Factors affecting the quality and elemental composition of milk

Olha Iakubchak[1], Valentina Korniyenko[2], Svitlana Midyk[3], Serhii Senin[4], **Anastasiia Ivaniuta[5],** Tetiana Naumenko[6], Oksana Pylypchuk[7], Petro Drozd[8]

[1]Doctor of Veterinary Sciences, Professor of the Department of Animal and Food Hygiene named after Professor A.K. Skorokhodko, **Faculty** of Veterinary Hygiene, National University of Life and Environmental Sciences of Ukraine, Kyiv, Ukraine

[2]Doctor of Biological Sciences, Professor, Director of the Ukrainian Laboratory of Quality and Safety of Agricultural Products National University of Life and Environmental Sciences of Ukraine

[3]PhD in Veterinary Sciences, Associate Professor of the Department of Animal and Food Hygiene named after Professor A.K. Skorokhodko, **Faculty** of Veterinary Hygiene, National University of Life and Environmental Sciences of Ukraine

[4]PhD **in Biological Sciences**, Senior Researcher of the Research Department for Monitoring the Safety of Agricultural Products of the Ukrainian Laboratory of Quality and Safety of Agricultural Products, National University of Life and Environmental Sciences of Ukraine

[5]Candidate of Technical Sciences, Associate Professor, Department of Technologies of Meat, Fish and Marine Products, Faculty of Food Technology and Quality Control of Agricultural Products, National University of Life and Environmental Sciences of Ukraine

[6]PhD in Engineering, **Department of Standardization and Certification of Agricultural Products, Faculty of Food Technology and Quality Control of Agricultural Products, National University of Life and Environmental Sciences of Ukraine**

[7]Candidate of Agricultural Sciences, Associate Professor, Department of Technologies of Meat, Fish and Marine Products, Faculty of Food Technology and Quality Control of Agricultural Products, National University of Life and Environmental Sciences of Ukraine

[8]Associate Professor, Candidate of Historical Sciences, Department of Administrative Management and Foreign Economic Activity, Faculty of Agricultural Management, National University of Life and Environmental Sciences of Ukraine

Abstract.

The relevance of the study is due to the growing demand for natural milk, which, in turn, contributes to the study of its nutritional and nutritional value and factors that affect the quality and composition of raw milk. In this regard, this article aims to identify changes in raw milk, taking into account the seasonality factor. The leading approach to studying this problem is to determine the quality indicators by ultrasonic method and the elemental composition by atomic emission spectrometry with inductively coupled plasma of raw milk from cows of the Ukrainian black-and-white breed and establish the dynamics of changes by seasons of the year. The involvement of smart and information technologies in monitoring the main quality indicators of milk in dynamics during the year provides the opportunity to trace seasonal fluctuations in the composition of milk, identify key influencing factors and create predictive models that allow adapting the conditions of feeding and keeping animals to increase the stability and quality of milk. The use of these methods in combination allows not only to detect seasonal variability in the physicochemical and elemental characteristics of milk with high sensitivity and accuracy but also contributes to a scientifically grounded approach to optimizing technological processes in dairy production and managing milk quality in accordance with changes in natural and climatic conditions.

It was found that the dry defatted milk residue in milk significantly decreased in the summer (by 19.3%) compared to the winter period. The highest mass fraction of fat in raw milk was found in the winter period (it is 19.7% higher compared to the summer period). The density of raw milk varies within insignificant limits. The lowest mass fraction of protein was found in the summer (3.28%), the highest - in winter and spring (3.40 and 3.39%, respectively). The mass fraction of minerals in cow's milk in winter significantly increased by 26.5% ($P<0.01$) compared to milk collected in the summer period. The materials of the article are of practical value and can be used for further scientific research, for example, during the stay of cows in conditions of chronic heat stress.

Keywords: macroelements, microelements, atomic emission spectrometry, dairy cows, seasonality

1. Statement of the problem.

From the point of view of physiology, the value of milk as a food product is explained by its universal composition and unique technological properties. Milk contains complete protein, which is rich in essential amino acids, milk fat (saturated and unsaturated fatty acids), lactose, water- and fat-soluble vitamins, macro- and microelements, etc.

M. Rashid et al. (2024) argued that cow feeding affects milk quality as well as quantity. Feeding an optimal carbohydrate content without fibre can help increase milk fat and protein content. Protein and fat content can also vary due to the physical form of the feed fed.

According to research by S. Lashkari et al. (2024), increased crude fat levels in the feed resulted in increased milk yield. An interaction was found between the fat source and the level of milk fat percentage. Specifically, the feeding of saturated fatty acids (SFAR) increased the percentage of milk fat, while the addition of other fatty acids resulted in a decrease in the milk fat percentage. Dry matter intake (DMI) decreased when the inclusion of raw fat in the diet was increased. With increased crude fat levels, the percentage of milk fat in calcium soaps of fatty acids CaFA and in polyunsaturated fatty acids (PUFAR) decreased. At the same time, the content of milk fat and the percentage of milk protein did not change.

A. M. Bales et al. (2024) demonstrated that the addition of hydrogenated fat calcium gluconate increased milk protein yield and tended to increase milk fat yield during the first 8 weeks of lactation in multiparous Holstein cows.

S.S. Koli et al. (2024) studied the effect of feeding a mixed herbage complex supplement to dairy cows in India on their milk composition and found that the fat, protein, and lactose content of milk increased when the corresponding plants were fed.

W. Boonkum et al. (2024) found that milk production and milk quality can also be affected by breed genetics, as well as heat stress.

V. Danchuk et al. (2024) argued that grazing cows in contaminated areas can lead to the accumulation of radioactive strontium, cesium in raw milk. These elements affect the qualitative content of fat, i.e., the fatty acid composition of milk. Exceeding the permissible level of 137Cs activity concentration of 100 Bq/kg in cow's milk causes a decrease in the relative content of polyunsaturated fatty acids (due to omega-6 fatty acids) and the omega-3/omega-6 ratio. Also, the relative content of linoleic acid decreased several times when the permissible level of 137Cs concentration in cow's milk was exceeded; while the concentration of stearic acid, which immediately exceeds physiological limits at a 137Cs concentration of about 110–130 Bq/kg, gradually increases to a 137Cs activity concentration of 270–330 Bq/kg and reaches 600 Bq/kg. That is, the factor of the duration of the effect of radioactive contamination on the physiological state of the mammary gland is obviously decisive and is responsible for the degree of biochemical transformations.

Milk contains macro- and microelements such as sodium, potassium, calcium, magnesium, phosphorus, copper, manganese, iodine, and zinc, which are vital for the normal growth, development, and functioning of a living organism. Calcium, phosphorus, magnesium, sodium, and potassium are especially important from the point of view of nutritional value since they participate in the formation of bone tissue, water-salt balance, and nervous and muscular activity.

However, the salt composition of milk is not constant - it varies depending on the stage of lactation, season, feeding conditions and physiological state of the animals. Changes in mineral composition are especially noticeable at the beginning and end of the lactation period. At the same time, the salt content in milk affects not only its nutritional value but also the stability of the colloidal structure of proteins and the ability to coagulate, which is critically important for the dairy industry.

In this regard, the use of highly sensitive research methods, such as ultrasonic analysis to determine the main quality indicators of milk, as well as inductively coupled plasma atomic emission spectrometry (ICP-OES) to accurately determine the content of macro- and microelements, is relevant. The combination of these methods allows for a comprehensive assessment of both the technological and nutritional characteristics of raw milk from cows of the Ukrainian black-and-white breed.

2. Analysis of recent research and publications

D. Nandan et al. (2022) noted that due to its widespread application and use in human nutrition, milk and products made from it always remain at the centre of scientific research.

O.M. Yakubchak et al. (2021) emphasised that the main indicators of the nutritional value of milk are the content of protein, fat, micro- and macroelements, vitamins and other nutrients. In clinically healthy cows, these indicators are stable and within appropriate limits.

E.E. Newton et al. (2023) believed that the importance of minerals in the vital activity of the body is difficult to overestimate. An important feature of milk as a source of macro- and microelements is that it contains mineral salts in precisely such proportions that are necessary for the human body. Milk, as the most balanced product in terms of all the components necessary for the body, with its daily consumption can fully satisfy the needs of the human body in mineral salts.

In the scientific work of J. B. Magan, et al. (2021) noted that there is growing consumer interest in organic milk from pasture-raised cows. Studies describe the effects of different feeding strategies on milk composition and focus on comparing pasture-based and concentrate-based feeding regimens.

M. Kamal et al. (2020) argued that due to the easily digestible proteins, fats, carbohydrates, minerals and vitamins present in milk, it is an integral part of children's nutrition. In addition, milk is considered a powerful protective factor, especially for people working in harmful production conditions, particularly in the chemical and metallurgical industries.

Milk protein neutralises toxic heavy metals, their traces, and other substances that are harmful to health. It should be noted that milk contains unique substances that are not found in any other products, in particular, casein, lactose and milk fat.

F. Ahtesh et al. (2018) stated that dairy products, particularly those containing probiotics, as well as fermented milk, are currently popular.

As summarised in the work of E. Feeney et al. (2020), the dairy matrix is unique and differs in many respects across various categories of dairy products. Dairy, for example, is an important source of a variety of microelements in the Irish diet, such as calcium and vitamin B12. Dietitians have traditionally recommended the consumption of milk, yoghurt and cheese (low fat) and advised limiting butter and cream intake.

However, recent studies on the impact of saturated fats on the incidence of cardiovascular diseases present a different theory.

S. Dunne et al. (2021) studied the effects of saturated fat intake from dairy products on markers of cardiovascular disease. Recent studies suggest that cholesterol particle size (LDL) is a more sensitive marker of cardiovascular disease risk, as smaller, dense LDL particles are considered more atherogenic.

Research by A. Astrup et al. (2020) focused on the modulation of cholesterol concentration ((total cholesterol (TC), LDL-C). It has been shown that when saturated fats are consumed, the increase in LDL cholesterol concentration may be due to an increase in large LDL particles, which are much less associated with the risk of cardiovascular disease than small, dense LDL particles.

J. Vekic et al. (2022) demonstrated that small, dense LDL is an independent risk factor for cardiovascular disease. This highlights the clinical importance of both LDL quality and quantity.

M. Perna et al. (2022) found an association between increased cardiovascular disease risk and long-chain saturated fatty acid intake, as well as a neutral (potentially beneficial) association with short- and medium-chain saturated fatty acids. Milk fat contains a large amount of short- and medium-chain fatty acids.

Duguma C. (2021) noted that feeding factors that affect milk protein content include the ratio of feed to concentrate, the amount and source of dietary protein, and the amount and source of dietary fat. Protein and fat content can also vary due to the physical form of the feed fed. Any situation that involves feeding interruptions or restricts feed intake can affect milk components.

V. Danchuk et al. (2024) draw attention to the fact that the qualitative composition of fat in milk, i.e. the content of fatty acids, can be affected by the consumption of radioactively contaminated feed by dairy cows.

Neto dos S. et al. (2021) conducted a meta-analysis and meta-regression to assess the effects of diets supplemented with calcium salts of palm fatty acids compared to control diets with low-fat supplements on nutrient digestibility and performance response in lactating dairy cows.

O. I. Kabul et al. (2015) determined the effect of seasonal (winter-spring-summer and autumn) fluctuations on the main components of raw cow's milk throughout the year in Egypt using a special database for the composition of raw cow's milk. Their studies showed that the average values of fat, dry defatted milk residue, protein and moisture of cow's milk in winter were 3.6±0.055, 12.4±0.071, 3.5±0.046 and 85.5±0.075, respectively, and in summer - 3.1±0.058, 11.1±0.092, 3.1±0.060 and 88.8±0.092, respectively. From this study, it can be concluded that the main parameters of milk (moisture, fat, protein and total solids) are affected by seasonal changes.

Therefore, there are many factors influencing the quality of milk, which is why we conducted research into the impact of seasonal changes on the quality indicators and elemental composition of milk.

The article provides a detailed examination of the impact of seasonality on changes in raw milk, including dry defatted milk residue, fat content, protein, lactose, minerals, freezing point, electrical conductivity, active acidity, as well as the content of macro- and microelements.

For reliable determination and comparison of seasonal changes in physicochemical parameters of milk, it is advisable to use the ultrasonic method, which provides rapid and reagent-free determination of such indicators as fat content, protein, lactose, density, acidity and freezing point. The advantage of this method is the possibility of prompt monitoring of qualitative changes in milk directly on the farm or in the laboratory.

The integration of ultrasound analysis with inductively coupled plasma atomic emission spectrometry (ICP-OES) enables highly accurate and sensitive determination of macro- and microelement content, which is critically important for assessing the mineral profile of milk across different seasons. The combination of these analytical approaches provides a comprehensive assessment of the quality of raw milk of the Ukrainian black-and-white breed in dynamics and allows for the identification of patterns of seasonal fluctuations associated with feeding, physiological state of animals and housing conditions.

3. Formation of the objectives of the article

The work aims to establish the influence of feeding ration and seasonal changes on the quality indicators and elemental composition of raw milk of Ukrainian black-and-white cows using the ultrasonic method to determine physicochemical properties and atomic emission spectrometry with inductively coupled plasma to analyse the content of macro- and microelements.

4. Research methods

The research was carried out during 2022 in a structural unit of the National University of Life and Environmental Sciences of Ukraine - the Ukrainian Laboratory of Quality and Safety of Agro-Industial Complex (accreditation in accordance with the requirements of the DSTU ISO/IEC 17025:2019 quality standard for performing analytical research).

Milk raw material for the research was selected from 5 dairy cows of the same age category. These were cows of the Ukrainian black and white breed of the 3rd–4th lactation, with a live weight of 600–630 kg, which belonged to LLC Mlynivskyi complex, Khoroshky village, Lubny district, Poltava region.

This farm practiced year-round tethered and free-range cow keeping. Dairy cows were housed in 3 barns of 200 heads each, the number of dairy herds was 600 heads, with a free range area. Feeding: haylage, hay, silage, and compound feed; during the summer, hay is replaced with green mass – lucerne. The diet of dairy cows is presented in Table 1.

Table 1. Feeding ration for dairy cows of LLC Mlynivskyi complex

Indicators	Hay from various grasses	Lucerne silage (haylage)	Corn silage	Compound feed for dairy cows
1	2	3	4	5
Amount of feed, kg/day	1.50	10.00	25.00	9.08
Amount of dry substances of feed, kg	1.30	3.50	7.30	6.40
Feed units	0.75	4.10	5.00	5.90
Exchange energy, cattle, MJ	10.70	28.70	77.93	50.22
Crude protein, g	227.00	598.50	609.00	1393.72
Crude fat, g	27.10	129.50	217.53	80.06
Starch, g	0.00	0.00	1522.56	1175.82
Crude fibre, g	363.83	1207.57	1703.8	156.90
Sugar, g	0.00	0.00	94.30	296.60
Ca, g	23.94	62.71	28.34	64.26
R, g	4.10	10.22	18.90	20.38
Salt, g	0.00	0.00	0.00	25.00

Notes: *The indicators of various components of the feeding ration for dairy cows are described.*
Source: *author's development.*

Milking was carried out twice a day at 6 a.m. and 5 p.m. using the Bratslav milk pipeline. The average annual yield is 7000 l. Disinfection of the farm was carried out with the Virosan F product (working concentration: 0.25%, consumption 0.5 l/m $^{2)}$.

Raw milk samples were taken from the same 5 cows but in different seasons, as well as from pooled raw milk samples (from a tanker of 200 cows). The obtained raw milk was placed in sterile glass containers with a capacity of 0.5 l. The samples were transported in a cooled form at a temperature of up to 4 ^{o}C.

In raw milk on the Master Classis LM2PI milk analyser ultrasonic method (in accordance with DSTU 70576:2009 Raw cow's milk. Ultrasonic method) determined the following quality indicators: dry defatted milk residue, mass fraction of fat, protein, lactose, milk density, mass fraction of water, minerals, freezing point, electrical conductivity and active acidity.

Determination of the content of macro- and microelements in raw milk was carried out by atomic emission spectrometry with inductively coupled plasma on the IRIS Interpid II XSP device (Termo), detection for silver was 0.05 mg/l, for all other elements – 0.01 mg/l.

Experimental studies involving animals complied with the requirements of the “European Convention for the Protection of Vertebrate Animals Used for Experimental and Scientific Purposes”, approved in Strasbourg in 1986 (European convention for …) and the Law of Ukraine No. 692 “On the Protection of Animals from Cruelty” (3447-IV) of 21.02.2006 (Law of Ukraine …). All necessary interventions on animals were carried out in compliance with the ARRIVE recommendations without violating the guiding principles of EU Directive 2010/63/EU (Council Directive 2010/63/EU of 22 September 2010) on the protection of animals used for scientific purposes.

Raw milk obtained from each cow was examined in 5 repetitions. Statistical processing of the results of the study of raw milk was carried out using a personal computer in the Excel program. To determine the statistical significance of the observed differences, the Tukey test was applied. We were guided by the fact that different superscript letters indicate values that were significantly different in the same row of the table ($P < 0.05$).

5. Results of the study

According to DSTU 3662:2018 Raw cow's milk. Technical conditions, the following indicators are standardised: crude fat content 3.4%; protein content 3.0% and freezing point - not lower than - 0.520, density - not less than 1027.0

kg/m ^{3} and active acidity for extra and higher grade raw milk - from 6.6 to 6.7 pH units and for first-grade raw milk – from 6.55 to 6.8 pH units.

According to organoleptic indicators, the milk under investigation complied with the relevant regulatory acts throughout all seasons, namely DSTU 3662:2018, and exhibited the following characteristics. The colour varied from white to light cream. The consistency of the tested milk is a homogeneous liquid without flakes and sediment; the taste and smell are characteristic of fresh milk, without foreign flavours and odours.

The data presented in Table 2 indicate that the dry defatted milk residue in the summer period decreased by 19.3% ($P < 0.05$) compared to the winter period, while in the spring and autumn its values did not differ significantly from the winter indicators. The decrease in this indicator in the summer may be due to the influence of high temperatures, changes in the dry matter content of feeds, and a decrease in the consumption of nutrients by animals, which leads to an overall decrease in the concentration of protein, lactose, and minerals in milk.

The determination of dry defatted milk residue was carried out using an ultrasonic method, which enables the rapid and accurate monitoring of changes in the physicochemical parameters of milk in real-time, without the use of chemical reagents. Due to the high sensitivity of ultrasonic technology to changes in the density and composition of milk, this method is an effective tool for detecting seasonal fluctuations in the quality of dairy raw materials and ensuring an objective comparative analysis of its component composition. R. Mylostyvyi *et. al.* (2023) noted a decrease in the dry defatted milk residue of raw milk.

Table 2. Quality indicators of raw milk (M±m, n=5)

Name of indicators, units of measurement	Time of year (seasons)			
	Winter	Spring	Summer	Autumn
Dry defatted milk residue,%	10.53 ± 0.32^{a}	10.11 ± 0.51^{b}	8.50 ± 0.03^{c}	10.06 ± 0.03^{b}
Mass fraction of fat,%	4.20 ± 0.02^{a}	3.58 ± 0.04^{b}	$3.37\pm0.\ 08^{c}$	3.67 ± 0.04^{d}
Density, kg/m ^{3}	1031.70 ± 1.07^{a}	1030.54 ± 1.42^{a}	1027.8 ± 0.21^{b}	$1028.60\pm0.19^{a,b}$
Mass fraction of protein,%	3.40 ± 0.02^{a}	3.39 ± 0.02^{a}	3.28 ± 0.02^{b}	3.32 ± 0.02^{c}
Mass fraction of lactose,%	5.67 ± 0.05^{a}	5.40 ± 0.08^{b}	5.10 ± 0.01^{c}	5.39 ± 0.05^{b}
Mass fraction of minerals,%	0.83 ± 0.04^{a}	0.70 ± 0.02^{b}	0.61 ± 0.02^{c}	0.74 ± 0.03^{d}
Freezing point, (minus) ^{0}C	0.600 ± 0.12^{a}	0.622 ± 0.004^{b}	0.655 ± 0.004^{c}	0.687 ± 0.15^{d}
Electrical conductivity, mS /cm	5.10 ± 0.03^{a}	5.33 ± 0.06^{b}	5.50 ± 0.03^{c}	5.30 ± 0.02^{b}
pH units	6.44 ± 0.04^{a}	6.60 ± 0.06^{b}	6.68 ± 0.06^{b}	6.61 ± 0.08^{b}

Notes: *Different letters in the superscripts indicate values that were significantly different within a row of the table ($P < 0.05$) based on the results of the Tukey test comparison.*
Source: *author's development.*

The minimum fat content in the milk of a healthy cow should not be lower than 3.2%. The mass fraction of fat in the milk of cows can fluctuate. This indicator can be influenced by the lactation periods of the cows and the composition of their diet. A. Maheshwari *et al.* (2024) found that the fat content in milk is affected by the age of the animals, and researchers M. Lorenzen *et al.* (2024) argued that in addition, the genetic characteristics of dairy cow breeds also play an important role.

M. Arif *et al.* (2024) concluded that the decrease in milk fat content in milk may be caused by biohydrogenation, i.e. diet. According to G. Ramsbottom (2021), low fat content in milk may indicate rumen acidosis. In our studies, the highest mass fraction of fat in raw milk was found in the winter period (it is 19.7% higher compared to the summer period). However, there was no significant difference between the summer, autumn, and spring periods.

Similar data on milk fat content were obtained by N. V. Zazharska *et al.* (2024). In their studies, regardless of the animal group, the fat content in cow milk was significantly lower in summer than in other seasons, and highest in winter.

R. Mylostyvyi *et al.* (2023) studied the conditions affecting the density of milk. This indicator is used to convert the amount of milk expressed in kilograms to liters and vice versa; to establish and control the naturalness of milk; calculations according to the formulas for dry matter, defatted dry milk residue (NFDMR) and other components. The density of raw cow's milk varies within 1.027–1.033 (sometimes from 1.026 to 1.031). The lowest density of milk is found in summer, it varies within insignificant limits: 0.38% lower than the density of milk in winter.

A. Runthala *et. al.* (2023) believe that the structure and properties of milk and dairy products are determined by the protein content and composition.

S.Warakaulle *et. al.* (2024) note that milk contains a myriad of different proteins, which are classified into caseins (αs1, αs2, β and κ-casein) and whey proteins (e.g. α- lactalbumin, β-lactoglobulin, serum albumin, lactoferrin, immunoglobulin), as well as non-protein nitrogen components.

The protein content in cow's milk affects the technological properties of milk, particularly the manufacture of dairy products. In addition, the mass fraction of protein in milk affects its quality. The lowest mass fraction of protein was found in summer (3.28%) and the highest in winter and spring (3.40 and 3.39%, respectively). Our results are consistent with the studies of N. V. Zazharska *et al.* (2024), where the lowest protein content (3.23±0.06%) in the mass of milk of primiparous cows compared to other seasons of the year was observed in the summer period.

Lactose content in milk decreases in the presence of mammary gland infection. Lactose is the main compound that determines the osmolarity of milk (it plays a crucial role in maintaining stable osmotic pressure in the cow's body). This is a relatively stable indicator that has biological limits. The lactose content in milk is almost constant throughout lactation. R. Antanaitis *et. al.* (2024) hypothesise that increased lactose content in milk indicates improved behaviour of dairy cows, including active chewing, feeding and locomotor activity, which, in turn, is reflected in improved general health and well-being of cows. Fluctuations in lactose levels in milk have a significant impact on the physiological and behavioural responses of dairy cows, thereby affecting the milk productivity of dairy cows. The mass fraction of lactose in the milk we studied did not change significantly, but its lowest content was noted in summer (5.10%) and the highest in winter – 5.67%.

The mass fraction of minerals is not regulated by the regulatory legal acts of Ukraine. In the study, the mass fraction of minerals in milk from cows in winter increased by 26.5% (P) compared to milk obtained from cows in the summer.

According to N. Rusko (2011), the freezing point is determined by the amount of soluble components of milk (lactose and mineral salts), the content of which in milk does not change significantly. The highest freezing point of the studied milk was established in the autumn period and the lowest in winter (Table 2).

J. Bonestroo *et al.* (2022) concluded that electrical conductivity plays an important role in identifying milk from cows with mastitis. In the milk we studied, this indicator decreased by 7.3% in winter compared to summer.

R. Mylostyvyi *et al.* (2023) noted that in fresh milk, the active acidity is within 6.6–6.8, i.e., milk has a weakly acidic reaction. With increasing milk acidity, this indicator gradually decreases. If the value is higher than 6.8, this indicates either the addition of substances to milk that prevent souring or the presence of mastitis. In the milk we studied, the active acidity fluctuated within 6.61–6.68 and did not differ significantly.

Micro and macroelements play an important role in the bodies of dairy cows and affect the quality and quantity of raw milk obtained from them.

O.V. Zhurenko (2020) established significant correlations between the content of specific macro- and microelements and the qualitative and quantitative performance indicators of cows when fed the feed additive Germacink. The use of Germacink led to a change in the ratio between productivity and the content of some minerals in the blood serum of cows. A weak correlation was also observed between phosphorus and calcium in blood serum and average daily milk yield ($r = 0.41$; $P<0.05$), and a reliable relationship with the potassium, magnesium and lithium content disappears.

I. Loboiko *et al.* (2024) also studied the level of mineral intake in blood plasma, colostrum and hair of cows using feed additives.

Given that milk is the main source of minerals in the human diet, and the fact that agricultural and seasonal parameters affect the concentration of micro- and macroelements in milk E.E. Newton *et al.* (2023) considered that the variation in mineral concentrations in milk is generally related to the feeding regimen of dairy cows. In most studies, milk collected in the summer season contained less Cu, I, Mn and Zn than milk collected in the winter.

I. Loboiko *et al.* (2024) have shown that milk type and season also influence the concentration of certain macrominerals and microelements. Modification of the mineral profile in milk is possible for many macro- and microelements, but it is likely to depend on genetics (e.g. breed, selection) and environmental factors.

According to the assessment of the elemental composition (Table 3) of raw milk obtained from cows, it was determined that the potassium content increased in the autumn period compared to the spring by 53% ($P<0.001$) and relative to the summer - by 28% ($P<0.01$).

Table 3. The content of macro- and microelements in raw cow milk (M±m, n=5)

Mass fractions of elements	Time of year (seasons)			
	spring	summer	autumn	winter
Potassium (K), g/l	$1.09±0.05^{a}$	$1.31±0.06^{b}$	$1.67 ±0.05^{c}$	$1.41 ±0.21^{b}$

Calcium (Ca), g/l	1.06±0.07[a]	1.20 ±0.03[b]	1.02 ±0.04[a]	1.15±0.03[b]
Sodium (Na), mg/l	391.9±10.8[a]	411.9± 13.2[a]	373.4±9.05[b]	480.1±18.6[c]
Magnesium (Mg), mg/l	108.3±3.3[a]	100.6±12.7[a]	96.9± 5.2[a]	118.3±3.4[b]
Zinc (Zn), mg/l	4.11±0.13[a]	3.93±0.49[a]	3.71±0.25[a]	4.12±0.08[a]
Aluminum (Al), mg/l	0.81±0.02[a]	0.92±0.03[b]	0.65±0.04[a]	0.10±0.01[a]
Strontium (Sr), mg/l	0.48±0.02[a]	0.56±0.04[a]	0.79±0.03[b]	0.34±0.02[c]
Iron (Fe), mg/l	0.43±0.03[a]	0.61±0.02[b]	0.55±0.07[b]	0.85±0.04[c]
Boron (B), mg/l	0.41±0.05[a]	0.49±0.03[a]	0.58±0.04[b]	0.30±0.01[c]
Lithium (Li), mg/l	0.086±0.017[a]	0.076 ±0.0 11[a]	0.077 ±0.012[a]	0.104 ±0.009[a]
Barium (Ba), mg/l	0.053±0.006[a]	0.056 ±0.001[a,b]	0.075 ±0.009[a]	0.048 ±0.008[b]
Chromium (Cr), mg/l	0.051±0.015[a]	0.043 ±0.008[a]	0.048±0.013[a]	0.058±0.009[a]
Copper (Cu), mg/l	0.038±0.008[a]	0.031 ±0.009[a,b]	0.026 ±0.005[a]	0.054 ±0.007[b]
Manganese (Mn), mg/l	0.037±0.007[a]	0.025 ±0.005[a]	0.042 ±0.013[a]	0.026 ±0.006[a]

Notes: *Different letters in the superscripts indicate values that were significantly different within a row of the table (P < 0.05) based on the results of the Tukey test comparison.*
Source: *author's development.*

The revealed seasonal fluctuations in the content of macro- and microelements in raw milk from cows of the Ukrainian black-and-white breed indicate a clear influence of natural and climatic factors and feeding ration on the mineral composition of milk. Thus, the calcium content in autumn decreased by 15% (P<0.01) compared to the summer period and by 11% (P<0.05) compared to the winter period. The sodium content in cow's milk in winter increased by 29% (P<0.001) compared to the autumn period and by 17% (P<0.05) compared to the summer period, and by 23% (P<0.01) compared to the spring season. The magnesium content decreased in autumn by 18% (P<0.01) compared to the winter season. The mass fraction of aluminium in milk decreased in winter by 88% (P<0.001) compared to the spring period, by 89% (P<0.001) compared to the summer season, and by 85% (P<0.001) compared to the autumn. Strontium in milk increased in autumn by 41% (P<0.01) compared to the summer period, and by 65% (P<0.001) compared to the spring and 2.3 times (P<0.001) compared to the winter period. Iron indicators in milk decreased in spring by 49% (P<0.001) compared to the winter period, and in summer by 30% (P<0.01), in autumn by 23% (P<0.05). The boron content increased in autumn by 1.9 times (P<0.001) compared to the winter season and by 42% (P<0.05) compared to the spring period. The mass fraction of lithium in milk was the highest in the winter period. The barium content in milk increased in autumn by 56% (P<0.05) compared to the winter period. The highest chromium and copper content in raw milk was observed in the winter period. The lowest manganese content was found in the summer period.

Studies of the elemental composition of pooled raw milk (Table 4) obtained from cows (n = 200) showed that the potassium content decreased by 31% (P<0.01) in the spring period and by 28% (P<0.01) in the summer compared to the autumn period.

Table 4. Content of macro- and microelements in pooled raw milk (M±m, n=200)

Mass fractions of elements	Time of year (seasons)			
	spring	summer	autumn	winter
Potassium (K), g/l	1.14±0.11[a]	1.58±0.05[b]	1.64±0.04[b]	1.35±0.09[c]
Calcium (Ca), g/l	1.08±0.04[a]	1.04±0.06[b]	1.01±0.03[a]	1.41±0.05[b]
Sodium (Na), mg/l	392.9±5.13[a]	405.4±8.88[a]	371.53±7.79[b]	536.7±18.47[c]
Magnesium (Mg), mg/l	108.9±3.52[a]	98.7±2.09[b]	93.9±2.06[b]	112.7±7.76[a]

Zinc (Zn), mg/l	4.08±0.05[a]	3.91±0.17[a]	3.68±0.18[b]	4.32±0.06[c]
Aluminum (Al), mg/l	0.78±0.03[a]	0.84±0.04[a]	0.61±0.02[b]	0.81±0.11[a]
Strontium (Sr), mg/l	0.52±0.03[a]	0.62±0.04[b]	0.77±0.06[c]	0.42±0.03[d]
Iron (Fe), mg/l	0.48±0.04[a]	0.58±0.07[b]	0.52±0.04[a,b]	0.92±0.08[c]
Boron (B), mg/l	0.36±0.02	0.45±0.05	0.55±0.04	0.41±0.03
Lithium (Li), mg/l	0.086±0.011[a]	0.078±0.008[a]	0.106±0.011[b]	0.108±0.013[b]
Barium (Ba), mg/l	0.057±0.011[a]	0.066±0.012[a]	0.067±0.012[a]	0.078±0.008[a]
Chromium (Cr), mg/l	0.051±0.007[a]	0.045±0.005[a,b]	0.039±0.009[a]	0.076±0.011[b]
Copper (Cu), mg/l	0.034±0.006[a]	0.044±0.009[a]	0.025±0.005[a]	0.072±0.015[b]
Manganese (Mn), mg/l	0.041±0.010	0.033±0.007	0.037±0.006	0.026±0.005

Notes: *Different letters in the superscripts indicate values that were significantly different within a row of the table (P < 0.05) based on the results of the Tukey test comparison.*
Source: *author's development.*

In addition, in winter, the calcium content in milk increased by 36% (P<0.01), and in autumn - by 40% (P<0.001) compared to the summer period. The sodium content in milk in autumn decreased by 31% (P<0.001 compared to the winter period. The magnesium content in winter increased by 20% (P<0.05) compared to the autumn season. The mass fraction of aluminium in autumn decreased by 22% (P<0.01), and in summer - by 27% (P<0.01), in winter - by 25% (P<0.001) compared to milk obtained in the spring period. The strontium content in autumn increased by 48% (P<0.01), compared to its content in milk in spring and in winter - by 83% (P<0.01). The iron content in spring decreased by 48% (P<0.001) compared to the winter season, and boron in spring - by 20% (P<0.05) compared to its content in milk in summer, and by 35% (P<0.01) compared to the autumn period. The mass fraction of lithium, chromium and copper in milk decreased in the winter period, and the manganese content in this period was the lowest. The mass fraction of potassium in the collected raw milk was the highest in the autumn and the lowest in the spring. The calcium content in milk was the highest in the winter, and there were slight differences in spring, summer and autumn. The mass fraction of sodium in milk was the highest in the winter, and the lowest in the autumn and spring periods. The magnesium content was the highest in the winter and spring periods and the lowest in the summer and autumn periods (Figure 1).

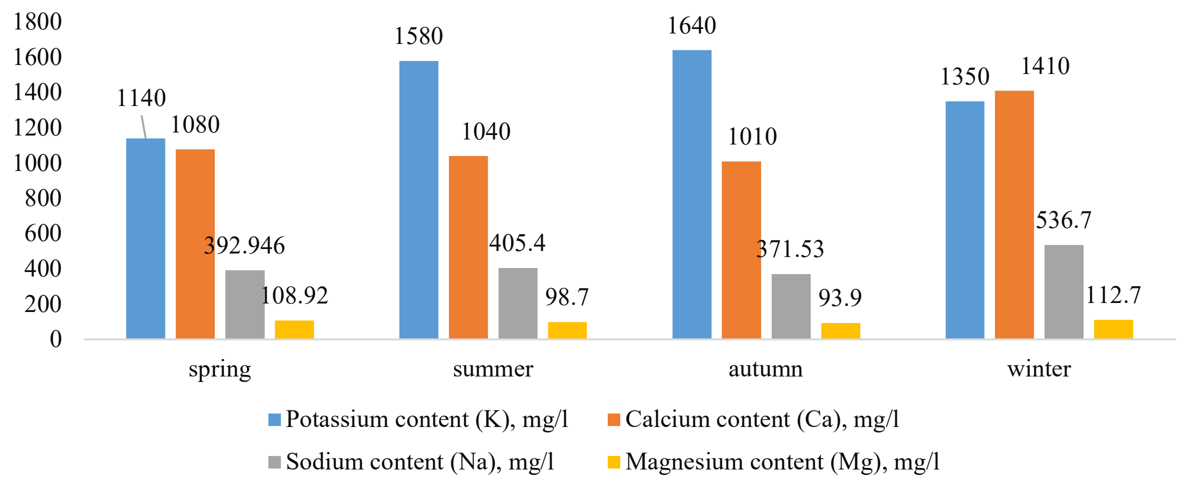

Fig. 1. The content of basic elements in pooled raw milk, depending on the season of the year (n=200).
Notes: *The studied elements are shown in different colors: blue - potassium, orange - calcium, gray - sodium, yellow - magnesium.*
Source: *author's development.*

Throughout the year, regardless of the season, in the milk of cows of the experimental group, as well as in samples of pooled milk, the content of silver (Ag) did not exceed 0.05 mg/l, and the concentrations of such potentially toxic microelements as cobalt, nickel, lead, cadmium and bismuth were lower than 0.1 mg/l, i.e. remained below the detection limits of the analytical equipment used.

The quantitative content of the specified microelements, determined by inductively coupled plasma atomic emission spectrometry, is characterised by high analytical sensitivity, the ability for simultaneous multi-element analysis, and low detection limits even for trace amounts of metals. Due to these properties, the method ensures reliable control of milk safety for heavy metals, which is extremely important in the context of food safety and compliance with sanitary requirements.

The results obtained indicate the absence of contamination of raw milk with heavy metals within the sensitivity range of the ICP-OES method, which confirms the ecological purity of production and the safety of the studied dairy products for consumption.

Analysis of the elemental composition of the water for drinking cows showed that the potassium content was 10.86 g/l, calcium 79.58 g/l; mass fraction of sodium – 99.81 mg/l, magnesium – 16.92 mg/l. Microelements were also found in the following quantities: mass fraction of strontium was 0.49 mg/l, iron – 0.26 mg/l, manganese – 0.24 mg/l, boron – 0.17 mg/l, lithium, barium 0.04 mg/l each, aluminium – at a concentration of 0.02 mg/l. Chromium, copper, silver, cobalt, nickel, lead, cadmium and bismuth were also found in the water, but in concentrations lower than 0.01 mg/l.

According to our research, the elemental composition of water for drinking cows did not depend on seasonality, that is, it did not change significantly throughout the year.

Therefore, minerals, as indispensable components of all living organisms (their content in the body of animals is 2.4–4.8%), play an extremely important and multifaceted role, and their metabolism in the body is considered as one of the links of the general metabolic pathway in it. M. O. Khomenko *et al.* (2023) noted that minerals participate in the construction of micro- and macrostructures (in the formation of bone tissue, the construction of cell membranes), in the regulation of osmotic pressure in biological fluids, in maintaining acid-base balance, the reaction of the environment (pH) at a certain level, due to their participation in the formation of buffer systems of biological fluids and tissues. They affect the permeability of cell membranes and vessels and perform important functions in creating the stability of biological colloidal systems. O.M. Yakubchak *et al.* (2021) emphasised that mineral elements are part of proteins (selenium, sulfur), coenzymes (phosphorus, cobalt), hormones (iodine, zinc), take an active part in various metabolic links (calcium, phosphorus, sulfur, manganese, magnesium). They activate a number of enzymatic systems and may be incorporated into the active site (zinc, copper, nickel, molybdenum, iron), regulating the activity of the symbiotic microflora of the gastrointestinal tract.

E.E. Newton *et al.* (2023) believe that the quality of milk is influenced by its mineral composition. Thus, the high availability of calcium and phosphorus from milk is, to some extent, due to their association with casein. The iron content performs versatile functions. Its low content in milk is not able to satisfy the calf's needs, but this level inhibits the reproduction and growth of many types of bacteria in milk. The formation of the mineral composition of milk is carried out in the epithelial cells of the alveoli of the mammary gland. The concentration of calcium, phosphorus, potassium, magnesium, zinc and iron in milk is much higher, sodium - 12 times lower than in arterial blood plasma, which is evidence of the active role of mammary gland cells in the secretion of these elements. The concentration of potassium, sodium, and chlorine in milk does not depend on the productivity of cows, the structure of the diet and the content of these electrolytes in it, but naturally changes over the lactation periods. The content of crude protein, iron, copper, zinc and manganese in the diet does not significantly affect the content of microelements in milk. The content of many microelements in milk is relatively constant and at different levels of their consumption changes only in the case of significant deficiencies. In this case, a decrease in productivity is detected much earlier than a decrease in the concentration of minerals.

Thus, the use of atomic emission spectrometry with inductively coupled plasma has become a key analytical tool in the study of the mineral profile of raw milk, allowing not only to identify reliable differences between seasons, but also to lay the foundation for further optimisation of feeding and production technologies for dairy products with predicted quality characteristics.

Conclusions

The dry defatted milk residue of raw milk was significantly lower in the summer (by 19.3%) compared to the winter period. In spring and autumn, it did not differ significantly from the winter period. The highest mass fraction of fat in raw milk was found in the winter period (it is 19.7% higher compared to the summer period). The density of raw milk in different seasons of the year varies slightly. The mass fraction of protein in milk was the lowest in the summer (3.28%) and the highest in the winter and spring (3.40 and 3.39%, respectively). The mineral content in the milk of cows increased significantly by 26.5% in winter compared to the milk obtained in the summer period. The highest freezing point of the milk we studied was in the autumn period, the lowest in the winter. The electrical conductivity of milk is 7.3% lower in winter compared to summer. Active acidity ranged from 6.61 to 6.68 and did not differ significantly by season.

The lowest potassium content in milk was found in the spring, the highest in the fall. As for calcium content, its content was 15% higher in the summer than in the fall. The mass fraction of sodium, magnesium, and zinc was the highest in milk in the fall. The highest aluminum and strontium content was found in the summer, the lowest in the winter. The iron content in milk was 49.4% lower in the spring compared to the winter, and the copper content was 51.9% higher in the winter compared to the autumn. The boron content was 1.9 times higher in the fall compared to the winter ($P<0.001$) and 42% higher in the fall compared to the spring ($P<0.05$). The mass fraction of lithium in milk was the highest in the winter. Barium content was higher in autumn compared to winter by 56% ($P<0.05$). The highest chromium and copper content in raw milk was in winter. The lowest manganese content was found in summer.

An analysis of the elemental composition of water for drinking cows revealed that the potassium content was 10.86 g/l, calcium – 79.58 g/ l; sodium – 99.81 mg/l, magnesium – 16.92 mg/l.

The combination of ultrasonic technologies, atomic emission spectrometry, and smart and information technologies creates an effective ecosystem for continuous monitoring and forecasting of milk quality indicators. This allows not only to optimise production but also to reduce costs, improve milk quality, and adapt production to changes in the external environment, including seasonal fluctuations.

The results we obtained can be used to study raw milk in the event of changes in various feeding factors or housing conditions, for example, when cows are exposed to chronic heat stress.

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