

Simple dose rate measurements for a very high synchrotron X-ray flux

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Dose measurements based on methylene blue (MB) bleaching, widely used for ultraviolet light, can also be applied to X-rays including very high flux levels. This method has been tested by using both MB bleaching and Fricke dosimetry for a conventional monochromatic X-ray source and then for 'white-beam' synchrotron radiation. The results show that MB bleaching dosimetry can easily measure X-ray doses up to at least 10^5 Gy s⁻¹, as long as the MB concentration is sufficiently high. This condition can be verified from the deviations from linearity of the bleaching *versus* exposure time.

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1. Introduction

In our synchrotron-based research, we routinely encountered a problem that affects many investigators: how to quickly and simply evaluate very high 'white-beam' X-ray flux levels with reasonable accuracy. This problem is becoming increasingly acute because of the improving source performances and new biomedical applications, such as imaging (Hwu *et al.*, 2004a,b; Margaritondo *et al.*, 2004; Chen *et al.*, 2008) and synthesis (Wang *et al.*, 2008; Liu *et al.*, 2008; Weon *et al.*, 2008), and is likely to explode with the forthcoming X-ray free-electron lasers.

We recently found a simple solution that we would like to share with other synchrotron users. The common dosimetry method for ultraviolet radiation, MB bleaching (Lafuente *et al.*, 1958; Kovacs *et al.*, 1998; LaVerne *et al.*, 2005; Day & Stein, 1957), can be extended to high flux levels of synchrotron X-rays. We reached this conclusion by testing and calibrating the method at lower dose levels with a conventional monochromatic source, then extrapolating the results to synchrotron-level fluxes and cross-checking them with Fricke dosimetry.

Other X-ray dosimetry technologies such as film badges, ionization chambers or Geiger counters are not helpful at high white-beam fluxes. In fact, they are affected by saturation and other problems. We shall see that even Fricke dosimetry is more problematic than MB bleaching at high flux levels.

We specifically targeted quantitative measurements without attenuation of the 'white-beam' dose rate emitted by the high-brightness superconducting wiggler light source at the 01A

beamline of the NSRRC, Hsinchu, Taiwan (Wang, Chien *et al.*, 2007; Wang, Hua *et al.*, 2007). We wanted to determine the amount of energy transferred from the radiation source to the absorbing material, *i.e.* the absorbed dose per unit mass. Since the spectral distribution of synchrotron radiation *versus* the photon energy is accurately known, the absolute photon flux as a function of the photon energy can be extracted from this result.

MB was previously used as a dosimeter for high-energy photons including γ -rays (Lafuente *et al.*, 1958; Kovacs *et al.*, 1998; LaVerne *et al.*, 2005) and X-rays (Day & Stein, 1957). However, it was never tested for the very high white-beam flux levels of advanced synchrotrons. Our present results show that MB bleaching can indeed be applied to high flux levels as long as the MB concentration is sufficiently high, as discussed below.

2. Experimental

Parallel measurements were performed at high flux levels using the Fricke (ferrous sulfate) approach (Fricke & Morse, 1927). The results yielded a much lower estimated dose than the MB approach. This discrepancy indicates that Fricke dosimetry is more affected by saturation problems at very high dose rates than MB bleaching.

The first tests were performed on a laboratory-based Cu $K\alpha_1$ (1.54056 Å wavelength, ~8 keV photon energy) X-ray source (in a Bruker D8 diffractometer) working at 45 kV and 40 mA. Then, for the synchrotron test we used unmonochromatized ('white') X-rays with no optical elements except one

set of beryllium and Kapton windows. A slit system was used to obtain a transversal beam section of 13×9 mm.

All the dye and chemicals were of reagent grade and used with no additional purification. All solutions were prepared using de-ionized water ($18.2 \text{ M}\Omega \text{ cm}$, Millipore, Milli-Q, MA, USA). Two types of solution containers were used: polypropylene (PP) conical tubes and PMMA cuvettes. The MB hydrate was from Sigma-Aldrich and we used MB aqueous solutions concentrations of 0.125, 1.25, 2.5 and 20 mM. The Fricke test was an air-saturated diluted solution (total volume 1 L) of 1 mM hexahydrated ferrous-ammonium sulfate $[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$, Showa Inc.] and 0.4 M sulfuric acid (Showa Inc.).

The MB bleaching was measured with a UV-VIS JASCO V-570 absorption spectrophotometer. The decolouration was evaluated from the changes in absorbance at 664 nm wavelength. UV-VIS absorption spectrometry was also used for the Fricke dosimetry by monitoring the yielded ferric ions in a quartz cuvette based on the 304 nm absorption peak.

Both the MB and Fricke solutions were freshly prepared before each irradiation test. The absorbance measurements were performed within a few minutes after irradiation.

3. Results and discussion

Figs. 1 and 2 show the results of low-flux-level tests with the conventional monochromatic source. Specifically, Fig. 1 shows the Fricke-measured absorbed dose *versus* the exposure time. These results are based on measured parameters (Law, 1969) including (i) the difference of the molar extinction coefficient between ferric and ferrous ions ($2204 \text{ L mol}^{-1} \text{ cm}^{-1}$); (ii) the density of the Fricke solution (1.024 g cm^{-3}); (iii) a *G* value of ~ 13 (chemical yield of Fe^{3+} in ions/100 eV); this value is independent of the photon energy in the relevant spectral range and was measured for similar source conditions for 25 and 48 keV photons (Law, 1969).

Fig. 1 reveals a rather linear behavior. The dose rate extracted from this figure is $146 \pm 3 \text{ Gy s}^{-1}$. Fig. 2 shows the MB bleaching data expressed as bleached micromoles (μM); the horizontal scale was converted from exposure time to the dose measured with the Fricke method. The three curves correspond to three different MB solution concentrations.

We see in Fig. 2 that the two lower concentrations are affected by saturation problems as the dose increases. On the contrary, the higher-concentration curve is linear up to high doses; the deviation from linearity is $< 1\%$ at 350 kGy. The curves in Fig. 2 also show that the initial bleaching rate, *i.e.* the slope of the MB bleaching *versus* the Fricke-measured dose, is independent of the initial concentration. This is reasonable since at low doses the number of bleached molecules by each photon is the same independent of the concentration.

From the highest-concentration curve of Fig. 2 (20 mM), we estimate a slope of $\sim 0.00404 \mu\text{M Gy}^{-1}$ corresponding to a *G* value of ~ 0.0390 molecules/100 eV. Note that this *G* value is much smaller than that for Fricke dosimetry. This reflects the fact that bleaching affects a smaller proportion of molecules in the solution than Fricke dosimetry. This led us to the idea that

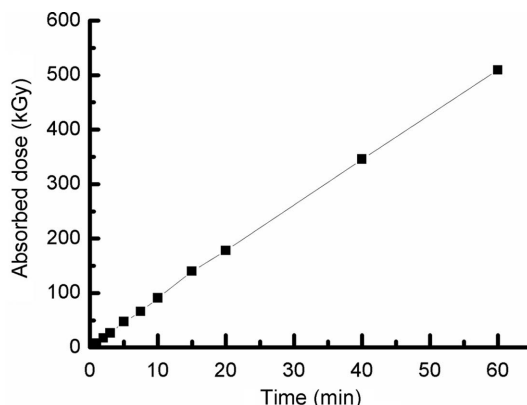


Figure 1 Absorbed dose as a function of the exposure time measured with the Fricke method using a conventional X-ray source.

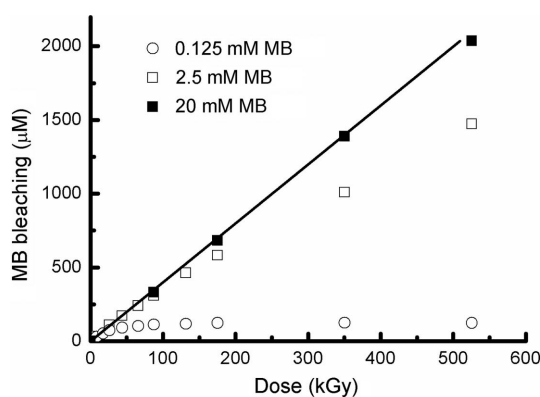


Figure 2 MB bleaching for the conventional X-ray source; the horizontal scale was obtained by converting the exposure time to the absorbed dose measured with the Fricke method. The three curves correspond to three different MB solution concentrations.

MB bleaching is more suitable and less affected by saturation than the Fricke method at high doses or high dose rates, as confirmed below.

We now discuss the high-flux-rate measurements with synchrotron radiation. Typical results are shown in Fig. 3 as bleaching *versus* the irradiation time for three MB solution concentrations. We can see that the white synchrotron beam

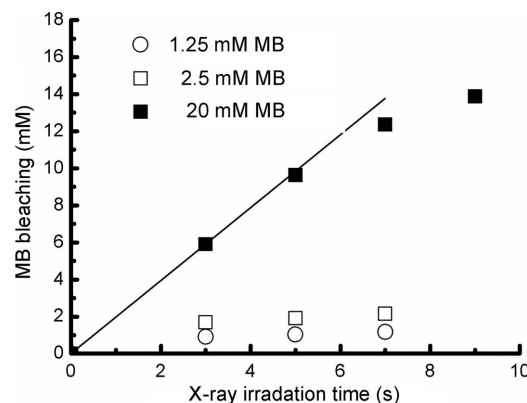


Figure 3 MB bleaching of MB for the synchrotron 'white' beam as a function of the irradiation time. The three curves correspond to three different MB solution concentrations.

bleaches the MB almost instantaneously because of its high dose rate, much larger than the conventional X-ray source. It is thus difficult to catch during the bleaching of a non-saturation regime except for very short exposure times. For example, Fig. 3 shows that even the 2.5 mM MB solution concentration is already clearly saturated even after 3 s of exposure. It is therefore not possible to extract the dose rate from the linear portion of the curve. However, with the 20 mM MB concentration solution, the linearity is quite good, within 2%, even up to 5 s of exposure. Note that such a measured dosage is three times more than that measured using the 3 s data point from 2.5 mM MB concentration and highlighted the problem of measuring very high radiation dosage precisely.

From the higher-concentration curve of Fig. 3 and using the G value obtained from Fig. 2, we estimate that the 7 s irradiation time corresponds to a total dose of $\sim 3.1 \times 10^6$ Gy. From the 3 s point, we estimate a dose rate of $\sim 4.7 \times 10^5$ Gy s⁻¹. The conservative accuracy limit of this result, linearly interpolated from the 7 s point, is 6% or 2.8×10^4 Gy s⁻¹ and is less than 2% or 9×10^3 Gy s⁻¹.

Quite interestingly, when we measured the dose and the dose rate of Fig. 3 with the Fricke method we obtained $\sim 0.6 \times 10^5$ Gy s⁻¹. This much lower value corroborates our hypothesis that Fricke measurements are more likely than MB bleaching to underestimate the dose rate because of saturation problems.

Note that the saturation problems for MB bleaching and for Fricke dosimetry cannot be solved at these high flux levels by simply limiting the exposure time. In fact, the time would become too small and difficult to measure accurately.

4. Conclusion

In summary, we found that dose rates at very high synchrotron fluxes can be measured with reasonable accuracy using the following method. The MB bleaching is measured as a function of time for different MB concentration, increasing as much as possible the highest concentration. The bleaching is then converted to doses using the conversion factor

$0.00404 \mu\text{M Gy}^{-1}$. The dose rate is derived from the highest-concentration curve and the accuracy is estimated by assessing the deviations from linearity of the bleaching *versus* exposure time curves.

For the present synchrotron sources, we estimate that the above accuracy can probably be improved to 1% if proper concentration is used. This method will become even more interesting for the future free-electron laser sources, offering a limited but still reasonable accuracy while measuring the dose rate with a rather simple method.

References

- Chen, Y. T. *et al.* (2008). *Nanotechnology*, **19**, 395302.
 Day, M. J. & Stein, G. (1957). *Radiat. Res.* **6**, 666–679.
 Fricke, H. & Morse, S. (1927). *Am. J. Roentgenol. Radium Ther. Nucl. Med.* **18**, 430–432.
 Hwu, Y. *et al.* (2004a). *Biophys. J.* **87**, 4180–4187.
 Hwu, Y., Tsai, W. L., Je, J. H., Seol, S. K., Kim, B., Groso, A., Margaritondo, G., Lee, K. H. & Seong, J. K. (2004b). *Phys. Med. Biol.* **49**, 501–508.
 Kovacs, A., Wojnarovits, L., Kurucz, C. N., Al-Sheikhly, M. & McLaughlin, W. L. (1998). *Radiat. Phys. Chem.* **52**, 539–542.
 Lafuente, B., Goldblith, S. A. & Proctor, B. E. (1958). *Int. J. Appl. Radiat. Isot.* **3**, 119–124.
 LaVerne, J. A., Tandoin, L., Knippel, B. C. & Montoya, V. M. (2005). *Radiat. Phys. Chem.* **72**, 143–147.
 Law, J. (1969). *Phys. Med. Biol.* **14**, 607–614.
 Liu, C. J. *et al.* (2008). *Nanotechnology*, **19**, 295014.
 Margaritondo, G., Hwu, Y. & Je, J. H. (2004). *Riv. Nuovo Cimento*, **27**, 7–40.
 Wang, C.-H., Chien, C.-C., Yu, Y.-L., Liu, C.-J., Lee, C.-F., Chen, C.-H., Hwu, Y., Yang, C.-S., Je, J.-H. & Margaritondo, G. (2007a). *J. Synchrotron Rad.* **14**, 477–482.
 Wang, C. H., Hua, T. E., Chien, C. C., Yu, Y. L., Yang, T. Y., Liu, C. J., Leng, W. H., Hwu, Y., Yang, Y. C., Kim, C. C., Je, J. H., Chen, C. H., Lin, H. M. & Margaritondo, G. (2007b). *Mater. Chem. Phys.* **106**, 323–329.
 Wang, C. H., Liu, C. J., Wang, C. L., Hua, T. E., Obliosca, J. M., Lee, K. H., Hwu, Y., Yang, C. S., Liu, R. S., Lin, H. M., Je, J. H. & Margaritondo, G. (2008). *J. Phys. D*, **41**, 195301.
 Weon, B. M., Je, J. H., Hwu, Y. & Margaritondo, G. (2008). *Phys. Rev. Lett.* **100**, 217403.