A new, highly-sensitive dosimetric composition based on a solution of rhodamine B lactone in chloroform

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A dosimetric composition based on a solution of rhodamine B lactone in chloroform saturated with water and air has been developed; this allows measurement of absorbed doses within the range 0.04–38 Gy at dose rates up to 6×10^8 Gy s^{-1}.

A large number of dosimetric systems allowing measurement of absorbed doses of several kilograys in magnitude is known (see, *e.g.*, refs. 1 and 2). Systems which can be used for the determination of doses < 1 Gy are considerably less common (see, *e.g.*, ref. 1). Previously in ref. 3, carried out with the participation of the present group, a dosimetric system based on an aqueous–alcoholic solution of tetrazolium salt for the determination of doses of -radiation within the range 1–50 Gy was described. Continuing this study, we observed that a solution of rhodamine B lactone in chloroform saturated with water and air can be used for the measurement of absorbed doses within the range 0.04–38 Gy at dose rates up to 6×10^8 Gy s^{-1}. The use of this system is based on the conversion of colourless lactone to rhodamine B, which has an intense purple colour, upon reaction with the acid formed during radiolysis of chloroform in the presence of water and air.

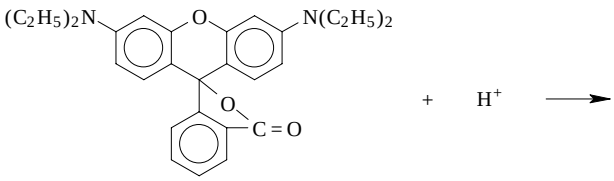
^{60}Co -radiation (dose rates 2×10^{-5}–3×10^{-1} Gy s^{-1}) and electron pulses (dose rates 2×10^6–6×10^8 Gy s^{-1}) generated by linear electron accelerators U-12 (electron energy 5 MeV, pulse duration 2.3 s) and 'Elektronika' (electron energy 8 MeV, pulse duration 8.9 ns) were used. Dosimetry was conducted with the usual or modified Fricke dosimeters,[1,2] the difference between the densities of the studied and the dosimetric solutions being taken into account.

Rhodamine B and chloroform were 'for quantum electronics' and 'for medical purposes' grades, respectively. The latter was washed with twice distilled water to remove traces of acid and alcohol. The solutions of rhodamine B lactone were prepared based on spontaneous conversion of the dye to lactone in proton-accepting solvents (chloroform is such a solvent). Equal volumes of aqueous dye solution and chloroform were mixed in a separating funnel and shaken for 5–10 min. The mixture was left to stand for 1 min for segregation. The aqueous solution became discoloured as a result of these operations, and the lactone formed was in the lower (chloroform) layer. After separation, this system was used as a dosimetric system [a solution of rhodamine B lactone in chloroform saturated with water (5.4×10^{-2} mol dm^{-3} at 293 K[4]) and air (2.48×10^{-3} mol dm^{-3} at 293 K[5])].

The yields of rhodamine B were determined from the difference in the absorbances of irradiated and unirradiated solutions at the dye optical absorption band maximum (550 nm). The value of the molar absorption coefficient of this dye in chloroform determined by us (7.1×10^3 m^2 mol^{-1}) was used in the calculations. The measurements were performed on a 'Specord M-40' spectrophotometer.

It was found that lactone **1** upon irradiation of the afore mentioned solution was converted to rhodamine B **2** by reaction with the acid formed from radiolytic decomposition of solvent, reaction (1). As an example, Figure 1 shows the optical absorption spectra of an unirradiated 2.5×10^{-5} mol dm^{-3} solution of rhodamine B lactone in chloroform saturated with water and air and the same solution after irradiation with dose 1.6 Gy.

The formation of dye also continues after irradiation. The duration of the process after irradiation was not more than 30 min at used concentrations of lactone (2.5×10^{-5} to 2×10^{-4} mol dm^{-3}), doses and dose rates. It was observed that the yield of dye (24.0±2.4 molecule/100 eV) did not depend on the concentration of the solution within the range studied and



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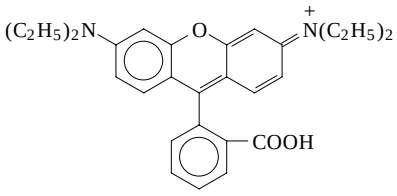

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(1)

dose rates from 2×10^{-5} to 6×10^8 Gy s^{-1}. Some data obtained are shown in Table 1.

The higher limit of measured dose increases proportionally with lactone concentration in solution. This is illustrated by Figure 2 in which the dependences of optical absorption of formed dye at various lactone concentrations are presented. A bend in the curves is caused by conversion of the greater part of lactone to dye. It is seen that a 2×10^{-4} mol dm^{-3} solution can be used for measurement of absorbed doses within the range 0.04–38 Gy. Use of a cell with an optical path length of 10 cm allowed us to determine a dye concentration of 10^{-7} mol dm^{-3} that corresponds to dose of *ca.* 0.02 Gy. This value can be considered as the sensitivity level of the system. The lower the concentration of the solution, the lower the optical absorption of the unirradiated solution. Because of this, solutions with lactone concentrations < 2×10^{-4} mol dm^{-3} are more suited to a determination of low doses and to use of the system as a personnel dosimeter.

Table 1 Yields of rhodamine B *G*(Dye) upon irradiation of solutions of its lactone in chloroform saturated with water and air at room temperature.

[Lactone]/ mol dm^{-3}	Radiation type	Dose/Gy	Dose rate/ Gy s^{-1}	*G*(Dye), molecule/100 eV
2.5×10^{-5}	-Radiation	0.02	2×10^{-5}	23.0
2.5×10^{-5}	-Radiation	1.0	1.3×10^{-4}	24.3
2.5×10^{-5}	-Radiation	1.0	1×10^{-3}	24.3
2.5×10^{-5}	-Radiation	1.0	1×10^{-2}	24.3
2.5×10^{-5}	-Radiation	8.5	1.5×10^{-2}	26.2
5×10^{-5}	-Radiation	18.5	1.5×10^{-2}	26.2
1×10^{-4}	-Radiation	0.3	2×10^{-3}	24.8
1×10^{-4}	-Radiation	10.0	1×10^{-2}	24.5
1×10^{-4}	-Radiation	10.0	5×10^{-2}	25.0
1×10^{-4}	-Radiation	10.0	3×10^{-1}	24.3
1×10^{-4}	Electron pulses (5 MeV)[a]	16.6	2.2×10^{-6}	25.0
1×10^{-4}	Electron pulses (8 MeV)[b]	14.1	5.8×10^{8}	23.0
1×10^{-4}	Electron pulses (8 MeV)[b]	15.0	6.2×10^{8}	22.0
2×10^{-4}	-Radiation	37.5	2.4×10^{-1}	24.0

[a] Pulse duration is 2.3 s. [b] Pulse duration is 8.9 ns.

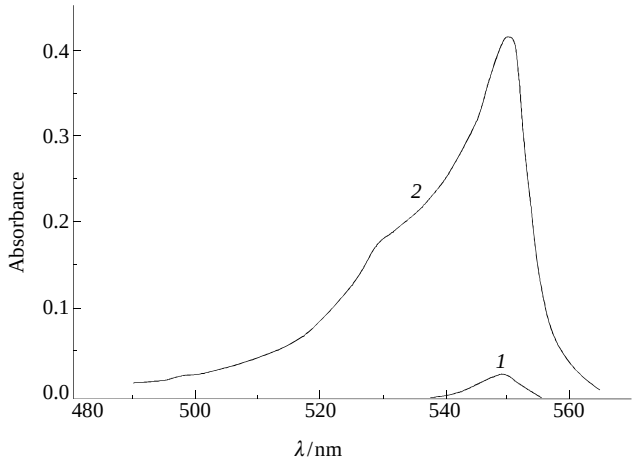

Figure 1 Optical absorption spectra of a 2.5×10^{-5} mol dm^{-3} solution of rhodamine B in chloroform saturated with water and air: *1* – initial solution, *2* –sol ution after irradiation to dose 1.6 Gy (optical path length *l* 1 cm).

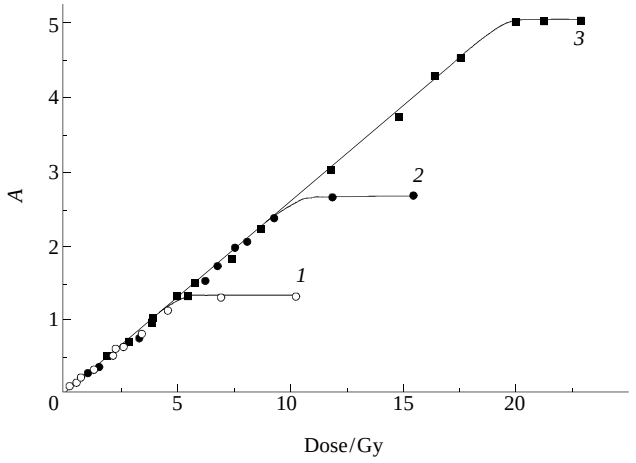

Figure 2 Dependence of variation of absorbance *A* for a solution of rhodamine B formed *vs.* absorbed dose upon -irradiation of 2.5×10^{-5} (*1*), 5×10^{-5} (*2*) and 1×10^{-4} (*3*) mol dm^{-3} solutions of its lactone in chloroform saturated with water and air (λ = 550 nm, *l* = 1 cm, 293 K).

The yield of dye formation depends somewhat on the temperature of the solution upon irradiation. Temperature also has an influence on the duration of the post effect, *i.e.* the formation of dye after irradiation. The respective data are given in Table 2. From Table 2 it follows that the irradiation of the system must be conducted at 274–308 K and that determination of the optical absorption of irradiated 2.5×10^{-5}–2×10^{-4} mol dm^{-3} solutions must take place 45 min after exposure. Under such conditions the reproducibility error at confidence level 0.95 is ±6–8% at doses over 1 Gy and ±10–12% at doses 1 Gy.

The lactone solutions are stable for a long time. It was found that they experienced no change upon storage in sealed ampoules and in the dark for 5.5 years. However, the stability becomes noticeably worse upon storage in day light. For example, the optical absorbance of a 1×10^{-4} mol dm^{-3} solution of lactone increases by 13% upon storage in day light for 9 days. The colour of the irradiated solution after finishing the post effect changed little 15 days after irradiation. During this time, its intensity increased by 12%.

The conversion of lactone to dye is also observed in deaerated solutions. However, in this case the yield of rhodamine B is noticeably lower, but a post effect is absent. In addition, solutions in other proton-accepting solvents were studied. It was found that the yields of dye were equal to 9, 11 and 14 molecule/100 eV in dichloroethane, trichloroethylene and tetrachloromethane, respectively, *i.e.* considerably lower than in chloroform.

The concentrations of lactone recommended for dosimetric measurements range from 2.5×10^{-5} to 2×10^{-4} mol dm^{-3}. The lower limit is due to the fact that at lower concentrations, the duration of the post effect increases considerably. For instance, the duration of the post effect at room temperature is 2 h at a lactone concentration of 1×10^{-5} mol dm^{-3}. The higher limit is caused by the confined solubility of rhodamine B in water from which the dosimetric system is prepared by extraction of dye to chloroform and, as a consequence, by the necessity of using large water volumes.

It is possible to present the following interpretation of the data obtained. It is known (see, *e.g.*, refs. 6–8) that the primary products of chloroform radiolysis are Cl, $CHCl_2$, CCl_3, CCl_2 and HCl, their total yield being equal to 11.9 molecule/100 eV. In the absence of oxygen, the main final products are HCl, CH_2Cl_2, $C_2H_2Cl_2$, C_2HCl_5, C_2Cl_6 and CCl_4. In the presence of oxygen, hydroperoxide and phosgene are formed. If chloroform also contains water, hydroperoxide and phosgene are hydrolysed with formation of HCl, reactions (2) and (3).

$$CCl_3OOH + H_2O \longrightarrow 3HCl + CO_2 + 1/2O_2 \quad (2)$$

$$COCl_2 + H_2O \longrightarrow 2HCl + CO_2 \quad (3)$$

Based on this mechanism, it is possible to observe that the yield of HCl in chloroform containing water and air must be equal to 26 molecule/100 eV. The yield of dye is close to this value. Therefore, it may be concluded that rhodamine B appears in reaction (1) and the presence of post effect is caused by the low rate of hydroperoxide and phosgene hydrolysis [reactions (2) and (3)].

The dosimetric system developed can be used for monitoring nuclear accidents, in radiobiology, radiation chemistry and some areas of radiation technology (for example, in radiation treatment of food).

Table 2 Influence of temperature on yield of rhodamine B formation and duration τ of the post effect upon -radiolysis of a 2.5×10^{-5} mol dm^{-3} solution of lactone in chloroform saturated with water and air (dose 1.8 Gy, dose rate 5×10^{-3} Gy s^{-1}).

Temperature/K	*G*(Dye), molecule/100 eV	τ/min
253	18	50
274	21	45
293	24	30
308	27	20
323	34	15

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