

Exploring the dose response of radiochromic dosimeters

PS Skyt^{1,2}, I Wahlstedt², ES Yates¹, L P Muren¹, JBB Petersen¹ and P Balling²

¹Dept of Medical Physics, Aarhus University /Aarhus University Hospital, Denmark

²Dept of Physics and Astronomy, Aarhus University, Denmark

E-mail: skyt@phys.au.dk

Abstract. The aim of this study was to explore the dose response of a newly developed radiochromic hydrogel dosimeter based on leuco malachite green dye in a gelatine matrix. The original dosimeter composition was first investigated in terms of dose response and dose-rate dependence. In addition, the initiating compounds producing chlorine radicals were substituted with compounds producing fluorine radicals, oxygen-centered radicals, carbon-centered radicals and bromine radicals. Also the surfactant was substituted by other compounds of different molecular size and charge. The original composition gave a dose response of $3.5 \cdot 10^{-3} \text{ Gy}^{-1} \text{ cm}^{-1}$ at 6 Gy/min with a dose rate dependence giving a 27 % increase when decreasing the dose rate to 1 Gy/min. None of the substituted initiating components contributed to an increase in dose response while only one surfactant increased the dose response slightly.

1. Introduction

Radiochromic dosimeters are promising tools for three-dimensional dosimetry [1] since they i) are insensitive to oxygen, ii) offer non-scattering dose response, and iii) are well suited for optical read-out [2]. In recent years, new dosimeter compositions have been proposed based on leuco malachite green dye suspended in a gelatine gel [3, 4]. However, the dosimeters suffer from low dose response, dose-rate dependence, and a relatively high auto-oxidation. To assess these issues we have in this study investigated the effect on the dose response when substituting chemical components of the dosimeter. Two components were substituted, the initiator in order to change its reactivity, as well as the surfactant to change the micelle structures.

2. Materials and Methods

2.1. Dosimeter fabrication

The original composition used in this study is based on that proposed in [4]. It consists of 6 % (w/w) gelatine that forms the matrix of the volume dosimeter. The active component is 0.37 mM leuco malachite green (LMG) dissolved in 80 mM trichloromethane (CHCl_3) while 5 mM trichloroacetic acid (TCA) was added as an initiator. To dissolve the LMG and CHCl_3 in the gelatine solution 50 mM sodium dodecyl sulfate (SDS) was added as a surfactant. Since SDS consists of a hydrophilic head region and a hydrophobic tail these molecules forms so-called micelles, making it possible to dissolve the non-polar LMG and CHCl_3 in an aqueous solution. A description of the procedure for manufacturing the dosimeter can be found in [4]. The gel was prepared in standard PMMA cuvettes (1x1x4.5 cm) and placed in a refrigerator until the next day.



2.2. Substituting initiator

The initiator, TCA, was substituted to investigate the effect of changing the reactivity of both the compound and the radicals produced. TCA was substituted with trifluoroacetic acid (TFA) to yield fluorine radicals, 2,4-pentadione peroxide (abbreviated 2,4-peroxide) and hydrogen peroxide (H_2O_2), to yield oxygen-centered radicals, 2,2'-azobis(2-methylpropionamide) dihydrochloride (abbreviated 2,2-azo) and 4,4'-azobis(4-cyanovaleric acid) (abbreviated 4,4-azo) to yield carbon-centered radicals, and HBr and CBR_4 to yield bromine radicals. NaOH was added to very acidic gel formulations since such acidic solution gave a thick opaque gel with two phases. The change in pH was not observed to affect the dose response for the original version.

In addition, a batch without TCA as well as batches with both TCA and $CHCl_3$ substituted with CCl_4 or dimethylformamide (DMF) were made to investigate the initiating effect of TCA and $CHCl_3$.

2.3. Substituting the surfactant

Since LMG is expected to be inside the micelles due to its non-polarity, the shape of the micelles might be of influence for the sensitivity of the dosimeter. Therefore the surfactant SDS was substituted in order to change the micelle size. It was hypothesized that larger heads or shorter tails of the surfactant would lead to smaller micelles increasing the surface-to-volume ratio. Three surfactants were investigated: Sodium dodecylbenzenesulfate (SDBS), sodium octyl sulfate (SOS), and dodecyltrimethylammonium bromide (DTAB). SDBS contains a larger head region since unlike SDS a benzene ring is present in the head region while SOS has a shorter tail than SDS. DTAB was similar to SDS but with a cationic head contrary to the anionic SDS.

2.4. Irradiation

Irradiation of the dosimeters was performed with x-rays from a linear accelerator set at 6 MV. The dosimeters were placed in a source-to-surface distance of 94.5 cm behind 5 cm of solid water. Additionally 5 cm solid water was placed behind the dosimeters to ensure backscatter. The dose rate was 6 Gy/min and dose sequences up to 80 Gy were given.

2.5. Read-out and data analysis

The optical densities of the dosimeters were measured with a spectrophotometer (Helios Alpha, Thermo Spectronic) at 633 nm both a few hours before irradiation and about 16 hours after irradiation. The two measurements were subtracted in order to obtain the optical response, i.e. the optical density change caused by the irradiation. The dose response was then obtained by plotting the optical response as a function of dose and fitting to a linear equation. The dosimeters were assessed in terms of dose response as well as transparency.

3. Results

The mean dose response of 9 batches of the original composition was found to be $(3.5 \pm 0.1) \cdot 10^{-3} \text{ Gy}^{-1} \text{ cm}^{-1}$ at a dose rate of 6 Gy/min that increased with 27% when the dose rate was decreased to 1 Gy/min. When TCA was omitted the dose response was $(2.78 \pm 0.05) \cdot 10^{-3} \text{ Gy}^{-1} \text{ cm}^{-1}$ and when both TCA and $CHCl_3$ were substituted by DMF or CCl_4 dose responses of $(1.7 \pm 0.2) \cdot 10^{-3} \text{ Gy}^{-1} \text{ cm}^{-1}$ and $(1.72 \pm 0.07) \cdot 10^{-3} \text{ Gy}^{-1} \text{ cm}^{-1}$ were obtained. The dose response of all other dosimeter formulations where the initiator TCA was substituted is summarized in table 1.

When adding TFA at the same concentration as that used for TCA in the original formulation, a 12% lower dose response was observed. When doubling the concentration the gel turned opaque, but by adjusting the pH by adding NaOH the transparency was increased. The dose response, however, decreased with increasing concentration. Similar tendencies were observed for both HBr and 4,4-azo with a decreased dose response of 3% and 18%, respectively. CBR_4 , 4,4-azo, and both peroxides gave lower responses even at the original TCA concentration.

The highest dose response (15% increase compared to the original formulation) and the only increase compared to the original formulation was obtained with SDBS which, however, resulted in opaque

gels. Of the three surfactants only DTAB resulted in transparent gels but gave very low dose response. The results for dosimeter formulations with substitutes for the surfactant SDS are summarized in table 2.

Initiators	Concentration	Notes	Dose response ($10^{-3} \text{ Gy}^{-1} \text{ cm}^{-1}$)
TFA	5 mM		3.09 ± 0.06
	10 mM	Hazy	2.91 ± 0.05
	10 mM	pH adjusted	2.2 ± 0.1
2,4-peroxide	5 mM		1.86 ± 0.05
	10 mM		2 ± 1
H_2O_2	5 mM	Hazy	2.4 ± 0.3
	10 mM	Hazy	1.7 ± 0.1
2,2-azo	5 mM	Opaque	2.6 ± 0.8
4,4-azo	5 mM		2.86 ± 0.02
	10 mM	Opaque	0.4 ± 0.6
CBr_4	5 mM		2.4 ± 0.2
	10 mM	pH adjusted	No response
HBr	7 mM		3.39 ± 0.04
	30 mM	pH adjusted	2.9 ± 0.2

Table 1: The original initiator, TCA, was substituted with the compounds and concentrations shown in this table. In addition, notes on their appearance as well as the dose response are shown. 4,4-azo was dissolved in DMF since it could not be dissolved in CHCl_3 .

Surfactants	Concentration	Notes	Dose response ($10^{-3} \text{ Gy}^{-1} \text{ cm}^{-1}$)
DTAB	40 mM		0.42 ± 0.02
	80 mM		0.3 ± 0.1
SOS	80 mM	Opaque	2.07 ± 0.04
SDBS	25 mM	Opaque	3.2 ± 0.1
	50 mM	Opaque	3.91 ± 0.05
	100 mM	Opaque	4.1 ± 0.2

Table 2: The original surfactant, SDS, was substituted with the compounds and concentrations shown in this table.

4. Discussion

In this study we have explored the dose response of a radiochromic hydrogel dosimeter using a range of different compositions including a range of initiators as well as surfactants. Initially, using the same composition as Vandecasteele et al. [4] resulted in a mean dose response 20 % lower than that reported in [4]. However, this difference is probably partly due to a difference in the dose rate used. In addition, only half the dose response was observed with CCl_4 as initiator compared to the same study.

In [3] the surfactant Triton X-100 was used instead of SDS which resulted in a dose response similar to Vandecasteele et al. [4]. In addition, in both [4] and [5] a dosimeter based on leuco crystal violet dye instead of LMG was investigated, resulting in higher dose responses. They are, however, still lower than that of the commercially available LMG based polyurethane dosimeter Presage™ where a dose response of $(2.2 \pm 0.3) \cdot 10^{-2} \text{ Gy}^{-1} \text{ cm}^{-1}$ has previously been reported for photon irradiation [6]. A similar

dose response for Presage™ was obtained in [7] and this study showed, in addition, a high sensitivity to irradiation temperature. The mentioned dose responses from [6] and [7] as well as all measurements in this study were all performed at room temperature.

When modifying the original composition by omitting the initiator TCA a 21% lower response than the original formulation was obtained. However, the fact that a response is observed even without TCA as initiator indicates that a considerable part of the LMG reaction is not caused by TCA but by CHCl_3 and other components. Substituting both TCA and CHCl_3 with DMF or CCl_4 decreased the dose response to half that of the original version. However, adding DMF or CCl_4 to the original composition (data not shown) did not considerably change the dose response and it therefore seems that they do not contribute. A considerable part of the dose response therefore has to be ascribed to other components than TCA and CHCl_3 .

When substituting the initiator TCA with other compounds the general trend was that the dose response decreased when the initiator concentration was increased. At the same concentration as TCA all initiators gave lower dose response, however, considerably closer to the original response than with higher concentrations. It therefore seems that the chemical reaction scheme does not depend on the specific initiator used. The initiator is therefore probably not the limiting factor for the chemical reactions causing the dose sensitivity.

Of the three surfactants used, only DTAB produced transparent gels but the dosimeters gave very low dose response. Only the surfactant SDBS gave a slightly higher dose response than the original version, but at all concentrations the gels were opaque. Large structures therefore must be present in the gel maybe due to large micelles or micelle aggregates. Since opaque dosimeters cannot be used for optical read-out this was not investigated further.

5. Conclusion

The measurements in this study indicate that while a part of the dose response originates from the initiator TCA and CHCl_3 , a considerable part of the dose response originates from other components. In addition, it was not possible to increase the dose response by substituting the two compounds. When substituting the surfactant a small increase was observed and it cannot be concluded whether the micelle structures are connected with the limitation in dose response. However, due to the dose rate dependence, it seems that the dose rate and the reaction rates giving the dose response are on similar time scales.

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7. References

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