Practical aspects of the application of radiation processing of raw milk

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Abstract. The use of modern technology for food processing by ionizing radiation is due to their high efficiency to reduce microbiological contamination. The purpose of the research was to study the effect of different doses of ionizing radiation when processing raw (unpasteurized) cow's milk of different fat content (2.5% and 3.2%) in various media (air, carbon dioxide) on milk freshness indicators. The studies have been carried out in accordance with the requirements of GOST R 52054-2003 and TR TS 033/2013. Raw (unpasteurized) cow's milk treated with doses of up to 2.2 kGy and 2.4 kGy in air and carbon dioxide, respectively, refers to fresh milk with lower quantitative characteristics of titratable acidity, content of malondialdehyde (MDA), and microbiological parameters when treated with ionizing radiation in carbon dioxide gas. No significant differences have been found for titratable acidity and malondialdehyde content depending on milk fat content, however, titrated acidity and malon dialdehyde content in milk with 2.5% fat have lower quantitative indicators compared to milk with 3.2% fat content. The determination of rational doses of ionizing radiation is of practical importance to ensure that the freshness indicators of raw (unpasteurized) cow's milk processed with ionizing radiation meet the requirements of regulatory documents. The following doses of ionizing radiation are recommended: for the milk of the highest and first grade when processed with radiation in the air medium—a dose of 1.2 kGy and for milk of the second grade—a dose of 2.0 kGy, for radiation processing in a carbon dioxide medium—a dose of 1.4 kGy and 2.2 kGy, respectively.

1. Introduction

The entry of the Russian Federation into the sixth technological paradigm requires an organic transition from the technologies of the fifth and fourth technological paradigms in order to increase the competitiveness of the domestic economy. The use of modern industrial conservation technologies in the food and processing industry allows providing high quality characteristics of food raw materials and food products over the entire shelf life [1].

Milk is a unique food product with a balanced chemical composition and high nutritional value, which requires the use of effective production technologies from the moment of milk yield and primary processing of raw (unpasteurized) milk to the arrival of finished dairy products in the consumer market.

The choice of applied methods of processing milk related to a highly perishable product according to the requirements of SanPiN 2.3.2.1324-03 Hygienic Requirements for Shelf Life and Storage Conditions for Food Products is determined by the need to ensure safety and to maximally preserve its nutritional and biological value, as well as to create optimal conditions for its storage and adverse
conditions for the microbial environment in order to reduce the risk of contamination by pathogenic and opportunistic pathogenic microorganisms, moldy fungi and yeast.

Common methods for processing raw (unpasteurized) milk include pasteurization, sterilization, and UHT (ultra-high temperature) sterilization, the technologies of which are energy intensive in the production process. Less common methods are infrared heating; sonication, ultraviolet radiation and ozone; electromagnetic methods. As a result of research by a number of authors [2], a slight change in the organoleptic characteristics of goat’s milk was found when processed with ultraviolet radiation with a wavelength of 254nm due to an increase in the concentration of alcohol isomers—pentanal, hexanal, and heptanal. However, the detected increase in free fatty acids does not affect the change in the smell of milk.

The use of high-frequency acoustic cavitation, according to [3], leads to a decrease in the number of Escherichia coli group bacteria (CGB (coli-forms)) up to 40%.

Widespread worldwide radiation technologies for processing food resources are due to the high efficiency in reducing microbiological contamination and ensuring a high degree of sterility. At the same time, microorganisms differ in different resistance. Thus, it was found that Salmonella strains turned out to be the most resistant to ionization irradiation, and S. aureus was less resistant [4].

A study of the effect of ionizing radiation on raw (unpasteurized) goat’s milk showed an increase in free radical oxidation, which can lead to denaturation of the protein fraction [5].

The mechanism of ionizing radiation exposure is associated with the ionization of molecules of microorganisms, which leads to the suppression of their development and even death. When irradiating a food product, the maximum dose should be less than that at which a consumer hazard could appear or which could adversely affect the functional or organoleptic properties of the product [6].

Gamma irradiation of raw (unpasteurized) whole milk in doses of 1-3kGy, providing lower bacterial contamination rates compared to unirradiated milk, does not impair organoleptic characteristics during storage of milk irradiated with a dose of up to 2kGy for up to 60 days. Upon irradiation with a dose of 3kGy, the appearance of a rancid odor was established as a result of the formation of free radicals and changes in the lipid fractions of milk [7]. Similar data, which indicate minor changes in the molecular structure of milk fat when irradiated with doses up to 2kGy without changing organoleptic parameters, have been obtained [8,9]. As identified by [10], a dose of 5 kGy is possible to reduce the microbiological population for casein and milk powder. There are research results on the protective role of ascorbic acid when it is added to cow’s milk irradiated with a dose of 4 kGy by protecting casein from reactive oxygen species (ROS) formed during irradiation, while reducing the number of bacterial colonies to 88% [11].

The use of ionizing radiation processing for various types of food products and agricultural raw materials is officially regulated in the Russian Federation: spices, fresh agricultural products, meat and meat products, fish and seafood since 2017. Despite the fact that in the Russian Federation, there is no guidance on the irradiation of milk and dairy products, scientific research in this direction can be defined as timely and relevant.

In this regard, the aim of the research is to study the effect of different doses of ionizing radiation when processing raw (unpasteurized) cow’s milk of different fat content in various media on freshness indicators.

2. Materials and methods
The subject of the study is raw (unpasteurized) cow’s milk with a fat mass fraction of 2.5% and 3.2%, processed with different doses of radiation from 0.2 kGy to 2.4 kGy for 2 hours after milking operation. The temperature of the initial milk is (4.0±0.5)°C. The groups have been formed: group 1 — a control group of milk samples with a fat content of 2.5%, which was not exposed to radiation; groups 2 and 3 — experimental groups of milk samples with a fat content of 2.5%, irradiated with doses from 0.2 kGy to 2.4 kGy in various environments: air medium — group 2 and carbon dioxide medium—group 3; group 4—a control group of milk samples with a fat content of 3.2%, which was not exposed to radiation; groups 5 and 6 — experimental groups of milk samples with a fat content of 3.2%, irradiated with doses from 0.2 kGy to 2.4 kGy in various environments: air medium — group 5
and carbon dioxide medium — group 6. The processing of milk in carbon dioxide was used to level the so-called “oxygen effect” in radiobiology, which is associated with the hydrolysis of phospholipids and triglycerides and the release of fatty acids. Samples of the experimental milk groups were treated with ionizing radiation at the Center for Radiation Sterilization at UrFU using the UELR-10-10S2 (УЭЛР-10-10С2) linear electron accelerator. Assessment of freshness of cow's milk (organoleptic and microbiological indicators, titratable acidity, and content of malonaldehyde) has been carried out in accordance with the requirements of GOST R 52054-2003 Raw (Unpasteurized) Cow's Milk. Specifications and TR TS 033/2013 On the Safety of Milk and Dairy Products. The titratable acidity has been determined by the method, according to GOST 3624-92 Milk and Dairy Products. Titrimetric Acidity Determination Methods using the phenolphthalein indicator; the content of malonaldehyde (MDA) has been determined spectrophotometrically by reaction with thiobarbituric acid. Studies have been carried out in 5-fold repetition.

3. Results and its discussion

According to the results of organoleptic evaluation, it was found that control and experimental samples of raw (unpasteurized) cow's milk with a fat content of 2.5% and 3.2% met the requirements of TR TS 033/2013 On the Safety of Milk and Dairy Products. The appearance of milk is an opaque liquid, its chewy texture is liquid, homogeneous, non-viscous. It is denser compared with milk samples of 2.5% fat in milk samples with a fat content of 3.2%. The color is intensely white in milk samples with a fat content of 3.2% and white — in milk samples with a fat content of 2.5% (in samples irradiated with doses above 1.4kGy, a light cream hue appeared). Its taste and smell are typical of milk, without foreign flavour and smell a typical of milk (in samples irradiated with doses above 1.4kGy, a subtle slight taste of pre-boiling appeared).

Titratable acidity in milk samples irradiated with a dose of up to 1.2kGy in the air and a dose of up to 1.4kGy in carbon dioxide, met the requirements of GOST R 52054-2003 Raw (Unpasteurized) Cow's Milk. Specifications for the milk of the highest and first grade; milk samples irradiated with doses of 1.4-2.0kGy in air and milk samples irradiated with doses of 1.6-2.2kGy in carbon dioxide—for the milk of the second grade. An increase in titratable acidity by 30.6% to (20.9±0.1)°T has been established upon irradiation of milk samples with a fat content of 3.2% with a dose of 2.0kGy in the air compared with unirradiated samples and samples irradiated with a dose of 2.2kGy, and by 28.8% to (20.6±0.1)°T when irradiated with carbon dioxide, at a dose of 2.2kGy; in milk samples with a fat content of 2.5%—by 26.9% to (20.3±0.1)°T and by 27.5% to (20.4±0.1)°T, respectively. An increase in the radiation dose in excess of 2.2 kGy and 2.4 kGy when processed in air and in carbon dioxide leads to an excess of the titratable acidity threshold for raw (unpasteurized) cow's milk with a fat content of 3.2% — (22.0±0.2)°T and (21.1±0.1)°T, respectively, for raw (unpasteurized) cow's milk with a fat content of 2.5% — (21.0±0.2)°T and (20.7±0.1)°T (Table 1). A high degree of correlation between the dose of milk samples of different fat content (3.2% and 2.5%) and titratable acidity has been established: in the air—0.954-0.956, in the carbon dioxide—0.938-0.941, respectively (the degree of the Cheddock's statistical link strength is very high).

A polynomial model of the change in titratable acidity upon irradiation of milk with a fat content of 3.2 % is provided:
• in the air: \( y=0.056x^2 - 0.191x + 16.10 \) (1),
• in the carbon dioxide: \( y=0.047x^2-0.218x+16.19 \) (2).

A polynomial model of the change in titratable acidity upon irradiation of milk with a fat content of 2.5 % is provided:
• in the air: \( y=0.043x^2 - 0.117x + 15.99 \) (3),
• in the carbon dioxide: \( y=0.047x^2-0.232x+16.21 \) (4).

The results obtained by processing with ionizing radiation in the air are comparable with the studies [7].
Table 1. Titratable acidity of raw (unpasteurized) cow’s milk unprocessed and processed with ionizing radiation in various media, °Т (p < 0.05)

| The radiation dose, kGy | Fatness 2.5 % | Fatness 3.2 % |
|------------------------|--------------|--------------|
|                        | the air      | the carbon dioxide | the air      | the carbon dioxide |
| 0                      | 16.0±0.1     | 16.0±0.1     | 16.0±0.1     | 16.0±0.1           |
| 0.2                    | 16.0±0.1     | 16.0±0.1     | 16.0±0.1     | 16.0±0.1           |
| 0.4                    | 16.1±0.1     | 16.0±0.1     | 16.1±0.1     | 16.0±0.1           |
| 0.6                    | 16.1±0.1     | 16.0±0.1     | 16.2±0.1     | 16.0±0.1           |
| 0.8                    | 16.3±0.2     | 16.2±0.2     | 16.4±0.2     | 16.2±0.1           |
| 1.0                    | 16.7±0.1     | 16.4±0.2     | 16.8±0.3     | 16.5±0.1           |
| 1.2                    | 17.3±0.3     | 16.8±0.3     | 17.5±0.2     | 16.9±0.2           |
| 1.4                    | 18.1±0.2     | 17.4±0.3     | 18.3±0.2     | 17.5±0.2           |
| 1.6                    | 18.5±0.3     | 18.1±0.2     | 19.1±0.2     | 18.1±0.3           |
| 1.8                    | 19.2±0.1     | 18.6±0.3     | 19.9±0.2     | 18.7±0.3           |
| 2.0                    | 20.3±0.1     | 19.3±0.3     | 20.9±0.1     | 19.5±0.2           |
| 2.2                    | 21.0±0.1     | 20.4±0.2     | 22.0±0.2     | 20.6±0.1           |
| 2.4                    | 21.6±0.1     | 21.0±0.2     | 23.0±0.3     | 21.1±0.2           |

The integral characteristic of lipid peroxidation (LPO) processes in raw (unpasteurized) cow’s milk when processed with ionizing radiation is the accumulation of the final LPO product—malon dialdehyde (MDA). The MDA content in the processing of milk with a fat content of 3.2% in the air increased by 43.9% to (721±5) nmol/L in comparison with the control samples and in the carbon dioxide—by 28.3% to (643±3) nmol/L, respectively (Figure 1); when processing milk with a fat content of 2.5%—by 32.5% to (636±3) nmol/L and by 25.1% to (601±6) nmol/L (Figure 2).

The polynomial model of MDA changes during irradiation of milk with a fat content of 3.2% has been shown:

- in the air: \( y = 0.8001x^2 + 5.1429x + 504 \) \( (5), \)
- in the carbon dioxide: \( y = 0.3317x^2 + 6.7632x + 407.84 \) \( (6). \)

Figure 1. The content of malon dialdehyde of raw (unpasteurized) cow’s milk with a fat content of 3.2% unprocessed and processed with ionizing radiation in various media.
The polynomial model of MDA changes during irradiation of milk with a fat content of 2.5 % has been shown:

- in the air: \( y = 0.1588x^2 + 9.8531x + 475.56 \) \( (7) \),
- in the carbon dioxide: \( y = 0.0719x^2 + 9.0809x + 473.06 \) \( (8) \).

**Figure 2.** The content of malon dialdehyde of raw (unpasteurized) cow's milk with a fat content of 2.5% unprocessed and processed with ionizing radiation in various media.

The microbiological safety indicators for all samples of raw (unpasteurized) cow's milk were within the standard parameters set for premium milk of the highest grade, according to the requirements of GOST R 52054-2003 *Raw (Unpasteurized) Cow's Milk. Specifications* with lower levels of QMAFAnM (Quantity of Mesophilic Aerobic and Facultative Anaerobic Microorganisms) and the number of somatic cells in milk samples processed with high doses of ionizing radiation up to 2.2–2.4 kGy. The data obtained confirm the effectiveness of ionizing radiation treatment to reduce the microbiological contamination of raw (unpasteurized) cow's milk. No significant differences in microbiological parameters in milk of different fat content have been found.

**4. Conclusions**

As a result of the processing of raw (unpasteurized) cow's milk of different fat content (2.5% and 3.2%) by ionizing radiation, it was found that the applied radiation dose (from 0.2 to 2.4 kGy) and the composition of the medium in which the irradiation is carried out (air or carbon dioxide) affect the change in freshness and, accordingly, the grade of milk. The milk samples after irradiation with doses up to 2.4 kGy, according to organoleptic indicators, meet the requirements of TR TS 033/2013 *On the Safety of Milk and Dairy Products* with a slight change in taste and smell after irradiation with doses above 1.4 kGy. After irradiation with doses of up to 1.4 kGy in the air and doses of up to 1.6 kGy in the carbon dioxide in terms of titratable acidity, raw (unpasteurized) cow's milk belongs to the highest and first grade milk; when irradiated with doses of 1.4-2.0 kGy and 1.6-2.2 kGy in the air and the carbon dioxide, respectively,—for the milk of the second grade, according to the requirements of GOST R 52054-2003 *Raw (Unpasteurized) Cow's Milk. Specifications*. Lower quantitative indicators of titratable acidity in the processing of milk by ionizing radiation in the carbon dioxide are due to the “additive effect”. When irradiated with doses in excess of 2.2 kGy in the air and doses in excess of 2.4 kGy in the carbon dioxide, the titratable acidity did not meet the requirements of GOST R 52054-2003. A high degree of correlation between the dose of milk samples of different fat content (3.2% and 2.5%) and the content of malon dialdehyde as a product of lipid peroxidation has been set: in the
air—0.984-0.996, in the carbon dioxide—0.991-0.998, respectively. Despite the fact that no significant differences were found in titratable acidity and malondialdehyde content depending on the fat content of milk treated with different doses of ionizing radiation, it was found that titrated acidity and malondialdehyde content in milk with 2.5% fat have lower quantitative indicators for compared with a milk fat content of 3.2%. The high efficiency of ionizing radiation processing as a result of a decrease in microbiological contamination with an increase in the radiation dose up to 2.4 kGy has been proved. Lower quantitative indicators of microbiological contamination have been identified upon exposure in the carbon dioxide medium. According to the results of the studies, it was found that in order to ensure the freshness of raw (unpasteurized) cow’s milk processed with ionizing radiation meets the requirements of the regulatory documents. The following doses of ionizing radiation can be recommended: for the milk of the highest and first grade when processed with radiation in the air—a dose of 1.2 kGy and for milk of the second grade—a dose of 2.0 kGy, for radiation processing in the carbon dioxide medium—1.4 kGy and 2.2 kGy, respectively.

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