New 3D radiochromic gel dosimeters with inhibited diffusion

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Abstract. Two new radiochromic gels for 3D dosimetry, both with inhibited diffusion, are described. The first dosimeter is based on the radiation-induced creation of a dye Turnbull blue. The dose sensitivity of the gel measured in terms of spectrophotometric absorbance is $(5.0 \pm 0.1) \times 10^{-3}$ Gy$^{-1}$ cm$^{-1}$ (1σ) and the background value 24 h after gel preparation is 0.14 cm$^{-1}$. The diffusion coefficient of the gel stored at 24°C is less than $4 \times 10^{-3}$ mm$^2$ h$^{-1}$ (1σ). The second dosimeter makes use of the radiation-induced formation of insoluble mercurous chloride which creates a fog inside an originally bright gel. The dose sensitivity of the dosimeter is $(3.8 \pm 0.2) \times 10^{-2}$ Gy$^{-1}$ cm$^{-1}$ (1σ) and its background value 24 h after preparation is 0.18 cm$^{-1}$. The diffusion coefficient is less than $2 \times 10^{-4}$ mm$^2$ h$^{-1}$ (1σ).

1. Introduction

Gel dosimeters are integral chemical dosimetry systems with the unique ability to record and retain information about a spatial distribution of dose. Radiochromic gels which change color during irradiation represent one class of these dosimeters. The main advantages of radiochromic gels include the possibility to evaluate their response using relatively cheap optical methods, e.g. cone-beam optical computed tomography (CT) [1]. So far, a Fricke-gel dosimeter with xylene orange indicator incorporated into a gel matrix (FXG dosimeter, [2]) has come into widespread use only, but its disadvantages are the fast spontaneous increase of the background value and the significant feathering of dose patterns owing to ferric ions diffusion [3]. This work describes basic characteristics of two newly developed radiochromic gels with inhibited diffusion of dose patterns.

2. Materials and methods

2.1. Dosimeter based on Turnbull blue

The first new radiochromic gel dosimeter is based on the radiation-induced creation of an insoluble dye Turnbull blue, K[Fe$^{II}$Fe$^{III}$ (CN)$_6$] (the TB dosimeter, see Figure 1, [4]). Basically, the TB dosimeter is composed of a gel matrix, potassium ferricyanide, and a ferric compound dissolved in an acidic medium. During irradiation ferric ions (Fe$^{III}$) are reduced to ferrous ions (Fe$^{II}$) which subsequently interact with potassium ferricyanide forming Turnbull blue.

Various compositions and concentrations of compounds were tested in order to achieve high sensitivity and low background simultaneously. Three versions of the gel are suggested (see Table 1).
Table 1: Composition of all three versions of the TB dosimeter

| Compound                        | Version 1 | Version 2 | Version 3 |
|---------------------------------|-----------|-----------|-----------|
| gelatin (300 bloom)             | -         | 3 % w/w   | 5 % w/w   |
| agarose (phytagel, [5])         | -         | -         | 0.4 % w/w |
| potassium ferricyanide          | K₃Fe(CN)₆ | 3 mM      | 1.5 mM    |
| ferric chloride                 | FeCl₃.6H₂O| 1.5 mM    | 0.45 mM   |
| ferric ammonium citrate         | C₆H₈O₇FeNH₃| 1.5 mM   | 1.5 mM    |
| sulphuric acid                  | H₂SO₄     | -         | 15 mM     |

2.1.1. Gel preparation. Gelatin (or agarose) was completely dissolved in distilled water (half of the total gel volume) at ~50°C (or at ~80°C in case of agarose). All other compounds were prepared separately as solutions in distilled water. It was difficult to dissolve ferric chloride hence its solution was heated and stirred while hydrochloric acid was being slowly added until the precipitate disappeared. The final mixing of the gel was carried out in semi-darkness. Gelatin (or agarose) was cooled down to 35-40°C and during its intensive stirring, the solutions were added successively into the gel as follows: ferricyanide and ferric chloride (version 1), or ferricyanide, sulphuric acid, and ferric ammonium citrate (version 2), or ferricyanide, ferric ammonium citrate, and ferric chloride (version 3). The gel was filled up with distilled water to the final volume, then separated into vials, and refrigerated. No special atmosphere is needed but it is desirable to use compounds in a high degree of purity.

2.2. Dosimeter based on mercurous chloride
The second presented radiochromic gel dosimeter is based on formation of mercurous chloride, Hg₂Cl₂ (the Hg dosimeter, see Figure 2, [6]). Hg₂Cl₂ is an insoluble compound created by radiation-induced reduction of Hg²⁺ contained in acidic solution of mercuric chloride, HgCl₂. Composition of the Hg dosimeter is shown in Table 2.

Table 2: Composition of the Hg dosimeter

| Compound               | Concentration |
|------------------------|---------------|
| gelatin (300 bloom)    | -             |
| mercuric chloride      | HgCl₂         |
| oxalic acid            | (COOH)₂.H₂O   |
|                        | 3 % w/w       |
|                        | 50 mM         |
|                        | 65 mM         |

2.2.1. Gel preparation. Gelatin was completely dissolved in distilled water (half of the total gel volume) at ~50°C and all other compounds were prepared separately as solutions in distilled water. In addition, a ~0.5 M solution of sodium hydroxide, NaOH, was prepared for adjustments of the pH of the gel. This solution was subsequently used for increasing the pH of oxalic acid to the value of ~2.7. The final mixing of the gel was again carried out in semi-darkness. Gelatin was cooled down to 35-40°C and during its intensive stirring, at first oxalic acid and then mercuric chloride were added into the gel. While still stirring, the pH of the gel was slowly adjusted to the value of 3.6. In the end, the gel was filled up with distilled water to the final volume, then separated into vials, and refrigerated.

2.3. Measurement of dosimetric characteristics
Several basic dosimetric characteristics of new gels were determined: the dose sensitivity, the background value, the gel ageing, and the diffusion rates. The dose sensitivity was calculated as a slope of dependence of the spectrophotometric absorbance on dose; the background value was given...
as absorbance of an unirradiated gel sample, and the gel ageing was determined by measuring absorbance of an unirradiated gel sample during several days after manufacture. Gel samples were prepared into short spectrophotometric plastic optical cuvettes (1x1x4.5 cm$^3$ inner dimensions) and their absorbance was evaluated by a spectrophotometer Helios $\beta$. The method of measuring the diffusion rate was as follows: gel samples in long plastic columns (1x15x1 cm$^3$) were irradiated over half their length to form an edge spread function (ESF). The rate of change of the ESF over a period of one month was determined from profiles of intensity of grey taken from black-and-white photographs [7]. The intensity profiles were fitted with a curve approximating the error function and subsequently the diffusion coefficients were calculated according to equations presented in [8].

3. Results and discussion

3.1. TB dosimeter

3.1.1. Gel composition. Optimization of composition of the gel was focused mainly to suppression of increased background. It was found that gelatin negatively influences the background values hence its concentration was held as low as possible. In the version 2 ferric chloride was replaced by ferric ammonium sulfate which led to slight decrease of the gel sensitivity but also to significant decrease of background. However, this dosimeter is highly light-sensitive and should be always stored in a dark place. In the version 3 gelatin was replaced with agarose which is able to solidify in much lower concentration. Unfortunately, even during intensive stirring agarose was lumping when the acidic solution of FeCl$_3$ was being added to the gel. That is why the concentration of FeCl$_3$ had to be lowered, but for maintaining the sensitivity ferric ammonium citrate was added into the gel. This version of the TB dosimeter shows the lowest background and the slowest ageing although its manufacture is a bit complicated due to a high melting temperature of agarose.

3.1.2. Dosimetric characteristics. Absorption spectra of the TB dosimeter are shown in Figure 3. Peak of the absorption band of Turnbull blue corresponds to 690 nm therefore all values of absorbance were measured at this wavelength.

The dose dependence of the TB dosimeter version 3 is presented in Figure 4. The dependence is linear from 0 Gy up to at least 400 Gy. The dose sensitivity is equal to $(5.0 \pm 0.1) \times 10^{-3}$ Gy$^{-1}$ cm$^{-1}$ (1$\sigma$) and the background value 24 h after gel preparation is 0.14 cm$^{-1}$ and 0.19 cm$^{-1}$ if stored in a dark place at 5°C and 24°C, respectively. Ageing of a gel stored at three different conditions is shown in Figure 5. The gel is very stable if stored in a refrigerator but, however, the background values are significantly increasing if the gel is stored in the light.

The diffusion coefficients were measured for gels stored in a dark place at 5°C and 24°C and in both cases the absolute value was lower than its uncertainty. It was found that the diffusion coefficient is less than $2 \times 10^{-3}$ mm$^2$h$^{-1}$ (1$\sigma$) and less than $4 \times 10^{-3}$ mm$^2$h$^{-1}$ (1$\sigma$) at 5°C and 24°C, respectively, hence the diffusion is practically negligible. This is caused by the nature of molecules of Turnbull blue which create huge clusters preventing the diffusion through the gel matrix.

Characteristics of all versions of the TB dosimeter are summed up in Table 3.
3.2. Hg dosimeter

3.2.1. Gel composition. It was observed that the dose sensitivity of the gel depends on its pH and it was found that an optimal value of pH is ~3.6. Unfortunately, from the point of view of the user the gel contains toxic mercury and so after use it should be treated as a toxic waste.

3.2.2. Dosimetric characteristics. Absorption spectra of irradiated gels are presented in Figure 6. Hg\(_2\)Cl\(_2\) emerging during irradiation creates insoluble particles with dimensions comparable to the wavelength of light therefore the gel scatters the light resulting in an increase of absorbance at all wavelengths. The consequence is that this gel cannot be evaluated with the cone-beam optical CT. Unfortunately, the gel gives no response on magnetic resonance imaging too.

The dose response is linear and the gel sensitivity is highest at the wavelength of 850 nm where the linearity of the dose response extends to at least 30 Gy and the sensitivity reaches (3.8 ± 0.2)\(\times\)10\(^2\) Gy\(^{-1}\) cm\(^{-1}\) (1σ; see Figure 7). If stored in a dark place at 24°C, the background value is very low: 0.04, 0.08, and 0.18 cm\(^{-1}\) 1, 5, and 24 h after gel manufacture, respectively. The ageing of the gel measured at 850 nm is very slight if the gel is stored in a refrigerator but increases if stored at a higher temperature or in the light.

![Figure 4: The dose dependence and the sensitivity of the TB dosimeter version 3 measured at the wavelength of 690 nm. Data dispersion is caused by slightly different light-history of each gel sample due to very long (3 days) irradiation.](image)

![Figure 5: The ageing of three unirradiated samples of the TB dosimeter version 3 stored in a refrigerator (red), in a dark place at 24°C (blue), and in the indirect light at 24°C (green).](image)

![Figure 6: Absorption spectra of the Hg dosimeter. An unirradiated sample (red) and samples irradiated to 5 Gy (blue), 20 Gy (green), and 40 Gy (cyan).](image)

![Figure 7: The dose dependence and the sensitivity of the Hg dosimeter measured at 850 nm.](image)
The diffusion rate was determined for a gel stored in a dark place at 24°C only. Again, it was found that the absolute value of the diffusion coefficient is lower than its uncertainty because solid particles of Hg₂Cl₂ are much larger than the pores in the gel and cannot move through. The result is that the diffusion coefficient of the Hg dosimeter is lower than \(2 \times 10^{-4}\) mm²·h⁻¹ (1σ).

All characteristics of the Hg dosimeter are summed up in Table 3.

**Table 3** *the FXG dosimeter is presented for comparison (composition used: 5% w/w gelatin, 0.1 mM xylenol orange, 0.5 mM ferrous ammonium sulphate, 25 mM sulphuric acid)*

| Dosimeter | Sensitivity \( (\text{Gy}^{-1}\text{cm}^{-1} \cdot \text{Gy}^{-1}) \) | Background value 24 h after manuf. \( \left(5^\circ\text{C}/24^\circ\text{C}\right) \) (cm⁻¹) | Linearity of the dose response | Diffusion coeff. at \(5^\circ\text{C}/24^\circ\text{C}\) \( (\text{mm}^2 \cdot \text{h}^{-1}; 1\sigma) \) | Ageing at \(5^\circ\text{C}\) | Light sensitivity |
|-----------|-----------------|---------------------------------|-----------------|-----------------|-----------------|----------------|
| FXG*      | \(7.6 \pm 0.1\times10^{-2}\) \( (585 \text{ nm}) \) | 0.25/0.35 \( (585 \text{ nm}) \) | 3 - 30 Gy | \(0.60 \pm 0.02)/\(0.74 \pm 0.03\) | medium | medium |
| TB dos. ver.1 | \(6.3 \pm 0.3\times10^{-3}\) \( (690 \text{ nm}) \) | 0.65/0.75 \( (690 \text{ nm}) \) | 0 – min.400 Gy | \(<2 \times 10^{-3} / <4 \times 10^{-3}\) | medium | medium |
| TB dos. ver.2 | \(4.4 \pm 0.2\times10^{-3}\) \( (690 \text{ nm}) \) | 0.17/0.64 \( (690 \text{ nm}) \) | 0 – min.400 Gy | \(<2 \times 10^{-3} / <4 \times 10^{-3}\) | slow | high |
| TB dos. ver.3 | \(5.0 \pm 0.1\times10^{-3}\) \( (690 \text{ nm}) \) | 0.14/0.19 \( (690 \text{ nm}) \) | 0 – min.400 Gy | \(<2 \times 10^{-3} / <4 \times 10^{-3}\) | very slow | higher |
| Hg dos. | \(3.8 \pm 0.1\times10^{-2}\) \( (850 \text{ nm}) \) | 0.15/0.18 \( (850 \text{ nm}) \) | 0 – min.30 Gy | \(<2 \times 10^{-4} / <2 \times 10^{-4}\) | slow | low |

4. Conclusions

Two new radiochromic gel dosimeters with inhibited diffusion were described. The dosimeter based on Turnbull blue is suitable for cone-beam optical CT evaluation and could be used in high dose measurements with steep gradients, e.g. dose distribution measurements around brachytherapy sources. The second gel, the dosimeter based on formation of mercurous chloride, possesses high dose sensitivity and could be of use, for example, in measurements of beam profiles, depth dose curves, etc.

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