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Investigation of antioxidant properties of cerium oxide nanopowders under nanosecond bremsstrahlung

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Abstract. This paper presents a method for measuring the effectiveness of radiomodification using a ferrous sulfate dosimeter, including evaluating the antioxidant activity of the radiomodifying agent. The effect of adding cerium oxide nanoparticles at the concentration of 100 μg/ml on the change in the absorbed dose recorded by the ferrous sulfate dosimeter when irradiated with inhibitory radiation with doses of 25, 50 and 75 Gy was investigated. The results showed low antioxidant activity of the examined nanoparticles and the effect of increasing the absorbed dose in proportion to the irradiation time.

Keywords: cerium oxide nanoparticles, radiomodification, ferrous sulfate dosimeter, absorbed dose.

1. Introduction

Cerium oxide nanoparticles (CONPs) due to the unique structure of the crystal lattice can inhibit free radicals [1]. In particular, this feature of cerium nanoparticles can be used in radiation therapy. As is known, the effect of ionizing radiation on bio-objects leads to the formation of free radicals, such as reactive oxygen species (ROS). In turn, the ability of CONPs to react with ROS strongly depends on their size, specific surface area, and the pH of the environment [2]. Since the environment of most tumor growths has a low pH, the use of CONPs will protect the surrounding healthy tissues from exposure to ionizing radiation.

The antioxidant activity (AA) of CONPs has been well studied [3], but quantitative and comparative assessment of the antioxidant properties of these and other nanoparticles is difficult, due to the imperfection of the current methods [4].

This paper proposes the use of a ferrous sulfate dosimeter (Fricke) to assess the change in the effect of ionizing radiation on a bio-object when adding CONPs resulting from their antioxidant properties.

2. Materials and methods

The study of cerium oxide nanopowders produced by pulsed electron beam evaporation (PEBE) method in vacuum [5] was carried out. Various methods for producing nanopowders can significantly affect their properties. The PEBE method makes it possible to produce CONPs with a high specific surface area (up to 190 m^2/g) [5], which ensures their high AA. The specific surface area of the studied nanopowders was ~97 m^2/g.

For measurement, nanoparticle suspensions were prepared using an ultrasonic dispersant, “FOTEC”. The resulting suspensions were added to the ferrous sulfate dosimeter (FSD) solution to obtain a CONPs concentration of 100 μg/mL for subsequent irradiation.

The principle of operation of FSD is based on the oxidation of three-shaft iron ion Fe^{3+} with free radicals formed under the action of ionizing radiation. The AA of CONPs makes it possible to change the amount of free radicals, which is expressed in the change in the absorbed dose. In this case, irradiation occurs in a tissue equivalent solution of the dosimeter, what simulates bio-object irradiation. The absorbed dose of FSD is proportional to optical density at a wavelength of 304 nm and can be calculated using the formula [6]:

$$D(Gy) = 9,65 \cdot 10^6 \frac{d - d_0}{lG\rho\mu(Fe^{3+})}, \quad (1)$$

where d – the optical density at wavelength λ = 304 nm; d_0 is the optical density of the non-irradiated solution at wavelength λ = 304 nm; l – length of optical path of ions - thickness of cuvette in cm; G – radiation-chemical yield; ρ – density of the solution; $\mu(Fe^{3+})$ is the molar extinction coefficient of Fe^{3+} ions at 304 nm.

Samples of a Fricke dosimeter with and without nanoparticles of 8 ml were prepared for the study. Samples were prepared and irradiated under the same conditions to ensure the accuracy of the experiment. The produced samples were irradiated with bremsstrahlung on a pulsed electron accelerator "URT-1M" [7], using a convector made of steel with a thickness of 1 mm. The initial energy of the electrons ≈700 keV, the frequency was 35 Hz. Irradiation was performed for 3, 6 and 9 minutes, one sample was a control one. The absorbed dose was previously measured by a dosimeter of type "ID-1" and calculated from a ratio of 0.4 Gy to 100 pulses. Accordingly, the estimated radiation doses are 25, 50 and 75 Gy.

After irradiation, the optical density of the samples was measured using an "Ecroschem PE-5400UF" spectrophotometer. Quartz cuvettes were used for measurement, since they are transparent at the wavelength of 304 nm. The results of the experiment were obtained in the form of optical density spectra of FSD from 200 to 400 nm, where the wavelength of interest 304 nm is in the middle of the spectrum. The measurement error was 11.82 % with a confidence probability of 0.95.

The results were processed with the "OriginPro® 2018" software package.

3. Results and discussion

The absorbance spectra of the FSD without nanoparticles (Fig.1) and when adding CONPs (Fig.2) are given below.

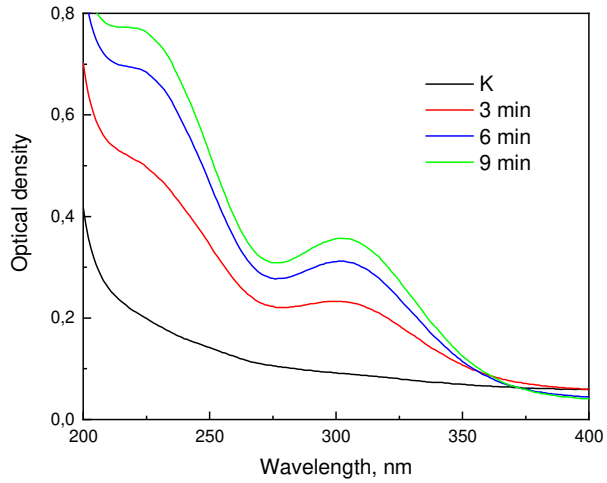

Fig.1. Optical density spectra of FSD without nanoparticles after irradiation. K – non-irradiated samples.

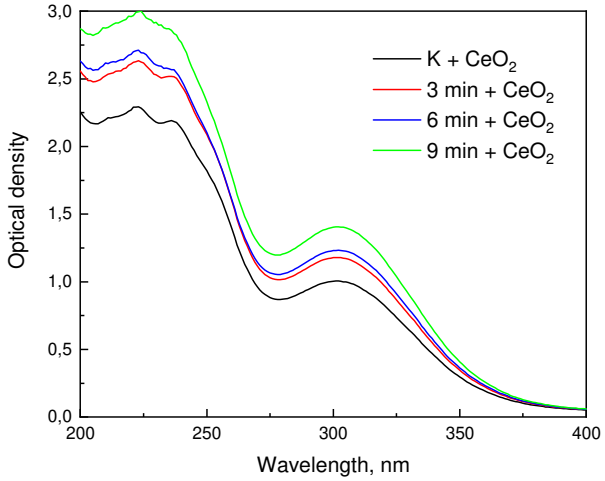

Fig.2. Optical density spectra of FSD with cerium oxide nanoparticles after irradiation. K – non-irradiated samples.

Both diagrams clearly show the local maximum absorbance at 304 nm increasing in proportion to the irradiation time, which indicates the operability of this technique. The optical density values of the non-irradiated nanoparticles-containing sample differ from the corresponding ones without CONPs. The difference arises from the intrinsic absorption of CONPs, as well as the interaction of particles with iron ions.

To compensate for these effects, and to take into account the effects of cuvette absorption and possible impurities, subtract from the absorbance data of the irradiated samples the values of the non-irradiated ones. The results of spectrum processing are shown in Fig.3.

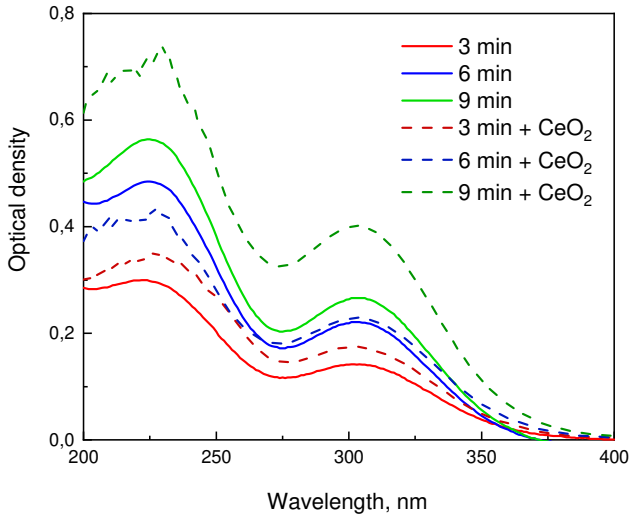

Fig.3. Result of processing optical density spectra of FSD with and without nanoparticles after irradiation.

The results of the treatment showed that the addition of CONPs resulted in an increase in absorbance, and thus an absorbed dose. This effect can be explained by the acidic environment of the dosimeter, in which the antioxidant properties of CONPs are weakly manifested [2]. In addition, increased uptake of low-energy photons by heavy cerium atoms may contribute further to the uptake of the absorbed dose [8].

To evaluate the effect of adding cerium oxide to the dosimeter solution, compare the absorbance values of samples with CONPs and without at the wavelength of 304 nm at different irradiation times (Fig.4).

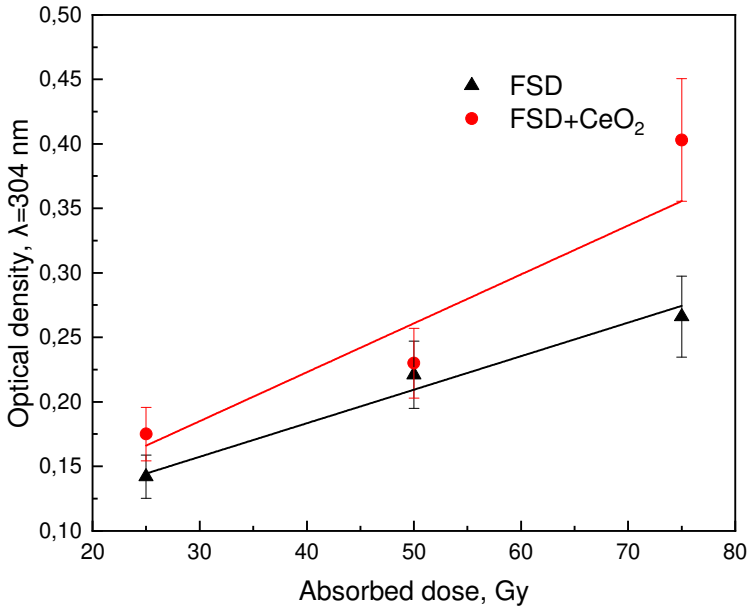

Fig.4. Optical density of FSD at wavelength 304 nm with and without nanoparticles after irradiation.

Fig.3 also indicates the presence of a local maximum at the wavelength of 225 nm increasing in proportion to the irradiation time. We examine this peak for dependence on the absorbed dose. The resulting spectra were decomposed into two-peak Gaussians at 304 and 225 nm. The results of calculations of maximum values of optical density and area under curves are given in Table 1.

Table 1. Values of maximal optical densities and area of gauss curves of examined samples

Time of irradiation	Max OD		Area of gauss curve	
	225 nm	304 nm	225 nm	304 nm
3 min	0.306	0.140	24.54	7.58
6 min	0.493	0.219	39.23	12.85
9 min	0.573	0.264	44.09	15.94
3 min (CeO_2)	0.351	0.171	28.46	8.73
6 min (CeO_2)	0.431	0.227	32.42	13.55
9 min (CeO_2)	0.728	0.398	56.05	22.86

To clarify the dependence of the area of the Gaussian curves on the absorbed dose, we present the results from Table 1 as diagrams (Figs.5 and Fig.6).

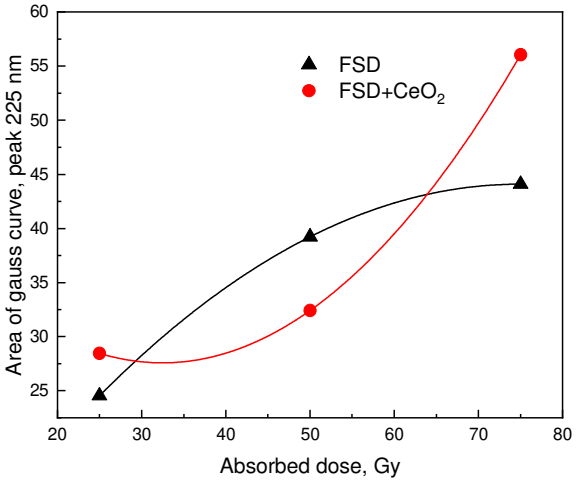

Fig.5. Dependence of the area of the gauss curves in peak 225 nm on the absorbed dose with and without nanoparticles.

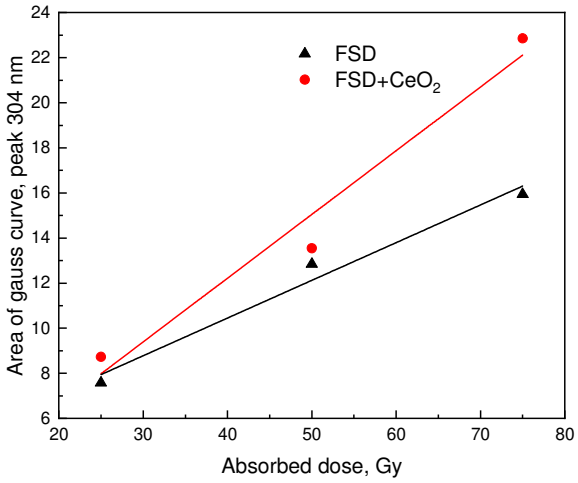

Fig.6. Dependence of the area of the gauss curves in peak 304 nm on the absorbed dose with and without nanoparticles.

Based on the results shown in Fig.5 and Table 1, it can be concluded that the optical density of the FSD at the wavelength of about 225 nm cannot be used to assess the effectiveness of radiomodification of bio-objects. The data did not show a linear dependence of absorbance on the absorbed dose, moreover, the absorbance of samples containing no nanoparticles at the wavelength of 225 nm and an irradiation time of 6 minutes exceeds the corresponding value for samples with the addition of CONPs, which contradicts the results of the experiment.

The areas under the Gaussian peak curves at 304 nm were linearly dependent on the absorbed dose. Moreover, the coefficient of determination R^2 with linear approximation of the obtained values of the area under the curves turned out to be closer to 1, relative to the approximation of peak values: 0.967 for the sample with CONPs and 0.978 without, against 0.874 and 0.981, respectively.

According to the results of the experiment, the absorbed dose recorded by the ferrous sulfate dosimeter when cerium oxide was added to the CONPs solution increased by a maximum of 1.51 times.

4. Conclusion

The study showed the possibility of using a Fricke dosimeter to assess the effectiveness of radiomodification of biological objects with cerium oxide nanoparticles when irradiated with pulsed inhibitory radiation. It has been demonstrated that the CONPs added to the tissue equivalent dosimeter solution did not show high antioxidant activity, which is expressed by increasing the

absorbed dose. This effect can be explained by inhibition of the anti-radical properties of CONPs in environment with low pH and low specific surface area of the test particles. Further studies of substances with antioxidant properties are needed to better assess the effectiveness of this technique.

Acknowledgements

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5. References

[1] Ivanov V.K., Shcherbakov A.B., Usatenko A.V., *Russ. Chem. Rev.*, **78**(9), 855, 2009; doi: 10.1070/RC2009v078n09ABEH004058
[2] Vazirov R., Sokovnin S., Ulitko M., *J. Rad. and App.*, **2**(2), 139, 2017; doi: 10.21175/RadJ.2017.02.029
[3] Rajeshkumar S., Naik P., *Biotechnology Reports*, **17**,1, 2018; doi: 10.1016/j.btre.2017.11.008
[4] Retif P., Pinel S., Toussaint M., Frochot C., Chouikrat R., Bastogne T., Barberi-Heyob M., *Theranostics*, **5**, 1030, 2015; doi: 10.7150/thno.11642
[5] Il'ves V.G., Sokovnin S.Yu., *Nanotechnol Russia,* **7**, 213, 2012; doi: /10.1134/S1995078012030068
[6] Schreiner L., *J. Phys.: Conf. Ser.*, **3**, 9, 2004; doi: 10.1088/1742-6596/3/1/003
[7] Sokovnin S.Y., Balezin M.E., Shcherbinin S.V., *Instrum. Exp. Tech.*, **56**, 411, 2013; doi: 10.1134/S0020441213040106
[8] Gerasimov A.S., Vazirov R.A., *AIP Conf. Proc.,* **2313**, 08001, 2020; doi: 10.1063/5.0035406