COLOR AND UV-VIS SPECTRAL CHANGES IN IRRADIATED NACRES

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INTRODUCTION

Nacre is a beautiful and shiny material. It can be found in a variety of colors and two samples of the same type of nacre practically never look the same. Because of its beautiful appearance it is often used for decoration on different cultural heritage (CH) objects. This way conservators have to deal with it when treating a variety of objects. In these cases the conservator usually does not know neither the origin of the nacre, weather its color is natural or obtained by one of the common treatments, like heating for enhancing colors, or if it was already treated as part of a previous restoration.

Gamma radiation is a very convenient and modern method for disinfection and disinsection of different biodegradable organic materials like wood, textile, paper, leather etc. Since nacre is a common ornament material that often cannot be removed from the treated object the question arises weather it is acceptable to irradiate nacre at all and if yes up to which doses.

This is the reason we chose to study how nacre's color is affected by irradiation. We selected nacres from the stock for conservation in a museum because such are most likely to occur on CH objects being radiation treated.

EXPERIMENTAL

Two different types of nacre were obtained as relatively large pieces from the conservation stock of Museum of Arts and Crafts in Zagreb, one white and the other with a yellowish tone (yellow). For colorimetric measurements samples of each nacre were cut to appropriate dimensions and irradiated to doses common in CH treatment and to much higher doses to ensure development of radiation induced effects: 0.5, 1, 2, 6, 10, 22, 54 kGy.

Dose rate~ 0.32 kGy/h, at room temperature, in air

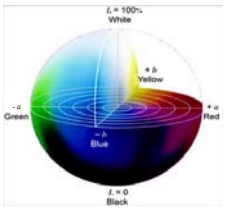
Instrument: Ocean Optics USB4000 spectrometer with a HL-2000 halogen source and test probe connected via fiber optics

To quantify the color the three-dimensional colorimetric system CIE-$L^*a^*b^*$ was used. This color space consists of three mutually perpendicular axes: axis L^* determines the lightness from 0 (black) to 100 (white), axis a^* determines the ratio of red (positive) to green (negative), and axis b^* specifies the ratio of yellow (positive) to blue (negative). To assess the difference between two colors a total color difference ΔE^* was used, which expresses the distance between two points in the CIE-L*a*b* system calculated according to the formula:

$$\Delta E^* = \sqrt{(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2}$$

where L^*, a^*, b^* are differences in individual axes (differences between the values measured after and before irradiation).

The color of each sample was measured prior to irradiation and after irradiation care was taken to replicate measurement conditions (position and orientation) as much as possible. Color assessments were repeated at selected periods during post-irradiation period.



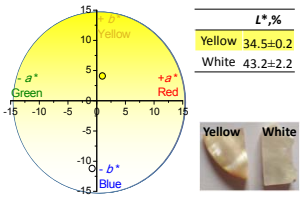
According to Mahy et al. [1]:
ΔE^* = 2.3 JND (just noticeable difference).

Simple evaluation of colour deviation according to Hardeberg [2]

ΔE^*	< 3	3-6	> 6
Colour difference	Hardly perceptible	Perceptual but acceptable	Not acceptable

RESULTS

Color charecteristics of the nonirradiated nacre



	L*,%
Yellow	34.5±0.2
White	43.2±2.2

Both nacres lightness is less than 50 % meaning that they both are gray leaning more to the black direction that the absolute white one. As expected the "white" nacre is as expected lighter than the "yellow" one.

The values of a^* and b^* are close to 0 indicating that the present colors are present only as soft tones while gray tones prevail. The yellow nacre has as a slightly yellow tone, while the white one has a somewhat stronger blue tone.

Figure 2.
Appearance of non-irradiated and irradiated samples of nacre. The marks indicate position and orientation for colorimetric measurements.

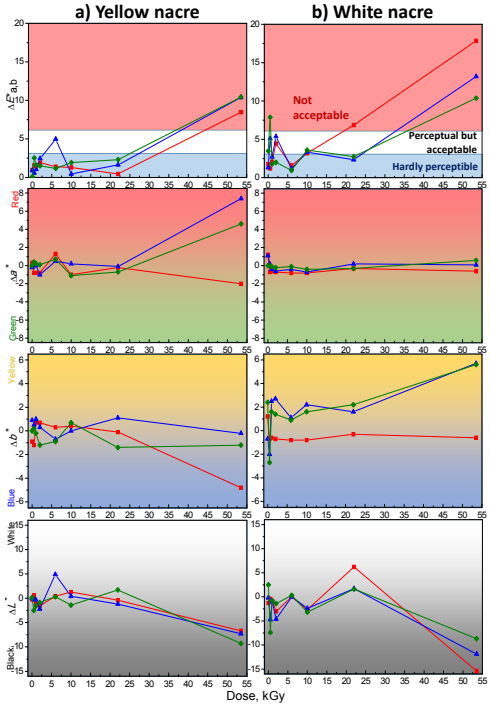


Figure 1.
Radiation dose dependence of the colorimetric parameters compared to those of the same non-irradiated samples immediately after irradiation and during post-irradiation period:
Red – immediately after irradiation; **Blue** - after 1 month; **Magenta** - after 2 months

Scattering of the results is partly due to non-homogeneity of a natural material with a complex visual appearance, which makes reproducibility of results a challenge.

Yellow nacre:

- $\Delta E^*_{a,b}$ values are more or less similar and below $\Delta E^*_{a,b}$ = 2.3 for all samples up to 22 kGy. A large increase of $\Delta E^*_{a,b}$ is noticed only for the dose of 54 kGy. For this sample $\Delta E^*_{a,b}$ is greater that 8. Compared to the Mahy et al. evaluation [1] the values are all under $\Delta E^*_{a,b}$ = 2.3 i.e. under JND (just noticible difference) disregarding the scatterings.
- Small variations in a^* and b^* can be noticed for all doses except the largest one. At 54 kGy a significant change is observed only in the value a^* but only after one month. The nacre gets a reddish tone. b^* values indicate that right after irradiation a bluish tone appeared, that disappeared during post-irradiation time. The largest impact of irradiation is observed for L^*. The nacre darkens with irradiation. Significant effect is observed only on the sample irradiated with 54 kGy.
- The color difference has increased and become constant within a month of post-irradiation.

White nacre:

- Its color is apparently more susceptible to irradiation. Even at the lowest dose of only 0.5 kGy $\Delta E^*_{a,b}$ becomes greater than 2.3 (JND) and all samples irradiated up to 10 kGy fall in the range "Perceptual but acceptable" according to Table 1 [2].
- The color change decreases particularly during the first month and somewhat less after two months. The values of $\Delta E^*_{a,b}$ in the case of the sample irradiated with 22 kGy have actually decreased to 2.3-2.7 and thus fall in the "hardly perceptible" category according to Hardeberg.
- The a^* difference can be completely disregarded since the values are too small. b^* values show the white nacre gets a slight yellowish tone, but only with time. As in the yellow nacre case the largest impact can be noticed on L^*, where the largest dose offers significant darkening of the surface.

There is significant variation of color properties already in non-irradiated samples, as can be seen in Fig. 2. Visually a real difference can be observed only on the samples that were subjected to 54 kGy.

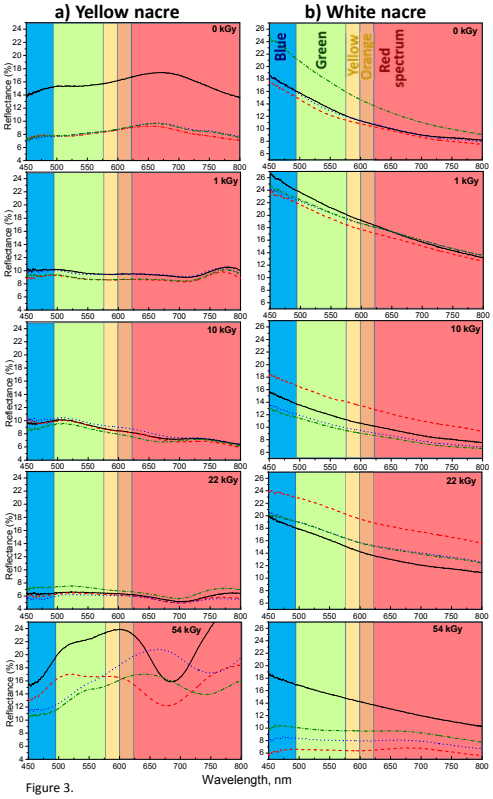


Figure 3.
Change of the reflectance of each sample after irradiation and with time:
Black – before irradiation; **Red** – immediately after irradiation; **Blue** - after 1 month; **Olive** - after 2 months

- At 54 kGy a weak wide absorption peak (minimum peak) can be observed at around 600 nm, in the yellow and orange region. This peak can be attributed to a carbonate radical anion according to Behar et al. [3]. The same peak can be observed at somewhat lower wavelength in the yellow region at 22 kGy. This is in accordance with the color parameter b^* measurements.
- The same peak can be observed at the same dose on yellow nacre, just not as a separate peak but as a shoulder of the peak at ca. 670 nm, in the red region. This is also in accordance with the results of a^* measurements. This band shifts to larger wavelengths, to the red region, in the post-irradiation period.
- Reduction in reflectance can only be observed at 54 kGy immediately after irradiation. During the post-irradiation period the reflectance increases again indicating that bleaching of the effect is taking place.

CONCLUSIONS

- The main radiation induced change in color properties of studied nacres is the change in brightness (L^*). Both types of nacre darken after irradiation. The color changes are observed only at the highest irradiation doses.
- The results indicate that only at doses of 22 kGy and higher not acceptable long term color change occurs and this is much above the dose range for CH object treatment.
- The post-irradiation effect is observed on both nacre types. In the case of yellow nacre the color change increases with time, while in the white nacre's case it decreases with time.
- UV-VIS reflectance data have shown a carbonate radical anion absorption after irradiation to high doses. This explains the changes in the color parameters (a^*, b^*). The carbonate radical anion absorbs in the red region on yellow nacre and in the yellow region on the white nacre.
- Reflectance increases again in the post-irradiation period going toward the values before irradiation, i.e. bleaching.

[1] M. Mahy, L. Van Eycken, and A. Oosterlinck, "Evaluation of uniform color spaces developed after the adoption of CIELAB and CIELUV," Color Research and Application, vol. 19, 2, pp. 105-121, 1994.

[2] J. Y. Hardeberg, Acquisition and Reproduction of Color Images, Colorimetric and Multispectral Approaches Dissertation.com, 2001.

[3] D. Behar, G. Czapski, and I. Duchovny, J. Phys. Chem., 74, 2206 (1970).