The effect of sunlight and UV lamps on EPR signal in nails

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Abstract

The effects of illumination of nail clippings by direct sunlight, UV lamps and fluorescent bulbs on native and radiation-induced electron paramagnetic resonance (EPR) signals in nails are presented. It is shown that a few minutes of exposure of the nail clippings to light including a UV component (sunlight and UV lamps) generates a strong EPR signal similar to the other EPR signals observable in nails: native background (BKG), mechanically induced (MIS) or radiation-induced (RIS). This effect was observed in clippings exposed and unexposed to ionizing radiation prior to the light illuminations. An exposure of the clippings to fluorescent light without a UV component generated, within the examined range of the light fluences (up to 240 kJ/m²), an EPR signal with considerably lower yield than UV light. The light-induced signal (LIS) decayed after 10 min of water treatment of the samples. In contrast, it was still observable 3 months after illumination in samples stored in air at room temperature, and 3 weeks in frozen samples, respectively. It is concluded that the LIS can considerably affect assessment of the dosimetric RIS components in irradiated nails, and of the background signals in unirradiated nails, thus contributing to errors in EPR dosimetry in nails.

Keywords EPR · Nails · ESR · Dosimetry · Radiation

Introduction

Recent studies suggest applicability of electron paramagnetic resonance (EPR) signals generated by ionizing radiation in nails for radiation dosimetry (Trompier et al. 2014a; Reyes et al. 2012; Sholom and McKeever 2016; Marciniak and Ciesielski 2016; Marciniak et al. 2018). The use of nail samples as a personal biodosimeter in emergency situations has many obvious advantages. Because of simple, non-invasive sampling, and easy and quick sample preparation, the dosimetry in nails potentially can provide a fast determination of radiation dose, provided problems resulting from the instability of the radiation-induced signal (RIS) and from

the complexity to determine its magnitude are solved. So far, EPR dosimetry in nails was applied to reconstruct doses in three radiation accidents, when individuals were overexposed to various radiation levels due to misuse of isotope sources (Trompier et al. 2014b; Romanyukha et al. 2014). It should be noted, however, that human nails, in particular those from hands, are also exposed to sunlight and may undergo different types of cosmetic treatments involving artificial light, such as hardening of nail polishes in cosmetic salons or UV exposures in solariums. Such treatments potentially can generate additional unwanted EPR signals that may overlap with the spectral components used in radiation dosimetry.

EPR signals measured in nail clippings can originate from native paramagnetic centers present in the nails' substance (the intrinsic background, the BKG spectral component) and from radicals induced by physical factors exerted on the nails: mechanical stress, e.g., caused by cutting the clippings (mechanically induced signal, the MIS spectral component), or ionizing radiation (radiation-induced signal, the RIS spectral component). All those signals, after their stabilization in air at room temperature, when measured in X-band are overlapping singlets. In addition, recent reports of Sahiner

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et al. (2015) and Sholom and McKeever (2017) show that illumination of nails by light can also induce EPR signals overlapping with the background and radiation-induced signals. This is an additional, serious confounding factor in potential EPR dosimetry in nails, which is based on reliable measurements of the RIS component used to determine the radiation dose.

In this study, effects of X-ray exposure of irradiated and unirradiated nail samples to light from four sources are reported: the cosmetic UV lamp, CLEO UV lamp used in solarium, fluorescent bulbs and direct sunlight on their EPR signals.

Materials and methods

Seventeen samples of nail clippings, each of 7–23 mg total mass, were obtained from six healthy volunteers (three females and three males). The samples marked with the same capital letter (A, B, C, D, E or F) were taken from the same donor. For example, the samples A1, A1a, A1b, A1c and A1d were all collected from donor (A) at the same time, while the sample A4 came from the same donor (A) but was cut on another day. The samples were cut off by scissors, similarly as during regular hygiene or cosmetic procedures. To reduce mechanical stress in nails caused by the cutting, the clippings were obtained by a single cut.

Irradiations of the samples by ionizing radiation were performed in the Department of Oncology and Radiotherapy, Medical University of Gdańsk, Poland, with 6 MVp photons from a Clinac 2300 medical accelerator. The samples were irradiated at electron equilibrium conditions (at beam axis, on the surface of a 10 cm thick PMMA block, under 1.5 cm buildup material), and at a dose rate 7.6 Gy/min. The accuracy of the delivered doses to individually irradiated samples was $\pm 2\%$. In time periods between clipping of the nails and all subsequent procedures (EPR measurements, irradiations, water treatments), the samples were stored in small (3×4 cm) tightly closed polyethylene bags in darkness at room temperature of about 24 °C (the samples encoded A1, A1a, B1, C1, C1a, D1, D1a, D2, E1, E1a, F1, F1a, and A1d) or in a freezer at -26 °C (samples A1b, A1c, A4 and A4a)—these samples were brought to room temperature directly before EPR measurements and put back to the freezer immediately afterwards. All steps of the experimental procedures were performed under air conditions. EPR measurements (those before or after the exposure of the samples to light or X-rays) were performed from 1 to 7 days after collection of the samples; only the samples C1a and D1a were measured 12 and 19 days after clipping, respectively.

The light exposures were performed using three types of lamps and the direct sunlight. Some of the samples were irradiated through a 1.6-mm glass plate (a Petri dish) to

check the effect of a partial filtering of those spectral components with the shortest wavelength (UV). The irradiances were measured at the samples positions with an ORION-TH power meter (OPHIR). The artificial light sources were:

- (1) an UV lamp commonly used in cosmetic nail salons for hybrid nail polishing (Ultraviolet Radiant Lamp AP-111, Alle Paznokcie) with four bulbs, 9 W each. The irradiance at the sample position was 164 W/m², or 48 W/m² (when filtered by the glass plate).
- (2) A lamp made of two parallel CLEO Advantage 80W-R lamps (Philips), 80 W each. The irradiance at the sample position was 48 W/m², or 20 W/m² (when filtered by the glass plate).
- (3) A lamp made of six fluorescent Duluxstar (OSRAM) bulbs, 24 W each. The irradiance at the sample position was 110 W/m², or 62 W/m² (when filtered by the glass plate).

The exposure of the nails to sunlight was done by placing the clippings on a white paper attached to a window sill outside the building at about noon. The irradiance measured during the exposure was about 800 W/m², or about 450 W/m² when filtered by the glass plate. The total fluences (J/m²) were calculated by multiplication of the measured irradiances by the corresponding time of the exposures. The temperature of the samples during the illuminations did not exceed room temperature by more than 1 °C for the artificial lamps and 5 °C for the sunlight.

The emission spectra of the artificial sources used in this study are presented in Fig. 1.

The EPR measurements were performed at room temperature (about 24 °C) using a Bruker EMX-6/1 (Bruker BioSpin) spectrometer at X-band (9.85 GHz) with a cylindrical 4119HS W1/0430 cavity. The nail clippings were measured in a quartz EPR tube (inner diameter: 5 mm) positioned in the central region of the cavity. The EPR cavity was equipped with an internal standard (ER 4119HS-2100 Marker Accessory, Bruker BioSpin GmbH). Quantitative analysis of the spectra was carried out using Microsoft Office Excel 2010. The acquisition parameters for the nails' spectra were: modulation frequency – 100 kHz, modulation amplitude – 0.5 mT, microwave power – 2.58 mW, time constant – 81.92 ms, sweep time – 41.94 s, number of scans – 10. The peak-to-peak amplitude of the central spectral line was taken as the magnitude of the EPR signals in the samples. Each sample was measured three times after rotation of the EPR sample tube in the cavity, and the measured amplitudes were divided by the amplitude of the internal standard, averaged and normalized to the sample mass. The uncertainties in the presented figures, marked by error bars, show repeatability (one standard deviation) of EPR amplitudes at the different orientations of the samples in

Fig. 1 Emission spectra of the applied light sources: **a** cosmetic UV lamp, **b** philips CLEO advantage lamp, **c** duluxstar fluorescent lamp. The insets in **a** and **b** enlarge the UV region of the spectra. All spectra were normalized to the peak at 431 nm

the cavity. The first EPR measurements of the water-soaked samples were performed always after having dried the samples in air for 20 min.

Results

Examples of EPR spectra of unexposed samples and of samples exposed to light or X-rays are presented in Fig. 2. Figure 3a shows the effect when three nail samples (from three donors) stored at room conditions were exposed to the light of the cosmetic lamp. For samples B1 and C1, the entire

Fig. 2 EPR spectra of two fingernail samples A1a and A1d before (A1a_BG and A1d_BG) and after their exposure to the CLEO lamp (A1a sample, 60 min., 172 kJ/m²) and to X-rays (A1d sample, 40 Gy), respectively. The spectra are normalized to the amplitude of the standard line marked by S

Fig. 3 **a** Effect of exposure of three nail samples (obtained from three donors) stored at room condition in darkness, to light from the cosmetic UV lamp. The A1 sample (black squares) was illuminated up to 492 kJ/m² on the first day, followed by illumination on the next day up to the total of 885 kJ/m². **b** Changes in the EPR signals for the samples from **a** the B1 sample was treated for 10 min with water (WT) 1 day after illumination, while the C1 sample was irradiated with X-rays to 40 Gy 6 days after illumination

procedure of light exposures and subsequent EPR measurements lasted about 3 h, while for the A1 sample it lasted about 3 h on the first day and another 3 h on the next day. EPR measurements of these samples were continued for the following 3 months, including soaking of the sample B1 for 10 min in water, and irradiation of the sample C1 with 40 Gy X-rays (see Fig. 3b).

The increase in EPR amplitude induced in nails from four donors (for six examined samples stored at room temperatures: A1a, C1a, D1, D1a, E1 and E1a) by the CLEO lamp is presented in Fig. 4a. The evolution in time of these amplitudes is shown in Fig. 4b. The arrows marked by ‘WT’ (the last data points for samples D1 and E1a) show the drop of the amplitudes after 10 min of water treatment followed by 20 min of drying in air.

The data presented in Fig. 5a, b show the corresponding results for two samples stored in the freezer after completing the light exposures. Illumination of the sample A1c was performed in two long 60-min fractions, while for the A1b

Fig. 4 **a** Effect of exposure of six nail samples obtained from three donors to light from the CLEO lamp. The upper timeline axis does not refer to the results of the samples D1a and E1 (i.e., those exposed through the Petri dish). **b** Time evolution of amplitudes in the illuminated samples. The last data points for the D1 and E1a samples (“WT” marked with arrows) show the effect of a 10-min water treatment of the samples

Fig. 5 **a** Effect of light from the CLEO lamp on two samples from one donor illuminated with different fractions. **b** Fading of the peak to peak amplitudes in the samples from **a** when stored in a freezer at -26°C

sample it was performed in six short fractions (5, 5, 10, 15, 15, and 10 min).

The effect of light from the Duluxstar bulbs on nail samples obtained from two donors and the corresponding evolution in time of their EPR amplitudes after illumination is shown in Fig. 6a, b, respectively. To compare the effect of light exposure from different sources (Duluxstar bulbs vs CLEO lamp) on the nails collected from the same donor, the data for sample D1a (from Fig. 4a) are also shown in Fig. 6a.

The effect of sunlight exposure on the EPR amplitudes and their fading after illumination in samples stored in the freezer are presented in Fig. 7a, b. Before illumination the sample A4a was irradiated with 20 Gy X-rays.

Discussion

The spectra in Fig. 1 demonstrate that a UV component (mainly UV-A in the 300–400 nm range) is generated only by the CLEO lamp and the cosmetic lamp. In contrast, the fluorescent source (Duluxstar) emits only visible light. The EPR spectra generated by light and X-rays are similar with respect to their g-factor and line-shape, as can be seen in

Fig. 6 **a** Effect of light from the Duluxstar bulbs on EPR amplitudes in nail samples obtained from two donors. Data from Fig. 4a (for the sample D1a) are added for comparison. **b** Time evolution of the EPR amplitude in the samples exposed to light. The end point for the sample D2 was measured after a 10-min water treatment of this sample (WT) followed by 20 min of drying

Fig. 2. Estimated LIS magnitudes due to 5 min of illumination with the applied light sources that do include a UV component (on the basis of the first two, left-hand data points in Figs. 3a, 4a, 7a) were approximately the same as the RIS magnitudes generated by 20–40 Gy of X-rays (as shown by the increase of the signal due to 40 Gy X-rays in Fig. 3b, and due to 20 Gy in Fig. 7a). The response curves presented in Figs. 3a, 4a and 5a reach their saturation after about 15 min of light exposure. The differences in the individual maximum saturation levels of EPR signals in Figs. 3, 4, 5, 6 and 7 can be due to inter-sample variations in the inherent sample sensitivity to light and/or in different sample geometries (sample thickness). Qualitatively, the results described in this study are consistent with observations of Sahiner et al. (2015), who also observed an effect of saturation using a different UV lamp than what was used in the present study.

The results presented in Fig. 4a show that the LIS amplitude was almost the same in clippings irradiated by direct light from the CLEO lamp or in clippings irradiated through 1 mm glass of a Petri dish (at the same fluence). Apparently,

Fig. 7 **a** Effect of sunlight on EPR amplitudes in nail samples obtained from one donor. Prior to sunlight exposure, the sample A4a was irradiated with 20 Gy X-rays. **b** Fading of the peak to peak amplitudes of the EPR signals in samples exposed to sunlight and stored in the freezer

the small filtering of the UV component by the glass (see inserts in Fig. 1) did not change noticeably the efficiency of the light in generating the LIS.

Both samples presented in Fig. 5a, b were obtained from the same individual and illuminated and measured on day 5 after cutting. As can be inferred from Fig. 5a, the data points for the sample A1c correspond to those for sample A1b, thus suggesting that the LIS is independent on the dose fractionation. In samples kept in the freezer at -26°C , the LIS signal decayed to BKG level in about 30 days (Fig. 5b).

The results presented in Fig. 6a show that visible light without a UV component does not increase the EPR amplitude in illuminated nails considerably, at least at the fluences where sources including a UV component did generate a strong LIS (as can be seen in Fig. 6a for the D1a sample). However, there is a noticeable, small but statistically significant, increase in EPR amplitude when the sources without UV were used (see the three dashed lines in Fig. 6a), indicating at least some LIS induction, although with much lower yield. This is concurrent with observation of Sholom and McKeever who reported induction of LIS by a 3-h exposure of nails to incandescent lamps (Sholom and

McKeever 2017). The much higher LIS yield in nails by the light modalities with a UV component can be related to a significant increase in light absorption of keratin below 350 nm (Bendit and Ross 1961).

It is interesting that the LIS saturation levels correspond to RIS amplitude caused only by about 40–70 Gy of X-rays. Those signal levels are still within the range of monotonic increase of the RIS with dose of ionizing radiation (Black and Swarts 2010; Trompier et al. 2009; Sahiner et al. 2015; Marciniak and Ciesielski 2016). A plausible explanation of this effect of such an “early” saturation (i.e., at such low signal amplitudes) could be related to a shallower penetration depth of UV light in the nails’ material as compared to the penetration of the X-rays, which deposit dose rather homogeneously in the nails. Stern et al. (2011) demonstrated a complete blocking of UVB radiation and an almost complete blocking (more than 96% of the incident beam) of UVA radiation by nail layers as thin as 0.025 μm . In the superficial layer of the illuminated nails, the local concentration of paramagnetic centers probably reaches saturation levels, but the “targets” in the deeper layers are still available to be transformed by X-rays into observable radicals [assuming the theoretical model of generation of radiation-induced radicals described in Ciesielski (2006)]. This hypothesis is supported by the data for sample C1 in Fig. 3: the EPR amplitude, which reached saturation level after light exposure (Fig. 3a), still increased remarkably after the following X-ray irradiation of that sample (Fig. 3b), obviously because the X-rays generated radicals in the whole volume of the nails (i.e., also in the deeper layers).

The EPR signal generated by light is eliminated completely by water treatments, as is indicated by the downward arrows in Figs. 3b, 4b and 6b. For those illuminated samples that were sealed in polyethylene bags at room temperature, the LIS stabilized after an initial decay in the first 20 days, at levels significantly higher than the background signal (Figs. 3b, 4b). In contrast, in the samples kept in the freezer after illumination the decay was much faster—the signal returned to background levels within about 30–40 days (Figs. 5b, 7b). This result shows that the stability of EPR signal in nails kept frozen as reported by Trompier et al. 2009; and Reyes et al. 2012 is not always observed. Note that, for example, a fast decay of LIS in frozen samples was also reported by Sahiner et al. (2015). The present results on samples irradiated by ionizing radiation also indicate a decay of RIS in frozen samples (data not presented here). These results are concurrent with those reported by Sahiner et al. (2015), who observed LIS decay in the first 24 h after illumination in samples stored at $-4\text{ }^{\circ}\text{C}$. The present results show that this fading continues (for samples kept at $-26\text{ }^{\circ}\text{C}$) for the next 3–4 weeks. These different findings regarding the magnitude and stability of the EPR signals in nail clippings are probably related to individual, physiological conditions

of the nails, and to details of the storage conditions; in particular to the water content in the nails and air humidity (if not stored in vacuum).

Conclusion

It was shown here that even a short (a few minutes) exposure of nail clippings to sunlight or artificial light with a UV component can generate a strong EPR signal overlapping with the other signals recorded in nails: BG, MIS and RIS. This effect inevitably influences EPR dosimetry of ionizing radiation in nails and may cause a significant inaccuracy in reconstructed doses.

Because fading of the introduced EPR signals in nail samples during storage after exposure also turned out to be critical in the present study, it is concluded that determination of reliable, reproducible conditions of sample storage after cutting and irradiation of nails still requires dedicated studies. This is a crucial issue for potential dosimetric applications of EPR in nails.

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