A Simple \( \gamma \)-ray Dose Threshold Detector Using a Dye

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Received April 30, 1965

A low cost, simple, convenient and quick readout dose detector whose color change indicates a threshold dose is developed. This detector is a paraffin base film made from polyvinyl chloride (PVC) powder and Congo red. The detector is based on the liberation of chlorine from PVC under irradiation, proportional to absorbed dose, leading to the formation of acid which can cause color change of Congo red.

The \( \text{H}^+ \)-ion yield from PVC powder (mean grain size=120 microns) by irradiation (G(\( \text{H}^+ \))-value) is determined from the pH-value of irradiated PVC powder in water. The film made from PVC powder 50 w\%, Congo red 0.1 w\% and paraffin 50 w\% shows a distinct color change at \( 3 \times 10^4 \) r of \( \gamma \)-irradiation, where the dose rate is \( 6.5 \times 10^4 \) r/hr. It is possible to make a film which changes its color at a higher threshold dose by adding NaOH in Congo red in advance. This threshold dose where color change of the detector initiates is able to be controlled by changing an amount of NaOH. Properties of this detector are reported.

1. Introduction

The sterilization of medical equipments by irradiation may be adopted in practical use also in Japan. For the sterilization by \( \gamma \)-irradiation, \( 2.5 \times 10^6 \) r (the dose selected in the U.K.) is accepted as the optimum dose. It must be assured that every unit of package of products has been irradiated up to a given dose in case of practical sterilization.

The dose measurement with ferrous sulfate solution or ceric sulfate solution gives accurate results, but it does not provide a visual indication and also is sometimes difficult to use. The integral dose measurement with an ionization chamber is not an economical way in case of determining the dose of every package. The glass dosimeter is most suitable for the dose measurement in practical sterilization under present conditions, but needs some instrument such as spectrophotometer and takes time for dose measurement. It has been desired to develop a low cost, convenient and quick readout dose threshold detector or dosimeter.

The result of a dose threshold detector developed by the present authors is as follows. The detector is based on the dehydrochlorination of halogenated polymers under irradiation, proportional to absorbed dose, leading to the formation of acid. If a proper pH-sensitive dye is mixed with halogenated polymers in advance, isolated acid will react with the dye to change its color. J. J. Farrel and R.L. Vale reported radiation sensitive films made from polymer dye solutions prepared with organic solvents. PVC (polyvinyl chloride), copolymer of PVC and PVA (polyvinyl alcohol), copolymer of PVC and polyvinylidene chloride, etc. and several azo dyes were used as polymers and coloring agents respectively. The detector used in our experiments is a simple paraffin base film made from PVC powder and Congo red.

2. Experimental Results

2.1 G(\( \text{H}^+ \))-value of PVC powder

The mechanism of dehydrochlorination of PVC by irradiation was reported by G.J. Atkinson, L. Huckel, et al. It is not argued here. The \( \text{H}^+ \)-ion yield of PVC powder by \( \gamma \)-irradiation is able to be determined from the pH-value of irradiated PVC powder in water. Fig. 1 shows the relation between G(\( \text{H}^+ \))-value of PVC powder (mean grain size=120 microns) and the dose irradiated, when PVC powder in water was irradiated with a 1,000 curies \( ^{60} \text{Co} \) source at the dose rate of \( 6.5 \times 10^4 \) r/hr. The dose rate was measured with the ratemeter of Victoreen, and all the experiments in this paper were made at the same dose rate.

Fig. 1 The relation between $G(H^+)$-value of PVC powder (mean grain size = 120 microns) and the dose irradiated, when PVC powder in water was irradiated with a 1,000 curie $^{60}\text{Co}$ source at the dose rate of $6.5 \times 10^4$ r/hr.

100 eV of energy absorbed in PVC powder. In this case, it had been assured that $G(H^+)$-value of water and polyethylene (used as a vessel of PVC powder and water) was negligible.

2.2 pH-sensitive dyes

Since it may be convenient for the detector to have the form of film, it is necessary for dyes that they behave in a dry polymer film as they do in the presence of water. It is also necessary for dyes themselves to be stable against radiation, and that a color change of a dye is a distinct one. Congo red (Fig. 2) was selected as an indicator satisfying above requirements.

2.3 Preparation of films and their color changes

PVC powder 50 w%, paraffin (used as a base) 50 w% and Congo red 0.1 w% were mixed at about 70°C, and made into the form of film with $0.5 \sim 1.0$ mm thickness. This film sealed in an air-tight envelope of polyethylene or PVC film changed its color from red to blue-violet by irradiation of $3 \times 10^4$ r. Next, NaOH 2.5 mg per PVC powder 1.0 g (this amount of alkali is equivalent to neutralize H$^+$-ions liberated from PVC powder by irradiation of $3.0 \times 10^6$ r, when $G(H^+)$-value is 25.0) was added to the mixture above mentioned with a very small amount of water, and a film made from this second mixture changed its color by irradiation of $2 \times 10^6$ r, which showed a comparatively good agreement with the value calculated. From above experiments, it is possible to prepare a film which changes its color at a dose desired by controlling an amount of alkali contents.

4. Properties of the Detector and Discussion

Color change and accuracy The color change is a distinct one and no neutral tints between the two colors are observed. The changed color (blue-violet) was not intensified by more irradiation. In case of films added alkali spotted color change appeared near at the threshold dose where color change initiated, while not in case of films not containing alkali. It is probably due to ununiformity of mixing of alkali and Congo red. Because of this spotted color

Fig. 2 Congo red (<pH 5.0 red—pH 3.0 blue-violet>)

Fig. 3 (A) The film under irradiation with a 500 curies $^{60}\text{Co}$ source. The film consists of PVC powder (mean grain size = 120 microns) 50 w%, Congo red 0.1 w%, paraffin 50 w% and NaOH 2.5 mg per PVC powder 1.0 g.

(B) The color change after 24 hours irradiation. Dark area is blue-violet and the rest is red. Where the threshold dose for color change is $2 \times 10^6$ r.
change, an accuracy of dose determination from color change is rather poor, about ±25%. However it may be improved by the careful mixing of alkali and Congo red.

*Stability of unirradiated films* Films stored 3 weeks in room temperature changed their colors at the same dose as in films irradiated immediately after production.

*Stability of color* The unirradiated color and the changed color have not faded at least 1 year in room temperature.

*Detectable dose range* Above the dose of about $2 \times 10^7$ r, it is difficult to discriminate the color change of film due to coloration of PVC itself. Therefore the detectable dose range of film is below $10^7$ r. However using a thin film, it is possible to extend this upper limit to some extent.

*Advantages of the detector* The advantages of this detector include good reproducibility, low cost, capability of being manufactured in arbitrary sizes and shapes, and no special skill in measurement.

5. Photographs for Demonstration

Photographs for demonstration of this detector are shown in Fig. 3 and Fig. 4.

![Fig. 4 The color change of film after 31 hours irradiation. The film has the same composition as the sample shown in Fig. 3.](image)

References

3) L. Huckel: *Isotopentechnik*, 4, 112 (1961)