Effect of the exothermal polymerization reaction on polymer gel dosimetric measurements

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Abstract. Discrepancies in polymer gel dosimetric measurements have been observed between containers of different sizes receiving the same radiation dose. We hypothesized that these deviations are caused by a change in the rate of polymerization due to internal heat increase in the gel containers resulting from the exothermic polymerization of monomers. Here, we test this hypothesis in a polyacrylamide gel dosimeter by recording the temperature in glass phantoms of different sizes during and after irradiation. The dose response of the samples was determined with magnetic resonance imaging. The difference of $R^2$ values along the depth of the containers was below ±1%. We discuss that this small difference can be attributed to variations in the rate of gelatin cooling during manufacture rather than to the measured heat increase during irradiation.

1. Introduction
Other authors and ourselves have already shown that a significant internal temperature increase can be measured during irradiation of polymer gel dosimeters due to release of energy from carbon-carbon double bond breaks (C=C) in exothermal polymerization reactions [1,2,3]. The temperature increase in the gel containers depends on three major factors: i) the ratio of volume to surface area (V/A) of the containers, ii) the volume of gel that receives radiation and iii) the type of monomers used. Other factors that influence the temperature increase are concentration of monomers, dose rate as well as material and thickness of the container walls.

Our hypothesis is that heat inside a gel container of interest can favour either propagation or inhibition reactions, leading to a different amount of polymer, which in turn modulates the dosimeter dose response as a function of gel volume. This becomes important not only for absolute dose determination but also relative dose evaluation since the relationship between transverse relaxation rates ($R_2$) and dose will consequently be modified by this effect.

Our previous attempts to pinpoint the effect of heat in normoxic gel dosimeters were not conclusive as the gel containers we had constructed were made of either Plexiglas® or Delrin® [1,4]. Oxygen can accumulate within these materials and may be returned to the gel before irradiation, hence interfering with the potential temperature effect on the dose response. We have reported elsewhere in these proceedings that traces of oxygen can increase the sensitivity of normoxic polymer gel dosimeters,
thus creating ambiguity in the interpretation of the results. We re-investigated the possible effect of temperature increase in an anoxic PAG dosimeter.

2. Materials and methods

Four cylindrical gel containers were constructed from borosilicate glass. The containers were 20 cm long with internal diameters of 5.65, 3.65, 2.35 and 1 cm as shown in figure 1(a). The thickness of the glass was 4 mm. In order to insert temperature probes into the gel, four entries on the side of the cylinders were designed by sealing tiny glass tubes at different heights from the bottom of the cylinders. Eight MRI-compatible optical temperature sensors (NeOptix Inc, Quebec, Canada, accuracy ±1°C, resolution 0.1°C, length 5 m) were used to monitor temperature variations inside the containers during irradiation. Before gel fabrication, two temperature probes were inserted into the entries at 15 mm and 35 mm from the bottom of each container. The probes were passed through plastic holder pipes which were fixed to the side entries. The containers were transferred into a nitrogen-flushed glove box and filled with a PAG dosimeter prepared with 5% gelatin (type A, 300 bloom, Sigma-Aldrich, Ontario, Canada), 3% acrylamide (AA) (electrophoresis grade, Sigma-Aldrich, Ontario, Canada) and 3% N,N’-methylene-bis-acrylamide (BIS) (99+, Acros Organics BVBA, Geel, Belgium). A set of glass calibration vials (2.5 ml) was also filled with the gel. The containers were left in the glove box overnight for the gel to set in an anoxic environment. All gel samples were transferred to the radiotherapy department the day after gel fabrication and placed into a water tank. A second water tank was also filled with water and both were left to equilibrate to the ambient temperature for 12 h. The gel containers and calibration vials were irradiated with a Siemens Oncor™ linear accelerator (Siemens Medical Solutions AG, Germany). Irradiation set up for the gel containers is depicted in figure 1(b). The uniformity of the depth dose profiles in all four glass phantoms had been verified to be within 1% by Gafchromatic® EBT2 (International Specialty Products, NJ, USA) film dosimetry. Doses of 10 and 15 Gy to $D_{\text{max}}$ in water were delivered using 6MV photons with a dose rate of 3 Gy/min and a $10 \times 10 \text{ cm}^2$ field. The SSD was set to 100 cm on the surface of water. Two probes at two different depths from the surface of water recorded the temperature changes in each container. The probe in position 1 was 15 mm lower than the point of maximum dose ($D_{\text{max}}$) and the probe in position 2 was 35 mm lower. This corresponds to a dose of 96% and 87.4% of $D_{\text{max}}$ at the position of each probe, respectively.
Temperature measurements started 30 min before irradiation and continued for 1 h after irradiation. Each gel container was transferred from the first water tank to the second water tank under the radiation field and was transferred back to the first water tank 20 min after the end of irradiation. The gel containers were scanned 24 h after irradiation using a Siemens Sonata (Siemens Medical Solutions Erlangen, Germany) 1.5 T clinical imager with a multi-echo spin echo protocol. The temperature probes were not removed to avoid distortions to the surrounding gel. Phantoms were scanned before irradiation to determine that the $R_2(0)$ values did not depend on phantom size. Data were analyzed with software developed for radiotherapy gel dosimetry in the MATLAB® environment.

3. Results

A summary of the results is presented in figure 2. Figure 2(a) shows internal temperature changes in the four gel containers for a dose of 10 Gy prescribed to $D_{max}$ in water. Start and end of irradiation is illustrated by two dotted vertical lines. The temperature increased very rapidly after the start of irradiation.
irradiation. The time to reach a maximum depended on the container volume and the position of the probe inside the container. The temperature increased by ~1.0°C, 2.0°C, 2.6°C and 3.0°C for increasing container volume. The difference between the temperature in the smallest and largest container is 2°C for this radiation dose.

Figure 2(b) shows the internal temperature increase in the four gel containers when a dose of 15 Gy was delivered. In the smallest gel container the temperature increased by 1.3°C during the course of irradiation. As the gel container volume increased, the maximum temperature rise was of 3.1, 4.0 and 5.0°C. The internal temperature difference between the smallest and largest gel container in this case was 3.7°C. While the temperature inside the largest container is still increasing after 10 min, the smallest container has almost reached equilibrium with the ambient temperature after this time.

Figure 2(c) shows the $R_2$-dose response of the PAG dosimeter as determined from small calibration vials. Figure 2(d) shows the profiles of $R_2$ along the depth of the gel containers scanned before irradiation and the gel dosimeters irradiated to 10 and 15 Gy. The upper axis in figure 2(d) shows the percentage depth dose (PDD) of the linac in water. The PDD of the Siemens linac in water decreases by 52.5% at a depth of 15 cm from the surface. As our glass phantoms were 20 cm long, the gel at this depth was well preserved from the diffused oxygen from the caps of the containers. We discarded the data from the last 5 cm gel near the caps due to oxygen inhibition effects. The position of the probes in the gel containers is also shown by vertical dotted lines. $R_2$ profiles of the gel dosimeters before irradiation are uniform at about 1.30 s⁻¹. $R_2$ profiles of the gel dosimeters irradiated to 10 Gy start at 3.46 s⁻¹ and end at 2.73 s⁻¹. For the dosimeters irradiated to 15 Gy, the profiles start from 3.69 s⁻¹ and end at 3.28 s⁻¹. Profiles of each group have a similar shape and slope but the profile of the largest gel container is lower than the other 3 gel containers by roughly 1.5%. Comparing $R_2$ values in figure 2(c) and 2(d) reveals that figure 2(c) systematically shows higher $R_2$ of about 3% for all doses.

4. Discussion

The highest temperature was recorded in the largest container in position 2, which was 35 mm below the point of maximum dose. This suggests that the maximum temperature is not at the same position as $D_{\text{max}}$, suggesting that heat is rapidly lost at the extremity of the phantoms and/or that heat is flowing from $D_{\text{max}}$ to larger depths. If the values of $R_2$ were directly correlated with the temperature rise, then we would expect a distortion of the profiles as a function of the container size, since the location of the maximum temperature rise depends on the container size. Such a trend is not observed in our results. It is important to note that the $R_2$ values in the largest container are actually lower by roughly 1.5%. This is consistent with the $R_2$ values of the small calibration vials that are higher by about 3% compared to the four larger containers. We recall that both the calibration vials and the gel dosimeters were irradiated with the same photon beams and identical setup in one session. Our results suggest that the $R_2$ values are most influenced by differences in the cooling rate of the gel in the phantoms and the calibration vials during and after manufacture.

To our knowledge, the effect of cooling history has not been studied for anoxic gel dosimeters. For a normoxic PAG dosimeter the $R_2$ values were about 7% higher in samples cooled at room temperature compared to those cooled in a refrigerator [5]. Although the study in [5] shows deviations between the dosimeters that have been subjected to different temperature history during storage, a consistent trend was not established between cooling rate and the $R_2$-dose response. In our experiments with an anoxic PAG dosimeter, faster cooling (i.e., for smaller samples) always produces higher $R_2$ values of up to about 3%. This explains the deviation observed in figure 2(d) between the four gel containers and between small calibration vials in figure 2(c) and phantoms in figure 2(d).

For the anoxic PAG dosimeter, a temperature increase of up to 12°C has been reported for a volume of 160 ml of gel receiving a high dose of 52 Gy [3]. However, the changes of $R_2$ values at such a high dose would be below the uncertainty of the $R_2$ estimation, such that any temperature-induced variations could not be observed. The situation is different for normoxic PAG dosimeters and methacrylic acid-based dosimeters. The $R_2$ values of normoxic PAG dosimeters prepared with 10 mM of tetrakis(hydroxymethyl) phosphonium chloride (THPC) saturate at about 30 Gy such that
temperature effects, if any, should be observed in the dose range below saturation. In separate experiments, we have observed that PAGAT dosimeters prepared in the same conditions as PAG dosimeters cooled slower, suggesting that heat conductivity of PAGAT dosimeter is lower. This may contribute to a detectable temperature induced effect. On the other hand, methacrylic acid-based dosimeters produce much higher heat during polymerization [1]. We have already measured temperature increases of up to 15°C in PAGAT and MAGAT dosimeters. Whether these internal temperature variations affect the final dose determination in PAGAT and MAGAT dosimeters is still under study.

5. Conclusion
The effect of internal temperature increase was studied in anoxic PAG dosimeter. For the range of doses between 10 – 15 Gy, no variations in the \( R_2 \) values could be attributed to the temperature increase resulting from the exothermal polymerization reaction in the gel dosimeter. An average discrepancy of 1.5% between the \( R_2 \) values of the four gel containers and discrepancies of up to 3% between the calibration vials and the dosimeter gel were instead attributed to differences in cooling history of the gel after filling the containers. Faster cooling always results in slightly higher \( R_2 \) values in anoxic PAG dosimeters. This may lead to dose inaccuracies of about 5%.

References
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