

RADIOCHROMIC BLUE TETRAZOLIUM FILM DOSIMETER

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Hungarian Academy of Sciences, Budapest, Hungary**Abstract**

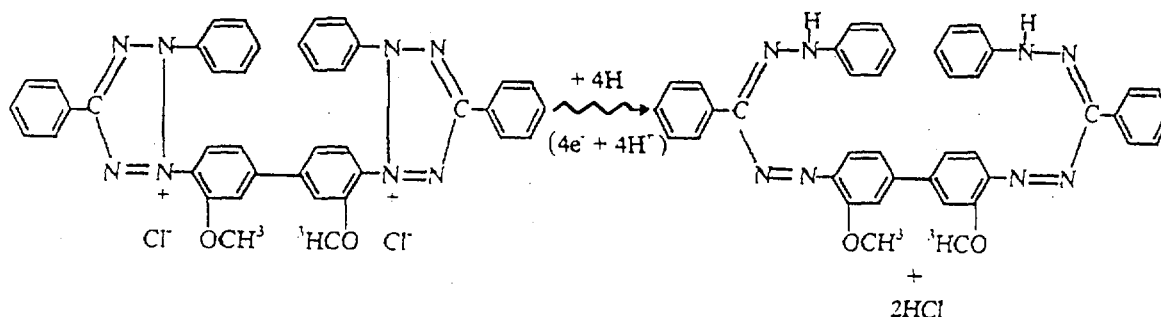
The colourless radiochromic chloride salt of blue tetrazolium (BT^{2+}) is reduced radiolytically to the deep violet-coloured formazan. Dosimeter films of this radiation sensor can be produced by dissolving polyvinyl alcohol (PVA) in a heated aqueous solution of the salt, and, upon cooling, by casting the solution on a horizontal glass plate. In the present development, the resulting flexible transparent film is readily stripped from the plate, with a thickness of 0.045 mm. Upon irradiation with gamma rays or electron beams, a permanent image is produced with a broad absorption band in the visible spectrum. The radiation response is approximately a linear function in terms of the increase in optical absorbance (ΔA) measured at $\lambda_{max} = 552$ nm wavelength versus absorbed dose (D) over the range 5 to 50 kGy. The radiochromic image has a relatively high spatial resolution and can be used to register dose distributions and beam profiles. The value of ΔA shows a gradual increase for the first 24 hours after irradiation but is stable thereafter. The variation of response with irradiation temperature is negligible over the temperature range -20 °C to $+30$ °C, but displays a pronounced positive temperature dependence at higher temperatures. The response to gamma radiation shows negligible dose-rate dependence as long as the radiochromic sensor concentration in the PVA matrix is sufficiently high (> 6 % by weight).

1. INTRODUCTION

The ditetrazolium chloride salt, $C_{40}H_{32}Cl_2N_8O_2$ is referred to in dye literature as *blue tetrazolium* (BT^{2+}) [1,2]. It has been used histochemically and cytochemically as a biological stain with oxidative enzyme systems, especially nicotinamide coenzyme-formed dehydrogenase reactions, for the past 50 years [3,4]. BT^{2+} is an analogue of the more familiar mono-tetrazolium form, in particular the triphenyl-tetrazolium chloride (TTC) salt, used as a radiochromic dosimeter by means of radiolytic reduction to triphenyl-formazan pigment. Slightly soluble in aqueous or alcohol solution and in hydrogels, BT^{2+} forms a nearly colourless, pale yellow medium. When irradiated with short-wave ultraviolet or ionizing radiation, however it is reduced irreversibly to a deep-violet di-formazan pigment. This reaction is similar to radiation chemical reactions studied by pulse radiolysis of other tetrazolium salt solutions, e.g. the mono-form 2,3,5-triphenyl-tetrazolium chloride [5-7]. Aqueous solutions of BT^{2+} have recently been investigated at the University of Maryland and NIST by pulse radiolysis [8], which gave results similar to those reported by Bielski's group at Brookhaven National Laboratory with another aqueous di-tetrazolium, nitro blue tetrazolium (NBT^{2+})[9]. It is shown that the reactions of BT^{2+} or NBT^{2+} with the hydrolytic hydrated electron and hydrogen atom proceed by rapid reduction at a rate constant of about $10^{10} M^{-1}s^{-1}$, with protonation occurring at the nitrogen closest to the unsubstituted phenyl group. This reaction involves the step-wise addition of four electrons and the formation of two transient tetrazole ring-shared free radicals, BT^{\cdot} or NBT^{\cdot} and the mono-formazan, MF, leading to the opening of one of the rings to a formazan cation centre MF^+ and an intermediate tetrazolium centre consisting of

the tetrazolinyl radical. These can be further reduced radiolytically to the stable hydrophobic product, di-formazan (DF) [8].

This reduction occurs via the two intermediate tetrazolinyl radicals shared by the di-tetrazole ring nitrogens, by the pH-dependent second-order disproportionation reaction producing mono-formazan and the *blue tetrazolium* cation cited below.



The aim of the present study is to evaluate a polymeric film containing BT^{2+} as a radiochromic dosimeter. The effects of BT^{2+} concentration, absorbed dose and dose rate, storage conditions, and irradiation temperature on dosimeter performance are investigated by gamma-ray sensitometry.

2. EXPERIMENTAL PROCEDURES

The blue tetrazolium salt (MW 727.66) was used as received from Aldrich Chemical Co., Inc.¹ without further purification. Polyvinyl alcohol (PVA) (99.7 % mol hydrolyzed; average MW 108,000) from Polysciences, Inc.¹ was used as the film-formulator host material. Dextrose (MW 180,162) from Fisher Scientific Co. Inc.¹ was used as the precursor to the reducing radicals. Water purified by the Millipore Milli-Q system¹ was used as the solvent for both the BT^{2+} salt and PVA.

The PVA (2.5 g) was slowly dissolved in 50 mL of deionized water at 90 °C. The solution was kept well stirred in a 100-mL volumetric flask in which a pre-dissolved aliquot of BT^{2+} in water at a specific ultimate concentration value was added, in order to form a specific weight percentage (6.7 wt%) of radiochromic dye in the PVA solution. Stirring of this solution was continued at 60 °C for 30 minutes, to prevent precipitation of the polymer and in order to achieve a uniform viscous medium. This solution was then poured onto a horizontal glass plate and allowed to dry at room temperature for two days in a draft-free darkened room. The resulting non-tacky, flexible, colourless film could then be stripped from the glass surface and cut into 1 cm x 1 cm dosimeter film samples having a relatively uniform thickness of 0.045 (\pm 0.005) mm (1σ).

For gamma-ray irradiations, the films were held between 5-mm thick polystyrene layers, in order to maintain approximate electron equilibrium conditions simulating water for 1.25 MeV photons. The gamma-ray irradiations were made at a series of absorbed doses in water over a dose range of 1 to 75 kGy. The film sandwich assembly was placed for irradiation in an annular geometry using a thermostated shielded arrangement of twelve equally-spaced ⁶⁰Co source rods. Two Nordion International Gammacell Model 220 (GC-45 and GC-232) irradiators¹ were used, supplying absorbed dose rates in water of 0.95 and 3.15 Gy s⁻¹, respectively.

¹ The mention of commercial products in this paper does not imply recommendation or endorsement by the University of Maryland or the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

Before and after irradiation of the films, their absorption spectra and absorbance values at specific wavelengths were measured with a double-beam Cary Model 3E spectrophotometer (Varian Australia Pty. Ltd.)¹. For each measurement series, a stack of five 10 mm x 10 mm pieces of the film were irradiated together, and then were measured spectrophotometrically individually at room temperature. For both unirradiated and irradiated films at each dose, the average of the absorbance values of the five replicate film samples was used.

3. RESULTS

The gamma-ray response characteristics of the PVA film dosimeter containing 6.7 wt% BT²⁺ are shown in Fig. 1. The response curve measured spectrophotometrically at $\lambda = 552$ nm is presented on the left. The radiation-induced absorption spectra, where the ordinate on the left is given as the increase in

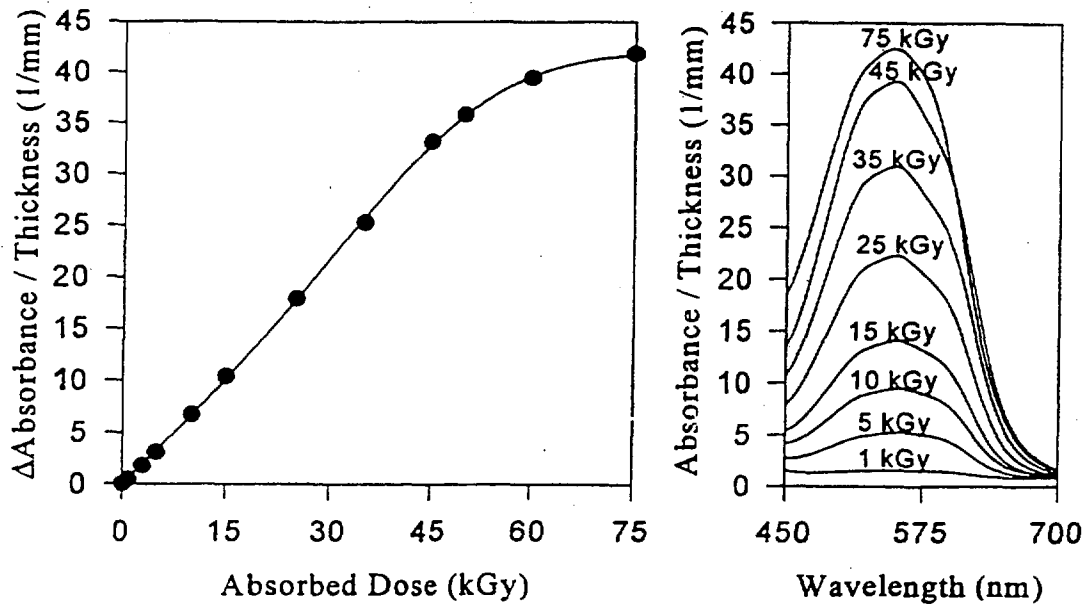


FIG.1. PVA films (6.7 wt% BT²⁺) exposed to gamma radiation from a ⁶⁰Co source: left – the calibration curve in terms of increase in absorbance per unit thickness of the film at 552 nm wavelength as a function of absorbed dose in water; right – the radiation-induced absorption spectra.

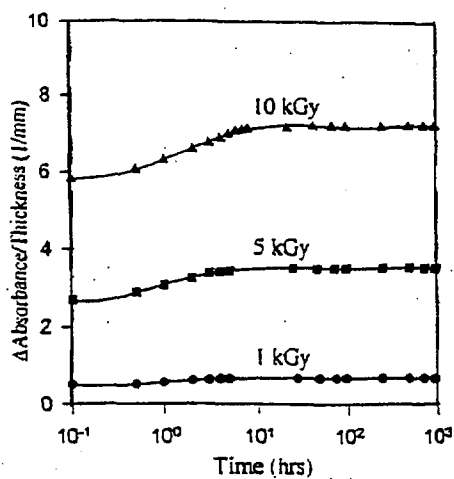


FIG.2 Stability of Δ A/l readings of BT²⁺ films stored in the dark at room temperature after irradiation to three different doses

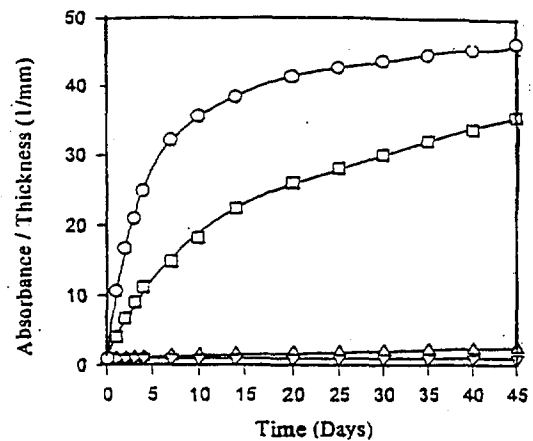


FIG.3. Instability of un-irradiated BT²⁺ films under different storage conditions.

○ direct sunlight; □ in the shade
 △ white fluorescent light; ▽ in the dark

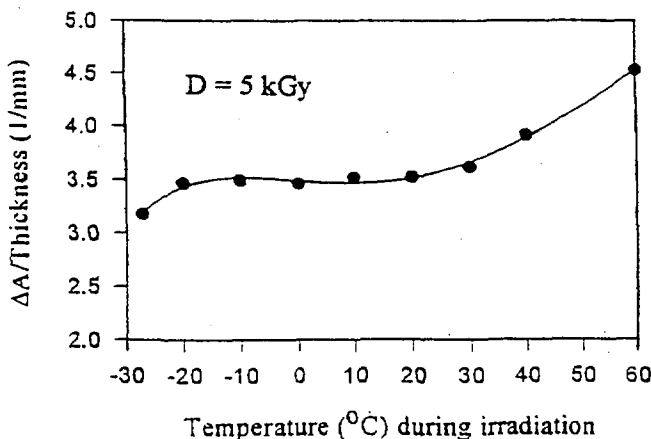


FIG.4. Variation in $\Delta A/l$ at 552 nm as a function of irradiation temperature for gamma-irradiated BT^{2+} radiochromic film.

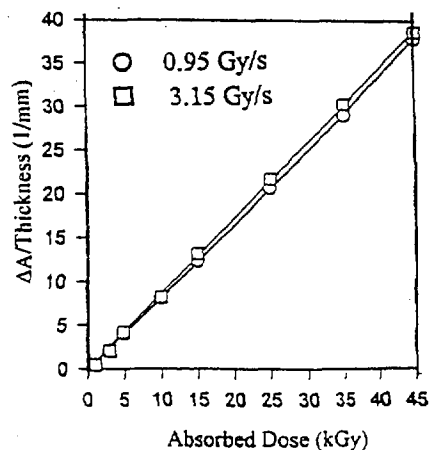


FIG.5. Gamma-ray response of the BT^{2+} radiochromic film at two dose rates.

absorbance per unit film thickness, $\Delta A/l$ are on the right. The irradiations were made at a temperature of 25 °C. The response curve in Fig. 1 is approximately linear in the dose range up to about 50 kGy, but it tends toward saturation at higher doses.

In order to study post-irradiation stability properties, the PVA- BT^{2+} films were irradiated with gamma rays to three doses, and then values of ΔA at 552 nm wavelength were monitored at different times after the end of irradiation. Between each ΔA reading, the films were stored in the dark at room temperature. Figure 2 shows that, at a dose of 10 kGy, the absorbance continues to increase by about 20 percent for about the first eight hours after irradiation and then becomes stable. The time for reaching a stable ΔA value is somewhat shorter at the lower doses.

In another stability study, the effects of ambient light conditions were investigated, as shown in Fig. 3. Here, the sensitivity of these films to the ultraviolet component of daylight is revealed by the increase in absorbance per unit film thickness. This indicates that the films should not be handled under bright light conditions, i.e. direct or indirect (shade) sunlight.

The irradiation temperature dependence of the film response to gamma radiation at a dose of 5 kGy was also studied over the temperature range -30 °C to +60 °C. The results shown in Fig. 4 indicate that, whereas a positive temperature coefficient is found at temperature extremes below -20 °C and above +30 °C, the response is relatively temperature-independent between -20 °C and +30 °C.

The film response was also studied at two absorbed dose rates 0.95 and 3.15 Gy/s. The results are shown for PVA film containing 6.7 wt% BT^{2+} (see Fig. 5) in terms of the increase in absorbance per unit film thickness measured at $\lambda = 552$ nm wavelength and as a function of absorbed dose administered at the two dose rates. The sensitivity at the lower dose rate is slightly less than that at the higher dose rate, but the difference is within the estimated uncertainty of the absorbance readings of the film dosimeter, i.e., within $\pm 4\%$ (1σ).

4. CONCLUSION

Radiochromic PVA – BT^{2+} films, with sensor concentrations of 6.7 wt %, are shown to be useful for routine gamma-ray dosimetry in the absorbed dose range of approximately 1 to 50 kGy, when measured at the peak of the radiation-induced absorption band.

The radiochromic response is dependent on extremes of irradiation temperature below -20 °C and above +30 °C. They must be shielded from direct or indirect sunlight because of their intrinsic sensitivity to ultraviolet light. Even when stored in the dark, they require several hours delay before readout because of a slow transient increase in absorbance immediately after irradiation. Further studies should be made with gamma radiation over broader ranges of dose rate and with electron beams at much higher dose rates, as well as with ultraviolet radiation curing sources, in order to expand the potential uses of this system for radiation processing applications.

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