Application of the electronic paramagnetic resonance method for detecting radiation-processed food products

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Abstract. This paper presents the results of work on studying the capabilities of EPR spectroscopy for identifying certain types of food products treated with ionizing radiation at various doses, determining the dose and time elapsed since the product was treated with ionizing radiation. The samples were examined for 270 days. For the prepared samples, the post-effect of irradiation with ionizing radiation was studied, which manifested itself in a change in the number of paramagnetic centers in the sample.

1. Introduction
Radiation treatment of food products is a process in which products are treated with ionizing radiation in order to extend shelf life, improve their safety and quality. In 69 countries, such treatment has already been standardized, in some countries it has been adopted as a phytosanitary norm for international import/export quarantine control. More than 100 types of food products are processed in this way in the world.

More than 220 specialized centers for irradiation of agricultural products and foodstuffs have been established. Most of them are located in China and the USA. The volume of irradiated products by now has a steady growth trend [1].

For food processing, radiation-technological installations are used with sources of ionizing radiation of three types: accelerated electrons, emission of hard photons and bremsstrahlung X-ray radiation.

Safety of food and agricultural products, i.e. the absence of unacceptable risk associated with harmful effects on humans during radiation processing can only be ensured with proper control of the processes of such processing. In addition, radiation processing of a number of products is prohibited by law in some countries [2-5].

The range of doses required for the effective processing of various types of food and agricultural products is well understood [5, 6]. These data are shown in the table 1 [3-6].
Table 1. The range of absorbed doses during irradiation of food and agricultural products in world practice

| Effect of exposure to ionizing radiation (technological purpose of radiation treatment) | Dose range, kGy |
|---|---|
| Disinfection from insects and destruction of parasites | 0.03 - 0.50 |
| Prevention of infestation by insects, parasites | 0.25 – 1.00 |
| Delay from rotting and spoilage of meat | 0.07–1.30 |
| Increased shelf life (meat, berries, mushrooms, etc.) | 1.50–7.00 |
| Reducing the risk of contamination with pathogens | 1.00 – 7.00 |
| Increased sanitation for spices and herbs | up to 10.00 |
| Sterilization of packaged meat | 25 - 70 |
| Sterilization (meat, seafood, poultry, etc.) | 30 – 50 |
| Disinfection, disinfection of individual additives and ingredients | 10 – 50 |

[1 Gy = 100 rad = 1 J / kg]

The presence of radiophobia among the population, the imperfection of legislative regulation, methodological and metrological support has led to the fact that food manufacturers do not properly label them when carrying out radiation processing.

Thus, the task of determining the fact of such processing and monitoring the compliance of the processing modes with the established requirements becomes urgent, as well as identifying food products in circulation, the processing of which with ionizing radiation (IR) is prohibited, and (or) food products that have been processed by IR, but do not have on the product of the international mark "Radura" and the corresponding information on the processing of IR on the label and (or) in the name of the product [1-6].

To control the magnitude of the absorbed dose during the processing of foodstuffs in the world practice, the method of alanine dosimetry or dosimetry using alanine-like substances is used [7]. This method is used directly for irradiation of products and consists in placing alanine (or similar) dosimeters together with the irradiated products into the installation.

The alanine dosimetry method is based on the fact that in a number of substances under the influence of radiation, paramagnetic centers are formed, the number of which depends on the radiation dose. The presence and number of such paramagnetic centers is established using electron paramagnetic resonance spectrometer (EPR spectrometers) - devices based on the phenomenon of electron paramagnetic resonance [8].

This same method is used to detect processed foods. For those food products for which this method is most applicable and relevant, appropriate standards have been developed and implemented [9-11]. The standards establish the method of electron paramagnetic resonance (EPR) for detecting the fact of irradiation (radiation sterilization) of meat of cattle and pigs containing bone tissue; products containing crystalline sugars; food products containing cellulose. These standards contain general information on the principles for the detection of some radiation-processed food products, however, the list of such products, after conducting appropriate research, can be expanded. At the same time, for each type of product, it is necessary to develop methods for sample preparation and measurements, including settings for EPR spectrometers.

Paramagnetic centers formed during irradiation can have different lifetimes; therefore, it is necessary to investigate the possibility of determining the fact of product irradiation depending on the time elapsed since the treatment with ionizing radiation.

In addition, in a number of cases, the EPR method allows not only to establish the fact of irradiation, but also makes it possible to quantitatively determine the absorbed dose during irradiation. This possibility, in particular, is based on the method of retrospective dosimetry [12], which makes it possible to determine the radiation dose from the EPR spectrum of tooth enamel.

Thus, the goals and objectives of this work were formulated.
2. Objectives of the work
Study of the capabilities of EPR spectroscopy to identify certain types of food products processed by IR in various doses, determine the dose and time elapsed since the processing of IR products.

Work tasks:
- study of the physicochemical composition of food products in order to identify materials and fragments suitable for EPR spectrometry;
- preparation of samples for research;
- processing samples with various doses of ionizing radiation;
- study of EPR spectra of samples for a long time;
- analysis of research results and establishment of the dependence of the intensity of the EPR signal on the time elapsed from the moment of processing.

3. Materials and methods
The products were selected by Rospotrebnadzor specialists (FBUZ Federal Center for Hygiene and Epidemiology of Rospotrebnadzor) directly from manufacturers that do not have processing centers (samples of pork and chicken meat containing bone tissue).

Irradiation was carried out using a Co-60 source in the range of 1-50 kGy at the gamma-installation for microbiological and radiation-chemical research MPX-γ-100 with Co-60 radionuclide sources traceable to the Russian State primary special standard of the unit of the absorbed dose rate of intense photon, electron and beta radiation for radiation technologies ГЭТ 209-2014. The dose range was chosen in accordance with the doses actually used for irradiation of meat (Table 1) and with the deliberate excess of the doses taken.

Dose and exposure time values are given in Table 2.

| Required dose, kGy | Dose rate, Gy / s | Irradiation time, s |
|-------------------|------------------|---------------------|
| 1                 | 3,57             | 280                 |
| 3                 | 3,57             | 840                 |
| 5                 | 3,57             | 1401                |
| 7                 | 3,57             | 1961                |
| 10                | 3,57             | 2801                |
| 25                | 3,57             | 7003                |
| 50                | 3,57             | 14006               |

The relative standard measurement uncertainty when reproducing the power unit of the absorbed dose of photon radiation, assessed by type A, does not exceed 0.2%, assessed by type B, does not exceed 0.3%.

The total standard measurement uncertainty does not exceed 0.4% when reproducing a unit of power and absorbed dose of photon radiation.

The expanded measurement uncertainty with a coverage factor K = 2 does not exceed 0.8%.

Thus, samples of pork bone tissue were prepared after irradiation with doses of 1, 5, 10, 25, and 50 kGy. And also samples of chicken bone tissue, irradiated with doses of 1, 3, 5, 7 and 10 kGy.

Follow-on studies were carried out using CMS 8400 ADANI EPR spectrometer, which is traceable to the Russian State Primary Standard of the unit of the number of paramagnetic centers ГЭТ 83-2017. In this case, the relative value of the number of paramagnetic centers in the irradiated and unirradiated samples and its change in time from the moment of irradiation of the sample were determined.
4. Research results
The samples were examined for 270 days. For the prepared samples, the post-effect of irradiation with ionizing radiation was studied, which manifested itself in a change in the number of paramagnetic centers in the sample.

The general view of the spectra obtained during operation is shown in Figures 1-2.

![Figure 1. General view of the EPR spectrum a sample of unirradiated bone tissue](image1)

![Figure 2. General view of the EPR spectrum bone tissue sample 1 hour after irradiation](image2)

When processing the EPR spectra, the relative intensity was taken into account - a parameter characterizing the number of paramagnetic centers in the sample, reduced to the sample mass. The results of changes in relative intensity over time are shown in Figures 3-4.

![Figure 3. Change in relative intensity for porcine bone samples over time.](image3)
5. Conclusions

The intensity of the absorption of electromagnetic radiation by the sample decreases over time (i.e., the number of free radicals decreases), while the EPR spectrometry method makes it possible to reliably detect irradiated food products (meat of various animals and birds containing bone tissue) for at least 270 days after treatment of products with ionizing radiation.

EPR spectrometers allow:
- determination of the dose with which the product was irradiated in the range of 1-50 kGy, provided that the processing date is known, the EPR spectrometer is traceable to ГЭТ 83-2017 (verified (calibrated) using measures of the number of paramagnetic centers of the approved type, traceable to the State primary standard of the number of paramagnetic centers ГЭТ 83-2017) and the post-effect of ionizing radiation has been studied for this product.
- control of food products and (or) unprocessed food (food) raw materials of animal origin (meat of various animals and birds containing bone tissue) for signs of ionizing radiation processing.

A advanced area of the research is the study of the applicability of the EPR method for monitoring the irradiation of dried fruits, nuts and other products of long-term storage.

Food safety is in the state regulation sphere on the territory of the Russian Federation (13) and, according to the requirements of the legislation (14), measurements should be traceable to state primary standards. Thus, the proposed methods of EPR control of radiation treatment products will establish an opportunity to ensure the traceability of measurements of EPR spectrometers to the State primary standard in Russia with use measures of the number of paramagnetic centers of the approved type.

References
[1] Kozmin G V, Sanzcharova N I, Kibina I I, Pavlov A N 2015 The development of the Russian market of radiation technology in agro-industrial complex Vestnik RAEN 15 (4) pp 24-30 (in Rus.), https://elibrary.ru/item.asp?id=24239517
[2] J. van Kooij 1981 Food preservation by irradiation *IAEA BULLETIN* Vol. 23 № 3
[3] Facts about food irradiation, https://www.nrc.gov/docs/ML0611/ML061170095.pdf
[4] ISO/ASTM 51900:2009(E). Guide for dosimetry in radiation research on food and agricultural products.
[5] GOST 34155-2017. Dosimetry Guidelines for the Study of the Effects of Radiation on Food and Agricultural Products (in Rus.)
[6] HIGH-DOSE IRRADIATION: WHOLESOMENESS OF FOOD IRRADIATED WITH DOSES ABOVE 10 kGy/ WHO, Geneva, 1999
[7] Donchenko S I, Leskov A S, Kuvykina M B, Tenishev V P 2019 Measurement of the absorbed dose of ionizing radiation using the reference measures of paramagnetic centers *Proceedings of the II International Scientific Forum "Nuclear Science and Technology"* June 24-27 (Almaty)
[8] Leskov A S, Kuvykina M B, Tenishev V P 2019 *J. Phys.: Conf. Ser.* 1420 011003, doi:10.1088/1742-6596/1420/1/012014
[9] GOST R 52529-2006 Meat and meat products. The method of electronic paramagnetic resonance for the detection of radiation-treated meat and meat products containing bone tissue (in Rus.)
[10] GOST R 52829-2007 Food products. Electron paramagnetic resonance method for detecting radiation-treated products containing crystalline sugar (in Rus.)
[11] GOST R 53186-2008 Food products. Electron paramagnetic resonance method for detecting radiation-treated cellulose-containing products (in Rus.)
[12] GOST R 22.3.04-96 Safety in emergency situations. Dosimetric control of the population. A method for determining the absorbed doses of external gamma radiation from the spectra of electronic paramagnetic resonance of tooth enamel (in Rus.)
[13] Technical Regulations of the Customs Union "On food safety" (TR CU 021/2011), https://docs.cntd.ru/document/902320560
[14] Federal Law of Russian Federation “On Ensuring the Uniformity of Measurements” (FZ-102) of 26.06.2008 (in Rus.), https://docs.cntd.ru/document/902107146