Evaporation and diffusion of chloroform with the deformable FlexyDos3D radiation dosimeter

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Evaporation and diffusion of chloroform with the deformable FlexyDos3D radiation dosimeter

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Abstract. Chloroform in the FlexyDos3D dosimeter acts as a radical initiator which brings about the colour change of the dosimeter when the radicals react with the leucomalachite green. However, the volatility of the chloroform likely results in a rapid loss of chloroform from the dosimeter. Gravimetric analysis and NMR diffusion-ordered coherence spectroscopy were used to measure the diffusion and evaporation rates of chloroform from the dosimeter and found that both rates were both significantly large resulting in a rapid loss of chloroform. Dose maps of irradiated phantoms aged for different times found a significant difference in the dose measurements of the dosimeter, likely a result of the different chloroform concentrations within the dosimeters.

1. Introduction

The FlexyDos3D dosimeter consists of an optically-transparent silicone elastomer (Sylgard® 184, Merck), chloroform, and a leucodye, leucomalachite green (LMG). The chloroform is used to produce radicals when irradiated that will react with the LMG, converting the LMG to malachite green (MG). This conversion of LMG to MG will result in the dosimeter changing from crystal clear to green.

Chloroform will evaporate rapidly when it is exposed to standard atmospheric conditions in an unenclosed space. Evaporation of chloroform from the FlexyDos3D dosimeter would likely result in less radicals being produced when the dosimeter is irradiated, resulting in less colour change in the dosimeter. This would likely also lead to spatial differences in the chloroform distribution within the dosimeter.

In this current study, the evaporation and diffusion rates of chloroform within the FlexyDos3D dosimeter were measured, both by gravimetric analysis and NMR diffusion-ordered coherence spectroscopy. Phantoms were also constructed and irradiated at different times after manufacture to see the effect of the evaporation of chloroform on the dose distributions within the dosimeter.

2. Methods and Materials

2.1 Dosimeter fabrication

The dosimeter, known as 'FlexyDos3D', consists of an optically-transparent silicone elastomer (Sylgard® 184, Merck), chloroform, and a leucodye, LMG. The silicone elastomer initially consists of a separate base and curing agent (CA), which cures when mixed together.

2.2 Irradiation

In fundamental studies, samples were irradiated with UVC light. For the final dosimetry tests, samples were irradiated with high-energetic X-rays on a linear accelerator (linac).

2.2.1 UVC irradiation. The cuvette samples were irradiated with a 9 W UVC germicidal lamp (TUV PL-S 9 W, Philips). The light intensity at 100 mm from the end of the lamp was measured with a UVC light reader (UVC-254, Lutron Electronic Enterprise Co., LTD) to be 5.22 W / m^2.

The cuvettes were placed 100 mm away from the UV lamp which was suspended in a polystyrene box. The box's internal surface was covered with aluminium foil to homogenize the UV flux. The cuvettes were enclosed on all sides but the one facing the UV lamp.

2.2.2 Linac irradiation. The cuvettes and phantoms were irradiated with high-energetic photon beams using a clinical Varian 21EX linac (Varian Medical Systems, Palo Alto, USA) with a beam quality of 6 MeV. All cuvettes were irradiated within a 10 cm × 10 cm field size at an SSD of 100 cm with the centre of the cuvettes positioned at 1.4 cm depth (Dmax). Cuvettes were each irradiated in 2 Gy increments up to a maximum dose of 20 Gy. The phantoms were irradiated with a photon beam with a 2 cm x 2 cm field size and an SSD of 100 cm and 2000 MU corresponding with a dose of 17.2 Gy (Dmax) at a depth of 1.4 cm (Dmax).

2.3 ^{1}H NMR diffusion study

5 mm NMR tubes were filled with different combinations of the FlexyDos3D dosimeter, deuterated water (D_2O), deuterated chloroform ($CDCl_3$), and chloroform ($CHCl_3$) (table 1). $CDCl_3$ or D_2O were used in the samples to lock the ^{1}H signal.

A diffusion-ordered spectroscopy (DOSY) sequence was used to measure the diffusion coefficients of the chloroform and water in the samples, and the sequence was based on a stimulated echo sequence with a gradient strength of 0.535 T / m, a gradient duration (δ) of 1 ms, and a diffusion time (Δ) of 1 s.

Samples S3 and S4 consisted of two layers of materials in the NMR tube; S3 had a layer of cured FlexyDos3D beneath a layer of deuterated water, and S4 had a layer of non-deuterated chloroform beneath a layer of deuterated water, with the deuterated water being used in both cases to lock the NMR signal. Samples S1 and S2 were used as an independent experimental control to determine the self-diffusion coefficient of pure chloroform. Sample S3 was cured in an oven for 2 hours at 60 °C.

Table 1. Mixtures for NMR measurements.

NMR Sample Name	$CDCl_3$ [% w/w]	$CHCl_3$ [% w/w]	D_2O [% w/w]	FlexyDos3D [% w/w]
S1	100	0	0	0
S2	50	50	0	0
S3	0	N/A	50	50
S4	0	50	50	0

2.4 Depth-dose profile over time study

Two 100 mm tall cylindrical phantoms with 58 mm diameters were constructed; one phantom was made 14 days before irradiation and the other on the day of irradiation. Cuvettes were also filled with the same

batch of dosimeter and were irradiated with a set of known doses which were used to calibrate the acquired phantom images from the optical cone-beam CT scanner to three-dimensional dose maps.

2.5 Evaporation of chloroform study

Open-topped cylindrical glass vials were filled with different amounts of the dosimeter which allowed chloroform to evaporate from the top surface of the dosimeter. Two groups of vials were made; one group was cured for 2 hours at 60 °C in an oven and the other was left to cure at room temperature. 15 samples were made with each containing up to 15 g of the dosimeter in 1 g increments. Another vial was also filled with 10 g of chloroform to measure the evaporation rate of pure chloroform.

The mass of each cylinder was measured immediately after manufacture and at various times over the next 2 months (60 days) to determine the mass loss relative to the first measurement. Another measurement was taken after 116 days to measure the final mass of the samples.

2.6 Measurements and imaging

2.6.1 Optical spectroscopy and absorbance measurements. LMG is transparent but when irradiated it converts to MG which shows an increase in absorbance at red wavelengths of light. The absorbance was compared at 630 nm, which showed a large increase, and 480 nm, which showed a minimal change in absorbance with increasing dose. The difference in these wavelengths could then be used to determine the dose delivered to the dosimeter.

$$\Delta OD = OD_{630\text{nm}} - OD_{480\text{nm}} \quad (1)$$

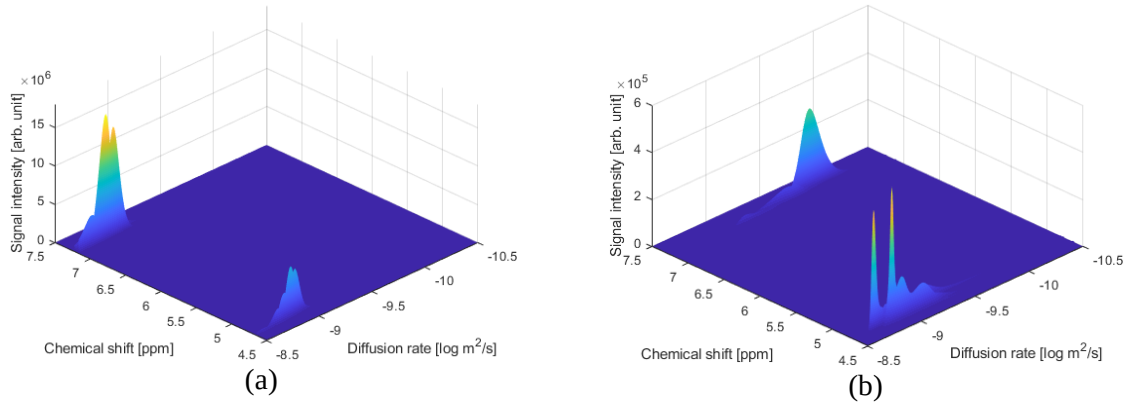
Optical spectra were acquired with a high-resolution spectrophotometer (USB4000, Ocean Optics) equipped with a cuvette holder.

2.6.2 Dual-wavelength optical cone-beam CT imaging. A modified dual-wavelength cone-beam optical scanner based on the Modus Vista™ scanner (Modus Medical Devices Inc, London, Canada) was used to image the phantoms and cuvettes. Optical CT images were constructed using an in-house developed cone-beam reconstruction software using the Matlab (The MathWorks, Inc.) environment.

Red and blue LEDs provided the two sets of wavelengths which were used to image the phantoms [1].

3. Results and Discussion

3.1 Diffusion NMR



(a) (b)

Figure 1. Two-dimensional DOSY spectra of a sample containing 50 % chloroform and 50 % deuterated water (a) and a sample containing 50 % FlexyDos3D and 50 % deuterated water (b).

The peaks for chloroform and water can be resolved at 7.2 ppm and 4.7 ppm, respectively (figure 1). The diffusivities of the chloroform and water sample (S4) were both measured as 1.61 x 10^{-9} m^2 / s (σ = 0.28 x 10^{-9} m^2 / s) and 1.36 x 10^{-9} m^2 / s (σ = 0.16 x 10^{-9} m^2 / s), respectively. The corresponding diffusion coefficients in the FlexyDos3D sample (S3) were measured as 0.15 x 10^{-9} m^2 / s (σ = 0.04 x 10^{-9} m^2 / s) and 1.48 x 10^{-9} m^2 / s (σ = 0.52 x 10^{-9} m^2 / s), respectively (figure 1b). The measured diffusion coefficient of the water is slightly less than that found in the literature (1.69 x 10^{-9} m^2 / s at 295 K (21.85 °C) [2]).

3.2Dose distribution of a photon beam

A noticeable difference is seen between the dose distribution obtained in a phantom irradiated 5 hours post-manufacture and in a phantom irradiated 14 days post-manufacture (figure 2).

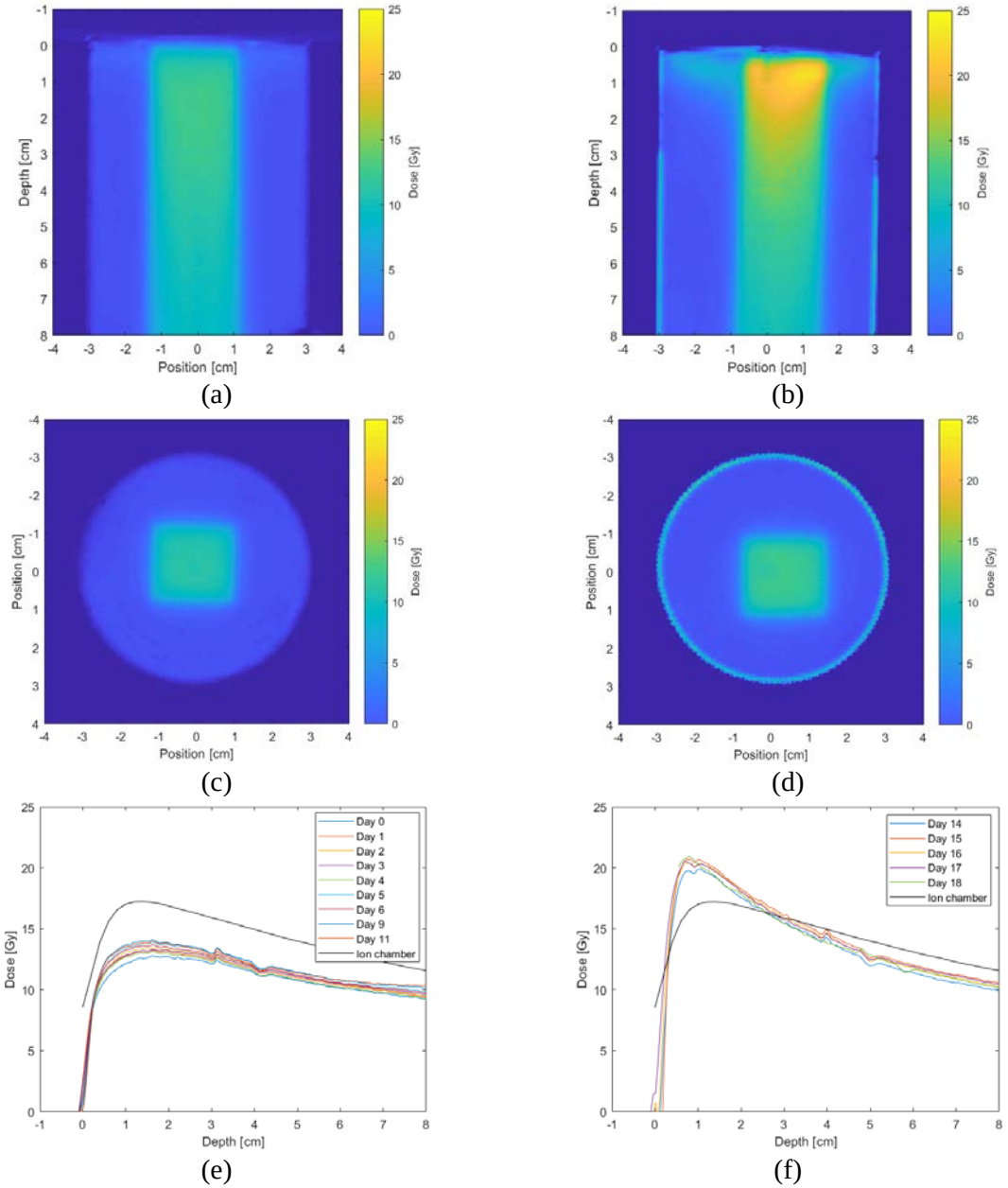
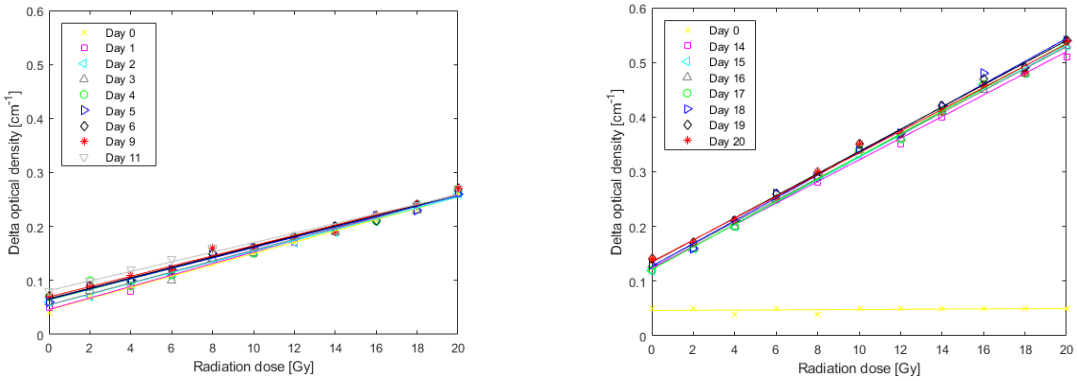


Figure 2. Depth-dose maps for the phantom irradiated 5 hours after manufacture (a) and for the phantom irradiated 14 days after manufacture (b), and corresponding cross-dose maps for the phantoms (c, d). Depth-dose profiles (e, f) for the phantoms over time with ionisation chamber measurements of the linac shown. Dark regions in dose maps correspond to areas outside of the phantoms.

The different responses between the two phantoms was also evident from the dose-response of both batches of calibration cuvettes (figure 3).



(a) (b)

Figure 3. Dose-response of the cuvettes irradiated on the day of construction (a) and 14 days after construction (b) using equation 1.

The phantom that was constructed 14 days prior to irradiation still showed a significant dose-response, as shown in figure 3b. The dose-response sensitivity was twice that of the phantom constructed on the day of irradiation, shown in figure 3a. A significant dose offset was also seen in the 0 Gy dose samples between the day of manufacture and 14 days later.

The depth-dose responses of the phantoms were calibrated using calibration curves obtained from the calibration cuvettes (figure 3). Dose profiles and maps of the two phantoms are shown in figure 2. The depth-dose profile in the dosimeter constructed on the day of irradiation is significantly less than that of the expected depth-dose response (figure 2e). The phantom constructed 14 days before irradiation has a depth-dose profile that is significantly larger near the surface than that the expected depth-dose response (figure 2f). A yet unexplained artefact appears at the surface of the aged dosimeter, as shown in figure 2d.

3.3 Chloroform evaporation

Measurements of the pure chloroform evaporation samples showed a constant mass loss rate over time of 0.19 g / hr. Using equation 1 and assuming the chloroform is very pure ($C_0(t)$ = 1 g / g) and that the chloroform concentration in the atmosphere is negligible at all times ($C_s(t)$ = 0 g / g), the dimension of proportionality (α) is equal to the mass loss rate [3].

$$M_t(t) = M_\infty \left(1 - \sum_{n=1}^{\infty} \frac{2L^2 \exp\left(-\frac{\beta_n^2 D\, t}{l^2}\right)}{\beta_n^2 \left(\beta_n^2 + L^2 + L\right)} \right) \tag{1}$$

$$\frac{dM_t(t)}{dt} = \alpha(C_0(t) - C_s(t)) \tag{2}$$

$$L = \frac{l\alpha}{D} \tag{3}$$

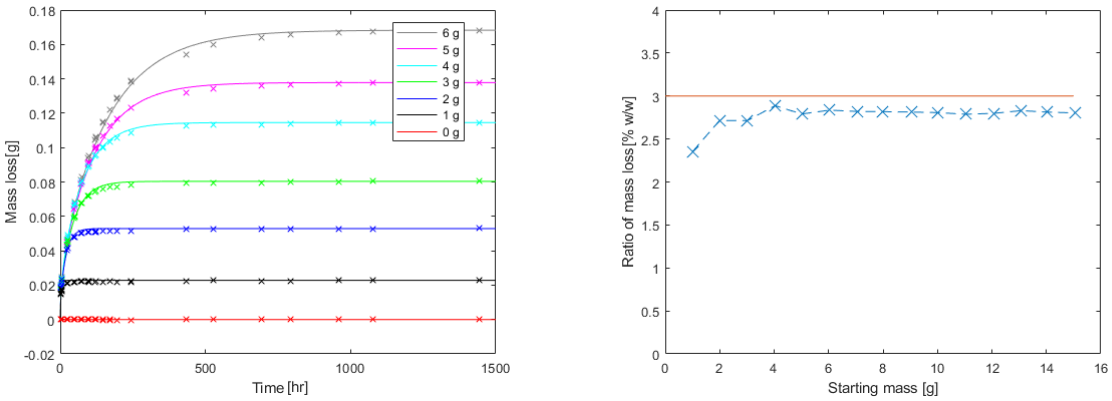
$$\beta_n \tan(\beta_n) = L \tag{4}$$

where: $M_t(t)$ is the chloroform mass loss at time t [g], M_∞ is the chloroform mass loss at an infinitely large time [g], $dM_t(t) / dt$ is the mass loss rate of chloroform [g / s], $C_0(t)$ is the concentration of chloroform within the material [g / g], $C_s(t)$ is the concentration of chloroform at the surface of the

material [g / g], α is a constant of proportionality which relates change in mass over time of the chloroform to the concentration difference between the inside and outside of the material [g / s], l is the height of the material [m], β_n are the roots of equation 4 [arb. units], and D is the diffusion rate of the chloroform [m^2 / s].

The samples all lost mass over time (figure 4a) and appear to approach a mass loss of 3 % which is equal to the amount of chloroform in the samples initially (figure 4b).

Apparent diffusion values were obtained by fitting the mass loss over time (figure 4a) using equations 1 – 4. The calculated diffusion values increased from 0.25 x 10^{-9} m^2 / s to 0.40 x 10^{-9} m^2 / s with higher initial masses of the dosimeter having a greater diffusion rate. The measured diffusion coefficient is dependent on the initial phantom volume indicates that the diffusion of chloroform in the elastomer is non-Fickian. No significant differences were observed between the diffusion rates of samples cured at different temperatures.



(a) (b)

Figure 4. Mass loss over time for the 60 °C cured samples up to 6 g (a). Fits using equations 1 – 4 are shown with the solid lines. Ratio of mass loss in the 60 °C cured sample after 116 days (b). A solid line has been added in (b) to show the 3 % mass loss value. The 120 °C results have not been shown as they are almost identical to the 60 °C results.

4. Conclusion

It was shown by gravimetric studies and two-dimensional NMR diffusion-ordered coherence spectroscopy that the evaporation of chloroform from the FlexyDos3D dosimeter is significant. The calibrated dose distributions of the phantoms did not match that of the expected dose distribution. The differences in the measured dose distributions in the phantoms that were irradiated at different times after manufacture were the likely result of evaporation of chloroform over time from the dosimeter.

5. Acknowledgements

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6. References

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