An investigation into the potential influence of oxygen on the efficiency of the PRESAGE® dosimeter

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Abstract. The influence of atmospheric oxygen on the efficiency of the PRESAGE® dosimeter was investigated. Batches of PRESAGE® and reporting system solution were deoxygenated using nitrogen and compared to similar batches that were exposed to atmospheric oxygen during fabrication. The overall results show little influence of oxygen on the characteristics of PRESAGE® with the radical initiator oxidizing the leucomalachite green in the presence of oxygen. However, when deoxygenating the reporting system the sensitivity to radiation dose increased by 30% compared to the non-deoxygenated system. A slight improvement in sensitivity (5%) was achieved by deoxygenating the PRESAGE® precursors prior to casting. The results suggest that the solid polyurethane matrix is not permeable to atmospheric oxygen. In addition, there were no observed changes in the dose linearity, absorption spectrum and post-response photofading characteristics of PRESAGE® under the conditions investigated.

1. Introduction
PRESAGE® is an exceptional 3D radiochromic dosimeter with unique characteristics that are desirable for clinical applications [1-4]. Unlike polymer gel dosimeters, PRESAGE® is composed of an optically clear polyurethane matrix that can be fabricated into any shape and requires no supporting container, a reporting system comprising of leucomalachite green (LMG) dye or one of its derivatives [5], and a halocarbon compound as a radical source [6, 7]. Free radicals produced from the radiolysis of the halogen-carbon bond upon irradiation oxidize the LMG dye leading to a change in optical absorbance, which is known to be linear with respect to the absorbed radiation dose [7]. One of the attractive features reported for PRESAGE® dosimeters over gel dosimeters is a lack of sensitivity to oxygen [7]; however, no experimental results have been documented in the literature to support such a claim. As part of a series of PRESAGE® component-specific optimization studies [5, 6, 8], the aim of this study was to investigate the influence of atmospheric oxygen on the efficiency of PRESAGE® as a dosimetric system and independently, on the reporting system (i.e., LMG and radical initiator).
2. Materials and Methods

2.1. PRESAGE® fabrication
The chemical agents used in this study were: Polyurethane resin (Crystal Clear 206, Smooth-On, Easton, PA, USA), which was supplied in two parts (Part A and Part B); the radical initiator, tetrabromoethane; and a commercial LMG dye (Sigma-Aldrich, St Louis, MO, USA). The dosimeters were prepared in poly(methyl methacrylate) spectrophotometer cuvettes with a wall thickness of 1 mm and internal dimensions of 1 × 1 × 4.5 cm. Detailed description of the fabrication procedure is described elsewhere [5, 6, 8]. The chemical composition of the PRESAGE® formula used was tetrabromoethane (1 wt%), LMG (2 wt%) and Crystal Clear 206/catalyst (97 wt%). Deoxygenation of the PRESAGE® was achieved by bubbling nitrogen (N₂) gas through the dosimeter precursor mixture for 10 min prior to casting. The reporting system was prepared by dissolving LMG 2% by mass in tetrabromoethane, which was then transferred into different glass vials fitted with PTFE caps. Deoxygenation of the reporting system was achieved by bubbling N₂ through each vial for 10 min by inserting two needles through the septa of each vial. One needle was connected to the N₂ source and the second needle acted as a vent.

2.2. Absorbance change measurements
Absorbance change measurements were acquired using a dual-beam Thermo scientific GENESYSTM 10S UV-VIS spectrophotometer (Thermo Fisher Scientific Inc, Waltham, MA, USA) over the visible wavelength region (450–750 nm) was measured to determine the absorption maxima of the PRESAGE® dosimeter cuvettes and vials of the reporting system. The optical absorption of each PRESAGE® cuvette was measured pre- and post-irradiation. To investigate the influence of deoxygenation of PRESAGE® on its post-response photo-fading, absorption acquisitions were acquired at different time intervals (1, 3, 6, 24, 48, 92, 120, and 168 hours post-irradiation).

2.3. Irradiation
The PRESAGE® cuvettes were irradiated with a 6 MV Varian True-Beam linear accelerator (Varian Medical Systems, Palo Alto, CA), using a dose rate of 5 Gy/min and a range of radiation doses (0, 1, 5, 10, 20 and 30 Gy). The field size was set to 10 × 10 cm. The dosimeter cuvettes and reporting system glass vials were sandwiched between two solid water phantoms with the top one measuring 1 cm in thickness so that the maximum dose occurred at the middle of each dosimeter. The SSD was set to 100 cm from the solid water surface.

3. Results and Discussion
Initially, the effect of dissolved oxygen on the reporting system, consisting of LMG dissolved in tetrabromoethane, was studied. The absorption spectra of the non-deoxygenated reporting system solution, and an identical solution deoxygenated using N₂, both after irradiation (20 Gy), are shown in figure 1a. For both cases, the absorption maximum (λmax) was found to peak at ca. 632 nm. A change in the solution colour was observed upon irradiation even in the non -deoxygenated solution (figure 1b). This suggests that, in contrast to polymer gel dosimeters, the presence of dissolved oxygen in PRESAGE® does not completely inhibit the oxidation reaction and formation of the chromatic cation, which occurs when the methine proton (C-H) of LMG is abstracted by carbon radicals generated by radiolysis of the halocarbons. However, deoxygenating the reporting system improved the sensitivity to radiation dose, with the change in optical density increasing by ~30% compared to the non-deoxygenated solution. This suggests partial oxygen sensitivity, however, this should not be considered a limitation since the colour formation reaction still proceeds in the presence of oxygen.

The measured absorbance changes at 632 nm versus the radiation absorbed doses for the deoxygenated and non-deoxygenated PRESAGE® dosimeters are displayed in figure 2. Absorption values were obtained by subtracting the relevant value of a reference cuvette from the same batch with zero radiation dose from that of the irradiated cuvettes. In both cases very good linearity (correlation
coefficient $R^2 > 0.99$) of the dose response was observed for PRESAGE® with/without deoxygenation indicating no influence on the linearity of the dose-response relationship (figure 2). However, it is important to point out that removing dissolved oxygen completely from the PRESAGE® precursors might be challenging because it is expected that oxygen might still diffuse into PRESAGE® during the curing process. Nevertheless, it is expected that potential diffusion of oxygen into the deoxygenated PRESAGE® batch is minimal and not sufficient to make an exact comparison between the two batches in terms of oxygen effects problematic.

Figure 1. (a) Absorption spectra of the deoxygenated and non-deoxygenated reporting system solutions after irradiation to a dose of 20 Gy. Reference solution (non-irradiated) for each formulation was used as a baseline to establish the zero value. (b) Photograph of the deoxygenated and non-deoxygenated reporting system solutions before and after irradiated to a dose of 20 Gy showing an increase in colour intensity in the deoxygenated solution.

Unlike the reporting system, a slight (~5%) increase in sensitivity was observed for the deoxygenated PRESAGE® compared to the non-deoxygenated batch. Such observation is consistent with the reporting system findings; however, the small variation between the deoxygenated and non-deoxygenated PRESAGE® could be attributed to the polyurethane matrix being solid and thus, minimizing the diffusion of atmospheric gasses.
Figure 2. Recorded optical absorbance changes as a function of absorbed radiation dose for the deoxygenated and non-deoxygenated PRESAGE® batches. Error bars represent the standard deviation in the measurement.

4. Conclusion
In this work, the potential influence of atmospheric oxygen on the overall characteristics of the PRESAGE® was investigated. In general, a noticeable oxygen influence on the sensitivity of PRESAGE® and its reporting system has been observed. However, no influence on the linearity, absorption spectra and stability of PRESAGE® has been reported. This confirmed yet another attractive feature of the PRESAGE® dosimeter; its insensitivity to oxygen. An increase in sensitivity to radiation dose could be achieved when deoxygenating the PRESAGE®. However, considering the complexity and time required to deoxygenate the PRESAGE® precursors and the fact that only a slight improvement in sensitivity is achieved, deoxygenation of PRESAGE® precursors is not justifiable and thus not recommended based on our observations.

5. References
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