Dose rate effects in fluorescence chemical dosimeters exposed to picosecond electron pulses: an accurate measurement of low doses at high dose rates – Supplementary Information

Martin Precek[1,2], Petr Kubelik[2,3], Ludek Vysin[2], Uli Schmidhammer[4], Jean-Pierre Larbre[4], Alexandre Demarque[4], Pierre Jeunesse[4], Mehran Mostafavi[4] & Libor Juha[2,5]

1) ELI Beamlines, Institute of Physics, Czech Academy of Sciences, Za Radnicí 835, 252 41 Dolní Břežany, Czech Republic

2) Department of Radiation and Chemical Physics, Institute of Physics, Czech Academy of Sciences, Na Slovance 1999/2, 18221 Prague, Czech Republic

3) Department of Spectroscopy, J. Heyrovsky Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 2155/3, 182 23 Prague 8, Czech Republic

4) Institut de Chimie Physique/ELYSE, UMR 8000 CNRS, Université Paris-Saclay, 91400 Orsay, France

5) Laser Plasma Department, Institute of Plasma Physics, Czech Academy of Sciences, Za Slovankou 1782/3, 18200 Prague, Czech Republic

Corresponding author: martin.precek@gmail.com

1 Details on fluorescence measurements

For the trimesic acid the issue of the unknown product of the irradiation somewhat complicates the process of performing reference fluorescence measurements. Fortunately, Matthews and Wilson (*1*) have already established that the fluorescence characteristics of the product are similar to quinine, with near identical wavelengths for the excitation and emission peak for both systems (see Table 1 in the paper, and Fig. S1 and Fig. S2 here). Hence, the fluorescence standard for both the terephthalate and the trimesic acid dosimeters was a solution of quinine in 0.01 M sulfuric acid (the standard reference quinine solution is usually 0.05 M sulfuric acid, but the value of the fluorescence yield of quinine in 0.01M sulfuric acid is identical (*2*)). The solution of sulfuric acid was checked and had no measurable fluorescence compared to pure water.

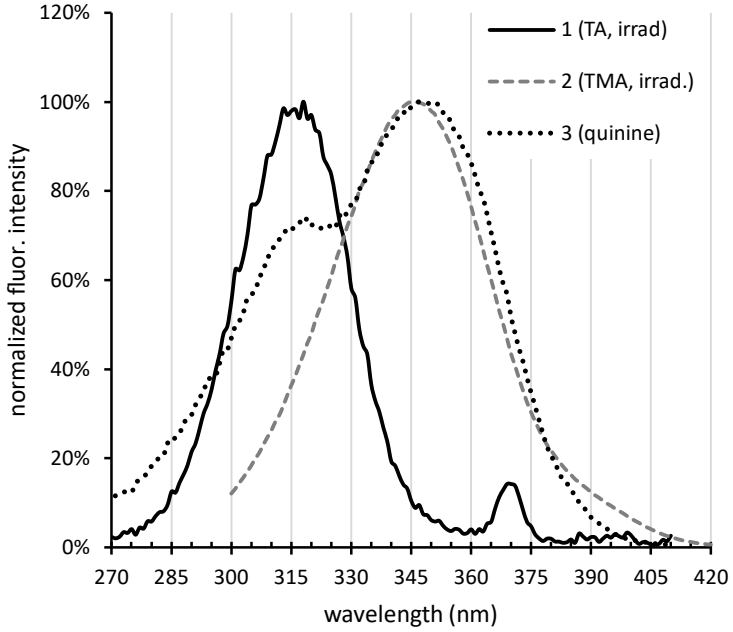

Fig. S1 - Fluorescence excitation spectra normalized to peak maxima for: 1) terephthalate dosimeter (TA, irradiated), 2) trimesic acid dosimeter (TMA, irradiated), 3) quinine reference; collection wavelength for emission was 420 nm for "1" and 440 nm for "2" + "3"; the peak at 370 nm for "1" is a result of water Raman scattering

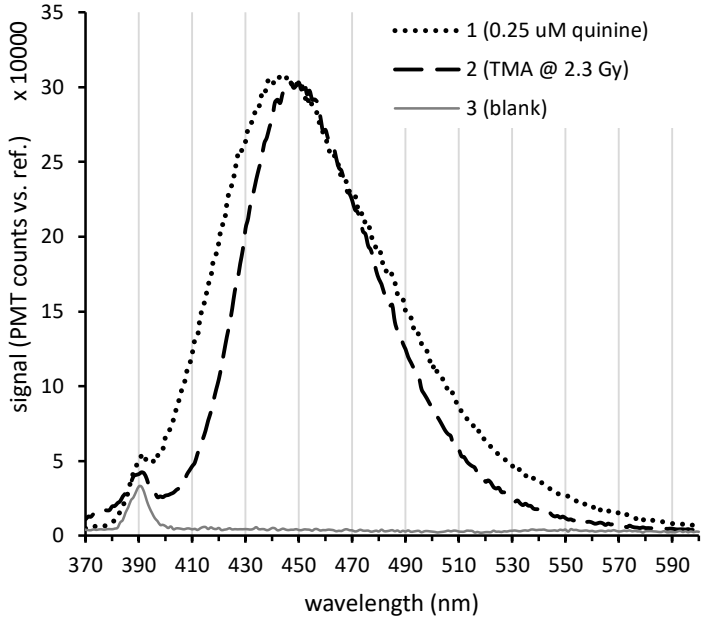

Fig. S2 - Emission spectra from 1) 0.25 µM quinine in 0.4 M H_2SO_4, 2) 1 mM trimesic acid (TMA) + 0.01 M H_2SO_4 irradiated to 2.2 Gy, 3) background noise and water Raman peak from scan of blank water solution; excitation wavelength = 345 nm

Although the fluorescent product for the terephthalate dosimeter, 2-hydroxy-terephthalate (HTA), is known, it was not commercially available to the experimenters during the preparation phase for the experiments, so the quinine solution was employed instead (as of the time of publishing of this work, the situation has improved and HTA is now available from multiple vendors). Utilization of quinine as

a reference for the terephthalate dosimeter was possible, because quinine has – in addition to the main maximum at ~350 nm – a secondary fluorescence excitation maximum at ~320 nm. This smaller maximum is fortunately located very near to the excitation maximum for HTA, i.e. the irradiated terephthalate dosimeter (see Fig. S1).

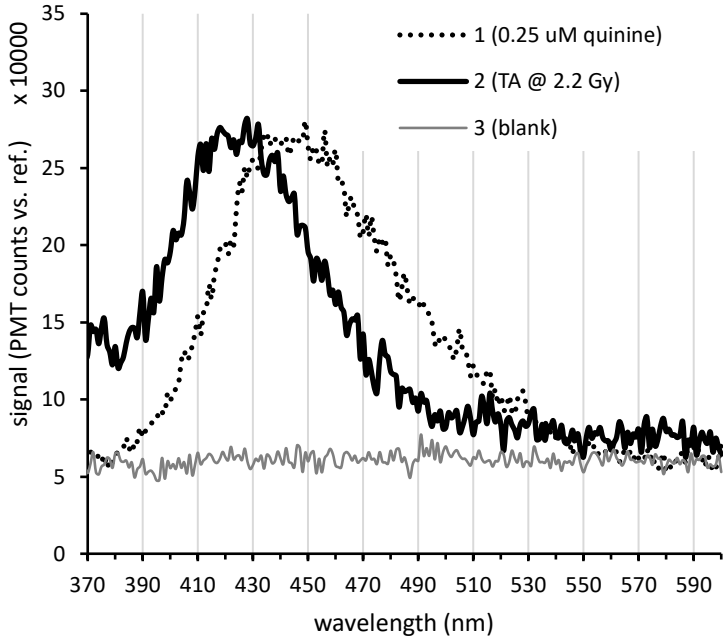

Fig. S3- Emission spectra from 1) 0.25 µM quinine in 0.4 M H_2SO_4, 2) 0.1 mM terephthalic acid (TA) + 0.4 mM NaOH irradiated to 2.2 Gy , 3) background noise from scan of blank water solution; excitation wavelength = 315 nm

For the coumarin-3-carboxylic acid (C3CA) dosimeter, the reference solution was the fluorescent radiolytic product – 7-hydroxy-C3CA (7-OH-C3CA) in a 10 mM equimolar phosphate buffer at pH = 6.8. As can be seen in Fig. S4, the irradiated C3CA solution cannot be excited on the primary maximum of 7-OH-C3CA – this is due to an absorption band from the C3CA molecule, so excitation centered approximately at 385 nm would be preferable. Unfortunately, there is an issue with the Raman scattering peak of water that can be observed at a wavenumber shifted by 3200-3600 cm^{-1} lower than the wavenumber of the incident light (*3*,*4*). In this case this would be 439-447 nm, overlapping with the peak of maximum emission for 7-OH-C3CA at 442 nm. Therefore, the excitation wavelength was selected to be 395 nm in order to shift the Raman peak to 452-460 nm, safely outside of the fluorescence maximum of 7-OH-C3CA (see Fig. S5).

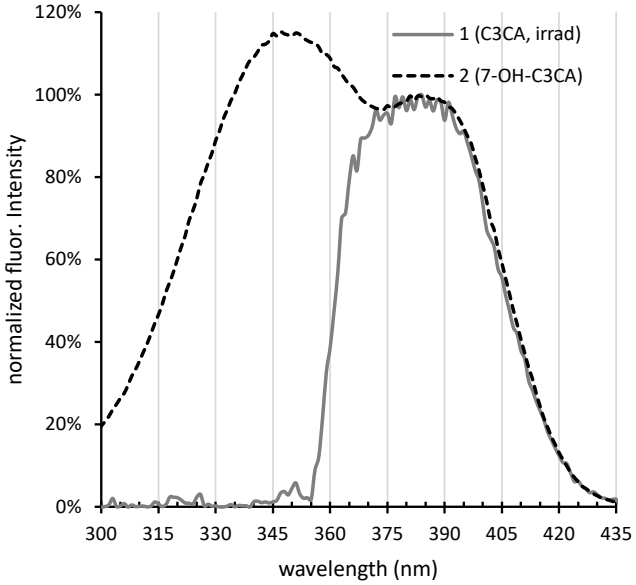

Fig. S4 - Fluorescence excitation spectra normalized to the local peak maximum at 387 nm for: 1) 1mM C3CA dosimeter irradiated by 2.3 Gy, 2) 1µM 7-OH-C3CA in 20 mM phosphate buffer; collection wavelength for emission: 445 nm (both spectra had been baseline corrected by subtracting the excitation spectrum of an unirradiated 1 mM C3CA dosimeter solution to remove the Raman scattering peak at 360 nm)

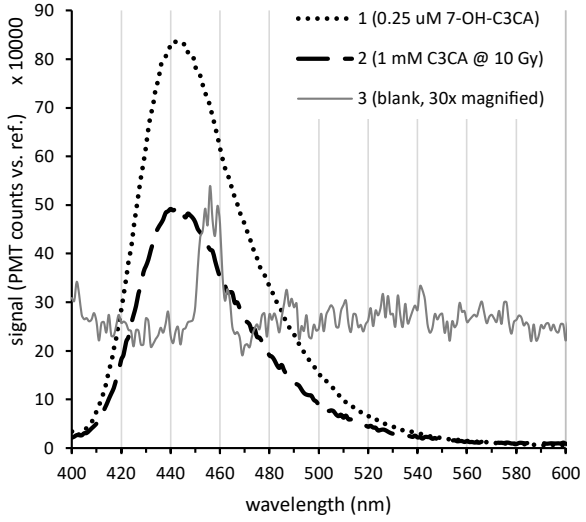

Fig. S5 - Emission spectra from 1) 0.25 µM 7-OH-C3CA in 20 mM PB of pH = 6.8, 2) 1 mM C3CA in 20 mM PB irradiated to 10 Gy, 3) 30-fold magnified background noise and water Raman peak from scan of blank water solution; excitation wavelength: 395 nm

Sets of cuvettes containing a linearly growing concentrations: 0 µM, 0.25 µM, 0.50 µM and 1.00 µM of the reference standard solution (quinine, 7-OH-C3CA) were freshly prepared prior to each measurement on the spectrofluorometer from their concentrated stock solutions. These reference sets were then measured prior to measuring the cuvettes with the samples of irradiated fluorescence dosimeters at the appropriate combinations of excitation and emission wavelengths and bandwidth selector slits. After baseline correction by subtracting the signal from the blank (0 µM) sample, a plot of the datapoints was made and the value of the slope of the linear trendline was utilized as the coefficient by which the

measured signal from the dosimeter samples were divided to calculate the relative fluorescence of the individual dosimeter samples vs. the fluorescence of an ideal 1 μM standard (see Fig. S6). The approach was taken to suppress random measurement errors and also to confirm the linearity of the photomultiplier signal response over the expected measurement range for each excitation and emission slit combination.

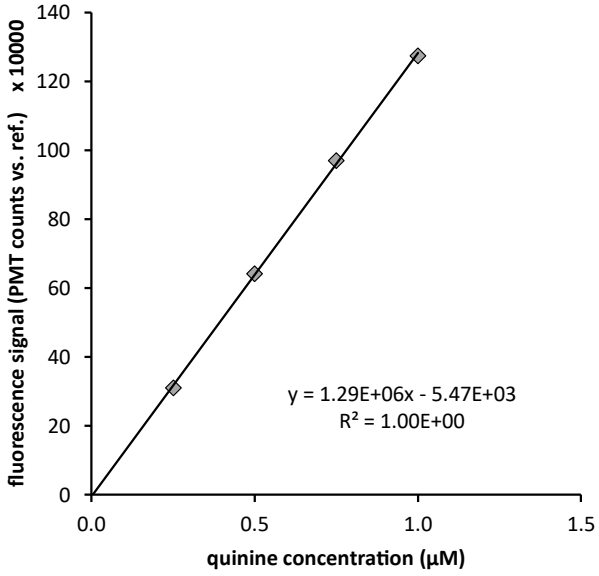

Fig. S6 – Example of the determination of the calibration coefficient (fluorescence signal vs. concentration) for the quinine reference set of standards for measuring the fluorescence of the samples trimesic acid dosimeters

2 Supplementary information literature

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