Utilisation des Rayonnements Ionisants dans les Procédés Industriels, Grenoble, 10-11 December, 1970.
7. McLaughlin, W.L., Miller, A., Fidan, S., Pejtersen, K., and Batsberg Pedersen, W., Radiochromic Plastic Films for Accurate Measurements of Radiation Absorbed Dose and Dose Distributions. Radiat. Phys. Chem., 1977, 10, 119-127.
8. Humpherys, K.C. and Kantz, A.D., Radiachromics: A Radiation Monitoring System. Radiat. Phys. Chem., 1977, 9, 737-747.
9. McLaughlin, W.L. and Chalkley, L., Low Atomic Number Dye Systems for Ionizing Radiation Measurement. Photographic Science and Engineering, 1965, 9, No. 3, 159-166.
10. McLaughlin, W.L. and Chalkley, L., Measurements of Radiation Dose Distributions with Photochromic Materials. Radiology, 1965, 84, 124-125.



11. McLaughlin, W.L., Microscopic Visualization of Dose Distributions. *Int. J. Appl. Radiat. and Isotopes*, 1966, 17, 85-96.
12. Harrah, L.A., Chemical Dosimetry with Doped Poly(halo-styrene) Film. *Radiation Research*, 1970, 41, 229-246.
13. McLaughlin, W.L., Radiochromic Dye-cyanide Dosimeters. In: *Manual on Radiation Dosimetry*, edited by N.W. Holm and R.J. Berry, Marcel Dekker, Inc., 1970, 377-385.
14. McLaughlin, W.L., Hussmann, E.K., Eisenlohr, H.H., and Chalkley, L., A Chemical Dosimeter for Monitoring Gamma-Radiation Doses of 1-100 krad. *Int. J. Appl. Radiat. and Isotopes*, 1971, 22, 135-140.
15. Hjortenbergh, P.E. and McLaughlin, W.L., Use of Radiochromic Dye Systems for Dosimetry. In: *Proceedings of the Regional Conference on Radiation Protection, Jerusalem, 5-8 March, 1973*.
16. McLaughlin, W.L. and Kosanić, M., The Gamma-ray Response of Pararosaniline Cyanide Dosimeter Solutions. *Int. J. Appl. Radiat. and Isotopes*, 1974, 25, 249-262.
17. Kosanić, M., M.T. Nenadović, Radak, B.B., Marković, V.M., and McLaughlin, W.L., Liquid Radiochromic Dye Dosimetry for Continuous and Pulsed Radiation Fields over a Wide Range of Energy Flux Densities. *Int. J. Appl. Radiat. and Isotopes*, 1977, 28, 313-321.
18. McLaughlin, W.L., Kosanić, M.M., Marković, V.M., Nenadović, M.T., Holcman, J., and Sehested, K., The Kinetics of Dye Formation by Pulse Radiolysis of Pararosaniline Cyanide in Aqueous or Organic Solution. *Risø-M-2202*, Risø National Laboratory, DK 4000 Roskilde, Denmark, November 1979.
19. Franks, L.A., Energy Sensitivity of Doped Poly(halo)-styrene Dosimeter Films. EGG 1183-2256, September 1970. EG&G, Santa Barbara Div., 130 Robin Hill Rd., Goleta, Calif. 93017, USA.

20. Humpherys, K.C. and Randtke, P.T., Doped Poly(halo)styrene Dosimeter Material Studies. EGG 1183-2267, September 1971. EG&G, Santa Barbara Div., 130 Robin Hill Rd., Goleta, Calif. 93017, USA.
21. Chappell, S.E. and Humphreys, J.C., The Dose-rate Response of a Dye-Polychlorostyrene Film Dosimeter. IEEE Trans. on Nuclear Science, 1972, NS-19, 175-180.
22. Bishop, W.P., Humpherys, K.C., and Randtke, P.T., Poly-(halo)styrene Thin-film Dosimeters for High Doses. Rev. Sci. Instr., 1973, 44, 443-452.
23. Miller, A., Investigation of the Radiochromic Dye Film Dosimeter under Process Conditions, Including Stability, Precision, Accuracy, the Influence of Dose Rate, and the Environment. IAEA Research Contract 2051/RB. Progress Report for the period August 1977 - May 1978.
24. Gehringer, P., Eschweiler, H., and Proksch, E., Dose-rate and Humidity Effects upon the Gamma-radiation Response of Nylon-based Radiochromic Film Dosimeters. SGAE-3058, Forschungszentrum Seibersdorf, Okt. 1979, Österreichische Studiengesellschaft für Atomenergie. Lenaugasse 10, A-1082 Wien, Austria.
25. Hansen, J.W., Jensen, M., and Katz, R., The Radiochromic Dye Film Dose Meter as a Possible Test of Particle Track Theory. Risø-M-2243, Risø National Laboratory, DK 4000 Roskilde, Denmark, November 1980.
26. Miller, A., Investigation of the Radiochromic Dye Film Dosimeter under Process Conditions, Including Stability, Precision, Accuracy, the Influence of Dose Rate, and the Influence of the Environment. IAEA Research Contract 2051/RB. Progress Report for the period May - October 1978 and November 1978 - April 1979.
27. Miller, A. and McLaughlin, W.L., Evaluation of Radiochromic Dye Films and Other Plastic Dose Meters Under Process Conditions. Paper presented at: Meeting of Advisory Group on Standardization and High-Dose Inter-comparison for Industrial Radiation Processing. IAEA, Vienna, September 25-29, 1978. Proceedings to be published.

28. Velarde, M.G. and Normande, C., Convection. *Scientific American*, 1980, Vol. 243, No. 1, 78-93.
  29. Levine, H., McLaughlin, W.L., and Miller, A., Temperature and Humidity Effects on the Gamma-Ray Response and Stability of Plastic and Dyed Plastic Dosimeters. *Radiat. Phys. Chem.*, 1979, 14, 551-574.
  30. Miller, A., Bjergbakke, E., and McLaughlin, W.L., Some Limitations in the Use of Plastic and Dyed Plastic Dosimeters. *Int. J. Appl. Radiat. and Isotopes*, 1975, 26, 611-620.
  31. McLaughlin, W.L., Humphreys, J.C., Radak, B.B., Miller, A., and Olejnik, T.A., The Response of Plastic Dosimeters to Gamma-Rays and Electrons at High Absorbed Dose Rates. *Radiat. Phys. Chem.*, 1979, 14, 535-550.
  32. Radak, B.B., private communication.
  33. Chappas, W.J., Accelerated Color Development in Irradiated Radiochromic Dye Films. 3<sup>rd</sup> Int. Meeting on Radiation Processing. Tokyo, Oct. 27-31, 1980. Proceedings to be published in *Rad. Phys. Chem.*
  34. Hansen, J.W. and Wille, M., private communication.
  35. McLaughlin, W.L. et.al. The Gamma-Ray Response of Radiochromic Dye Films at Different Absorbed Dose Rates. 3<sup>rd</sup> Int. Meeting on Radiation Processing, Tokyo, Oct. 27-31, 1980. Proceedings to be published in *Rad. Phys. Chem.*
  36. Wexler, A. and Hasegawa, S., Relative Humidity-Temperature Relationships of some Saturated Salt Solutions in the Temperature Range 0<sup>o</sup> to 50<sup>o</sup>C, *J. Res. NBS* 53, 19-26, 1954.
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| <p>Title and author(s)</p> <p>ON A RADIOCHROMIC DYE DOSE METER</p> <p>Arne Miller and William L. McLaughlin<sup>x)</sup></p> <p><sup>x)</sup> National Bureau of Standards<br/>Washington, D.C. 20234, U.S.A.</p>   | <p>Date December 1980</p> <p>Department or group<br/>Accelerator</p> <p>Group's own registration number(s)</p> |
| <p>34 pages + 2 tables + 12 illustrations</p>   |  |
| <p>Abstract</p> <p>Radiochromic dye dose meters made of polyvinyl butyral (PVB) with hexa(hydroxyethyl)para-rosaniline cyanide (HPR-CN) as the radiation-sensitive element are being developed and investigated at Risø. This report summarizes the present results and outlines plans for further research on this dose meter. Currently the response is found to be almost stable after irradiation, but recalibration of a given batch is needed every 3-6 months because of changes in response characteristics with age. Under typical laboratory conditions, the temperature coefficient is found to be about +1% per degree Celcius and the relative humidity coefficient +(0.4-0.5)% per percent change in relative humidity. The response drops ~ 15% when the dose rate is lowered from 1.1 Gy/sec to 0.2 Gy/sec.</p> <p>This research is supported by IAEA through research contract No. 2051/RB, and this report constitutes the progress report for the period November 1979 - October 1980.</p> <p>Available on request from Risø Library, Risø National Laboratory (Risø Bibliotek), Forsøgsanlæg Risø), DK-4000 Roskilde, Denmark<br/>Telephone: (02) 37 12 12, ext. 2262. Telex: 43116</p> | <p>Copies to</p>   |