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IMPROVING THE DESIGNING OF MECHANICAL TECHNOLOGIES THROUGH OPTIMIZED DIMENSIONAL STRUCTURES

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Abstract. Modern trends in technological development related to the use of numerical control machine tools are manifested by minimizing the number of technological operations, installations, operation elements. One of the most effective ways to improve the design of mechanical processing technologies is to create optimal technological dimensional structures. In the paper, optimality requirements are formulated in relation to the elementary dimensional structures and the entire structure. It is shown that a technological dimensional structure is optimal if it is similar to the constructive dimensional structure. Real constructive dimensional structures are very complex and varied, so that the optimality of some sequences of the structure excludes ensuring the optimality of other sequences. Reciprocal structural adaptations are required, which can be done by constructively resizing the equivalent part. As a criterion for the resizing, the non-admission of the increase in the tolerance of the machining allowance is manifested.

Keywords: *mechanical technologies designing, optimal dimensional structure, dimensional analysis, technological dimensional chain, machining allowance.*

Rezumat. Tendințele moderne în dezvoltarea tehnologică legate de utilizarea mașinilor-unelte cu comandă numerică se manifesta prin minimizarea numărului de operații tehnologice, de instalări, de faze tehnologice. Una dintre cele mai eficiente modalități de îmbunătățire a proiectării tehnologiilor de prelucrare mecanică este crearea structurilor dimensionale tehnologice optimale. In lucrare sunt formulate cerințe de optimalitate în raport cu structurile dimensionale elementare şi cu structura întreagă. Se arata ca o structură dimensională tehnologică este optimală daca este asemănătoare cu structura dimensională constructivă. Structurile dimensionale constructive reale sunt foarte complexe și variate, astfel încât optimitatea unor secvențe ale structurii exclude asigurarea optimității altor secvențe. Sunt necesare adaptări structurale reciproce, care se pot face prin redimensionarea constructivă echivalenta a piesei. În calitate de criteriu al redimensionării se manifesta neadmiterea creşterii toleranţei adaosurilor de prelucrare.

Cuvinte cheie: *proiectare tehnologii de prelucrare mecanică, structură dimensională optimală, analiză dimensională, lanț dimensional tehnologic, adaos de prelucrare.*

1. Introduction

One of the important tasks of mechanical engineering is to obtain competitive products in the sense of minimizing the total costs at the stages of the entire life cycle of the product. This is especially true for the stages of design, development of technological processes and production with the requirement of minimal cost, high quality workmanship while maintaining high productivity.

A characteristic feature of most technological problems is multi-variance. This is due to the possibility of manufacturing a product using a variety of equipment and tools with different structures of operations and their sequence in the technological process. And since there are several possible solutions, there are better and worse options, there is one best option.

Therefore, an important problem is the synthesis of the optimal dimensional structure of the technological process of machining, which allows, at the stage of preparation of production, to obtain an optimal technological process that ensures the achievement of the specified quality and precision of the part, with high productivity of their manufacture, taking into account specific production conditions [1]. The modern solution of such problems is carried out within the framework of the concept of concurrent engineering, developing mutually acceptable and mutually coordinated designs of parts and their manufacturing technologies.

The search for a technology option that ensures the quality and cost-effectiveness of manufacturing parts based on the optimization of dimensional-precision relationships requires finding the optimal technological parameters [2]. At this stage, the main issue is solved the technological support of the technical conditions for the manufacture of the part.

In chronological order, the process of enhancing the design of mechanical technologies was synchronized with the process of technical support of these technologies.

In the conditions of mass and large-scale production, the technological process was developed, and then tested and refined several times until a positive result was achieved. Due to the time and resources involved in production testing, the resulting successful technology was accepted without further optimization. This is also related to the fact that optimization requires a certain tactical behavior in the process of achieving the best result, when as a trial and error method it is based on experience and intuition.

The use of dimensional analysis has greatly simplified the task of designing mechanical technologies, eliminating the need for repeatable manufacturing tests. The latter were replaced by repetitive calculations, although such a synthesis of operating technologies is a rather complicated process due to the large number of parameters. The greatest difficulties arise in the development of schemes for setting technological sizes, the number of which, due to the many options for locating, is quite large. Analysis of all variants of schemes for setting technological sizes in order to find the optimal one requires a long time. Experience has shown that performing iterative dimensional analysis for multiple options leads not only to good solutions, but also to optimized technological structures.

2. Principles to improving the mechanical technologies designing

Changes in recent years, associated with a significant reduction in product series and the widespread use of CNC machines, **including machining centers, have led to the** need to develop technological processes with optimal dimensional structures in a limited time frame [3]. Thus, the dimensional analysis, which performs the function of checking technological

sufficiency, turns into an element of guaranteed design of the optimized technological process of machining.

The marked trend also consists in a rather strong decrease in the number of technological operations. On machining centers, technological processes are not uncommon, including 2-3 operations, there are often single-operation technological processes.

If the developed mechanical processing technology contains many operations, then separate partial dimensional structures are formed from many locating datum. The dimensional structure of a part is formed by "assembling" or coordinating the partial dimensional structures into a single whole (Figure 1). Such an "assembly" is carried out with errors, so the reliability and quality of the developed technology are not easy to achieve. Compliance with the principle of the unity of bases can significantly improve the process of "assembling" the particular dimensional structures, however, the errors of repeated installations affect (Figure 2). Obviously, the larger the partial dimensional structures, the more accurate the dimensional structure of the machined part will be.

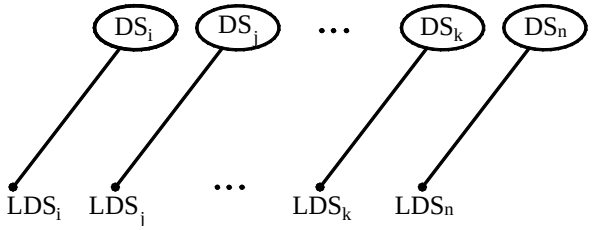

Figure 1. Formation of the part's dimensional structure by many reinstallations from various locating datum surfaces.

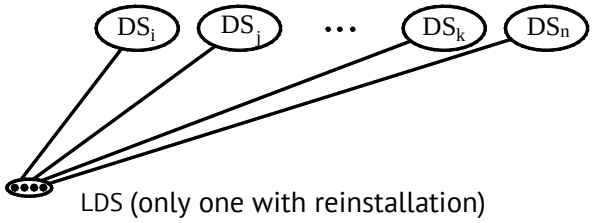

Figure 2. Formation of the part's dimensional structure by many reinstallations, but from only one locating datum surfaces.

For single-operation technologies, there is no need to assemble partial dimensional structures (Figure 3) and the dimensional structure of the part is completely determined by the dimensional structure of the technological system and by the measure of their consistency. The modern CNC machine-tools and machining centers provide significantly higher precision than classical ones, so dimensional precision can be achieved in fewer operatopnal elements. Thus, the first principle (direction) of designing optimization and, consequently, technological processes can be formulated as follows. *The number of technological operations, the number of installations and the number of operation elements throughout the entire technological process should be kept to a minimum* $\sum n_{op} \to min$, $\sum n_{inst} \to min$, $\sum n_{oe} \to min$.

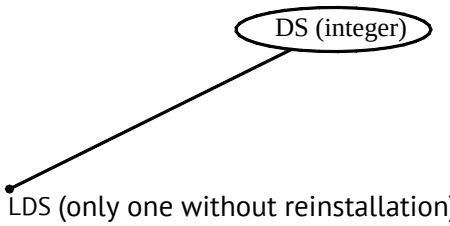

Figure 3. Formation of the part's dimensional structure through one installation.

The use of CNC machines and machining centers is justified for the manufacture of parts with complex dimensional structures. Probabilistic methods of dimensional analysis in conditions of a large number of sizes are not satisfactory for assessing the decisions made. Therefore, the worst case scenario is taken into account - the Worst-Case tolerancing method. Thus, the second principle (direction) of designing optimization and, consequently, technological processes provides for the following. *The sum of the tolerances of technological sizes that make up the links in the chain of the closing designing size must not exceed the tolerance of this size,* $T \geq \sum \omega_{t_i}$.

The dimensional structure of the part includes many design sizes with their own tolerances $A_c(T_{Ac}^{det\,ail})$, each of which is formed in technology by its own technological size with its own technological tolerance. Optimal is the dimensional structure in which the design dimension $A_c(T_{Ac}^{det\,ail})$ is formed only by it own technological size $A_t(\omega_{At})$ [4]. Then the precision of the technological size goes into the precision of the design size directly and without loss (Figure 4, a). The process involves the processing of surfaces connected by a design dimension with an alternation of a number of technological sizes $T_{A_c}^{det\,ail} = \omega_{A_t}$ (Figure 4, b).

Dimensional structures are often observed in which the technological dimensional chain is closed not only by the designing and its own technological dimensions , but with the involvement of an additional one (possibly several) already existing (historical) technological dimensions (Figure 5). Thus, the required precision of the design size is achieved by increasing the requirements for the precision of the technological sizes that make up the dimensional chain according to the inequality $T_{A_c}^{det\,ail} \geq \omega_{A_t} + \omega_{B_t}$ [4]. The precision of the designing size is ensured at the proper level by improving the precision of the execution of technological sizes.

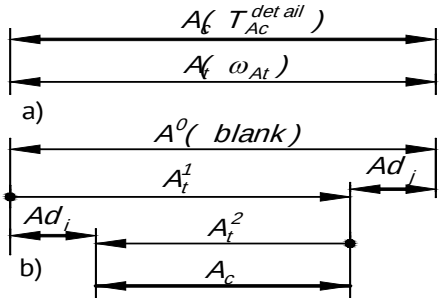

Figure 4. The constructive size is formed through: a) the only one technological size, $T_{A_c}^{det\,ail} = \omega_{A_t}$; b) when machining with the removal of machining allowances Ad, the constructive size is the result of alternating a series of own technological sizes.

The optimality of the above described option in Figure 3 a may be violated, since the locally optimal size A_t may enter as a historical one into another dimensional chain. It will require an increase in its precision and, as a result, a forced increase in the precision of its own designing size A_c. Thus, the third principle (direction) of designing optimization and, consequently, technological processes can be formulated as follows. *The optimal is the dimensional structure, in which each design dimension is formed only by its own technological dimensions*.

Any pair of technological sizes is formed due to the removal of the machining allowance, the goal being an increase in the precision of a certain technological size (Figure 6). The machining allowance in this case is the closing size of the dimensional chain. If both technological dimensions are formed from the same locating datum surface, then the machining allowance tolerance is defined as $\omega_{Ad_i} = \omega_{A_t^{i-1}} + \omega_{A_t^i}$.

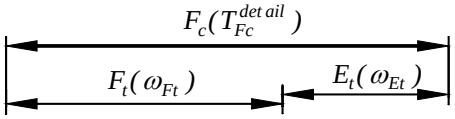

Figure 5. The constructive size is formed through the own technological size and another technological (historical) size.

If there is a change of locating datum surfaces, then the tolerance of the machining allowance increases by the tolerance of the distance between the accepted locating datum surfaces, $\omega_{Ad_i} = \omega_{A_t^{i-1}} + \omega_{A_t^i} + \Delta_{LDS}$.

An increase in the maximum machining allowance ($Ad_{\max} = Ad_{\min} + \omega_{Ad}$) is equivalent to an increase in the depth of cut and the need to increase the number of operation elements. The large depths of cut are especially unacceptable in terms of the use High Speed Machining concept.

From this the fourth principle (direction) of designing optimization and, consequently, technological processes can be formulated as follows. *The number of links in the technological dimensional chain, in which the machining allowance is the closing link, should be, if possible, equal to 3 (the size on the previous operation element, the size on the given operation element and the intermediate size between them - the machining allowance)* $\sum m_j = 3$. This is, in fact, a different formulation of the principle of unity of locating datum. The optimal technological process will consist of similar elementary technological blocks. At the same time, the locating datum must coincide with the designing and measurement datum surfaces.

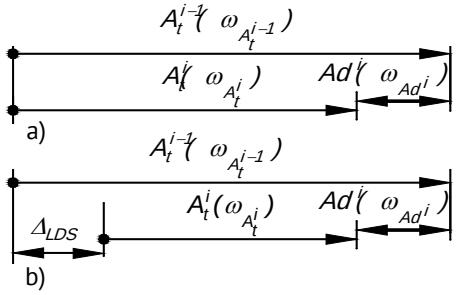

Figure 6. Target transformation of the technological size by removing the machining allowances: a) from only one locating datum surface; b) with the change of locating datum surfaces.

Note that the removal of the machining allowance in order to increase the precision of one technological size leads to a decrease in the precision of all other technological sizes associated with the machined surface (Figure 7). Non-target sizes (R_t^i), in this case, are closing in dimensional chains and their tolerance is increased by the tolerance of the machining allowance to be removed ($\omega_{A_t^i} = \omega_{A_t^{i-1}} + \omega_{Ad_i}$). The size takes on an intermediate value $R_t^{i\,int}$ and subsequently as a target size will be brought to the required precision [5].

The labor intensity of the technological processes is associated with the removal of machining allowances from the surfaces. And this is the time spent by technological systems, operators, tool consumption etc. The fifth principle (direction) of designing optimization and, consequently, technological processes can be formulated as follows. *The sum (volume sum) of the maximum machining allowances (*$Ad_{k\,max} = Ad_{k\,min} + \omega_{Ad_k}$*) removed from all surfaces of the part should be minimal (*$\sum Ad_k \to min$*) and each maximum machining allowance should not exceed the value allowed to achieve precision,* $Ad_{k\,max} \le [Ad_k]$.

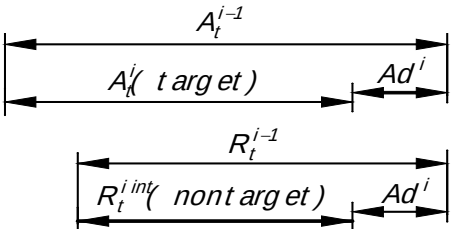

Figure 7. Non-target formed size.

The detail subjected to machining, is characterized by constructive dimensional structure which reflect, eventually, its functionality. The nature of the constructive dimensional structure is defined by the designer who takes into account the technological features of machine tools, but not in detriment of their functionality. The technological dimensional structure should ensure the formation of the dimensional structure of the part with restrictions imposed by the features of the dimensional structures of technological systems. This is optimally achieved if the designing and technological dimension structures are the same, so that each design dimension is formed exclusively by its own technological dimension [4].

The sixth principle (direction) of designing optimization and, consequently, technological processes can be formulated as follows. *The optimality of technological processes is achieved at the similarity of the technological and constructive dimensional links graphs* [4].

The technological system has its own possibilities for the formation of dimensional structures. The CNC machine-tools and machining centers are being programmed to form epy

dimensional structures in absolute and relative coordinates (Figure 8). Additional features are associated with the ability to use the floating zeros. In technological terms, this is the possibility of successive change of locating datum surfaces (locating datum - LD, adjustment datum - AD). The optimal technological dimensional structure in terms of similarity with the designing dimensional structure often must be adapted to the capabilities of the technological system. This can be done by recalculating the designing sizes so that the new designing dimension structure is equivalent to the original. The central problem of technological design optimization is the allocation of tolerances for technological sizes [6,7].

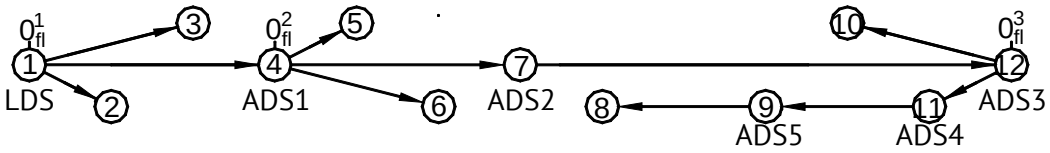

Figure 8. Formation of a dimensional structure on CNC machine-tools.

3. Adapting dimensional structures to the capabilities of CNC machine-tools

Below several variants of combinations of constructive and technological dimensional structures are analyzed. The dimensional chains have been solved at the machining the front surfaces 1, 2, 3 and 4 with the positioning coordinates in relation to surface 0 respectively at 200, 150, 100 and 50 mm in the dimensioning variants according to Figures 9, 11, 13, 15. For forming the constructive sizes A_c, B_c, C_c and E_c all end surfaces (1, - 4) are machined twice, first on the 13th grade, and then on the 11th grade. The cast blank is made with dimensional tolerances corresponding to 16th grade. Depending on the specific variant, each constructive size is formed either only by its own technological size or by its own technological size and other situational size. The need to improve the precision of technological sizes in comparison with the 13th grade for the first stage of machining and the 11th grade at the second stage of machining is analyzed. The number of tolerance units is used as a measure.

The tolerance values of the machining allowances removed at the first and second stages of machining are also analyzed. This is important because the depth of cut is assumed to be equal to the maximum machining allowance, $Ad_{max} = Ad_{min} + \omega_{Ad}$.

The analysis were performed using the worst-case method and worst-case method with error's compensation methods [8,9].

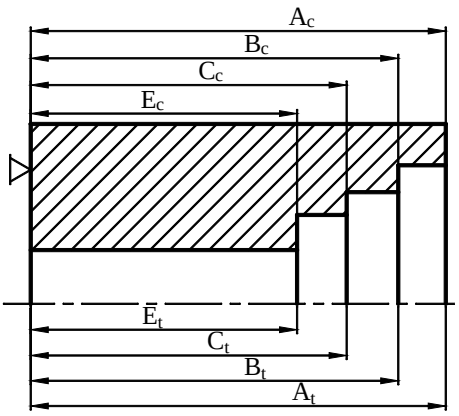

Figure 9. Dimensional constructive and technological structures (variant 1).

Variant 1, (Figure 9). The all constructive sizes are given from constructive base - surface 0 and the technological sizes are formed also from locating datum surface (LDS) – the same surface 0.

From the graphs of dimensional links (Figure 10 b, c) it's clear that the conditions for ensuring the size's precision are optimal because the precision of technological sizes is not greater than precision of constructive sizes:

$$\omega_{A_t^1} \le \omega_{A_c^1},\ \omega_{B_t^1} \le \omega_{B_c^1},\ \omega_{C_t^1} \le \omega_{C_c^1},\ \omega_{E_t^1} \le \omega_{E_c^1},$$
$$\omega_{A_t^2} \le \omega_{A_c^2},\ \omega_{B_t^2} \le \omega_{B_c^2},\ \omega_{C_t^2} \le \omega_{C_c^2},\ \omega_{E_t^2} \le \omega_{E_c^2}. \quad (1)$$

After the first stage of machining the tolerances of machining allowances for surfaces 1, 2, 3 and 4 should be determined as (Figure 10 d):

$$\omega_{Ad_1^1} = (\omega_{A_t^1} + \omega_{A_t^0}), \qquad \omega_{Ad_2^1} = (\omega_{B_t^1} + \omega_{B_t^0}),$$
$$\omega_{Ad_3^1} = (\omega_{C_t^1} + \omega_{C_t^0}), \qquad \omega_{Ad_4^1} = (\omega_{E_t^1} + \omega_{E_t^0}). \tag{2}$$

Here and below the sizes A_t^0 ,B_t^0 ,C_t^0 and E_t^0 are the dimensions of the blank.

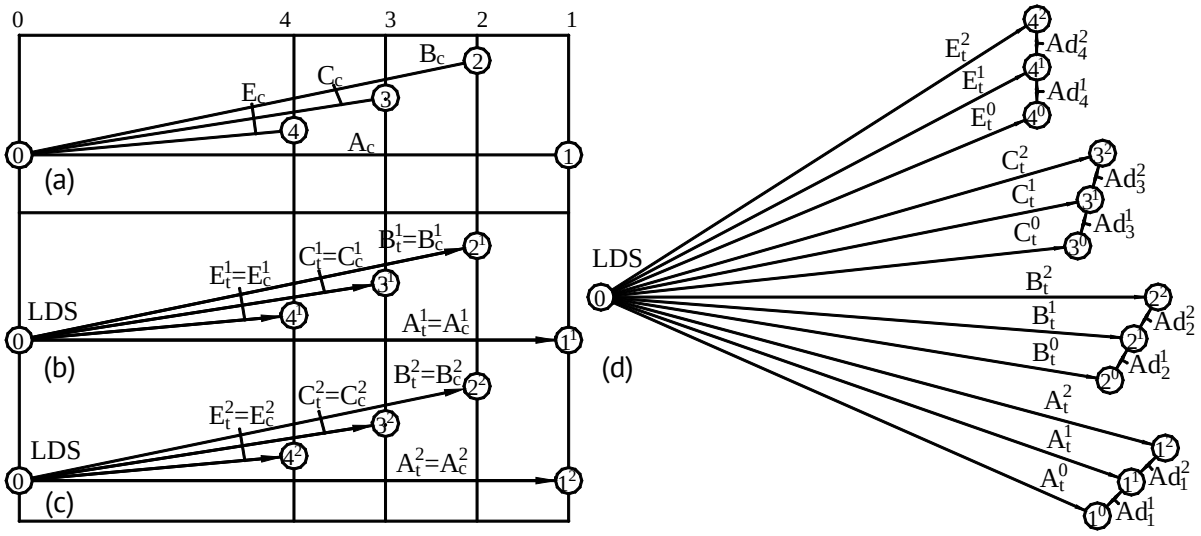

Figure 10. The graphs of dimensional links for: constructive sizes (a), technological sizes (b, c) and machining allowances (d) [10,11].

It can be seen that at the second stage of machining, the effect of error's compensating between the two succesive technological sizes formed by machining is manifested (Figure 10 d):

$$\omega_{Ad_1^2} = (\omega_{A_t^2} + \omega_{A_t^1}) - 2 \cdot \omega_{1^2 1^1}^{comp}, \qquad \omega_{Ad_2^2} = (\omega_{B_t^2} + \omega_{B_t^1}) - 2 \cdot \omega_{2^2 2^1}^{comp},$$
$$\omega_{Ad_3^2} = (\omega_{C_t^2} + \omega_{C_t^1}) - 2 \cdot \omega_{3^2 3^1}^{comp}, \qquad \omega_{Ad_4^2} = (\omega_{E_t^2} + \omega_{E_t^1}) - 2 \cdot \omega_{4^2 4^1}^{comp}. \tag{3}$$

It can be seen that there are not situations with fairly high values of the machining allowance's tolerances (greater than 3.62), consequently with fairly high values of the machining allowances (Table 1). The machining strategy according to Figures 9 and 10 is optimal.

Table 1

Variant 1. The values of machining allowance's tolerances

Stage	Machined surfaces							
	1	2	3	4	1	2	3	4
	Worst-case tolerances				Worst-case tolerances with error's compensation			
Ad^1	3.62	3.13	2.74	1.99	3.62	3.13	2.74	1.99
Ad^2	1.01	0.88	0.76	0.58	0.43	0.38	0.32	0.20

Variant 2 (Figure 11). One of constructive sizes is given from constructive base - surface 0 and the rest of the sizes are given from other constructive base - surface 4. The machining is realized by technological sizes formed exclusive from locating datum surface 0 (LDS).

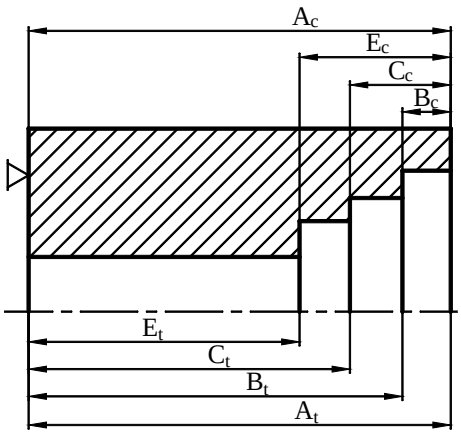

Figure 11. Dimensional constructive and technological structures (variant 2)

From the graphs of dimensional links (Figure 14, b, c) it's seen that the conditions for ensuring the size's precision are not optimal because the accuracies of technological sizes B_t, C_t and E_t are greater than the precision of respective constructive sizes (table 2).

From Figure 12 d should be that the dimension links for the machining allowances of surfaces 2, 3 and 4 include as constituent elements the machining allowances of surface 1 (Ad_1^1 or Ad_1^2). The tolerances of machining allowances for surfaces 1, 2, 3 and 4 after first stage of machining can be determined as:

$$\begin{aligned}
&\omega_{A_t^1} \le \omega_{A_c^1}, && \omega_{B_t^1} \le \omega_{B_c^1} - \omega_{A_t^1} + 2\cdot\omega_{1^1 2^1}^{comp},\\
&\omega_{C_t^1} \le \omega_{C_c^1} - \omega_{A_t^1} + 2\cdot\omega_{1^1 3^1}^{comp}, && \omega_{E_t^1} \le \omega_{E_c^1} - \omega_{A_t^1} + 2\cdot\omega_{1^1 4^1}^{comp},\\
&\omega_{A_t^2} \le \omega_{A_c^2}, && \omega_{B_t^2} \le \omega_{B_c^2} - \omega_{A_t^2} + 2\cdot\omega_{1^2 2^2}^{comp},\\
&\omega_{C_t^2} \le \omega_{C_c^2} - \omega_{A_t^2} + 2\cdot\omega_{1^2 3^2}^{comp}, && \omega_{E_t^2} \le \omega_{E_c^2} - \omega_{A_t^2} + 2\cdot\omega_{1^2 4^2}^{comp}.
\end{aligned} \tag{7}$$

$$\begin{aligned}
&\omega_{Ad_1^1} = (\omega_{A_t^1} + \omega_{A_t^0}),\\
&\omega_{Ad_2^1} = (\omega_{B_t^1} + \omega_{B_t^0}) + (\omega_{A_t^1} + \omega_{A_t^0}),\\
&\omega_{Ad_3^1} = (\omega_{C_t^1} + \omega_{C_t^0}) + (\omega_{A_t^1} + \omega_{A_t^0}),\\
&\omega_{Ad_4^1} = (\omega_{E_t^1} + \omega_{E_t^0}) + (\omega_{A_t^1} + \omega_{A_t^0})
\end{aligned} \tag{8}$$

Table 2

Variant 2. The measure of the growth of the precision of technological sizes

Stage	A_c, B_c, C_c, E_c	Worst-case method				Worst-case method with error's compensation			
		A_t	B_t	C_t	E_t	A_t	B_t	C_t	E_t
	Number of tolerance units, a; precision grade								
1	250; 13	72; 10 - 11	72; 10 - 11	153; 12	250; 13	81; 10 - 11	81; 10 - 11	184; 12 - 13	330; >13
2	100; 11	35; <9	35; <9	55; 9 - 10	95; 11	39; 9	39; 9	64; 10	114; >11

After the second stage of machining the situation is a similar, except that the phenomenon of error's compensation is manifested:

$$\begin{aligned}
\omega_{Ad_1^2} &= (\omega_{A_t^2} + \omega_{A_t^1}) - 2 \cdot \omega_{1^1 1^2}^{comp}, \\
\omega_{Ad_2^2} &= (\omega_{B_t^2} + \omega_{B_t^1}) - 2 \cdot \omega_{2^1 2^2}^{comp} + (\omega_{A_t^2} + \omega_{A_t^1}) - 2 \cdot \omega_{1^1 1^2}^{comp}, \\
\omega_{Ad_3^2} &= (\omega_{C_t^2} + \omega_{C_t^1}) - 2 \cdot \omega_{3^1 3^2}^{comp} + (\omega_{A_t^2} + \omega_{A_t^1}) - 2 \cdot \omega_{1^1 1^2}^{comp}, \\
\omega_{Ad_4^2} &= (\omega_{E_t^2} + \omega_{E_t^1}) - 2 \cdot \omega_{4^1 4^2}^{comp} + (\omega_{A_t^2} + \omega_{A_t^1}) - 2 \cdot \omega_{1^1 1^2}^{comp}.
\end{aligned} \tag{9}$$

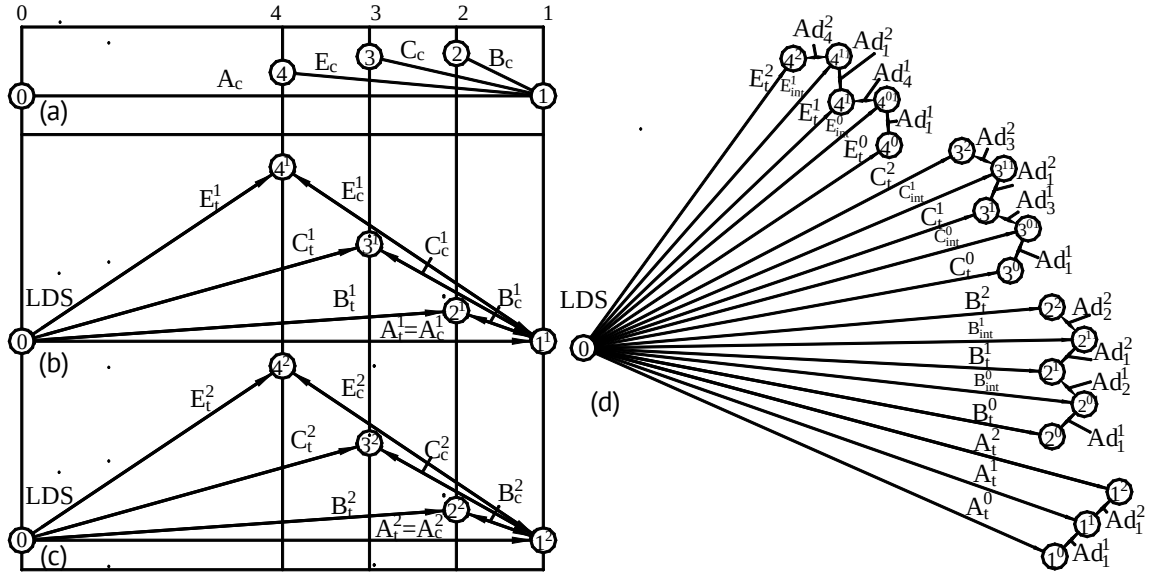

Figure 12. Example of the graphs of dimensional links for: constructive sizes (a), technological sizes (b, c) and machining allowances (d) [10].

Table 3

Variant 2. The values of machining allowance's tolerances

Stage	Machined surfaces							
	1	2	3	4	1	2	3	4
	Worst-case tolerances				Worst-Case tolerances with error's compensation			
Ad^1	3,62	6,75	6,36	5,61	3,62	6,75	6,36	5,61
Ad^2	1,01	1,89	1,77	1,59	0,43	0,81	0,75	0,63

$$\begin{aligned}
&\omega_{A_t^1} \le \omega_{A_c^1}, && \omega_{B_t^1} \le \omega_{B_c^1} - \omega_{A_t^1} + 2 \cdot \omega_{1^1 2^1}^{comp}, \\
&\omega_{C_t^1} \le \omega_{C_c^1} - \omega_{B_t^1} + 2 \cdot \omega_{2^2 3^1}^{comp}, && \omega_{E_t^1} \le \omega_{E_c^1} - \omega_{C_t^1} + 2 \cdot \omega_{3^1 4^1}^{comp}, \\
&\omega_{A_t^2} \le \omega_{A_c^2}, && \omega_{B_t^2} \le \omega_{B_c^2} - \omega_{A_t^2} + 2 \cdot \omega_{1^2 2^2}^{comp}, \\
&\omega_{C_t^2} \le \omega_{C_c^2} - \omega_{B_t^2} + 2 \cdot \omega_{2^2 3^2}^{comp}, && \omega_{E_t^2} \le \omega_{E_c^2} - \omega_{C_t^2} + 2 \cdot \omega_{3^2 4^2}^{comp}.
\end{aligned} \tag{10}$$

It can be observe that there are many situations with fairly high values of the machining allowance's tolerances (greater than 3,62), consequently with fairly high values of the machining allowances (Table 3).

Variant 3 (Figure 13). One of constructive sizes is given from constructive base - surface 0 and the rest of the sizes are given in chain from the surface 4. The machining is realized by technological sizes from locating datum surfaces 0 (LDS).

From the graphs of dimensional links (Figure 14, b, c) it's seen that the conditions for ensuring the size's precision are not optimal because the accuracies of technological sizes B_t, C_t and E_t are greater than the precision of respective constructive sizes:

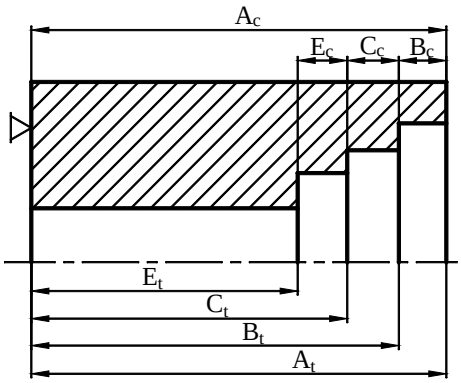

Figure 13. Dimensional constructive and technological structures (variant 3)

Table 4

Variant 3. The measure of the growth of the precision of technological sizes

Stage	A_c, B_c, C_c, E_c	Worst-case method				Worst-case method with error's compensation			
		A_t	B_t	C_t	E_t	A_t	B_t	C_t	E_t
	Number of tolerance units, a; precision grade								
1	250; 13	72; 10 - 11	72; 10 - 11	96; 11	116; 11 - 12	81; 10 - 11	81; 10 - 11	140; 11 - 12	130; 11 - 12
2	100; 11	35; <9	35; <9	47; 9 - 10	57; 9 - 10	39; 9	39; 9	68; 10	63; 10

From Figure 14 d should be that the dimension links for the machining allowances of surfaces 2, 3 and 4 include as constituent elements the machining allowances of previous machined surface. The tolerances of machining allowances for surfaces 1, 2, 3 and 4 after first stage of machining can be determined as:

$$\begin{aligned} &\omega_{Ad_1^1} = (\omega_{A_t^1} + \omega_{A_t^0}), && \omega_{Ad_2^1} = (\omega_{B_t^1} + \omega_{B_t^0}) + (\omega_{A_t^1} + \omega_{A_t^0}), \\ &\omega_{Ad_3^1} = (\omega_{C_t^1} + \omega_{C_t^0}) + (\omega_{B_t^1} + \omega_{B_t^0}), && \omega_{Ad_4^1} = (\omega_{E_t^1} + \omega_{E_t^0}) + (\omega_{C_t^1} + \omega_{C_t^0}). \end{aligned} \quad (11)$$

After the second stage of machining the situation is a similar, except that the phenomenon of error's compensation is manifested:

$$\begin{aligned} \omega_{Ad_1^2} &= (\omega_{A_t^2} + \omega_{A_t^1}) - 2 \cdot \omega_{1^1 1^2}^{comp}, \\ \omega_{Ad_2^2} &= (\omega_{B_t^2} + \omega_{B_t^1}) - 2 \cdot \omega_{2^1 2^2}^{comp} + (\omega_{A_t^2} + \omega_{A_t^1}) - 2 \cdot \omega_{1^1 1^2}^{comp}, \\ \omega_{Ad_3^2} &= (\omega_{C_t^2} + \omega_{C_t^1}) - 2 \cdot \omega_{3^1 3^2}^{comp} + (\omega_{B_t^2} + \omega_{B_t^1}) - 2 \cdot \omega_{2^1 2^2}^{comp}, \\ \omega_{Ad_4^2} &= (\omega_{E_t^2} + \omega_{E_t^1}) - 2 \cdot \omega_{4^1 4^2}^{comp} + (\omega_{C_t^2} + \omega_{C_t^1}) - 2 \cdot \omega_{3^1 3^2}^{comp} \end{aligned} \quad (12)$$

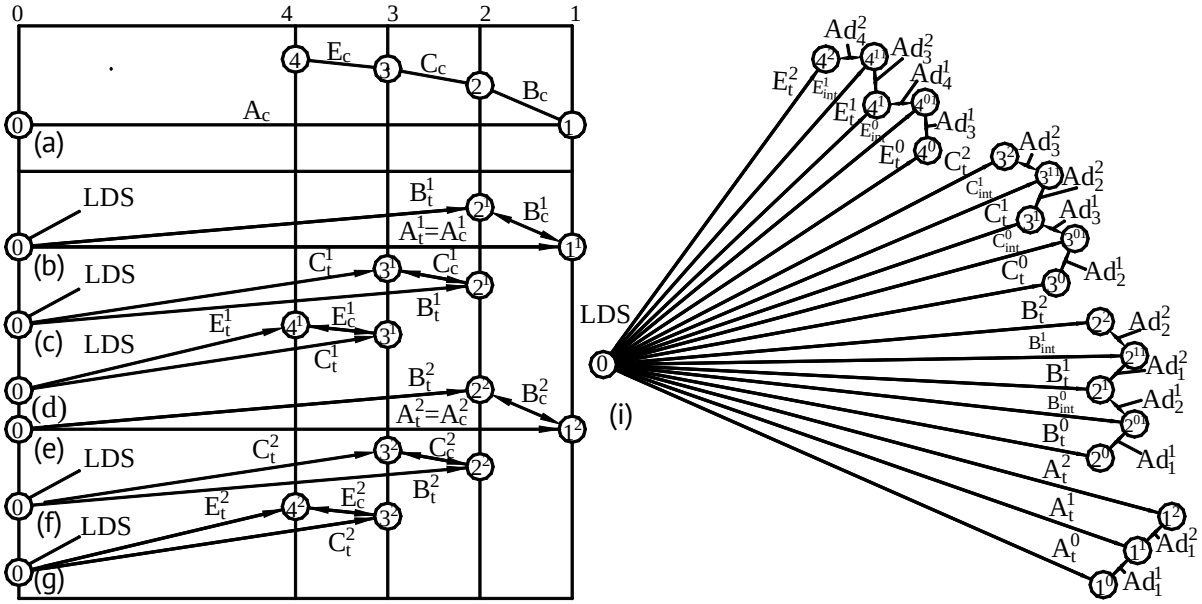

Figure 14. Example of the graphs of dimensional links for: constructive sizes (a), technological sizes (b, c, d, e, f, g) and machining allowances (i) [10].

Table 5

Variant 3. The values of machining allowance's tolerances

Stage	Machined surfaces							
	1	2	3	4	1	2	3	4
	Worst-case tolerances, mm				Worst-Case tolerances with error's compensation, mm			
Ad^1	3.62	6.75	5.87	4.73	3.62	6.75	5.87	4.73
Ad^2	1.01	1.89	1.64	1.34	0.43	0.81	0.70	0.52

It can be observed (Table 5) that there are many situations with fairly high values of the machining allowance's tolerances (greater than 3.62), consequently with fairly high values of the machining allowances.

Variant 4 (Figure 15). One of constructive sizes is given from constructive base - surface 0 and the rest of the sizes are given in chain from the surfaces 1, 2 and 3. The machining is realized by technological sizes formed from locating datum surface 0 (LDS) and in chain from adjustment datum surfaces 1, 2, 3 (ADS1, ADS2, ADS3).

From the graphs of dimensional links (Figure 16 b, c) it's seen that the conditions for ensuring the size's precision are optimal because the precision of technological sizes is not greater than precision of constructive sizes:

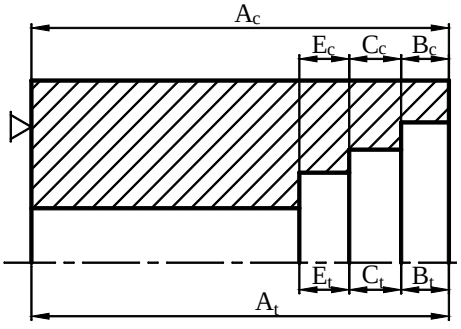

Figure 15. Dimensional constructive and technological structures (variant 4).

$$\begin{aligned} &\omega_{A_t^1} \le \omega_{A_c^1}, \quad \omega_{B_t^1} \le \omega_{B_c^1}, \quad \omega_{C_t^1} \le \omega_{C_c^1}, \quad \omega_{E_t^1} \le \omega_{E_c^1}, \\ &\omega_{A_t^2} \le \omega_{A_c^2}, \quad \omega_{B_t^2} \le \omega_{B_c^2}, \quad \omega_{C_t^2} \le \omega_{C_c^2}, \quad \omega_{E_t^2} \le \omega_{E_c^2}. \end{aligned} \tag{13}$$

From figure 16 d should be that the dimension links for the machining allowances of surfaces 2, 3 and 4 include as constituent elements the all machining allowances of previous machined surface. The tolerances of machining allowances for surfaces 1, 2, 3 and 4 after first stage of machining can be determined as [10]:

$$\begin{aligned} &\omega_{Ad_1^1} = (\omega_{A_t^1} + \omega_{A_t^0}), \qquad \omega_{Ad_2^1} = (\omega_{B_t^1} + \omega_{B_t^0}) + (\omega_{A_t^1} + \omega_{A_t^0}), \\ &\omega_{Ad_3^1} = (\omega_{C_t^1} + \omega_{C_t^0}) + (\omega_{B_t^1} + \omega_{B_t^0}) + (\omega_{A_t^1} + \omega_{A_t^0}), \\ &\omega_{Ad_4^1} = (\omega_{E_t^1} + \omega_{E_t^0}) + (\omega_{C_t^1} + \omega_{C_t^0}) + (\omega_{B_t^1} + \omega_{B_t^0}) + (\omega_{A_t^1} + \omega_{A_t^0}). \end{aligned} \tag{14}$$

After the second stage of machining the situation is a similar, but with the manifestation of the phenomenon of error's compensation:

$$\begin{aligned} &\omega_{Ad_1^2} = (\omega_{A_t^2} + \omega_{A_t^1}) - 2 \cdot \omega_{1^1 1^2}^{comp}, \\ &\omega_{Ad_2^2} = (\omega_{B_t^2} + \omega_{B_t^1}) - 2 \cdot \omega_{2^1 2^2}^{comp} + (\omega_{A_t^2} + \omega_{A_t^1}) - 2 \cdot \omega_{1^1 1^2}^{comp}, \\ &\omega_{Ad_3^2} = (\omega_{C_t^2} + \omega_{C_t^1}) - 2 \cdot \omega_{3^1 3^2}^{comp} + (\omega_{B_t^2} + \omega_{B_t^1}) - 2 \cdot \omega_{2^1 2^2}^{comp} + \\ &\quad + (\omega_{A_t^2} + \omega_{A_t^1}) - 2 \cdot \omega_{1^1 1^2}^{comp}, \\ &\omega_{Ad_4^2} = (\omega_{E_t^2} + \omega_{E_t^1}) - 2 \cdot \omega_{4^1 4^2}^{comp} + (\omega_{C_t^2} + \omega_{C_t^1}) - 2 \cdot \omega_{3^1 3^2}^{comp} + \\ &\quad + (\omega_{B_t^2} + \omega_{B_t^1}) - 2 \cdot \omega_{2^1 2^2}^{comp} + (\omega_{A_t^2} + \omega_{A_t^1}) - 2 \cdot \omega_{1^1 1^2}^{comp} \end{aligned} \tag{15}$$

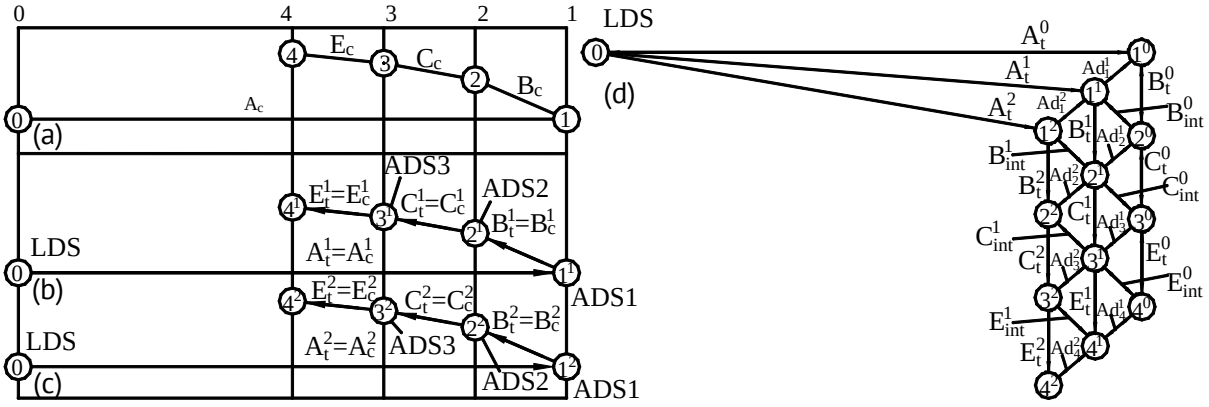

Figure 16. Example of the graphs of dimensional links for: constructive sizes (a), technological sizes (b, c) and machining allowances (d) [10,11].

Table 6

Variant 4. The values of machining allowance's tolerances

Stage	Machined surfaces							
	1	2	3	4	1	2	3	4
	Worst-case tolerances, mm				Worst-Case tolerances with error's compensation, mm			
Ad^1	3.62	5.61	7.60	9.59	3.62	5.61	7.60	9.59
Ad^2	1.01	1.65	2.26	2.84	0.43	0.57	0.74	0.94

It can be observe that there are many situations with fairly high values of the machining allowance's tolerances (greater than 3.62), consequently with fairly high values of the machining allowances (Table 6).

4. Conclusions

1. Modern trends in technological development are related to the increasing use of numerically controlled machine tools. This is reflected in the fact that the number of technological operations, the number of installations and the number of operation elements throughout the entire technological process should be kept to a minimum.
2. The reduction of product series implies higher requirements for the robustness of technologies designed in such a way that the worst case scenario is taken into account - the Worst-Case tolerancing method. So, the sum of the tolerances of technological sizes that make up the links in the chain of the closing designing size must not exceed the tolerance of this size.
3. One of the most effective ways to improve the design of mechanical processing technologies is the creation of optimal technological dimensional structures, which are based on optimal primary structural elements such as: a) the optimal is the dimensional structure, in which each design dimension is formed only by its own technological dimensions; b) the number of links in the technological dimensional chain, in which the machining allowance is the closing link, should be, if possible, equal to 3 (the size on the previous operation element, the size on the given operation element and the intermediate size between them - the machining allowance).
4. The optimality of technological processes is achieved at the similarity of the technological and constructive dimensional links graphs.
5. Real constructive dimensional structures are very complex and varied, so that the optimality of some sequences of the structure excludes ensuring the optimality of other sequences. Reciprocal structural adaptations are necessary.
6. The machining allowance is an indispensable element of the technological dimensional links and, in addition to the geometric character (value, tolerance), it also has the role of cutting depth, which is limiting for machining precision and for consumptions. So, each maximum machining allowance should not exceed the value allowed to achieve precision and the sum (volume sum) of the maximum machining allowances removed from all surfaces of the part should be minimal.

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Conflicts of Interest: The author declares no conflict of interest.

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EVALUATION AND MEASUREMENT OF TECHNOLOGICAL FUNCTIONS

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Abstract. Technological transfer is an important factor of technological development and requires assessment and measurement of effects. Evaluation and measurement can be done with the use of models, the most important being the model of the technology, i.e. of the object being transferred. In the paper, a version of technological function's model is developed, starting from the models of interaction, establishing links, choosing the mechanism and forming the interaction interface, forming the technological function by modifying the internal functions of the objects in interaction and modifying the properties them. The modifications of the properties of the object subjected to the action, of the object carrying technological tasks and of the object-interface serves as the basis for the evaluation and measurement of the technological function in all its complexity. It is shown that technological task bearers can be of two categories: physical-technical (materials, energy, processes, etc.) and immaterial (theories, concepts, data, knowledge, etc.). Both the mechanisms and the measure of manifestation of the technological functions for the two categories are different.

Keywords: *technological function, internal function, property, interaction, link, interface, physical-technical object, immaterial object, carrier of technological task.*

Rezumat. Transferul tehnologic este un factor important al dezvoltării tehnologice şi necesită evaluare şi măsurare a efectelor. Evaluarea şi măsurarea se pot realiza cu utilizarea de modele, cel mai importat fiind modelul tehnologiei, adică al obiectului ce se transferă. În lucrare este dezvoltată o versiune de model al funcţiei tehnologice, pornind de la modelele de interacţionare, de stabilire a legăturilor, de alegere a mecanismului şi formării interfeţei interacţiunii, de formare a funcţiei tehnologice prin modificarea funcţiilor interne ale obiectelor în interacţiune şi de modificare a proprietăţilor acestora. Modificarea proprietăţilor obiectului supus acţiunii, obiectului purtător de sarcini tehnologice şi a obiectului-interfaţă serveşte ca bază pentru evaluarea şi măsurarea funcţiei tehnologice în toată complexitatea sa. Este arătat că purtătorii de sarcini tehnologice pot fi de două categorii: fizico-tehnici (materiale, energetice, procese etc.) şi imateriali (teorii, concepte, date, cunoştinţe etc.). Atât mecanismele cât şi măsura manifestării funcţiilor tehnologice pentru cele două categorii sunt diferite.

Cuvinte cheie: *funcţie tehnologică, funcţie interioară, proprietate, interacţiune, legătura, interfaţă, obiect fizico-tehnic, obiect imaterial, purtător de sarcină tehnologică.*

1. Introduction

Technological transfer is an important aspect of technological development. It is often treated as an act of using a newly acquired technology, from which some positive results are expected. It is true that in many cases this approach manifests itself positively, but for short periods of time. The reality is more complex, because the sources of modern technologies increasingly represent not only physical-technical systems, but especially physical-technical-informational systems. Without knowing well what a technology represents, what are the sources and carriers of technology, how a source, a carrier of technology is manifested, it is difficult to carry out the assessment, especially based on measurement [1,2].

Technology and technology models. The term technology comes from the Greek language (tekhnë - craft, art and logos - word) with the initial meaning of "discourse on crafts, arts", being currently treated as "the sum of techniques, skills, methods and processes used in the production of goods or services or in achieving objectives, such as scientific research" [3]. In some works technology is treated as the totality of tools, machines, systems and processes used in practical activities and in engineering [4,5]. It is observed that the mentioned totality includes components of different origins (artifacts and processes), a fact that generates certain problems of perception. It goes without saying, however, that all components are interacting processes.

Technologies are process entities intended to reproduce artificial functions [6]. In this statement, the key words are "artificial functions", thus emphasizing the human role in selecting the process and its implementation. "The artificial" shows that the entities are either created by man, or are natural but are used differently than "natural". "Function" refers to how things are used.

The relationship between technology and applied research is one of asymmetrical reciprocity. Technology is not limited to applied sciences, because knowing how to reproduce a useful effect does not mean knowing how and why this effect is produced [6]. This distinction leads to the definition of technology in terms of artificial functions, which generate the necessary results. Often, based on observation and knowledge, the functions are artificially reproduced and understanding is not mandatory. At the same time, understanding serves as an active and organizational element for the next step in technological development.

Technological development activities are amplified by the need to solve certain problems. The observation, knowledge, understanding, research focus on the problem to obtain a predetermined result. Thus, technologies are process entities resulting from solving problems, which produce transformations and changes based on a preconceived idea, a plan or a project to give rise to the desired artificial functions [6].

The evaluation, in general, and the evaluation of technologies is done with the use of models, which reflect a connection between inputs and outputs, between cause and effect. Namely, the models make possible a structured understanding of the technologies and their effects.

Sharif N. [7] structured technology into four tools or forms of technology: technical (technoware), human (humanware), informational (infoware) and organizational (orgware). The technical form of technology (technoware) includes facilities in the form of capital resources, products, machines, machine-tools, robots, transport and storage units, physical equipment, tools, physical-technical processes, etc. The human form of technology (humanware) includes skills of understanding, applying knowledge, know-how, solving

problems, working in design, manufacturing, organizing, managing, etc. The informational form (infoware) is the form of technology incorporated through open or coded records about physical, technical, scientific relationships and principles, about standards, technical information, computer programs, etc. The organizational form of technology (orgware) is the form of technology that contains techniques for organizing work and processes, techniques for using, maintaining and controlling manufacturing factors.

The Sharif model is simple and clear, but it emphasizes components, tools, aspects, which makes them, in a way, static. It is important that these tools are effectively used [7], which can be achieved by considering them as correlated processes.

The evaluation of transfer technologies must be based on quantities that can be clearly identified, measured, and compared. In this sense, the notion of ownership is very attractive. In the field of machine building, to design and manufacture, is worked with many properties of the objects. For example, materials are characterized by properties classified into: physical, chemical, mechanical, technological, thermal, optical, electrical, magnetic, radiological, toxic hygienic-sanitary, etc. [8-11]. In the transfer process, the notion of property of the technology becomes a fundamental one, because the property is the vizible cause of the initiation of the transfer, it is also the main element for evaluation and measurement.

2. Properties of objects and their manifestation

In any object there is something "for itself" (the object in itself), something that is found within its limits (of the object) and does not depend on anything else. Simultaneously, in any object there is something "for someone else" (object for another object), something that is conditioned exclusively in relation to something else [11]. The property is not only an external manifestation, but also a unity of appearance and essentiality, being a messenger to the outside about the internal quality [12]. Thus, the property is born inside the quality of the object, in the sphere of its essence, and the genotype of the property is determined by the totality of all internal links.

According to [12] the property represents a moment of the own qualitative determinability of an object, which through the interaction with another object detaches from its own foundation, penetrates into that other object, acquires in it and through it visibility and already exists on a foreign basis, on a foreign carrier (Figure 1,a).

The interaction is reciprocal, so that in the eyes of the analyst both the property of the object A in the base B (Pr_B^A) and the property of the object B in the base A (Pr_A^B) are manifested. The interaction is, as a rule, multiple, it occurs through different physical channels (for example, mechanical force, mechanical friction, thermal, etc.), so the sets of properties of both objects ($\{Pr_B^A\}, \{Pr\,B\}$) are simultaneously manifested and observed. Interactions can occur simultaneously with several objects, so that each couple of objects generates properties, the multitude of the latter becoming very large [14,15]. Moreover, the interaction of object A with the set of objects B, generate interactions within this set with very varied effects for properties (Figure 1,b).

A property is a quality, a potential reflected in an object, it is a quality from the realm of the possible. A possible property is revealed externally in the interaction with another object and through this other object. Interactions are produced by establishing links between objects. Linkage is a way of the presence of one object in another, a means of the existence of different objects in their unity [12].

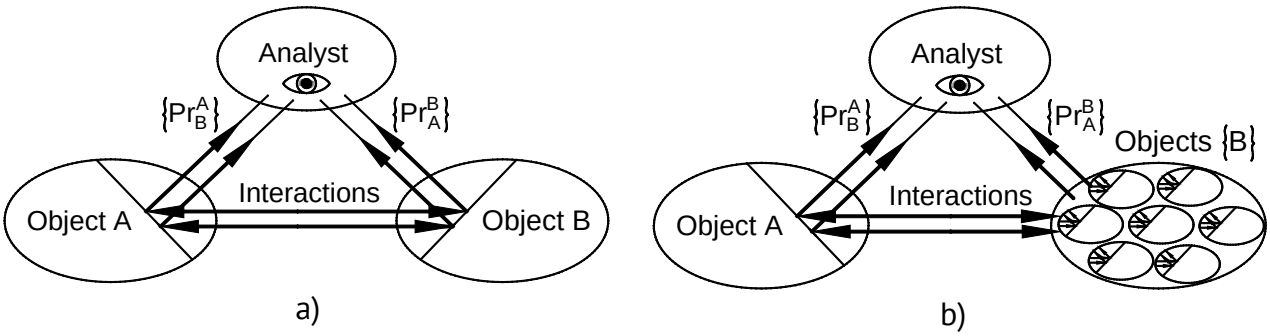

Figure 1. Formation of object's properties in the "mirroring" interaction: a) between objects A and B, b) between object A and the set of objects $\{B\}$.

There are two main types of links (Figure 2): 1) external link through force (energetic) contact of objects with mutual maintenance of the force effect in space and time; 2) the abstracted external link of the internal inherent essences of the objects, such as, for example, the connections "cause - effect", "general - particular", etc. The first type of links has a real character based on physical-technical laws, and the second has a virtual character, representing, in fact, the directions of change and oriented development.

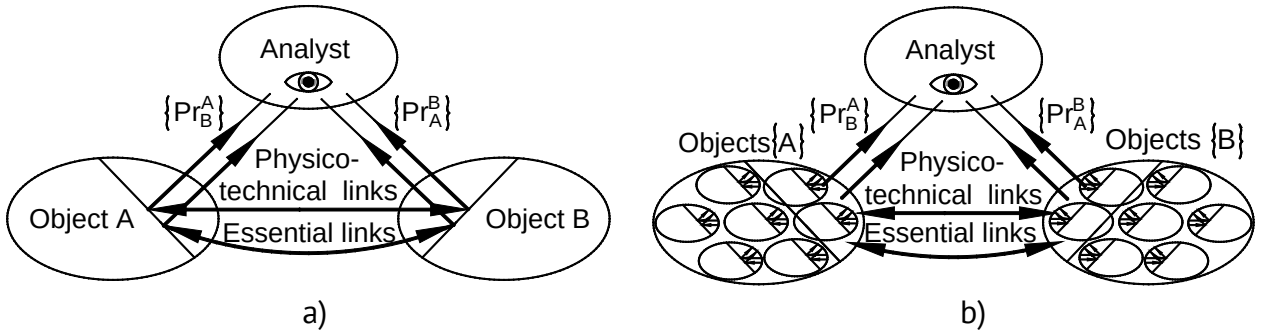

Figure 2. External physical-technical links and abstractized essential links: a) between objects A and B, b) between the sets of objects $\{A\}$ and $\{B\}$.

A link is understood as a mutual action of objects, so that, each of them changing quantitatively in alliance with the other, it nevertheless continues to clearly maintain its qualitative determinability.

Objects manifest their properties in interaction with other objects through the changes that produced. However, only the presence or absence of changes can be observed by comparing what was and what is. Thus, the property can be defined as the inherent ability of the object in certain interactions to produce (not to produce) some changes in another object and/or to change (not to changed) under the influence of other objects [11]. The change or lack of change in its essence is the property. There is no contradiction here, because at least two objects participate in the interaction and for each of them individual criteria and requirements for change or non-change and the measure of these phenomena can be formulated.

The properties can be internal and external [13]. An internal (intrinsic) property is one that the given object has by itself, a priori, independently of other objects. An external (extrinsic or relational) property is one that depends on the given object's connections with other objects.

If an object is something specific, different from what other objects are, then it has other properties. And vice versa, if an object manifests other properties than other objects

manifest, then it is something specific, different from what other objects are. In many cases, the identity of the objects is important. Two objects are identical, they have similar identities if they show the same properties.

It can be said that objects are made up of a nucleus, of an individualized substance, and around the nucleus is formed a cloud of interaction links, a cloud of properties, due to which the object preserves its identity.

Objects exist, interact and manifest through properties over time. Time represents a framework for carrying out interactions, for establishing links, a condition for changes, a measure of the existence of objects, a characteristic of the change of states of objects and their development. As a result, properties are the result of processes quantified over time and, in general, are variable. The state of an object, in this context, is nothing but the multitude of properties manifested by this object in the given amounts of time and space.

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Interaction of objects. The properties of the objects are manifested if there is interaction with the establishment of links, that is, if there is a task of sufficient size (physical and/or informational) capable of producing a state of mutual request [14,15]. As sources of the properties are both objects from the couple. In another couple other properties will be present. The same couple of mutually requested objects in another interaction will manifest other properties. From what has been reported, it follows that the interaction does not represent a source of appearance of the properties of the objects, but only a condition for their manifestation. This condition includes three elements: the presence of the actual interaction as a phenomenon, the selection of the interaction mechanism and the selection of the interaction interface.

The interaction can be defined as a specific material and/or energetic and/or informational impulse produced by one of the objects of the couple and perceived, supported by the other object of the couple. The effect of the perception, of the support of the impulse by the second object is also a reaction impulse perceived and supported by the first object.

The realization of an interaction between the objects of the couple is determined by the manifestation of compatible properties and relevant behaviors of the objects. At the same time, conditions, limitations, quantification of space and time, operating scenarios, compliance with which favors interaction must be specified.

The interaction mechanism qualitatively and quantitatively characterizes the specific impulse, the modes and parameters of the interaction, thus representing the concrete form of the interaction, a variety of the many possible ones.

In machine building, in mechanical engineering, the real interactions have a physical-technical character and are produced based on several physical laws. A physical-technical interaction is realized if a physical effect and an appropriate geometry are selected (for example, the physical effect of rolling the profiles of the teeth of the involute wheels).

Interface of the interaction. The notion of interface is common to the fields of mechanical engineering, systems engineering, and has a universal use, common to everyone.

Each field leaves a specific mark, thus mechanical engineering formulates the interface in several variants [11,14,15]:

- the place of passing the interaction beyond the spatial limits of the object;
- a physical or functional mating relationship between two objects through which the interaction are produced;
- a facilitating means that makes possible the interaction between two objects;
- an intentional relationship of interaction between two objects;
- the place where the properties appear, the means by which the object can be designed to fulfilling certain functional requirements;
- any physical or logical relationship necessary to bring together the boundaries of objects, including the object with its external environment.

At least two objects are simultaneously interacting, both having portions of common borders - interfaces. Each of the objects of the couple has its own portion of the common border, that is, it has its own interface. This one is an approach to define simple interfaces

Another approach considers that the interface is an object in itself, which at the same time unites objects and separates them. Being something separate, the interface is made up of the interacting objects and is complex [11,14,15].

In many cases, the originally intended interaction mechanism is supplemented with derivative mechanisms, so that additional interactions appear, new interfaces appear, possibly other objects are involved in the interaction. Derived interactions can be the reaction result of the mechanism of the intended interaction, they can also be a consequence of the mechanism of an already defined derived interaction. The mechanisms of intentional and derivative interactions and their physical-technical phenomena are all manifested together, so the analyst's task consists in establishing the order of manifestation of the phenomena and the objectivity of the "cause-effect" links of the interactions.

3. Technological function

The interactions between objects can be natural with useful effects or without them, but they can also be initiated, organized, carried out intentionally by humans, being artificial. Namely, these last interactions represent the beginning of any technology. Chronologically, this process includes the following actions: selecting the objects, initiating the interaction, choosing the interaction mechanism, forming the interaction interface, establishing links and observing the properties of the objects.

Once many properties of the objects are known, their degrees of compatibility are also known and this fact represents a potential for interaction. In the context of practical engineering activities, there is the possibility not only to select but also to oriented way create objects with compatible properties for certain interaction mechanisms and formed interfaces, so as to obtain a result, an anticipated effect. In this case, the chronology of actions changes: selection of compatible properties, choice of objects bearing such properties, choice of interaction mechanism and interface, initiation of interaction, establishment of links, observation and recording of anticipated formulated result (properties), verification (testing) of manifested properties.

It should be mentioned that mutual compatibility is necessary for both properties and interfaces. The lack of an element of compatibility leads to the non-formation of the link and the result, the expected effect is not obtained. To satisfy a need, an object with an appropriate set of properties is required. If such an object exists and is available, the need is satisfied.

More frequently, objects have sets of properties that do not satisfy the need, but can be modified oriented way for this purpose. Initially, the technological objective is formulated.

The technological objective represents a state of some (yet unspecified) object, a set of its properties $\{Pr^V\}$ that can be obtained or achieved through action directed at the object (Figure 3). The character of the objective is imaginary, virtual, not yet real, it corresponds to the question "what the?" and does not provide answers to other questions such as "how?" and "from what?" [11].

It is found that there is an object with a set of real initial properties that do not fully correspond to the need, but which can be modified up to the size of the set formulated by the technological objective (Figure 4).

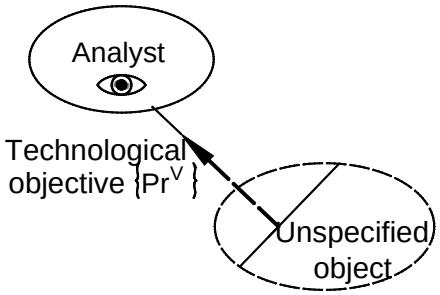

Figure 3. Formulation of the technological objective $\{Pr^V\}$.

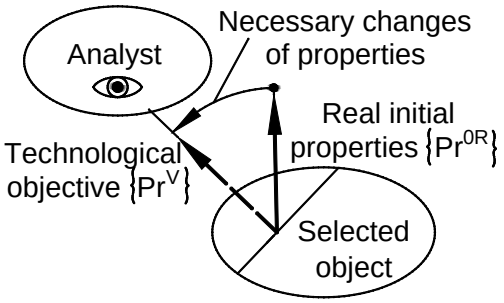

Figure 4. Object with real properties $\{Pr^{0R}\}$ that can be brought to the sizes formulated by the objective $\{Pr^V\}$.

Thus, to the question "from that?" an answer is given. Next is the selection of the method of action on the object to modify its properties. There are several modes of action, but only one is chosen, thus the answer to the question "how?" becomes concrete and unequivocal. The action, in turn, can be performed by several objects carrying technological tasks and follows the choice of only one. Once the actions are defined, the carrier of technological task is chosen, the mechanism and the interface of the actions are chosen, the actions are initiated, the links are established, the changes in the properties are observed and recorded, the real final properties are verified by testing (Figure 5).

The carrier of technological tasks realizes a continuous concretization of the way to modify the properties, is it a transformation system "how?" of entries "from what?" in outputs "what the?" [11]. The carrier of technological tasks has the capacity for the necessary transformations to achieve the objective.

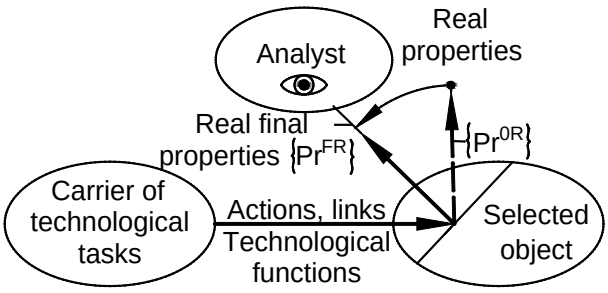

Figure 5. Establishment of technological functions.

When modifying the initial real properties, it must be taken into account that the useful ones must be kept, amplified, highlighted, and the useless ones with a negative influence must be diminished, liquidated, not admitted. The amplification of some properties and the concomitant decrease of other properties is rarely ensured by the same action. The difference between the values of the real initial properties and those formulated by the technological objective is also important. Consequently, the necessary modification of the properties is done through partial technological tasks with the establishment of intermediate objectives (Figure 6).

A technological task represents the difference that must be covered by action between a given real initial state and a virtual, possible, imaginary intermediate or final state [11]. As a result, the modification of properties is done in distinct and non-linear phases, that is, there are no changes only for the "good", there can also be "falls" of properties, which will later be recovered. In some phases, priority is given to actions for "good" properties, and in other phases - actions to combat "bad" properties.

The technological function characterizes the ability of the bearer of technological tasks to carry out the modifications of the initial real properties of an object in its final real properties. Technology, in this context, can be defined as a process structured in space, ordered in time and oriented to change the properties of the object.

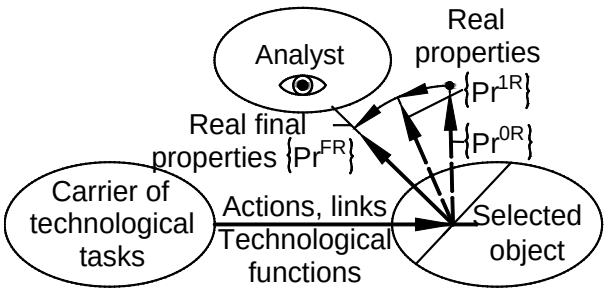

Figure 6. Achieving the objective through partial technological tasks.

For technology, the function resulting from the process is important and not the physical-technical phenomenon used for it. Functions define the essence of technologies, so that technologies represent artifacts, information and knowledge [6]. Because functions are externally oriented, technologies can be multiplied by many physical-technical options appropriate to functional functions and uses. The functional approach of the technological entity positions the technology in a system of values that allow assessments of the quality and efficiency of the technologies.

It is observed that the actions of the carrier of technological tasks have a reaction on the same or on other physical channels, thus becoming an object with properties in the process of modification (Figure 7). In both objects, phenomena with effects occur and the analysis can be focused on one or the other of them.

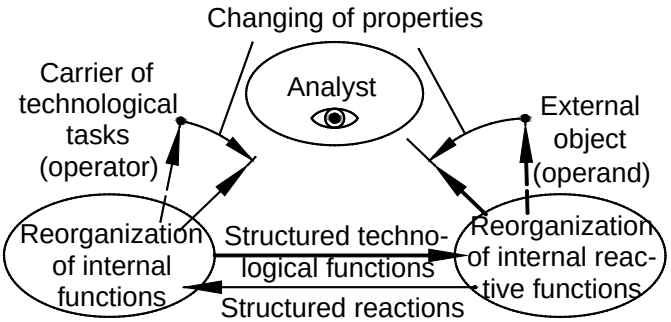

Figure 7. Reactions supported by the carrier of technological tasks.

The technological objective is defined as a set of properties that can be obtained or realized through actions, effort and has an imaginary, virtual character. Having specified an appropriate carrier of technological tasks, the objective from the set of imaginary initial properties is transformed into a set of real final properties. Thus, the technological task defines a requirement, and the technological function defines the reality in which the task is fulfilled, that is, it represents a response to the requirement.

At the base of the technological function are the actions that take place over time, thus the formulation of the technological function as the ability of the task's carrier to effectively give answers to the questions "from what?", "what the?", "how?" the time factor "when?" is also added.

The final performances of a technological function are generated in networks of cause-effect interactions, so that the results of a process represent the launch conditions for the next process. The interactions are not ideal and in order to obtain functional results, the

technological components must be of a certain quality and be placed physically, spatially and logically in certain positions to function [6].

Several special phases can be highlighted in the process of technology operation [11,14,15] (Figure 8):

- ✓ the interaction of the object carrying technological tasks with another external object, thus being initiated a technological function either as an influence from the external object, or as the tendency of the carrier of technological tasks to reach a more preferential state of its own, a tendency that causes action on the external object;
- ✓ the initiation by the object carrying technological tasks of a mechanism structured in space and time by interaction with the external object;
- ✓ the formation of a structured interaction interface between the carrier of the technological tasks and the external object;
- ✓ the mutual adaptation of the object carrying technological tasks and the external object through subordination, that is, through the intensive modification of the properties of the external object, and the modification occurs through the reorganization of its internal functions;
- ✓ perceiving the effect of the structured reaction from the external object by the internal structure of the object carrying technological tasks;

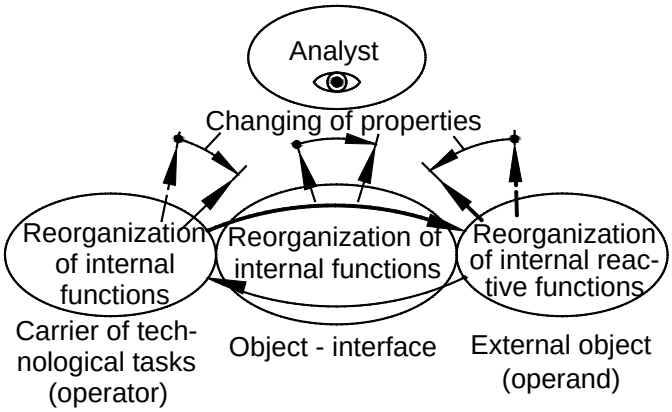

Figure 8. Realization of the technological function by reorganizing the internal functions of the external object, of the carrier of technological tasks and of the interface.

- ✓ the reorganization of the structure of the internal functions of the object carrying technological tasks with the redistribution of tasks on functional elements, with the coordination of actions to ensure its ability to perform the external technological function;
- ✓ the changing of the properties of the object carrying technological tasks (simultaneously with the changing of the properties of the external object) as a result of the reorganization of internal functions.

Thus, the structured technological functions cause structured reactions and the reorganization of the internal functions of both the external object and the carrier of technological tasks. At the same time, the technological functions are manifested through interfaces common to interacting objects and these (interfaces) can be considered separate objects. The act of realizing the technological function includes the reorganization of the internal functions with the modification of the properties of three distinct objects: of the carrier of technological tasks (the operator), of the external object (the operand) and of the interface (Figure 8).

The reorganization of internal functions, the modification of properties are processes that take place over time, so the mentioned objects are objects - processes, i.e. technological objects. Apart from the interactions the object - interface does not exist, the object carrying technological tasks has a defined internal functional structure, and the external object has a

defined internal reactive functional structure. These three objects, their properties and variation represent factors for the technological function.

If in an ordinary interaction process, without waiting for a desired result, the establishment of links is conditioned by the compatibility of the properties, then the realization of a technological function is possible if the compatibility of the internal functional structures of the factor objects is respected.

4. Defining and measuring the properties of technological functions

The defining of the properties of the technological functions is done in the form of the observable external manifestation of the reorganization of the internal functions of the operator, operand and interface.

The properties are important themselves, but more important is the extent of their modification, the amplification of the useful ones, the reduction (blocking) of the harmful ones, the formation of new properties, etc. This is ascertained by measurement. Measurement is a set of actions using different types of measurement scales.

The multitude of applications of technological functions is very large, because it is determined by the multitude and variety of objects that manifest themselves through technological functions, by the multiple variants of pairs of objects that can be put into interaction for the manifestation of properties. The interaction conditions, the mechanisms and interfaces, the links installed are also varied. The conditions may change as a result of the interaction. The analyst can change the places of the operator and the operand, if it is in the interest of a special research. Consequently, the number of properties manifested by the reorganization of the internal functions of the object carrying technological tasks, an external object and the interface is large.

A clarification of the notion of object is useful here. In the fields of technology and technique, processes and products, industry and enterprises, the multitude of objects considered and the interactions practiced have a common characteristic - the transfer of matter and/or energy and/or information. The particularities of the analysis will highlight one of the mentioned aspects (material, energetic, informational), and the other two being also imminently present.

Different categories of objects with a real character are manifested through technological functions [11,14,15]:

- *material physical-technical objects* (solid, liquid, gaseous, plasma, machine-tools, devices, tools, blanks, parts, assemblies, mechanisms, machines, products, etc.);
- *energetic physical-technical objects* (gravitational field, magnetic field, electric field, electromagnetic field, laser beam, electron beam, etc.);
- *objects-physical-technical processes* (mechanical, cutting, plastic deformation, welding, thermal, magnetic, electric, electromagnetic, wear, oxidation, cracking, coating, deposition, destruction, technological, manufacturing, production, transport, storage, etc.).

They are very important for technological development and immaterial objects with essence content, which are created, formulated by people through observation, analysis and research. Immaterial objects provide a general-methodological foundation for the development of new technologies and industrial products. In other words, these objects represent development environments. Among it are the following categories of objects [11]:

- *geometric objects,* which define the shape of other objects through spatial limits and associate them with graphically represented or mathematically modelled geometric idealities;
- *process-objects* (marketing, conception, constructive design, technological design, machining, manufacturing, logistics, organization, innovation, technological transfer, digitization, computerization, etc.);
- *organizational objects,* which reflect and regulate the existence and manifestation in time and space of objects from any category;
- *soft-objects* - a combination of coded instructions and data that allow a calculation or command system to perform calculations or command functions;
- *time is an object* - a factor that establishes the fact, the measure and the speed of change (unchange) of other objects in interactions with physical-technical effects (physical aging, natural aging of alloys, creep of materials, radioactive half-life t1/2, etc.), as well as with essential effects (moral aging, technical level, technological level, etc.);
- *technical-economic-social objects* - major phenomena such as, for example, Kondratiev economic cycles, industrial revolutions, production, marketing, economic strategy, quality, diversification and customization of markets, innovation and technology transfer, industry 4.0, ecology, sustainable development, etc.;
- *concept objects*, which represent generalizations and syntheses of new ideas, based on advanced experiences and forecasts such as:
  - ✓ *concepts of manufacturing technologies* (subtractive, additive, assembly, welding, moulding, punching, casting, injection, cutting at high speeds, dry cutting, etc.);
  - ✓ *manufacturing concepts* (mass, in series, unique, automated, flexible, digital, direct from the computer, advanced, smart, intelligent, etc.);
  - ✓ *industrial concepts* [16]*:* "Industry 4.0" (Germany, 2010), "Advanced Manufacturing Partnership 2.0" (USA, 2011), "Catapult Centers" (Great Britain, 2011), "Intelligent Factories Clusters" (Italy, 2012), "Made in China 2025" (China, 2014), "Intelligent Factories Clusters" (Belgium, 2014), "Industry of the Future" (France, 2015), "Revitalization/Robots Strategy" (Japan, 2015), "Manufacturing Innovation 3.0" (South Korea, 2015);
  - ✓ *concepts of new technologies of Industry 4.0* [17]*:* autonomous and collaborative robots, simulations and digital twins, augmented reality, vertical and horizontal systemic integration, industrial internet of things, additive manufacturing, big data analytics, cloud computing, cyber security, etc.
- *object-theories,* which represent an abstraction and a conceptualization of objective reality, thus becoming a form of rational knowledge and structured knowledge systems for describing and explaining the domains of reality.

These two large categories of objects manifest themselves through technological functions, but through different mechanisms.

Measuring the properties of real physical-technical technological functions. Objects with a real physical-technical character can be put into "live" or virtual interactions. The real properties of technological functions are manifested when both the bearer of technological tasks and the object on which they act are real. These properties are real measured, they are true, but they have a particular character to the interaction couple used. As an example, the mechanical processing of a piece on a machine tool can be given. Both the machine tool and

the part are real, but they have individualized characteristics even within the limits of the machine-tool classes and the types of parts.

For generalizations and for reducing the number of properties taken into account until "sufficient and necessary", there is the practice of representative properties evaluated and measured under the conditions of standardized tests. Standardization is necessary to have the possibility to compare the properties starting from a common base. A technological standard is a process of evaluation and measurement of properties, which stably reproduces a structured technological function and a structured technological reaction. A representative property is one that is similar to the real property to a degree of veracity considered acceptable. Representativeness is an evaluation of the similarity of properties starting from the idea that, once the causes and effects are similar, the properties must also be similar.

An example of determining the representative properties of the technological functions of mechanical processing on CNC machining centers is the measurement of the geometric precision parameters of a processed standardized artifact (Figure 9). The piece has surfaces of different shapes and placed in specific positions. If the processing of this part is according to the technical requirements [14], then it is considered that the CNC machining center performs appropriate technological functions for a class of parts with similar geometries and technical requirements. For other geometries, including more complex parts, other artifacts are used and correspondingly by higher complexity.

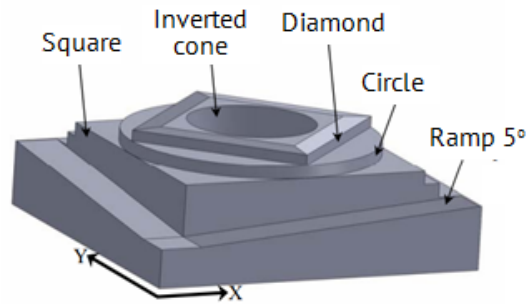

Figure 9. "Square diamond circle" machining artifact for establishing the properties of the technological functions of machining centers [17].

If in the case of traditional mechanical processing technologies, the physical-technical phenomenon of surface generation is predominantly cutting by various methods, then additive technologies are based on many more physical-technical phenomena with specific problems of creating shapes. For this field, which is developing very quickly, artefacts of geometric shapes specific to the realized technological functions are elaborated (Figure 10). Sometimes testing is done with real equipment on real parts. However, standardized artifacts are predominantly used, so the technological functions are evaluated representatively.

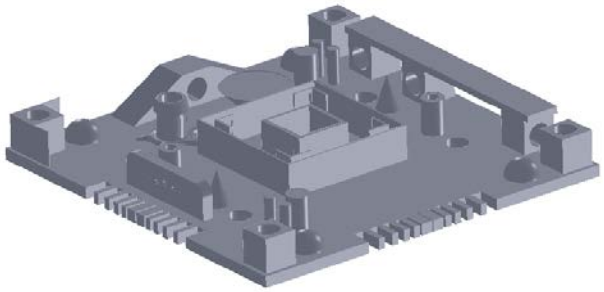

Figure 10. Artefact de testare a unei tehnologii aditive [18].

Modern engineering relies heavily on modelling with systematic parameter variations to map behavior and understand its underlying causes [6]. The properties of technological functions can be defined and measured through virtual interactions (simulations) based on geometric-mathematical models. The models, although they are digital, are based and mirror behaviorally the physical-technical phenomena, objects and real conditions. Models are defined as abstractions that reflect aspects of the entities to which they are similar. Entity properties are also component parts of models. The properties measured in this way are representative and require the determination of the level of veracity.

Measuring the properties of technological functions of immaterial complex objects. Immaterial complex objects are functionally manifested technologically in relation to other technologies through development impulses, through the opening of new possibilities and/or alternatives, through the challenge of technical, economic and social interests, etc. Approaching any technology in terms of a central nucleus around which a vital technology environment is formed means that technology cannot be seen in clear and well-defined boundaries [6]. The vital technology environment is one made up of coherent technologies already adapted to each other that work in a balanced way, but also one made up of new technologies, such as digital ones, which cause imbalance for development. Thus, a technology-environment co-evolution process is generated with incremental improvements in alternation. Technology is the result of this co-evolutionary process in which technological functions, knowledge, artefacts and their living environment adapt and improve each other.

The technological potential of these immaterial objects is multiplied by their own example - they are in permanent modification, change, they are dynamic, they present new and new versions. The properties of the technological functions of the older versions are already evaluated and measured. The effects and problems are well known. The properties of the newer versions have a degree of historical credibility and are qualitatively measured by the interest shown by representatives from industry, research, etc. The greater the interest, the more valuable the properties of technological functions are considered. The measurement is done by scientometry, which is a tool for quantitatively studying the evolution of scientific and technological fields, of industrial concepts through statistics of information published in certain reference time periods (theoretical and applied scientific works, citations, etc.).

The following measurement is made by analyzing successful experiences (so-called "good practices"), with real results of economic agents expressed in technical-technological and economic values. The absolute values are often not significant enough, so the sensitivity measurement is used. Sensitivity reflects the formation of an effect-value disproportionate to the cause-value. Good practices are disseminated, adapted to various concrete conditions, and the measure of properties becomes closer to the real one.

5. Conclusions

Technological transfer is an important aspect of technological development and as any process requires not only qualitative but also quantitative evaluation to appreciate the effects of the transfer. Quantitative evaluation by measurement can be done using different models, the most important being the technology's model, i.e. of the object being transferred.

Models based on the notion of property are very attractive for evaluating transferable technologies, properties being defined as the ability to change other objects, and the change is easy to measure. Based on the models of the manifestation of the properties in interactions with the establishment of physical-technical and essence (substance) links and through interfaces, the notion of technological function was defined.

The technological function model includes the interaction of three distinct objects: of the carrier of technological tasks (of the operator), of the external object on which the action is applied (of the operand) and of the interface. The technological function is defined as the reorganization of the internal functions of the operator, the interface and the operand caused by the interaction and has a character of modifying their properties, a fact that offers the possibility of measuring them.

The technological functions are performed by objects carrying technological tasks of two categories: physical-technical (materials, energy, processes, etc.) and immaterial (theories, concepts, data, knowledge, etc.). The measurement of the properties of technological functions is done with interactions of real or representative objects in real or representative conditions, in most cases the measured properties being representative. The measurement of the properties of the technological functions of complex immaterial objects is done with statistical scientometric tools (theoretical and applied scientific works, citations, etc.) and by analyzing successful experiences ("good practices").

An increasingly widely used field of measuring the representative properties of technological functions is digital simulation with the use of models that reflect the properties of real objects and their behavior.

Conflicts of Interest: The author declares no conflict of interest.

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NATIONAL AND INTERNATIONAL EXPERIENCE REGARDING DEVELOPMENT OF BICYCLE INFRASTRUCTURE

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Abstract. Cyclists, together with pedestrians, as traffic participants, are the most vulnerable. Every year in the world over 40000 cyclists die on the roads, which represents approximately 3% of the number of people who died in road accidents. Ensuring the safety, including of these road users, must be part of the basic priorities of any country.The development of bicycle infrastructure brings social, economic and ecological benefits. The article presents a brief description and analysis of state programs in some countries and in Republic of Moldova (the city of Chisinau) regarding the development of cycling in urban road traffic.

Keywords: *bicycle infrastructure, road accidents, traffic accidents, cyclists, traffic participants, cycle lane.*

Rezumat. Bicicliștii împreună cu pietonii, ca participanţi la trafic, sunt cei mai vulnerabili. Anual în lume mor pe drumuri peste 40000 de bicicliști, ceea ce reprezintă aproximativ 3% din numărul persoanelor decedate în accidentele rutiere. Asigurarea securității, inclusiv a acestor participanți la trafic, trebuie să facă parte dintre prioritățile de bază ale oricărei țări. Dezvoltarea infrastructurii de biciclete aduce beneficii atât sociale, cât economice și ecologice. Articolul cuprinde o descriere și analiză succintă a programelor de stat în unele țări și în Republica Moldova (orașul Chișinău) privind dezvoltarea ciclismului în traficul rutier urban.

Cuvinte cheie: *infrastructura de biciclete, accidente rutiere, accidente de circulație, bicicliști, participanți la trafic, pistă pentru bicicliști.*

1. Introduction

Modern cities are growing very rapidly, Chisinau not being an exception, and together with them the number of vehicles is growing, at a rate where the road infrastructure does not keep up with them. According to official data on 01.08.2022, 335617 vehicles were registered in Chisinau municipality [1] (239359 cars, 56000 trucks, 7106 minibuses and buses, 6006 tractors, 7480 motorcycles, 15036 trailers and 4630 semi-trailers) with an official population

of 870093 inhabitants [2]. So, in Chisinau there are about 386 vehicles per 1000 inhabitants, at the recommended norms of 60...80 cars per 1000 inhabitants [3].

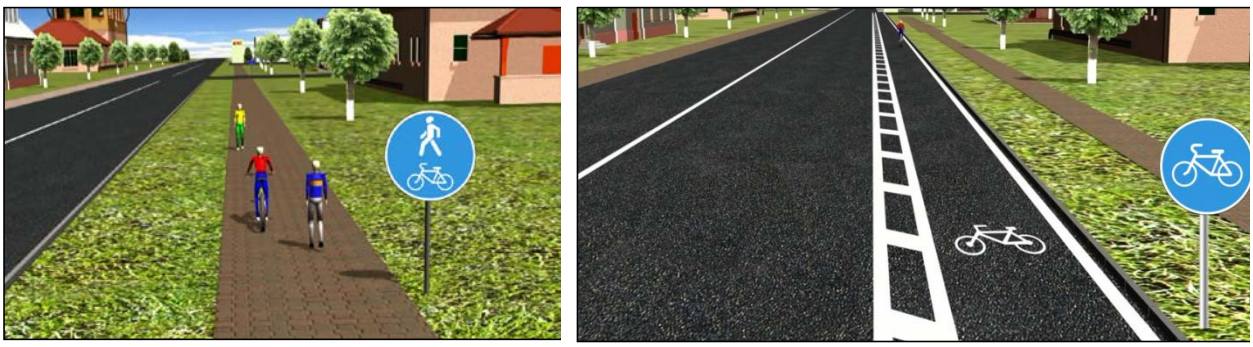
Despite the rapid motorization of most countries of the world, in many cases reaching the maximum value (over 600 automobiles per 1000 inhabitants), the bicycle as a vehicle has not lost its significance. In 1990, in the USA, the Netherlands, Japan, China, there were more than 400 bicycles per 1000 inhabitants. The largest area of bicycle use for work and business travel is typical for countries in the Asian region. For example, in Hanoi (Vietnam) the saturation level of these vehicles exceeds 480 bicycles per 1000 inhabitants, and in Ho Chi Minh City – 530 bicycles per 1000 inhabitants. At the same time, the maximum traffic intensity of cyclists on some streets reaches 5000...15000 un/h [4].

The safest are the bicycle lanes organized outside the carriageway of highways and city streets. The lane for cyclists must be allocated on the streets in the form of a lane separated from the roadway (*figure 1, a*) or an extreme lane of the sidewalk or parallel to the sidewalk and separated from the roadway by a green lane (Figure 1, b) [4-7].

a) b)

Figure 1. Lanes for cyclists [4-6]:
a) – track for cyclists separated from the road by a green strip; b) – track for cyclists parallel to the pavement and separated from the road by a green strip.

Also, tracks for cyclists can be combined with tracks for pedestrians (Figure 2, a). In restricted road conditions, including entrances to artificial constructions, the track for cyclists can, as an exception, be located near the edge of the road, but separated from it by a curb with a height of at least 0,25 m or by a road marking (Figure 2, b) [4-7].



a) b)

Figure 2. Tracks for cyclists [4-6]:
a) – track for cyclists combined with the track for pedestrians; b) – track for cyclists separated from the road by a curb or road marking.

Bike tracks can be designed for one-way traffic (with width not less than 1.2 m) or for two-way traffic (with width at least 2.5 m). The longitudinal gradients of the tracks for cyclists must not exceed 5%. The most difficult thing is to ensure safety at intersections with road flows. In accordance with international experience, it is possible to use traffic lights for cyclists on specially designed tracks that intersect the carriageway. Such directed intersections are unacceptable to be organized on streets with continuous traffic and high speed. As a rule, the green phase of the traffic light for cyclists must coincide with the red phase of the traffic light of the main direction of traffic.

2. Statistics of road traffic accidents

The rapid urbanization as well as motorization of the population in the world is accompanied by an rise of the number of road traffic accidents, which results in people die, people traumatized and people injured. According to apprisals, every year in the world in road traffic accidents die more than 40000 cyclists representing about 3% of the overall deaths in road traffic accidents (Figure 3). Among those who died in traffic accidents 29% belong to car drivers and passengers, 28% to motorcyclists, 23% to pedestrians, and the remaining 17% to other road traffic participants [8-14].

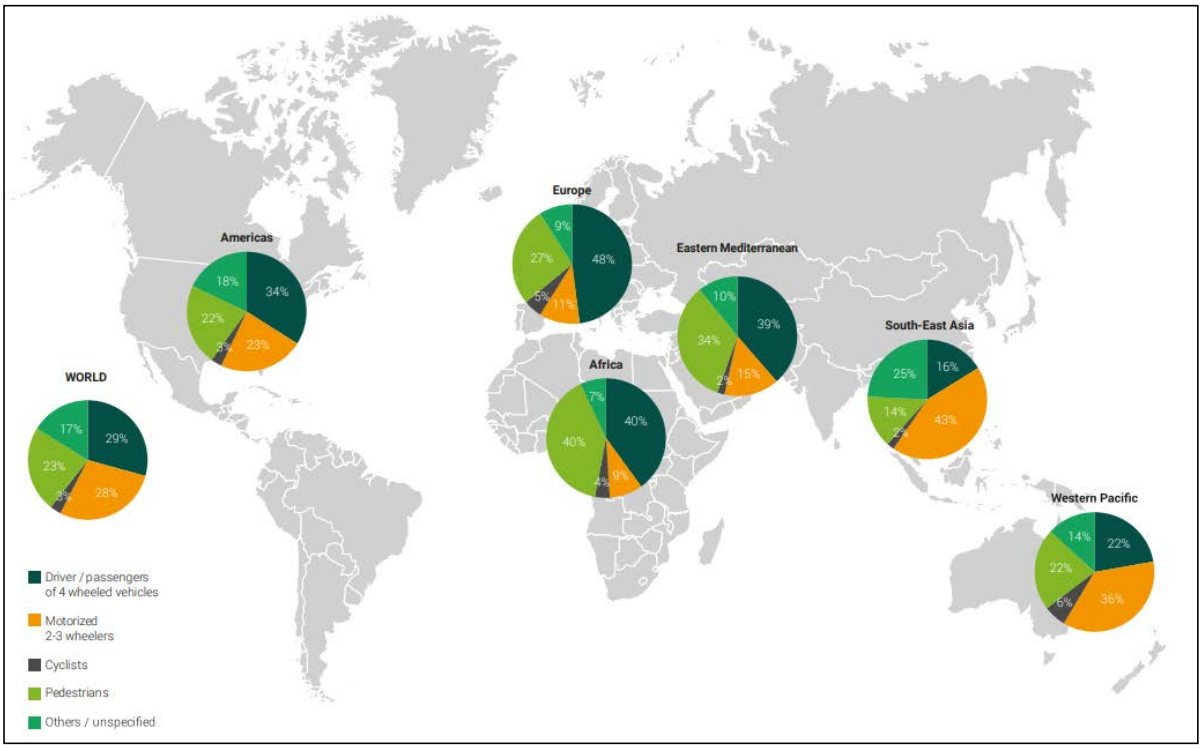


Figure 3. Distribution of deaths by categories of road users by WHO (World Health Organization) regions [9, 13, 14].

The situation differes significantly among world regions. The value of income influence the percent of the victims in traffic accidents. So, the low and middle-income countries has a higher rate victims, such as pedestrians, cyclists, drivers and passengers of motorized two and three-wheeled vehicles, than in high-income countries. For example, 40% of all road traffic fatalities are pedestrians according to WHO for African Region, and in the WHO Western Pacific Region 36% are motorcyclists, which are drivers and passengers of 2- or 3-wheeled motorized vehicles (Figure 3). Car drivers and an car passengers represent 16% of those killed in road traffic accidents in the Southeast Asian Region and 48% in the European Region [8-14].

The WHO region with the highest proportion of cyclist deaths in road accidents is the Western Pacific Region with 6%, followed by the European Region with 5%, the African Region with 4%, the American Region with 3%, the Eastern Mediterranean Region and the Asian Region with Southeast with 2% each [8-14].

Between 2000 and 2020, 2438 (about 106 per year) road accidents involving cyclists were recorded in the Republic of Moldova, which is about 4.11% of the overall accidents (Table 1) [13-27].

The accident situation in the Republic of Moldova took a negative direction during the last 5 years (Table 1), when the number of road accidents involving cyclists suddenly increased from year to year, registering 794 (about 159 per year) road accidents, which it is about 6.58% of the total number of accidents in the mentioned period, exceeding by 1.9 times the percentage average of the previous period (years 2000-2017). In the years 2020 and 2022, the highest annual share of the number of road accidents involving cyclists from the total number of accidents was recorded, respectively 8.09% and 7.92%. 2021 is the year with the highest number of road accidents involving cyclists in the period 2000-2022.

Table 1

Frequency of road accidents in the Republic of Moldova (years 2000–2022)

The year	Road accidents in total	Road accidents involving cyclists	% of the total number of road accidents	The year	Road accidents in total	Road accidents involving cyclists	% of the total number of road accidents
2000	2580	112	4.34	2012	2712	82	3.02
2001	2666	117	4.39	2013	2603	79	3.03
2002	2899	102	3.52	2014	2564	85	3.32
2003	2670	99	3.71	2015	2527	80	3.17
2004	2447	78	3.19	2016	2479	66	2.66
2005	2289	88	3.84	2017	2640	66	2.50
2006	2298	85	3.70	2018	2615	111	4.24
2007	2437	86	3.53	2019	2585	152	5.88
2008	2875	111	3.86	2020	2003	162	8.09
2009	2755	110	3.99	2021	2548	186	7.30
2010	2930	118	4.03	2022	2312	183	7.92
2011	2826	80	2.83	**Total**	**59260**	**2438**	**4.11**

The statistical analysis of road accidents involving cyclists in the period 2008–2022 (Table 2) [13-15, 17-19, 21-26] in the Republic of Moldova shows that 188 (about 13 per year) cyclists died as a result, and another 1516 (about 101 per year) were traumatized.

After a more disastrous period of the years 2008-2013, when between 14-18 cyclists died in road accidents, a more „quiet" period followed, the years 2014-2018 (except for 2016), when they were registered between 6-9 deceased cyclists (Figure 4). Starting from 2019, the number of cyclists who lose their lives in road accidents has started to increase sharply again. In 2022, the number of cyclists killed in road accidents is 2.3 times higher than in 2017 and 2.7 times higher than in 2014.

Table 2

Number of cyclists killed and injured in road accidents in the Republic of Moldova (years 2008–2022)

The year	Totally die in road accidents	Cyclists killed in road accidents	% of the total number of dead	Totally traumatized in road accidents	Cyclists injured in road accidents	% of the total number of traumatized	Coefficient of severity of road accident consequences
2008	508	15	2.95	3511	95	2.71	13.64
2009	487	18	3.70	3297	92	2.79	16.36
2010	452	14	3.10	3747	94	2.51	12.96
2011	443	14	3.16	3535	92	2.60	13.21
2012	441	16	3.63	3510	83	2.36	16.16
2013	295	17	5.76	3221	81	2.51	17.35
2014	324	6	1.85	3080	72	2.34	7.69
2015	297	9	3.03	3021	76	2.52	10.59
2016	311	13	4.18	2928	75	2.54	14.77
2017	302	7	2.32	2993	58	1.94	10.77
2018	274	8	2.92	3123	100	3.20	7.41
2019	277	10	3.61	3031	136	4.49	6.85
2020	245	10	4.08	2265	146	6.45	6.41
2021	257	15	5.84	2864	159	5.55	8.62
2022	217	16	7.37	2586	157	6.07	9.25
Total	**5130**	**188**	**3.66**	**46712**	**1516**	**3.25**	**11.03**

For the first time, the number of cyclists injured in road accidents in the mentioned period exceeded 100 in 2018, after which an even more pronounced increase followed. In 2022, the number of cyclists injured in road accidents is 3.1 times higher than in 2017 and 2.7 times higher than in 2014.

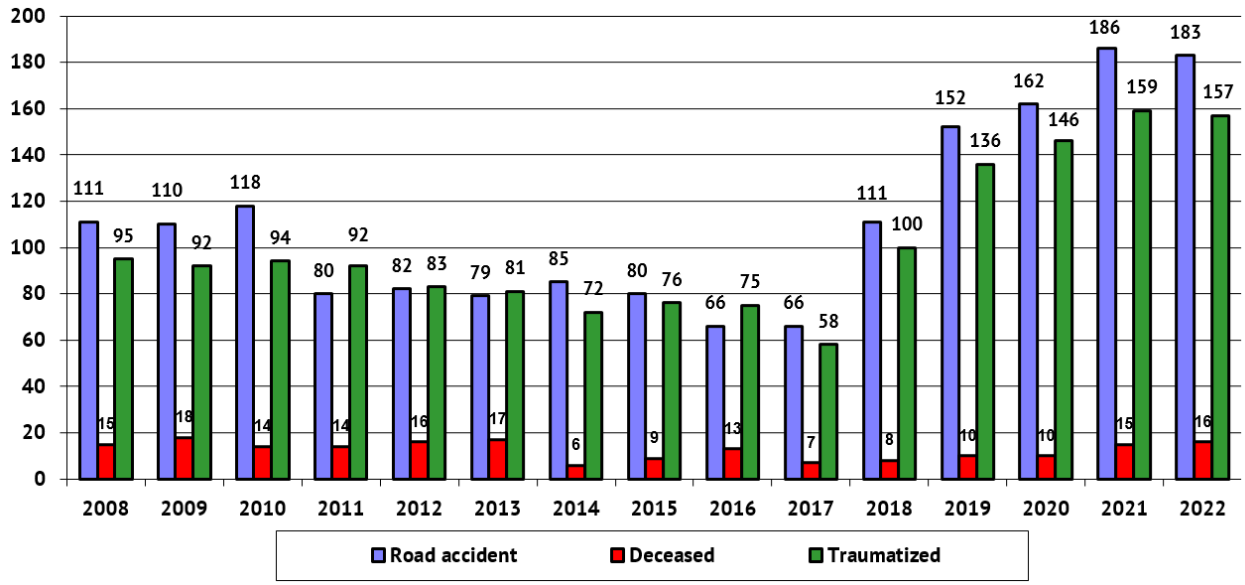


Figure 4. Frequency of road accidents involving cyclists in the Republic of Moldova (years 2008-2022).

The severity index of the consequences of road accidents involving cyclists in the period 2008-2022 is 11.03, being less than 10 percentage units in the last 5 years (2018-2022) and 2014 with an increasing trend in recent years, which puts us look with concern at the future traffic accident statistics.

Reducing the number of road accidents involving cyclists is a task of great socio-economic importance for all countries of the world, the Republic of Moldova not being an exception. Although the figures do not give us a complete picture of the real state of affairs in this field of human life, we cannot neglect the statistical data, which in the last 5 years are somewhat worrying.

3. The problem of transport in cities

The main negative factors of the transport problem in big cities are the following [28, 29]:

1. degradation of the ecological situation due to the large amount of concrete and concrete-asphalt pavement, without it being sufficiently compensated with green areas and parks;
2. pollution of the atmosphere with harmful exhaust gases and fuel vapors, especially in city centers, where a maximum accumulation of vehicles is aimed at;
3. pollution of the environment with dust and wear products of tires, brake shoes, clutch discs and road pavement;
4. the discomfort created by vibrations, electromagnetic waves and the high level of noise, which negatively affects the health of residents;
5. thermal emissions, which exceed the emissions of thermoelectric plants and liquid emissions, composed of leaks of fuels, lubricants, acids, alcohols, antifreezes, which pollute the air, soil and water bodies;
6. large losses of time of residents for traveling from home to work and vice versa, etc., which increase with the increase of cities and traffic jams;
7. the large number of road accidents, which affect the population both morally, socially and economically;
8. as cities grow, so does the need for automobiles, which requires an appropriate transport infrastructure (roads, parking spaces, gas stations, self-service etc.).

The main reasons for the formation of such a difficult road situation include: the lack of clear urban plans in the post-Soviet period; large-scale destruction of the former public transport infrastructure without adequate replacement with large modern vehicles; the imperfection of the traffic rules in relation to the existing traffic and the slow development of the road infrastructure etc. Public policies in the field of urban mobility in the city of Chisinau are focused on encouraging the use of private transport through the development of road infrastructure, widening of streets and the arrangement of parking spaces at the expense of the sidewalk. Although investments are also made in public transport, it remains uncompetitive and unattractive, stimulating citizens to invest in private transport [30].

The problem of modernizing the road infrastructure of cities and the country as a whole is a current one. The large volume of capital and the scale of infrastructure projects require significant investment. Historically, transport projects are initiated and financed by the state. The weak interest of private business to invest in infrastructure objects is explained by the uncertainty of investment recovery guarantees, by the non-competitive selection of contractors, as well as by the unclear understanding of infrastructure development priorities, which makes it difficult to evaluate the prospects of these investments [28].

4. The experience of the city of Chisinau regarding the development of bicycle infrastructure

The city of Chisinau can be classified in the category of cities that avoid investing or invest very little in urban cycling. Although thematic events, such as: Velo Hora (2009-2016) and Velo Fun (2015-2019), „Girls on Bikes", Chisinau Bike Tour (every year on October 14, Chisinau City Day, „World Bicycle Day" and „World Car Free Day" (within the European Mobility Week) etc. [31], manage to gather more and more bicycle fans, the municipality is in no hurry to develop this mode of travel. At the moment there are no official data on the number of cyclists in Chisinau, but indirect data suggest a constant increase of the interest of Chisinau residents in this type of travel, especially recently, favored by the effects of the „COVID" pandemic and high fuel prices. Although at the events dedicated to cyclists, their number is impressive, in everyday life cyclists represent an insignificant part of urban traffic and are very difficult to notice on city streets [28].

Cycling on the streets of Chisinau is a real challenge for cyclists. The lack of infrastructure and means of signaling traffic, damaged roads, but also less friendly drivers in traffic, endanger the lives of cyclists, whose number has increased recently. For these reasons, the number of road traffic accidents involving cyclists has also increased.

Analyzing the General Urban Plan [32] and the Public Transport Strategy of the City of Chisinau [33] until year 2020, it can be seen that all these strategic development documents of the city of Chisinau were focused exclusively on road traffic and the development of the infrastructure for motorized transport . Moreover, all the studies [34], research and public policy analyzes developed by non-governmental organizations and experts outside the Chisinau City Hall had the same priorities – the circulation of motor vehicles [30].

None of these documents provided for or mentioned the construction and design of bike lanes and parking, pedestrian infrastructure, or addressing alternative transportation as a means of getting around the city. However, despite the lack of strategic documentation, the municipal authorities regularly addressed the issue of bicycle infrastructure and experimented with their arrangement. However, due to a lack of experience, expertise and a systematic and serious approach, these attempts have proven to be ineffective further compromising the idea of urban cycling.

Among the most well-known examples of the arrangement of bike lanes is the experiment from 2014 with the application of yellow markings on the pavement on some streets in the city of Chisinau (Figure 5), which were drawn in hard-to-reach places with numerous impediments, bumps and dangerous crossings [30, 31].

Figure 5. Bicycle lanes marked with yellow paint [30, 31].

Another example took place in 2016 on Stefan cel Mare si Sfant Blvd., the bicycle track was laid out on the sidewalks, in the form of a strip of pavement of a different color, with a width of 1 m on each side of the street (Figure 6). In the absence of a physical demarcation, the track was always occupied by pedestrians, parked cars on the sidewalk or street vendors, which made it impossible for cyclists to use it [30, 31].

In 2018, in the Valea Morilor park, a bicycle lane was marked in the pedestrian zone (Figure 7), which, however, is designed semi-legally, due to the current road regulations that do not allow the circulation of cyclists in parks and on sidewalks. The lane is actively used for recreational purposes, but cyclists cannot move safely, being forced to always be cautious, as the lane is often occupied by people with strollers, minor children, pets etc. [31].

The practices of European and American cities demonstrate, however, that the arrangement of bicycle lanes on the sidewalk is inefficient and dangerous, as it generates a constant conflict between pedestrians and cyclists due to the difference in travel speed. While the average speed of a pedestrian is 4 km/h, cyclists can easily develop a speed of 20 km/h, which inevitably leads to accidents and serious trauma [30].

Figure 6. Bicycle lane laid out on sidewalks, in the form of a strip of pavement of a different color [31].

Figure 7. Bicycle path arranged in the pedestrian area [31].

In May 2020, the lane for public transport was demarcated on Alexandr Puskin Street, which offers the possibility of being used by cyclists as well (Figure 8). This pilot project presents a gradual inclusion of dedicated lanes for public transport and as well as for bicycles on other central streets, such as: Stefan cel Mare si Sfant Blvd., Gavriil Banulescu-Bodoni str. and Grigore Vieru Blvd. [31].

In September 2020, as part of the repair of the pedestrian zone, the construction of the bicycle path on the alley on Mircea cel Batran Blvd., which reaches a length of about 2 km (Figure 9). This variant is so far the best designed, but due to the lack of continuity of the route, the track exists only on the alley route [31].

Meanwhile, the situation started to evolve for the better. The City Hall of Chisinau with the support of the EcoPro Public Association in partnership with UNDP (United Nations Development Programme), Green City Lab, Automobile Club of Moldova and the help of experts in the field of bicycle infrastructure design and the cycling community in Chisinau in 2020 developed the „Infrastructure Development Strategy for Alternative Transport in the city of Chisinau", which has as its main purpose the development of bicycle infrastructure in the city of Chisinau.

Figure 8. Delimited lane for the shared circulation of road vehicles and bicycles [29].

Figure 9. Bike lane parallel to pedestrian lane [photo: Ziarul de Garda].

Following the surveys carried out by the „Working group for the development of alternative transport" and the organization EcoPro, the sectors with the greatest flow of cyclists were determined, as well as the most used streets for the movement of cyclists in the city.

Based on the statistical data and the projects to be carried out, 4 stages of bicycle infrastructure implementation were established [31].

STAGE 1, years 2020–2022.

- Implementation of shared lanes for public transport and bicycles (Figure 10):
  1. Gavriil Banulescu-Bodoni str.;
  2. Stefan cel Mare si Sfant Blvd.
- Implementation of bicycle lanes in the framework of street renovation (Figure 10):
  3. 31 August str.
- Realization and implementation of a route project for alternative transport, which will connect the 3 most popular sectors: Botanica, Centru, Rascani (Figure 10):
  4. Moscova Blvd., Kiev str., Renasterii Blvd., Grigore Vieru Blvd., Gavriil Banulescu-Bodoni str., 31 August str., Ciuflea str., Dacia Blvd.

STAGE 2, years 2022–2023.

Development of routes for alternative transport that will connect the Center sector with other sectors through streets with the greatest flow of cyclists (Figure 10). The total length of the routes – 50 km.

- Center:
  1. Alexei Mateevici str.
- Telecentre:
  2. Hancesti road;
  3. Gheorghe Asachi str.
- Buiucani:
  4. Ion Creanga str.;
  5. Alba-Iulia str.
- Sculeni:
  6. Calea Iesilor str.
- Posta Veche:
  7. Calea Orheiului str.;
  8. Socoleni str.
- Rascani:
  9. Bogdan Voievod str.;
  10. Alecu Russo str.

STAGE 3, 2023–2024.

Development of routes on the secondary streets inside the sectors (*Figure 10*). The total length of the routes – 46 km.

- Center:
  - 1 Constantin Negruzzi Blvd.;
  - 2 Iurii Gagarin str.;
  - 3 Ismail str.;
  - 4 Vasile Alecsandri str.
- Rascani:
  - 5 Florilor str.;
  - 6 Nicolae Dimo str.
- Botanica:
  - 7 Decebal Blvd.;
  - 8 Traian Blvd.
- Buiucani:
  - 9 Vasile Lupu str.;
  - 10 Nicolae Costin str.
- Telecentre:
  - 11 Miorita str.

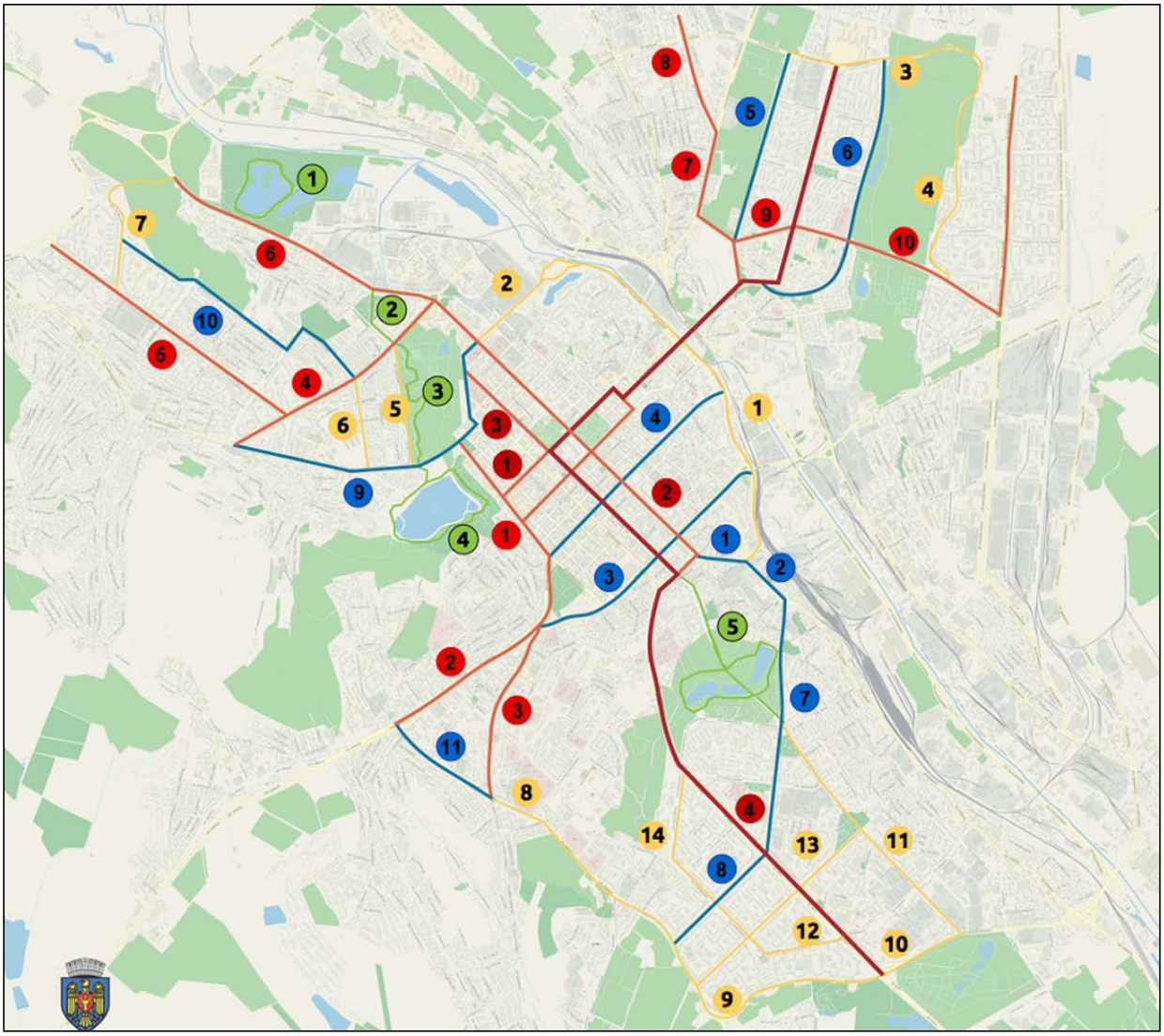


Figure 10. Map of bicycle routes in the city of Chisinau [31].

STAGE 4, 2024–2026.

Development of local and recreational routes (*Figure 10*). The total length of local routes – 65 km and recreational routes – 12 km

In total, for the period of implementation of the development strategy, it is planned to develop a network of trails with a length of 203 km and recreational trails with a total length of 12 km [31].

- Center:
  1. Albisoara str.;
  2. Mihai Viteazul str.
- Rascani:
  3. Studentilor str.
- Buiucani:
  4. Eugen Coca str.,
  5. Vissarion Belinski str.;
  6. Liviu Deleanu str.

- Ciocana:
  7. Mihai Sadoveanu str.
- Botanica:
  8. Grenoble str.;
  9. Valea Crucii str.;
  10. Gradina Botanica str.;
  11. Sarmisegetusa str.;
  12. Independentei str.;
  13. Cuza Voda str.;
  14. Hristo Botev str.

1. Park La Izvor
2. Park Alunelul
3. Park Dendrariu
4. Park Valea Morilor
5. Park Valea Trandafirilor

5. The benefits of bicycle infrastructure development

Authorities in several cities around the world have understood that the bicycle has not only fun and sporting functions, but is an efficient means of transport for covering short and medium distances. Therefore, suitable alternative transport infrastructures were created, which encouraged people to leave their cars at home and go around the city or to work by public transport, bicycle or scooter, and this reduced the pressure on road networks and prevented the formation of traffic jams.

Cycling is part of transport, urban and environmental policies, as well as health and tourism policies. It complements public passenger transport, providing mobility to the population over short and medium distances.

An analysis of experience in different countries of the cycling's development in large cities has shown that bicycle infrastructure can bring together the results in the development of the city obtained both in short-term and long-term, can improve the quality of life of its citizens.

The development of bicycle infrastructure can be viewed by 4 aspects [35]: transport, social, ecological and economic. By the transport view, we mean the impact of the development of the bicycle infrastructure on the indicators of the use of various types of transport or user preferences. One of the most important social and ecological consequences of using a bicycle is the improved health of city dwellers. It also make more accessibil the movement around the city for those who cannot get or drive a car, and also cannot use taxi services. The economic effect of the development of the bicycle infrastructure is evaluated from several directions: the economy of resources, due to the reduction of car traffic; reduced economic damages related, for example, to health or ecology; increased income of the city's, due to the better accessibility to transport and increasing the income of businesses, related to the development of cycling.

World experience shows that it takes about 10...15 years to create a developed bicycle infrastructure. The transition to cycling has a number of undeniable advantages [28, 31]:

- reducing harmful emissions in the atmosphere of cities and the noise level;
- reducing traffic jams in the city and the time spent in them;
- less need for parking spaces, because more bicycles can be parked on a place occupied by a car;

- the economy of budgetary resources for health, as a result of the increased physical activity of the population;
- significant resource savings for fuel, consumables and automotive components;
- reducing costs associated with road safety and environmental pollution;
- the possibility of closer communication with people and the study of new places and routes, which lead to an increase in the tourist attractiveness of cities;
- provides an additional impetus for the development of related branches and creates opportunities for the development of small business enterprises;
- greater mobility of this type of transport compared to a car;
- reducing social inequalities, giving people with lower incomes the ability to move from residential areas to the city center, integrating them into the full life of the community;
- increasing road safety, because with a maximum bicycle speed of 30 km/h and an average of 15...20 km/h, fatal accidents involving cyclists and pedestrians are minimal, and under the same conditions, the percentage of road accidents with serious trauma and less serious is significantly reduced etc.

Other health benefits of cycling [31]:

- at an average speed, a person burns from 500 to 700 calories per hour;
- the production process of endorphins („hormones of happiness") takes place, which help fight depression and increase immunity;
- reduces the risk of cancer by 45%, and the risk of cardiovascular diseases by 46%;
- increases the amount of „good" cholesterol, decreases the amount of „bad";
- strengthens the spine;
- regulates the activity of the circulatory system, lungs and improves the oxygen absorption process;
- strengthens bones and muscles, and keeps a good physical shape. And all this they give results without stressing the joints etc.

In many developed countries, bicycle transport is developing faster than car transport, and the number of bicycle trips is constantly increasing. Bicycles have gained more popularity in Northern and Western European countries, as well as in the USA and Canada, compared to Southern European countries. According to the number of bicycles and the diversity of bicycle infrastructure objects, the city of Helsinki leads, followed by the cities of Copenhagen, Stockholm and Hanover [28].

In most European countries, as well as in the USA, the development of bicycle transport has long been managed at the government level [28]. The network of bicycle routes must be based on subway and railway stations, large commercial and educational centers, parks, rest areas, recreation and residential spaces, to ensure optimal routes for people's travel.

It should be noted that the development of the bicycle infrastructure can serve as an impetus for the development of urban areas and constitutes a high demand on the service market: sports shops; technical services; construction of parking lots and bicycle rentals; storage of bicycle equipment as a service in the housing sector; secure parking service; cafes and grocery stores; production of bicycle components etc.

In order to use the positive potential of bicycle transport, it is necessary that the bicycle infrastructure be attractive and safe, allowing cyclists to reach their destination comfortably and quickly. In addition, in order to switch from automobile to bicycle in the

desired volume, it is necessary to form a positive attitude towards cycling in society, to raise the social status and prestige.

To use efficiently the bicycles in urban transportation, the organization of bicycle parking and storage is as important as the presence of bicycle infrastructure. Bicycle parking and storage are necessary to be able to rent a bicycle in crowded places such as shopping malls, subway stations, amusement parks, and residential areas, etc. The demand for bicycle parking spaces arises for two reasons: the possible theft of the bicycle and the need to organize the parking of a large number of bicycles in the urban space, especially in the city center. The organization of bicycle parking must be included in the city's parking organization policy, in the planning and design of streets, neighborhoods and separate buildings, similar to what happens with car parking.

An important factor that negatively affects the level of bicycle ownership is the lack of conditions for storing bicycles at home or near buildings. Currently, both in the neighborhoods of old buildings and in those with new buildings, there are no places to store bicycles. As a result, in new construction, building regulations should take into account the minimum requirements for providing bicycle parking and storage spaces.

The integrated development of bicycle infrastructure is an effective contribution of infrastructure investment, which can generate economic benefits, creating a reserve for further development of the city.

6. World experience on bicycle infrastructure development

Traditionally, a study of world experience of cycling starts with the „cycling cities" Amsterdam and Copenhagen.

In the mid-20th century, Copenhagen was plagued with transportation issues due to the mass carization of the city. However, in the 1990s, a movement to shift towards bicycle transportation began to emerge. Today, the distance traveled by cyclists in Copenhagen has increased by 36% compared to 1996. An astounding 52% of the city's residents use bicycles to commute to work or school. This is the highest percentage of bicycle commuters in any city in the world, with 650000 bicycles and only 125000 cars for a population of 550000. The growing number of cyclists has also led to a decrease of the number of road accidents involving cyclists. The city has adapted its transportation system to better accommodate cyclists, with an impressive cycling infrastructure that includes well-thought-out bike lanes, special steps at intersections, and bike pumps installed in various places on the tracks. Cargo bikes also have a special place in the city, with dedicated parking lots. In fact, 17% of families in Copenhagen now use cargo bikes. In addition to its impressive cycling infrastructure, Copenhagen is also developing an intelligent road system that uses special LEDs to determine the priority of certain types of transport on certain road sections. This system will help alleviate traffic congestion and is set to be fully operational by 2025. The city has also included its bike rental system as part of its public transportation network, giving it equal status alongside buses, trains, and the metro. Helsinki has taken a different approach to promoting cycling. Rather than a large number of bike lanes, the city has created a series of large lanes with one-way traffic along the main highways. The speed limit for all vehicles has also been reduced to 30-40 km/h. Intersections are equipped with special features, and the priority of traffic in Helsinki is as follows: pedestrians, cyclists, public transport, logistics, and private cars [36].

London faced significant traffic problems in the early 2000s, with constant traffic jams in the city center reducing the average speed of private cars to just 19 km/h. The city implemented restrictions on parking and circulation through the city center while promoting cycling as an alternative. The goal was to increase the number of cyclists by 400% by 2026. In 2001, Londoners made 320,000 trips by bicycle per day, which increased to 570000 trips in 2010. The share of bicycles in the city's volume of transport is currently 5% [36].

Hamburg is one of the largest cities in Europe that is actively promoting cycling. The city has a 12% share of bicycles in total traffic, with a network of 280 km of bicycle paths divided into 14 routes. Special bridges for cyclists and pedestrians have also been provided, and the bike rental system includes 130 stations and almost 2000 bikes. Hamburg is also working to improve legislative aspects of traffic to further improve cycling. Beijing is another city that is making a significant effort to promote cycling. In the past, bicycles were the primary mode of transportation in China, but the automobile started to be in the 1990s a symbol of success, as well as a symbol of prosperity, leading to restrictions on bicycles to allow for automobile circulation. However, this led to serious transportation issues and air pollution. In response, the city is working to modernize and expand its bicycle infrastructure, as well as improve the perception of cycling among its residents, as part of its goal to become the world's first "green civilization [36].

The Singaporean authorities have adopted an economic solution to the problem of traffic jams [37]: the customs duty of 40% for a car and the cost for registration – another 140%. Short distances between objects in Singapore, the accessibility of taxis, and an acceptable public transport system determines the use of bicycles.

Montreal has been recognized as North America's most bike-friendly city despite the dominance of automobiles and its hilly topography and cold, snowy winters. Bike infrastructure and culture are actively developed in the city. Other cities and countries also prioritize bike transport, and the government is involved in promoting this mode of transport. Austria has a cycling development plan called Masterplan Radfahren Strategie zur Forderung des Radverkehrs in Osterreich, which aims to achieve a 10% share of travel by bicycle. The strategy creates an attractive and safe infrastructure for bicycles, organizes traffic according to cyclists' needs, optimizes intermodal transport networks, and educates and informs all participants in urban traffic. Czech Republic adopted a strategy for the development of the cycling which the goal to increment the share of cyclists in the city's road flow up to 10% in 2020 and up to 25% in 2025. The other goal of the national strategy for the period 2013-2020 was to popularize the bicycle as part of the the city's transport system with equal rights to other ways of transportation, aiming to transform "popular and irregular" bicycle use into "civilized bicycle movement with continuous support". The Denmark's national strategy goal is to overcome the current trend of reducing the use of bicycles for city trips, although as early as 2014, the share of bicycle trips was 23%. Finland's National Action Plan for Walking and Cycling 2020 aimed to increase the political status and importance of walking and cycling and recognize them as equal types of travel to the city. The strategy provided for a 20% increase in the share of cyclists in 2020, compared to 14% in 2014. The France's national plan for cycling is aimed at revising existing policies and developing new types of mobility in cities. The strategy propose to include a mandatory exam in secondary school on the knowledge of traffic rules when traveling by bicycle. The National Cycling Plan in Germany until 2020 is part of a policy for mobility and integrated transport. Its proposed policies go beyond the boundaries of bicycle circulation and include in the development of the so-called

concept of "eco-mobility," which includes walking, cycling as well as local public transport. In the UK's 'A Sustainable Future for Cycling' document the results of the "Cycling England" program are presented. There are different strategies for the development of the cycle infrastructure for different parts of the the UK, such as England, Wales, Scotland, and Northern Ireland. The strategy for the development of cycling and pedestrian activity in England envisages an increase in segments traveled by bicycle from 800 millions in 2013 to 1600 millions in 2025. The development of cycling infrastructure and the promotion of cycling as a means of transportation is a global trend that aims to achieve a more sustainable society and a higher quality of life. Many countries have adopted national cycling strategies that aim to increase the number of bicycle riders and make cycling a safe and accessible transportation option for all [35].

These strategies include various objectives and tasks, such as increasing physical activity, developing urban and regional bicycle infrastructure, and promoting cycling among different age groups. For instance, the Hungarian cycling strategy aims to increment the relative amount of bicycle rides when considering the overall number of rides, while the goal of the Swedish national cycling strategy is to make the bicycle as a type of transport with equal rights and safety. Cycling can be used in different conditions, and cities around the world are finding innovative solutions to make cycling safe and comfortable for their residents. For example, the Norwegian city of Trondheim installed special bicycle lifts on difficult sections of the road to make cycling possible on hilly terrain, while the Finnish city of Oulu has achieved a high percentage of winter bicycle riders by providing snow-cleared tracks and winter tires. These examples show that cycling can be a viable option even in extreme conditions.

7. Conclusions

The car itself deals with comfort and speed, but in many transition economies, including also Republic of Moldova, it is also a social status as a symbol of success and prosperity of its owner.

The bicycle, as a means of transport, is still not part of the usual lifestyle of the majority of Moldovans, especially Chisinau residents, as in the Netherlands or Beijing, and the hills of Chisinau city differ significantly from the flat relief of Amsterdam or Copenhagen. Periods of cold weather and heavy rainfall should not be an obstacle to bicycle use, this can be overcome by better quality of bicycle infrastructure and better level of its maintenance. Being an ecological means of travel and replacing personal automobiles for short and medium-distance city travel, the bicycle also represents an effective way to increase the physical activity as well as time for rest and enjoyment.

A well-developed bicycle and pedestrian infrastructure is a sign of a modern city, where the administration takes care of the comfort, safety and health of the inhabitants. The city of Chisinau has potential and can become in the future a friendly and attractive city for pedestrians and cycling.

The distribution of deaths according to the categories of traffic participants shows, as mentioned above, that, according to estimates, more than 40000 cyclists die in road accidents annually, which constitutes about 3% of the total number of deaths in road accidents worldwide and about 5% at the level of the European Region. The analysis of the statistics regarding the deaths of cyclists as a result of road accidents in the Republic of Moldova during the years 2008-2022 finds that the Republic of Moldova exceeds the world share by 0.66%,

but it is below the share of the European Region. But, the last two years, especially the year 2022, should worry us, because the share of the European Region has been exceeded by about 1.5 times and almost 2.5 times the global one.

It is recommended to hurry the implementation of the bicycle infrastructure development plan in Chisinau city. or, at least compliance with the implementation schedule, as well as taking over the good practice for other localities in the Republic of Moldova, which would contribute to raising the level of road traffic safety and ecology. Also, the development of bicycle infrastructure facilitates the circulation of new means of transport for pedestrians – electric scooters, which are increasingly common on public roads.

Conflicts of Interest: The authors declare no conflict of interest.

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STRUCTURE OF POLYMER/CLAY NANOCOMPOSITES, A MOLECULAR MODELLING PERSPECTIVE

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Abstract. The search for renewable biodegradable materials to replace conventional oil-based plastics is a fast-growing research area as it provides an important factor for the sustainable growth of the packaging industry. In this regard, clay-containing composite materials have numerous current and potential commercial applications. However, the interaction between clay and polymer, i.e. Poly(ethylene glycol), is influenced by many factors, such as the nature of the clay, length and nature of the polymer chain, hence, in this work polymer/clay nanocomposite is studied both ex`perimentally and theoretically. Structural and thermodynamic properties of formulated nanocomposites are probed using XRD and TGA techniques and then compared with corresponding values derived from a series of Molecular Dynamics simulations of intercalated polymer/clay nanocomposites. For the first time, the developed potential models were able to predict realistic basal spacing of poly(ethylene glycol)/clay nanocomposite. The simulation also revealed the structure of the interlayer on a molecular level, which greatly benefited the understanding of the formation of polymer/clay coatings. The swelling dynamics, energetics and structure of the clay interlayers are examined. Particular attention is paid to the behaviour of polymer and water when they coexist in the clay interlayer.

Keywords: *molecular dynamics, montmorillonite, clay, water, polymer, composite, clay-coatings.*

Rezumat. Căutarea de materiale regenerabile biodegradabile care să înlocuiască materialele plastice convenționale pe bază de ulei este un domeniu de cercetare în ascensiune, deoarece oferă posibilitate pentru creșterea durabilă a industriei ambalajelor. În acest sens, materialele compozite care conțin argilă au numeroase aplicații comerciale actuale și potențiale. Cu toate acestea, interacțiunea dintre argilă și polimer este influențată de mulți factori, cum ar fi natura argilei, lungimea și natura lanțului polimeric. În această lucrare, nanocompozitul polimer/argilă este cercetat experimental și teoretic. Proprietățile structurale și termodinamice ale nanocompozitelor formulate sunt testate folosind tehnici XRD și TGA și ulterior comparate cu valorile corespunzătoare derivate dintr-o serie de simulări de dinamică moleculară a nanocompozitelor intercalate polimer/argilă. Pentru prima dată, modelele potențiale dezvoltate au reușit să modeleze distanța bazală realistă a nanocompozitului poli(etilen glicol)/argilă. Simularea a dezvăluit, de asemenea, structura stratului intermediar

la nivel molecular, ceea ce a avantajat înțelegerea formării acoperirilor de polimer/argilă. Se examinează dinamica gonflării, energia și structura straturilor intermediare de argilă. O atenție deosebită este acordată comportării polimerului și apei atunci când acestea coexistă în stratul intermediar de argilă.

Cuvinte cheie: *dinamică moleculară, montmorillonit, argilă, apă, polimer, compozit, acoperiri cu argilă.*

Abbreviations:

MD – Molecular Dynamics Simulation;
MC – Monte Carlo Simulation;
NaMt – Na^{+}-Montmorillonite;
CaMt – Ca^{2+}-Montmorillonite;
PEG – Poly(ethylene glycol)
XRD – X-ray Diffraction;
TGA – Thermogravimetric Analysis.

1. Introduction

One of the reasons that Clay Minerals are efficient adsorbents is that the interlayer spaces are potentially accessible not only for water molecules but for organic materials as well. Thus, it is necessary to investigate the adsorption between the layers to understand the structure of polymer/clay nanocomposite coatings.

Poly(ethylene glycol) (PEG, formula, $H\text{-}(O\text{-}CH_2\text{-}CH_2)_n\text{-}OH$) also known as poly(ethylene oxide) (PEO) or polyoxyethylene (POE) [1] is a non-toxic biodegradable polymer and is one of the most important polymers widely used in biotechnology, pharmaceutical compositions and as a food additive [2, 3]. In recent years, however, it has found popularity in biodegradable food packaging applications [4, 5] where it can be used as a plasticiser for polymer/clay-containing films which are otherwise notoriously brittle [6, 7].

The interaction between clay and polymer, i.e. PEG, is influenced by many factors, such as the nature of the clay, the length and nature of the polymer chain and any solvent present. There are different accounts of the intercalation of PEG in layered silicates in the available literature [8-11]. Studies based on X-ray diffraction propose a highly ordered polymer arrangement within the clay galleries.

One proposed structure of the intercalated PEG is a helix. In this model, the axis of the polymer chain is oriented parallel to the basal surface and exchangeable cations reside in the centre of the interlayer. It was first proposed by Ruiz-Hitzky et al. [12] and was believed to be plausible because only one plateau was observed in the adsorption isotherms, corresponding to the basal spacing of 18 Å. A second possible interlayer structure considers PEG chains to be organised in two extended chains parallel to clay surface layers. Here, exchangeable cations are also positioned in the middle of the interlayer [8, 9, 13]. Unlike the helix conformation, this model contemplates two stages of swelling depending on the amount of PEG available – a monolayer with a d_{001}-spacing of 14 Å and a planar bilayer with a d_{001}-spacing of 18 Å [4].

Using MD and MC simulations, Hackett et al. [14] showed that the intercalated PEG chains in clay-based nanocomposites were arranged parallel to the basal surface of the hectorite galleries. This structure agreed well with the results of neutron scattering

experiments, a review of which was given by Ray [15]. Further simulations of PEG/clay nanocomposites also suggested layered PEG structures [2, 9, 16-19].

Therefore, it is reasonable to take, from the literature, that PEG may adopt various conformations in the galleries of different clays. However, obtaining detailed molecular-scale insight into the structure and dynamics in the interlayer is difficult because of the static and dynamic disorder of these systems. Here, computational approaches, e.g. MD, can be highly informative, especially when considering both hydration and polymer intercalation processes simultaneously. In order to assess the ability of chosen models to simulate the swelling behaviour of PEG/Mt composite and rationalise the simulation observations, some experimental work on the swelling of various montmorillonite clays, when loaded with different amounts of PEG200, was performed.

2. Materials and Methods

A. Experimental techniques

All experimental PEG/clay nanocomposites presented in this work were prepared using the solvent casting method. The bentonite clay samples, Cloisite Na^+ (NaMt) and Cloisite Ca^{2+} (CaMt) were supplied by Southern Clay Products and used as received. The bentonite is predominantly composed of montmorillonite with CEC value of 92.5 meq/100g. PEG of molecular weight of 200 $g \cdot mol^{-1}$ was used as supplied by Aldrich.

For the nanocomposite preparation, the concentration of each component used was based on the total solid content. 3 ± 0.001 g of clay was initially mixed with 60 ml of distilled water in a beaker and agitated for 2 hours using a magnetic stirrer. The desired amount of PEG200 (PEG200, clay=0, 3, 9, 12, 18, 27 wt%) was mixed in 20 ml of distilled water and added to the clay suspension. The PEG200/clay solution was then stirred for a further 6 hours at room temperature before being cast onto a glass slide and placed into a Petri dish. All of the suspensions were dried in an oven at 40 °C for 3 h and then left at room temperature for 12 h before being analysed by XRD, TG and TG-MS. XRD, in particular, provides evidence for the formation of intercalated systems by allowing measurement of the interlayer spacing. In this study, all XRD measurements were undertaken on a X'Pert Pro Diffractometer, Philips. A copper tube CuK_α (1.54186 Å) as the source of X-rays was used with current and voltage of 40 mA and 40 kV applied to it respectively. A divergent slit of 0.5° and anti scatter slit of 1° were used. Data was collected in the 2Θ range of 2-45° with step size of 0.02° and a scan time of 1 second per step. The Petri dishes containing the dispersions were used for general characterisation after grinding.

B. Simulation details

A broad range of PEG200 and H_2O concentrations, ranging from 0 to 0.35 $g_{(PEG200)}/g_{clay}$ (0 to ~7.1 PEG200·uc^{-1}) and 0 to 0.2 $g_{(H2O)}/g_{clay}$ (0 to ~16.5 H2O·uc^{-1}) respectively were used. Range of clay models utilised to simulate PEG/water/Mt intercalated nanocomposite comprised of eighteen montmorillonite models. Molecular dynamics simulations were performed using the Nosé-Hoover thermostat and DL_POLY simulation package with 1.0 ps of relaxation time. For the NPT simulations, a Nosé-Hoover barostat was utilised to control the pressure with a barostatic relaxation time of 1.0 ps. Interatomic interactions were evaluated using a time step of 0.001 ps, and three-dimensional periodic boundary conditions were employed with a cutoff at 10 Å for short-range interactions. Long-range electrostatic interactions were calculated using the Ewald summation with an accuracy of 1×10^{-6}. All MD simulations were performed at 300 K and at 1 atm for the NPT ensemble. Statistical and

atomic position data were collected over the last 1 ns of the simulation and stored every 25 ps to obtain the thermodynamic and structural properties of the simulated systems.

3. Results and Discussion

A. Experimental Characterisation of PEG/water/Mt Intercalated Films

The XRD patterns for PEG/NaMt and PEG/CaMt with a range of PEG200 loadings are presented in Figure 1 and the corresponding calculated d_{001}-spacings are plotted in Figure 2. The diffraction profiles obtained are in very good agreement with numerous previous investigations of PEG intercalation into NaMt [8, 10, 11]. The shift of the XRD peak positions for Na^+ exchanged clay (Fig. 1(a)) indicates the presence of intercalated structures for the whole range of PEG loadings. Even a very small amount of PEG200 (3 wt%) forces the clay layers to expand from 12.7 Å to 13.6 Å (6.98° 2Θ and 6.46° 2Θ respectively). This continues with higher loadings of PEG which gradually fills the interlayer until a complete PEG200 monolayer in the interlayer is apparently formed at 12 wt% (6.22° 2Θ) with a d-spacing of ~14.4 Å (Fig. 2(a)). Further loading of PEG200 (18 wt%) results in the formation of two coexisting structures – monolayer (14.4 Å) and bilayer (16.7 Å) which are apparent from the two peaks in the XRD trace at 6.1° 2Θ and 5.1° 2Θ respectively. The bilayer polymer structure is completely formed when the PEG200 loading reaches 27 wt%, as evidenced by the narrow distribution of d-spacings and the high intensity of the XRD peak, corresponding to a d-spacing of 18.5 Å.

XRD traces suggest completely different behaviour for the Ca^{2+} exchanged clay upon intercalation of PEG200 (Fig. 1(b)).

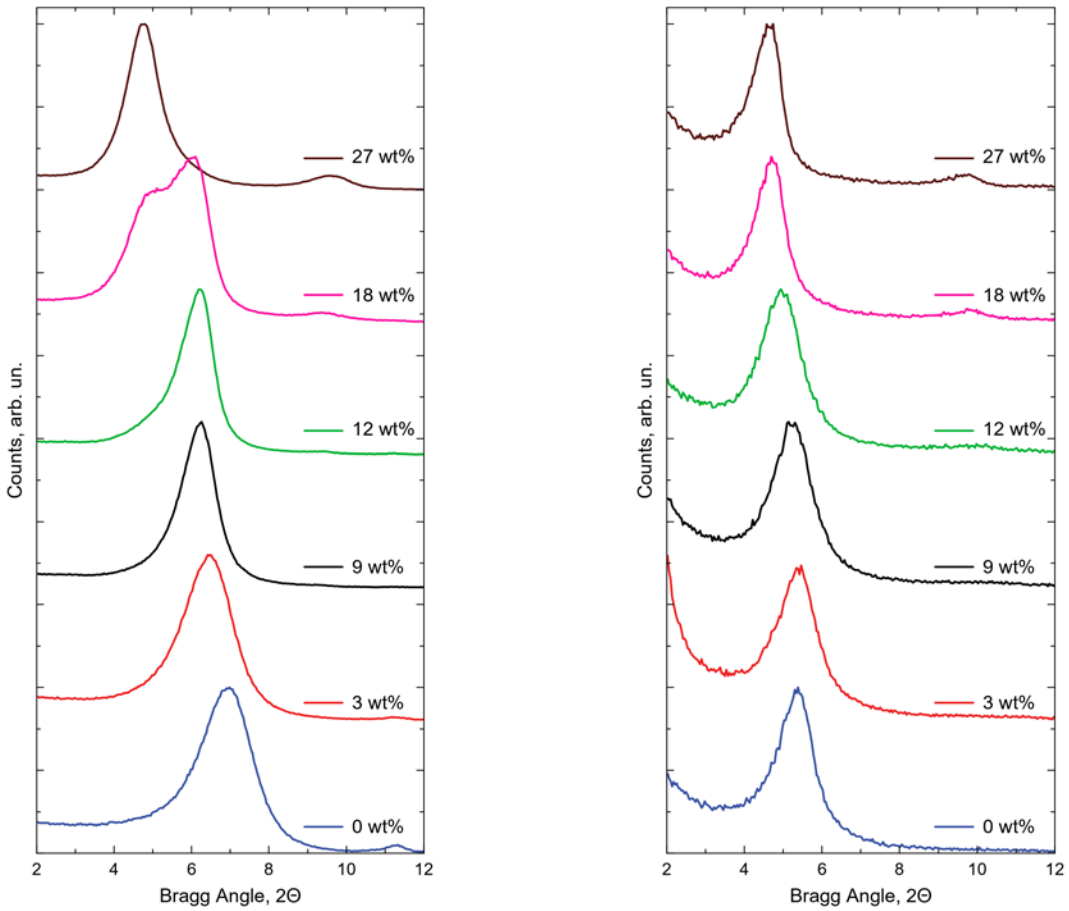

Figure 1. XRD patterns of PEG/Mt with 0–27 wt% PEG200 for a) Na^+-cloisite and b) Ca^{2+}-cloisite.

The XRD peak for the sample with 0 wt% PEG200 is located at 5.68° 2Θ which corresponds to d-spacing of 15.1 Å (Fig. 2(b)). At this point, only water and hydrated Ca^{2+} cations are present in the interlayer. The calculated d-spacing agrees with that of the simulated clay + water systems where it was concluded that CaMt always forms a bilayer hydrate interlayer at ambient conditions, due to the high hydration capability of bivalent the exchange cation. Upon introducing PEG200 into this system, the d-spacing of PEG/CaMt increases nearly linearly until it reaches a spacing of 18.8 Å at 18 wt%. It then levels off, presumably showing the limit of intercalation capability of Ca^{2+}-cloisite at room temperature and normal pressure.

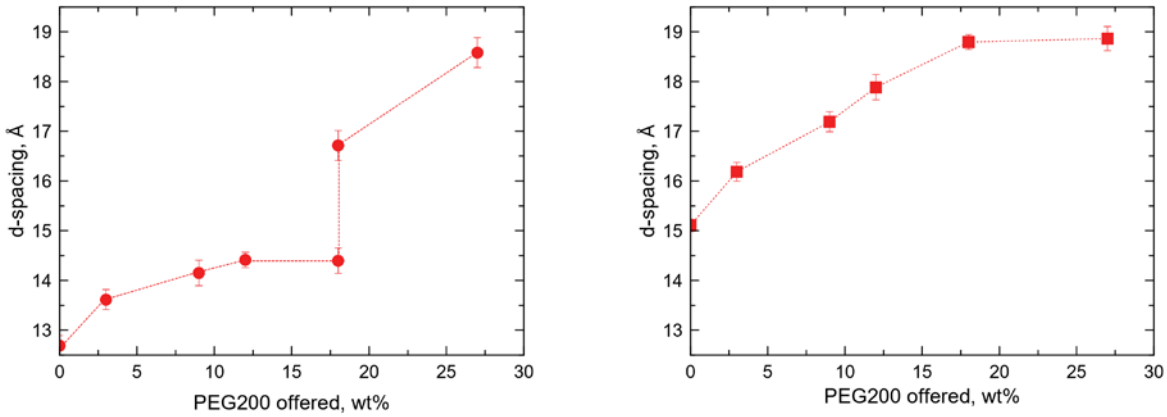

Figure 2. Summary of d-spacing observed in the XRD traces of PEG200/Mt for a) Na^{+}-cloisite and b) Ca^{2+}-cloisite.

Thermal Decomposition of PEG in Nanocomposites

The thermal stability of the formulated samples was investigated using the TGA technique. The thermograms (TG) and corresponding negative derivatives (dTG) for PEG/Mt nanocomposites are presented in Figures 3 and 4 and were utilised to quantify the amount of intercalated PEG and water present in the nanocomposites. Thermal decomposition of the PEG/Mt nanocomposites proceeds as a multiple-step process, (i) weight loss due to the release of water at a temperature less than 225°C; (ii) decomposition of polymer at 250–400°C forming monomers, small oligomers, and other decomposition products [8]; (iii) dehydroxylation of the Mt layer at ~ 700°C. These three processes are intrinsic for both Na^{+} exchanged and Ca^{2+} exchanged montmorillonites, as revealed by the TG curves shown in Figures 3(a) and 3(b) respectively.

The first major weight loss occurs between 35 and 150°C. The reciprocal dTG peak denoted as 1st peak in Figures 4(a) and 4(b), corresponds to the removal of water from the samples. The amount of released water decreases as the PEG concentration increases from 0 to 27 wt% (Fig. 4(a) and 4(b), 1st peak). This indicates that either some of the water present in clay is being replaced by PEG200 [10] or that more compact water aggregates are created which remain in place up to ~ 150°C [11]. A shoulder at ~ 140°C in dTG curve of pure Ca^{2+}-cloisite (Fig. 4(b)) is due to the decomposition of the relatively strong Ca^{2+} hydration shells [8].

Adding as little as 3 wt% of PEG200 to both clays reveals a 2nd weight loss peak between 300°C and 400°C (Fig. 4). The intensity of this peak increases as the amount of PEG in the nanocomposite increases – significantly, up to 7x for NaMt but to a much smaller extent for CaMt (up to 1.5x). The weight loss curves associated with the 2nd dTG peak (Fig. 4) correlate clearly to the shapes and progression of the corresponding XRD swelling curves

(Fig. 2). In particular, the weight loss curves of PEG/NaMt nanocomposites level off between 12 and 18 wt% PEG200 content, which corresponds to a monolayer polymer organisation within the interlayer. Further increase in PEG content results in a significant increase in the weight loss associated with this. The corresponding weight loss of the CaMt-based nanocomposites, on the other hand, reaches a plateau at a lower PEG200 content which corresponds to the formation of a PEG200 bilayer in the interlayer. Similar to the swelling curve, a further increase in PEG200 content does not influence the observed weight loss.

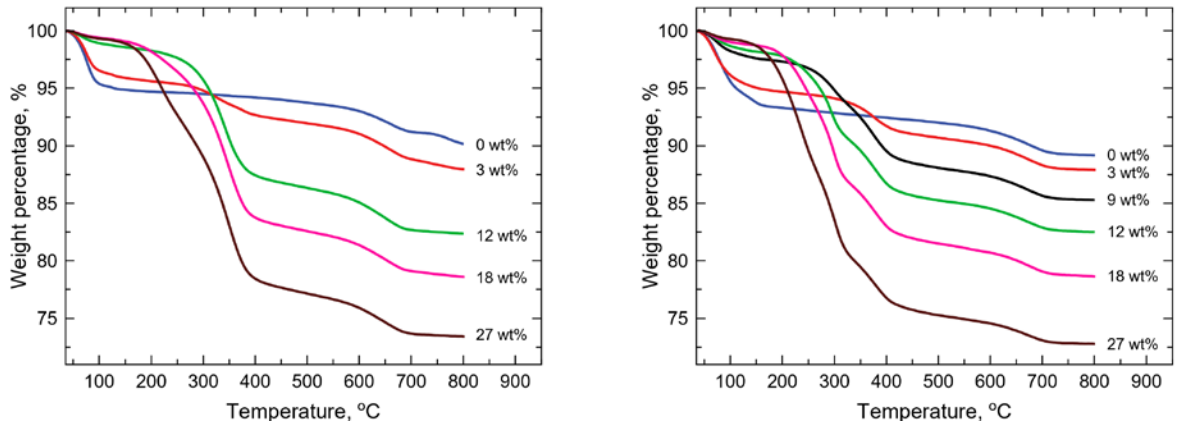

Figure 3. Thermograms of PEG200/Mt with different wt% PEG200 for a) Na^{+}-cloisite and b) Ca^{2+}-cloisite.

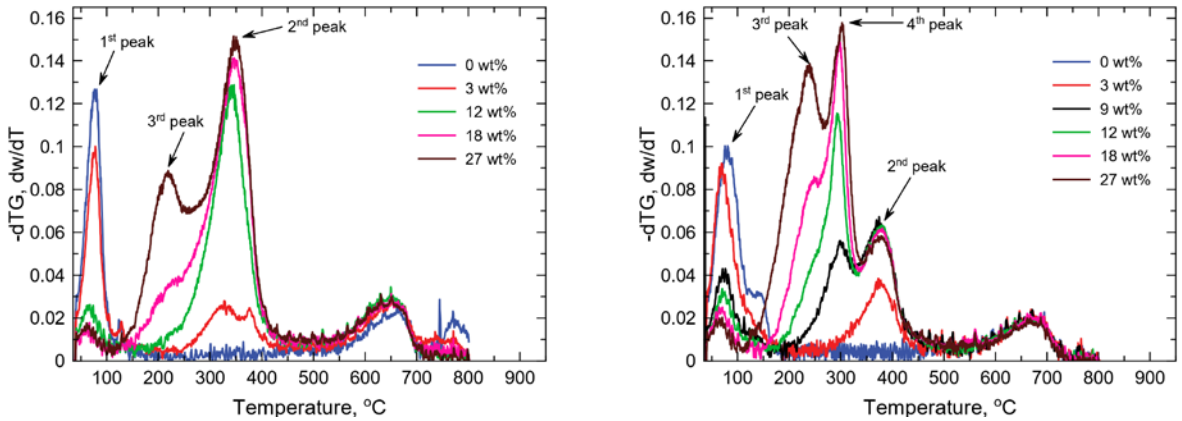

Figure 4. TGA negative derivatives of PEG200/Mt with different wt% PEG200 for a) Na+-cloisite and b) Ca2+-cloisite.

The third peak (Fig. 4(a)) becomes sizeable at PEG200 contents of 18 wt% for NaMt and 12 wt% for CaMt. These loadings correspond to the formation of the bilayer interlayer structure for clays in both exchanged forms (Fig. 2(a)). The weight losses at these corresponding temperatures are nearly linear, especially at high PEG content. One explanation of the 3rd weight loss peak could be not fully intercalated PEG, in which only a few polymer chain segments are occluded by the gallery and the bulk of each molecule remains in solution [9].

The amounts of water and PEG200 for all studied samples, calculated on the basis of TG curves and TGMS analysis, are presented in Table 1. Only the 1st, 2nd and 3rd weight loss peaks (Fig. 4) were taken into account here. It is rather important to recognise that these values do not relate exclusively to intercalated media, as there is no direct way to distinguish intercalated from supernatant adsorption configurations. CaMt retained a higher amount of water for all studied samples, as expected from hydration analysis. For example, pure NaMt

and CaMt contained 5.0% and 7.3% of water respectively. NaMt, on the other hand, adsorbed higher amounts of polymer, giving adsorbed PEG loadings very close to the percentages of offered polymer. As the PEG content in the nanocomposite increased the amount of water decreased for both exchanged clay forms. This suggests that PEG intercalates by replacing the free water molecules in the gallery as well as some water that is directly coordinated to the exchangeable cations.

Table 1

Amounts of PEG and water adsorbed from water solution on NaMt and CaMt, as determined by thermogravimetry

PEG200 offered (wt%)	NaMt		CaMt	
	H_2O amount (%)	PEG amount (%)	H_2O amount (%)	PEG amount (%)
0	5.0	-	7.3	-
3	4.1	3.8	5.4	2.7
12	1.2	10.2	2.2	9.1
18	0.5	17.3	1.5	15.8
27	0.4	23.6	1.1	21.0

Computational simulation of polymer/clay nanocomposite

Figure 5 presents the results of a series of simulations for the intercalation of PEG200 in the montmorillonite exchanged by Na^+ and Ca^{2+} cations. The calculated basal spacing of the clay complex is plotted as a function of polymer content along with experimental data presented previously in this chapter. Carefully selected variable amounts of water in the interlayer were based on experimental data obtained from TGA and TGMS calculations (Table 1). The simulations correctly predict a step-wise swelling behaviour for NaMt. Two plateaux around PEG200 contents of 0.10 and 0.25 gPEG200/gclay are observed (Fig. 5(a)), which supports interlayer polymer organisation in two extended layers parallel to the clay surfaces – monolayer and bilayer.

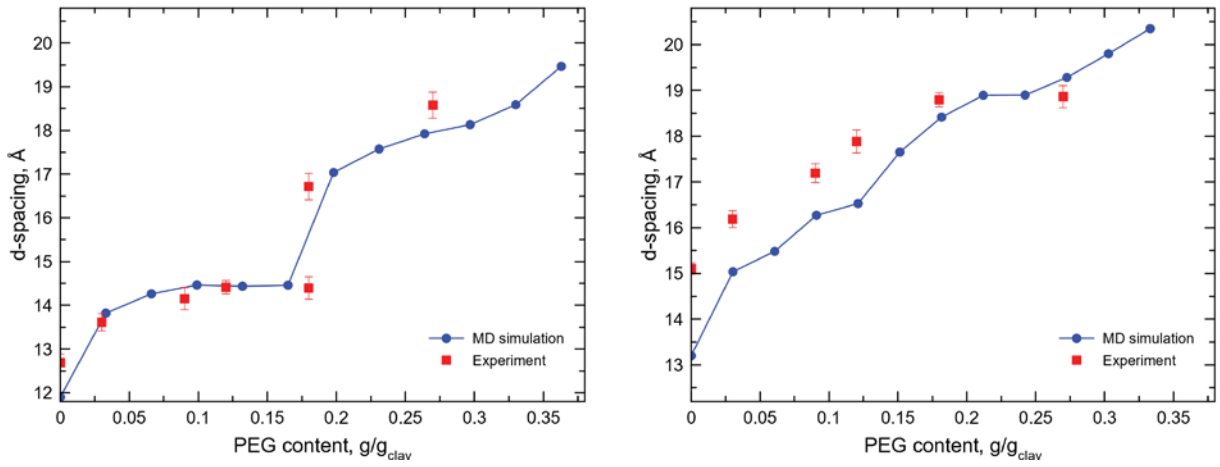

Figure 5. Simulated and experimental basal spacing of (a) NaMt and (b)CaMt as a function of increasing poly(ethylene glycol) (PEG200) content in the interlayer. Amount of water in the interlayer was selected according to experimental findings presented in Table 1.

More importantly, for the first time we have achieved realistic basal spacings from simulation for these two polymer arrangements. The first plateau on the swelling curve corresponds to a monolayer organisation of polymer with a d-spacing of 14.5 Å. This is an excellent match to the experimental observations presented in the previous section as well as previous experimental investigations. [7-9]. The simulated spacing that corresponds to the bilayer polymer structure is approximately 0.5 Å smaller than that obtained experimentally.

Similar to the clay hydration process, the exchangeable cation affects intercalation of PEG significantly (Fig. 5(b)). CaMt exhibits a nearly linear increase in d−spacing with the uptake of PEG200 until reaching a plateau at around 0.2−0.25 gPEG200/gclay with a spacing of 18.8 Å. This plateau corresponds to the formation of a bilayer polymer structure and again matches experimental observations. At lower polymer content, the swelling curve for CaMt is less accurate than for NaMt, however, the nearly linear swelling trend is similar to that observed experimentally. The absence of a stable monolayer polymer structure in the interlayer suggests that the level of uptake of PEG200 by CaMt is smaller when compared to that by NaMt. Similar behaviour was observed experimentally, where the ratio of the uptake of PEG1500 by NaMt to that by CaMt has been found to be about 2.3 [24].

4. Conclusions

Two types of commercially available bentonite clay were used to produce intercalated polymer/clay nanocomposites with a wide range of PEG and water concentrations. This was done to provide an evidence base for direct comparison with computer simulations of similar systems. Also, additional information on the processes involved in the collaborative intercalation of water and PEG into clay mineral was required. Through the use of XRD analysis, particular attention was paid to the interlayer structure of the formulated samples. Thermal stability and quantitative analysis of adsorbed organic material were assessed by TG and TGMS analysis.

XRD analysis indicated significant expansion of both clays studied upon increase of polymer content. Two stable polymer structures within the interlayer of NaMt were identified – a monolayer and a bilayer. The exchangeable cation has a significant effect on the expansion properties of montmorillonite. CaMt did not produce a stable monolayer, showing a linear increase of basal spacing as the polymer content in the system increased, until a stable bilayer polymer structure was created. The value of the d-spacing at 0 wt% of PEG200 was on par with that found in the simulations of the hydration process of clay layers, indicating the presence of a bilayer hydrate in the CaMt interlayer even at low relative humidity.

Experimental measurements of intercalated PEG/Mt nanocomposites showed that polymer chains replace some of the adsorbed water, filling the space between hydrated exchangeable cations. The amount of polymer adsorbed is influenced by the hydration enthalpy of the exchangeable cation, indicating possible associations between those exchangeable cations and the ether oxygen atoms of PEG chains. It was established that the uptake of PEG200 by NaMt is higher than that by CaMt.

The computational model of PEG200/Mt nanocomposites has proved both experimentally and theoretically to be successful at reproducing the structural and thermodynamic properties of all studied nanocomposites. It was shown that polymer chains replace some of the adsorbed water, filling the space between hydrated exchangeable cations. The amount of polymer adsorbed is controlled by the hydration enthalpy of the

exchangeable cation, indicating possible associations between the exchangeable cation and the ether oxygen atoms of the PEG chains. It was also found that montmorillonite mineral preferentially absorbs the high molecular weight fractions of PEG. From an engineering point of view, these results are significant because they suggest that nanocomposites with better barrier and mechanical properties could be obtained by controlling molecular weight distribution to avoid low polymer fractions.

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Conflicts of Interest. The author declares that they have no conflict of interest.

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PROCESSING OF MICROSTRUCTURES OF METAL SURFACES WITH CHEMICAL-THERMAL TREATMENT IN LOW VOLTAGE ELECTROLYTIC PLASMA

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Abstract. The main reason for these researches is to solve the problem of intensification of the alloying process by electric sparks by increasing the energy of the electric pulses. In relation to this, the purpose and object of the research is the need to assume a new concept of organizing the alloying process in order to intensify the strengthening of metal surfaces, excluding the negative effects. Among the electrophysical methods of layer formation, a special place is occupied by alloying by electric sparks of metal surfaces, considering the multitude of its characteristic advantages, which are the following: high adhesion of the deposited coatings, the possibility of depositing coatings of any conductive materials, the simplicity of the process and the low consumption of energy for its implementation. The main results are that after the heating in the electrolyte, the cooling takes place in the air, then in the superficial layers of the samples treated in this way residual tensile stresses act. In conclusion, it is important to mention that through the combined processing the properties of the superficial layers and the exploitation characteristics can be controlled.

Keywords: *metals, electrolyte, materials processing, electrolytic plasma, pressing, chemical-thermal, process.*

Rezumat. Motivul principal al acestor cercetări este acela de a rezolva problema intensificării procesului de aliere prin scântei electrice prin creșterea energiei impulsurilor electrice. În raport de aceasta, scopul și obiectul cercetării este necesitatea asumării unui nou concept de organizare a procesului de aliere în vederea intensificării întăririi suprafețelor metalice, excluzând efectele negative. Dintre metodele electrofizice de formare a straturilor, un loc aparte îl ocupă alierea prin scântei electrice a suprafețelor metalice, având în vedere multitudinea avantajelor sale caracteristice, care sunt următoarele: aderență ridicată a învelișurilor depuse, posibilitatea depunerii de acoperiri a oricărui conductor conductor. materialelor, simplitatea procesului și consumul redus de energie pentru implementarea acestuia. Principalele rezultate sunt că după încălzirea în electrolit are loc răcirea în aer, apoi în straturile superficiale ale probelor astfel tratate acționează tensiunile reziduale de tracțiune. În concluzie, este important de menționat că prin prelucrarea combinată se pot controla proprietățile straturilor superficiale și caracteristicile de exploatare.

Cuvinte cheie: *metale, electrolit, prelucrare materiale, plasmă electrolitică, presare, chimio-termic, proces.*

1. Introduction

The general name of "electrotechnologies" combines various technological processes, special features of which consist in the use of electricity to achieve technological transformation of materials (changes in condition, composition, structure, shape and operating properties, etc.) [1, 2].

Electrotechnologies as a separate field of materials technology has no strictly set limits, but in practice they can be classified into the following processes and methods:

1. Electric welding (with arc, contact, electric drill, etc.).
2. Galvanic deposits of metal coatings (electroplating, electroplating).
3. Induction heating, with high and high frequency currents (melting, soldering, heat treatments).
4. Methods of electron-ion technology (electrostatic painting electrophoresis, etc.).
5. Electrophysicochemical methods and combined processing of materials.

It is important to note that for a better acquisition of the theoretical material a special role is played by practical laboratory work and seminars in the research process have the ability to deepen their knowledge in the theoretical classes [3].

This guide proposes a cycle of works, which aims to familiarize students in theory and practice with laboratory techniques in the field of electrophysical methods of processing. It is addressed to future specialists, who want to deepen their knowledge in the field of high technologies.

The processing of metals and especially electrolytic plasma steels effectively solves complicated technological problems. Among the advantages of the method can be listed the following: obtaining high heating rates up to quite high temperatures, practically up to melting temperature, the possibility of a complete automation of the process in mass production, diversification of thermal and thermochemical processing operations, also soldering as well as making deposits by melting, etc., the possibility of locating and obtaining a strictly limited heating area; the ease of adjusting the thermal parameters by changing the electrical parameters; a specific energy consumption; non-aggressiveness of the work environment [4].

A simpler process for reducing the roughness is the subsequent sparking of the alloyed surface with a graphite electrode at a lower regime, than during the formation of the coating itself [6-8]. In this case, due to the substantial specific resistance of graphite compared to metals, in the places where the electrode contracts with the micro-irregularities, as a result of the release of Joule heat at the moment of the short circuit, the melting of these micro-irregularities takes place. However, since in the alloying by electric sparks with a graphite electrode as a result of the transfer of the electrode material to the cathode, there is no increase in the coverage, but only the diffusion of carbon atoms in the alloy surface, with a multiple action of electric pulses the roughness of this surface decreases. Thus, as a result of the sparking of the coatings with the use of the graphite electrode, not only the reduction of the surface roughness is obtained, but also the synthesis of different carbon compounds, which in the end, improve the physico-chemical and exploitation characteristics of the superficial layers [5].

However, these preliminary results did not allow for an in-depth knowledge of the laws of the processes that take place in the space between the electrodes and in the superficial layers of the cathode during the alloying by electric sparks during the simultaneous action of the magnetic field superimposed on the working area and the direct

passage of the current electrically through anode and cathode. These new knowledge can only be obtained in the case of systematic studies of all aspects of this new variant of the alloying process by electric sparks. Systematic studies on the influence of additional energy sources on the ASE process are being carried out for the first time [6]. Under these conditions, the opportunity for research is evident, and the objectives of the doctoral thesis refer to the following aspects:

- analysis and presentation of the results of worldwide research in the field of alloying by electric sparks;
- the development of the research method and the creation of specialized devices and installations for conducting experimental investigations and for the application of technology.
- establishing the legality of the formation of coatings on the surface of the cathode - part under different conditions of the action of continuous and pulsating electric current, as well as of the magnetic field;
- establishing the redistribution of elements and the transformations of structure and phase in the superficial layers subjected to AES in the magnetic field and when the electric current passes through the electrodes;
- evaluation of the structural, substructural, tensional, physical-mechanical and operational characteristics (microhardness, residual stresses, wear resistance, electroconductivity) of the layers obtained during complex processing:

a) alloying by electric sparks with the additional action on the AES of the magnetic field and the electric current;

b) alloying by electric sparks with subsequent plasma chemical treatment in electrolytes;

- the establishment of complex technologies with industrial applications for obtaining coatings on construction alloys [7, 8].

2. Materials and Methods

When carrying out the experimental part, certain technological parameters of processing were taken into account. Thus the voltage on the electrolytes must be adjusted between 0-300 V, the current density up to 50 A/cm^3 in the transaction mode, and up to 2 A/cm^3 in the heating mode and ensuring the fuselage of the electrolyte, the temperature of which in the processing process does not must exceed 30 °C. Steel 45 (0.45% C) was used to carry out the work and cutting knives were made directly to the right with the following construction elements [9].

Testing of 45 steel hardened electrolytic plasma hardened and Y13 heat-treated knives was performed on the 1K62 lathe on a 20 mm cylindrical rolled 45 steel semi-finished product at the following cutting speeds:

- cutting speed- v = 20 m/min;
- cutting depth t = 1 mm;
- federate S = 0.1 mm/rot.

The amount of wear was determined with the help of a laboratory microscope with a magnification of 25 times.

2.1. Theoretical-practical methods and variants of materials processing

At the continuous increase of the voltage on the electrodes of the bath, at the beginning, the normal electrolysis process takes place in this region, the dependence

between current and voltage has a linear character and is described by Ohm's law. A further increase in voltage leads to the beginning of the first phase intensive formation of gases on the surface of the cathode - is manifested by oscillations of the liquid in the cathode region, the appearance of spark discharges, and with characteristic cracks. The further increase of the voltage leads to the increase of the number of unit discharges and finally on the surface of the cathode the formation of a luminous coating takes place, the intensity of the current again increases. The second phase of the process begins, through which the heating of the cathode surface takes place. It is not recommended that the total voltage (e.g. 220 V) be applied to the electrodes, in which case the process will proceed abnormally in accordance with the first phase [10].

The method has its drawbacks, such as the need to make a special machine and certain devices for it: complicated machine to ensure a safe operation due to high voltages; difficulties in directly controlling the temperature of the parts to be processed; some difficulties in processing long profiled parts; a yield not exceeding (40-45 %).

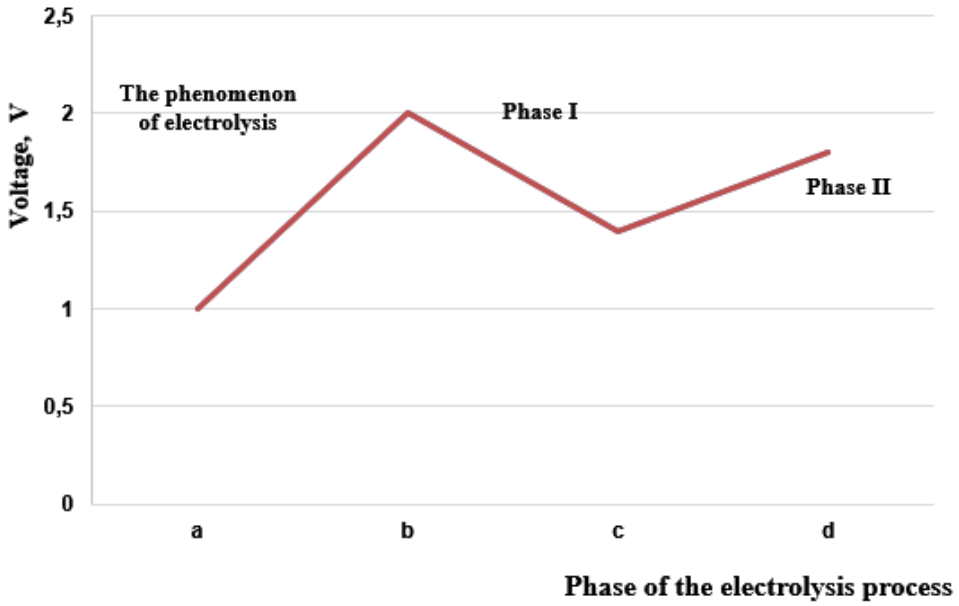


Figure 1. The typical volt-ampere characteristic of the phases of the plasma electrolytic processing process [10].

The typical volt-ampere characteristic of the phases of the electrolytic plasma processing process is shown in Fig.1. At the continuous increase of the voltage on the electrodes of the bath, at the beginning, the normal electrolysis process (a-b) takes place in this region, the dependence between current and voltage has a linear character.

A further increase in voltage leads to the beginning of the first phase (b-c) intensive formation of gases on the surface of the cathode - is manifested by oscillations of the liquid in the cathode region, the appearance of spark discharges, and with characteristic cracks. The further increase of the voltage leads to the increase of the number of unit discharges and finally on the surface of the cathode the formation of a luminous coating takes place, the intensity of the current again increases.

The second phase of the process (c-d) begins, through which the heating of the cathode surface takes place. It is not recommended that the total voltage (e.g. 220 V) be applied to the electrodes, in which case the process will proceed abnormally in accordance with the first phase [12].

2.2 Tempering the parts by the free end heating method

This method hardens the valve heads, bolt heads, screws, pushers, regulator clutch heads, etc. The high precision of the length of the end subjected to heating is maintained by ensuring the constant immersion depth of the part which is the cathode in the electrolyte. The metal bath connects to the positive pole of the DC circuit.

The depth of immersion of the part is determined by means of the fixing device. The possibilities of using the process are determined by the section, shape and length of the end of the part to be heated. When increasing the section and the length of the end subjected to processing, the current density is distributed unevenly. Such a condition leads to melting of the end and first of all of the parts that are sharp. Basically, this process is only used for machining the cylindrical and spherical ends of parts with a diameter of up to 15 mm and a length of 5-10 mm [11].

2.3 Hardening and annealing of the heads by shielding them

Expanding the region of the end use of heating contributes to its shielding and the extremities. To reduce the current density on the ends based on the sharp ones (edges), the parts are fixed on an electrically insulating refractory material. Using screens (screens) it is possible to evenly heat parts with a diameter of 30-35 mm when immersing in electrolyte up to 40 mm.

2.4 Processing of materials by pressing

The principles of metalworking in electrolyte before forging, stamping, bending, discharge are the same as in other cases. The only difference is that before pressing, the metal is heated to full volume, but not only on the surface, as in hardening. Such processing is carried out by the appropriate selection of heating regions and occurs in installations used for tempering. Semi-finished products with a diameter of 100 mm may be subjected to such processing.

When the constant conditions regarding the composition, concentration and temperature of the electrolyte are observed, the heating regimes are regulated only by changing the voltage of the current source and the heating time [12].

The advantages of the electrolyte heating method are manifested in the process of performing concrete operations in a certain way. Gluing excludes the need to use fluxes, reduce the use of soldering material, significantly increase productivity, the possibility of simple automation of lines in the torrent. Local or general heating, volume or surface heat treatment or mechanical heat treatment - this technology allows easy adjustment of heating rate, no surface oxidation, preservation of the initial roughness and accuracy of the parts to be processed, use for any electroconductive materials, simplicity of automation and simple operation. In the case of white incandescent annealing of wires, thin pipes, flexible shafts, etc. - high production quality and simplification of operations are achieved. In the process of baking and hot pressing of parts made by the powder metallurgy method - there is a correlation of the joining of the grains between them, with pressing in an operation, - simplification of technology, increase of quality of parts, articles. The basic conditions for obtaining a uniform and economical heating consist in creating a necessary current density on the cathode and maintaining a correlated ratio between the surface of the cathode and the anode [12].

The surface of the anode must exceed the surface of the cathode not less than 10 times. The uniformity of the heating of the surface of the piece of complex shape is carried

out by changing the distance between the different sectors of the anode and the cathode to obtain on the whole surface of the cathode approximately the same current density. The speed and temperature directly depend on the size and duration of the current flow, but in each case the absolute values of these indices are different depending on the type of items subjected to heating [12].

2.5 Wear resistance

The tribological tests of the superficial layers obtained from the additional energetic action on the alloying by electric sparks process were carried out in two stages. First of all, the wear resistance of the coatings was evaluated using the express method at the installation, the principle scheme of which is presented in Figure 2 [13].

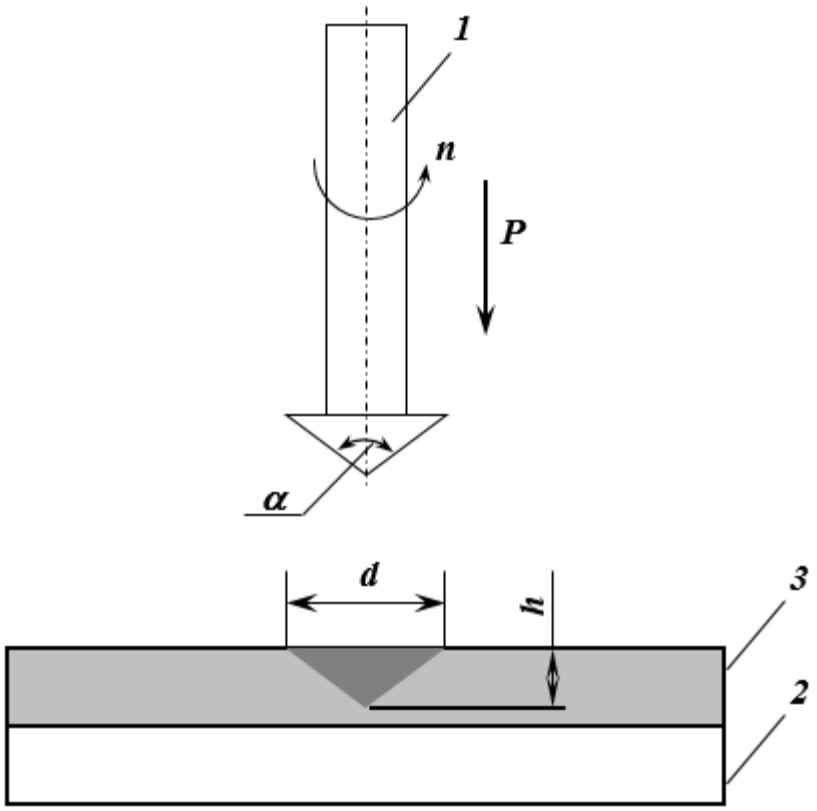


Figure 2. Scheme of the wear resistance measurement procedure: 1 - centering device with penetrator; 2 - sample; 3 - cover; *d* - diameter of the footprint; *h* - penetration depth of the penetrator: *n* - rotation frequency of the penetrator; P - force, applied to the penetrator; *α* - the angle at the tip of the penetrator (*α* = 90 - 1500) [14].

Depending on the thickness of the coating and the microhardness of the layer subjected to the test at different depths, the parameters that determined the wear of the layer were measured. The essence of the method of measuring the wear resistance of the material using this procedure consists in determining the diameter and depth of the imprint when rotating the diamond penetrator with an eccentricity of no more than 0.1 μm. The measurement accuracy is ~1.0 μm. The dimensions of the fingerprint on the sample-standard coated by the traditional method of spark alloying were taken as 100%, and the ratio of the dimensions of the fingerprint on the investigated samples with coatings obtained by alloying by electric sparks, in the magnetic field compared to the standard was chosen as the unit of wear resistance for the given test procedure [14].

The samples for the tests were made at optimal regimes of alloying by electric sparks in the magnetic field, for which conditions were created to obtain coatings with greater thicknesses and higher quality for the given pair of materials of the anode and the cathode. For example, when depositing silver coatings, the discharge energy (Wd) and magnetic field induction (B), superimposed on the processing area, were chosen, starting from the condition of minimal irrecoverable losses of silver and obtaining a uniform and continuous coating. These parameters were: Wd = 0.1 J and B = 0.06 T. When establishing these parameters in the case of alloying by electric sparks with Ni, Cr, Al, graphite electrodes, the discharge energy was 10 times higher and was 0.9-1.0 J for magnetic field induction 0.074 T.

In the second stage, the samples with similar coatings were tested for wear on the MI-1 and CMT-1 standard rubbing machines.

Under the conditions of friction without grease, the load was 140 N/cm^2 at the sliding speed of 0.3 m/s, and at the semi-liquid friction, respectively 700-750 N/cm^2 and the sliding speed 1.3 m/s. Such a regime was chosen in order to create conditions close to those of exploitation.

Industrial oil -20A was chosen as the grease, which was introduced into the friction area at the rate of 3-4 drops per minute. The coatings by electric spark alloying were deposited on the cylindrical generator of the 50 mm diameter roller. The contact surface of the track with the roller was approximately 100 mm, which made it possible to substantially save the running-in time.

In a series of cases alloying by electric sparks nickel, silver and chromium coatings were smoothed with a 12 mm diameter hard ball of 15 steel with a spring smoothing device at a load of 300 N. The rotation speed of the part (roller) and the advance of the support are established in accordance with the recommendations of D.D. Papsev and the support of the advance constitute 50-100 m/min and the rotation speed of the piece is 0.15-0.2 mm/rot. The hard layers, obtained by electric spark alloying with tungsten carbide-based hard alloys, were first smoothed with a hard ball, and then with a diamond grinder with a radius of 1.5 mm at a load of 15-20 kF and respectively the advance is 0.05 mm to obtain the roughness 3.0...0.32 μm is recommended for the surfaces of the friction pairs [15].

The results of the tests, in which the wear of the coating over time is determined, is presented on Figure 3.

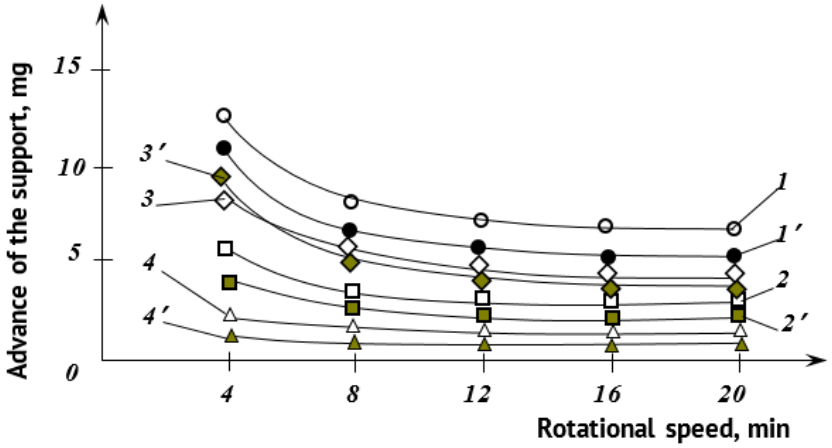


Figure 3. Wear over time of alloying process by electric sparks coatings in traditional airing: 1 - Al; 2 - Cr; 3 - Ni; 4 – graphite and at alloying by electric sparks in magnetic field: 1' - Al; 2' - Cr; 3' - Ni; 4' – graphite [15].

3. Results and Discussion

The obtained results show us that if, after heating in the electrolyte, the cooling takes place in the air, then in the superficial layers of the samples treated in this way, residual tensile stresses act. Tempering in the electrolyte, however, leads to the formation in them of residual compressive stresses with maximum values in the depth of the superficial layer.

Based on this, the conclusion can be drawn, that with the combined processing, possibilities are created to control the properties of the superficial layers, and therefore, the exploitation characteristics [17].

The chemical-thermal treatment is more fully performed under the regime of heating in low voltage electrolytic plasma.

The results of the calculations are shown in Table 1.

Table 1

Wearing the face of the lathe knives

The path taken by the cutting tool, m	The size of the back surface wear, mm
100	0.1-0.4
200	0.2-0.4
300	0.2-0.6
400	0.3-1.0
500	0.7-2.0

Considering the limit wear for knives hs = 0.5 mm, the length of was obtained cutting for 45 steel spindles, processed into voltage electrolytic plasma low equal to 465 m, and for heat-treated U13 steels equal to 260 m.

A considerable number of scientific papers have been written about the influence of the magnetic field on the mechanism and kinetics of transformations in the heat treatment process of steels, whose results are analyzed in the specialized literature [17].

In the previous chapter, the influence of the magnetic field on the initial and intermediate phases of alloying process by electric sparks was studied in detail: the erosion of the anode and the transfer of the eroded material to the cathode. But it is necessary to appreciate the influence of the magnetic field on the final phase of this process, that is, the formation of the superficial layer on the cathode.

Because in the process of alloying with electric sparks on the electrodes, in particular, in the superficial layers of the cathode as a result of the thermal action of the impulse discharges, micrometallurgical processes occur with phase and structure transformations, with diffusion phenomena, etc. The constant magnetic field on the alloying zone with electric sparks is applied in such a way that in one case it ensures the parallelism of the vectors of the magnetic induction and the discharge current, when they coincide ($\vec{B} \uparrow\uparrow \vec{I}_d$) or have opposite directions ($\vec{B} \downarrow\uparrow \vec{I}_d$), and in another case - their perpendicularity ($\vec{B} \perp \vec{I}_d$).

It should be mentioned that for the proposed energy and time parameters of the alloy with electric sparks, no displacements of the reflexes were observed on the radiographs, that is, they were not fixed to the voltage of the second degree. This was verified at AES with ammonium anodes of copper and iron samples. On fig. 4. the concentration curves of chromium distribution in St. 3 are presented in the case of the presence of the field and in its absence.

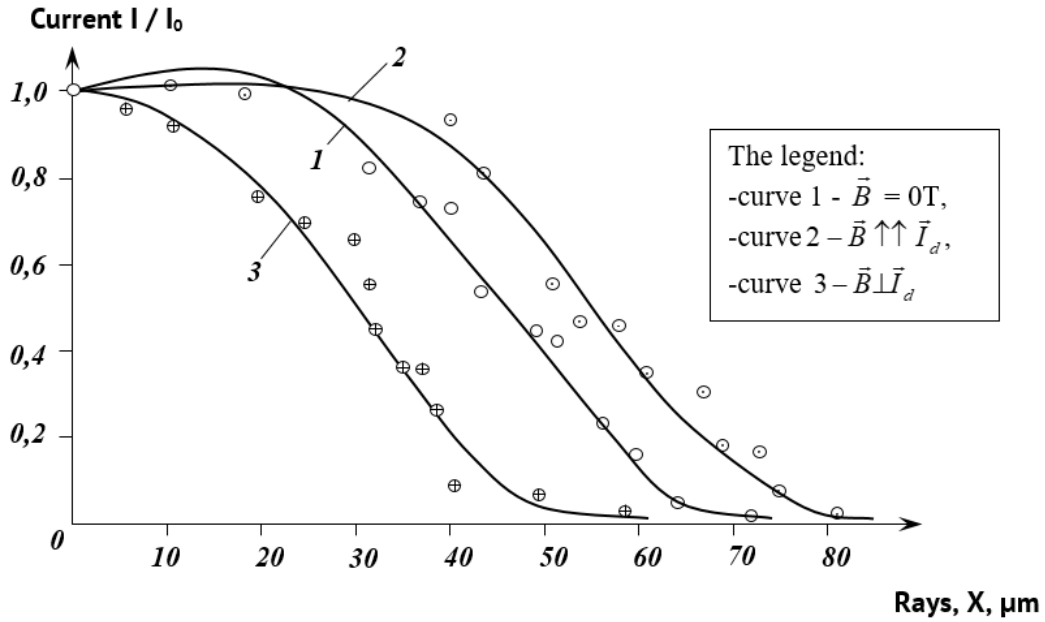
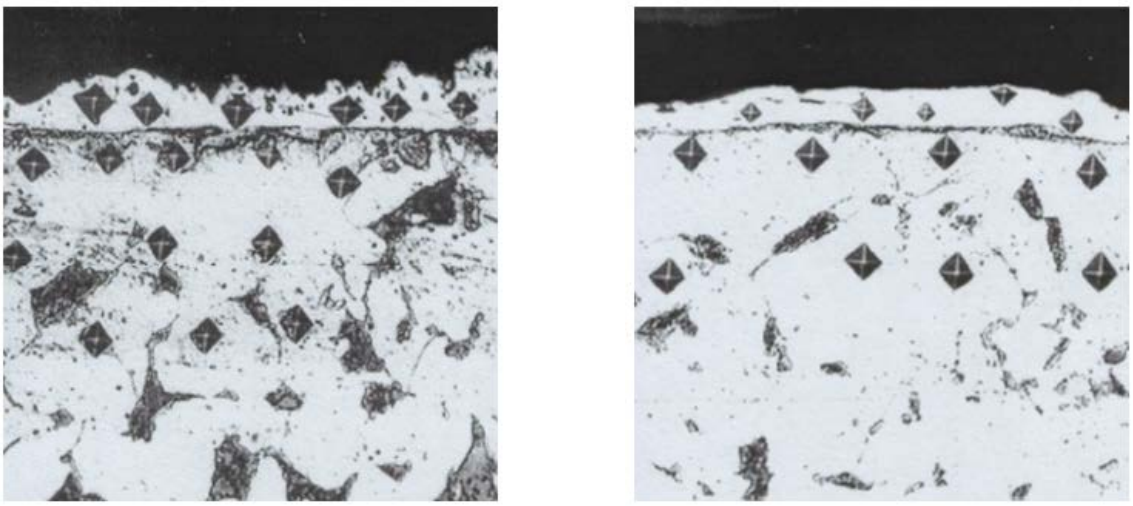


Figure 4. Chromium distribution curves in the coating at alloying process by electric sparks in a magnetic field.

From the analysis of fig. 4. it turns out that the application of the magnetic field parallel to the vector of the discharge current ($\vec{B} \uparrow\uparrow \vec{I}_d$) (curve 2), contributes to increasing the depth of chromium penetration. But when changing the direction of the magnetic field by 90^0 ($\vec{B} \perp \vec{I}_d$) (curve 3), the penetration depth of the chromium atoms decreases substantially.



a) b)

Figure 5. The microstructure of the sample from St. 3, subjected to AES with nickel under normal conditions (a) and in a magnetic field (b); discharge energy 0.3 J, specific alloying time – 1 min/ cm^2; x 500 (Made by the author).

The superimposition of the magnetic field also affects the solubility of the alloying element in the matrix. Thus, the parameter of the steel network, which in its initial state was 0.28771 nm, after alloying with electric sparks with chromium for γ = 0 decreases by 0.0006 nm as a result of the dissolution of chromium in it, and under the action of the magnetic field

- by 0.0010 nm, which speaks of the content in the solid solution of a larger amount of chromium [18].

Through the metallographic analysis and measurement of the surface roughness, it is confirmed that the magnetic field, superimposed on the processing area, influences the intensification of the mixing of materials, contributing to the increase of homogenization and the formation of more uniform coatings by thickness (fig. 5).

When alloying St.3 steel with electric sparks in a magnetic field with graphite anodes, the phase composition of the superficial layers changes less than in the usual alloying conditions. For example, the change of network parameters of the iron solid solution constituted 8×10^{-3} nm and 2×10^{-3} nm, respectively for the case of alloying with electric sparks in the absence of the field and in its presence. At the same time, the content of cementite and austenite in the diffusion zone is practically the same in both cases.

4. Conclusions

In conclusion, it should be noted that:

1. The dependences of the mass transfer and the intensity of the deposition of the hardened layer on the size and nature of the electric current passing through the electrodes as well as on the parameters of the magnetic field superimposed on the area of alloying by sparks were established.

2. The phenomenon of quasi-regular oscillation of the intensity of the anode material transfer in the process of pulse discharge and structure and phase transformations in the superficial layers of the cathode under the action of the magnetic field superimposed on the alloy area was discovered.

3. It was established that when the direct current with the density of 1 – 3 A/mm^2 passes through the anode, a maximum amount of material of the anode and respectively of the addition of the cathode was obtained, and the variation of the induction of the magnetic field within the limit of 0.01 – 0.1 T allows directing in a wide range the processes of physicochemical transformation in the surface layers of the cathode.

4. The dependence of the intensity of the coating formation on the surface of the cathode on the magnetic properties of the processing electrode and the matrix was established. Under equal conditions in the magnetic field of the St.3 matrix with a nickel electrode, the intensity of the eroded mass transfer in a unit of time is 3.5 - 4.0 higher than when processing with a silver electrode.

Conflicts of Interest: The author declares no conflict of interest.

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TRACTION CAPACITY OF RECHARGEABLE LFP BATTERIES FOR TROLLEYBUS

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Abstract. The article deals with the actual problem of reducing air pollution by internal combustion engines of public transport in urban and suburban traffic through the use of battery trolleybuses for passenger transportation. A method is proposed for calculating the capacity of batteries for the autonomous movement of trolleybuses, which can be used to calculate the required capacity of trolleybus batteries for use on city bus routes partially passing under the trolleybus overhead contact wires. The calculation of the required capacity of the lithium iron phosphate (LFP) battery for the operation of the battery trolleybus on the real bus route of the Chisinau municipality has been carried out.

Keywords: *Calculations of the energy consumed by a trolleybus, calculation of the capacity of storage LFP batteries, choose the optimal power of storage batteries*

Rezumat. Articolul este dedicat problemelor actuale a reducerii poluării aerului de către motoarele cu ardere internă ale transportului public în traficul urban și suburban prin utilizarea troleibuzelor cu baterii pentru transportul de persoane. Se propune o metodă de calcul a capacității bateriilor pentru deplasarea autonomă a troleibuzelor, care poate fi utilizată pentru a calcula capacitatea necesară a bateriilor de troleibuz pentru utilizare pe rutele autobuzelor urbane care trec parțial pe sub firele de contact aeriene ale troleibuzului. S-a efectuat calculul capacității necesare a bateriei litiu fier fosfat (LFP) pentru funcționarea troleibuzului cu baterii pe ruta reală de autobuz a municipiului Chișinău.

Cuvinte cheie: *Calcule ale energiei consumate de un troleibuz, calculul capacitatii acumulatorilor LFP, alegerea puterii optime a acumulatorilor.*

Abbreviations

Bl service life of lithium-iron-phosphate battery (LFP), years.
Ccell nominal capacity of LFP cells, Wh.
Cdc charge/discharge cycles of LFP battery.
Cstored electrical energy stored in the battery, kWh
Cstored, *one section* - electrical energy stored in one battery section, kWh.
DoD depth of discharge of LFP battery, %.
EFK number of discharge/charge cycles of LFP battery.

f rolling resistance coefficient.
fc coefficient of rolling resistance at low speed (fc = 0.015… 0.025).
G weight of the vehicle, N.
G_B weight of the bus Ikarus 260.0, N.
G_F weight fuel, kg.
G_T weight of the trolleybus RTEC 62321, N.
kf the coefficient of increasing the consumption of useful energy of the trolleybus for rolling additional mass.
L_A autonomous run of trolleybus (long autonomous mileage), km
L_R full length of bus route, km.
$Ndpy$ number of days of operation of a trolleybus, year.
η_{TOTB} coefficient of efficiency of a bus engine.
η_{TOTT} coefficient of efficiency of a trolleybus with a battery.
P_{fB} the power expended by the bus to overcome rolling resistance on a flat road surface, kW.
P_{fT} the power expended by a trolleybus to overcome rolling resistance on a flat road surface, kW.
P_f the power expended to overcome rolling resistance on a flat road surface, kW
Q_{TEF} the thermal energy of the diesel fuel, kJ.
Qy specific heat of combustion for diesel fuel, kJ/kg.
$Unom$ rated output voltage of one battery section,V DC.
v speed of the vehicle within the city, m/s.
W_{CET} the total energy consumption of a trolleybus, kWh.
W_{CETA} the total energy consumption of a bus, kWh.
W_{EEF} the electric equivalent of diesel fuel energy, kWh.
W_{UWB} useful work produced by the bus engine, kWh.
α angle of the road, angular degrees.
γ_{Fl} specific gravity of one liter of summer diesel fuel, kg/dm^3.

1. Introduction

The problem of air pollution in cities from internal combustion engines of vehicles has stimulated the search for alternative sources of energy for transport. Urban public transport buses, taxis and trolleybuses are equally good at transporting passengers. However, trolleybuses have an important advantage - they do not pollute the atmosphere. Research has shown that trolleybuses significantly help to reduce emissions of nitrogen oxides, non-methane volatile organic compounds and particulate matter, while increasing sulphur dioxide emissions on the served lines. They also generate lower specific emissions of carbon dioxide compared to diesel buses [1]. At the same time, trolleybuses have a drawback - they depend on power supply devices, that is, for their operation, it is necessary to build traction networks and substations. With the invention of batteries with a high energy capacity per unit weight, trolleybuses were able to move autonomously using the energy stored in the batteries.

The energy content of batteries has increased significantly due to the successful commercialization of lithium-ion batteries (LIB) in the 1990s. The LIB energy density has been increasing at a rate of less than 3% over the past 25 years [2]. Practically, the energy densities of 240–250 Wh kg–1 and 550-600 Wh L–1 have been achieved for power batteries.

Such battery trolleybuses, when moving on contact networks, use current both for movement and for charging batteries. This made it possible to lengthen urban transport routes to the suburbs without spending on the development of a contact network and to replace buses on these routes. For autonomous movement on long routes, it is necessary to install batteries of appropriate energy capacity on trolleybuses to cover energy costs for movement.

The determination of energy consumption for the autonomous movement of a trolleybus has been considered in numerous articles. Sinhuber, Rohlfs & Sauer (2012) [3] and Rogge, Wollny & Sauer (2015) [4] used a simulation model to determine the energy consumption on the route and to calculate the required battery capacity. Rogge et al. (2015) discussed the trade-off between passenger traffic, battery capacity and the relationship between charging power and battery capacity when electrifying the existing bus network. Battery capacity is investigated by Gao et al. (2017) [5] Researchers have concluded that operational requirements and charging concept have a significant impact on battery size and design. Safonau (2012) [6], believes that when calculating the energy consumed by traction vehicles, the following methods can be used:

- on the curves of currents I (t), obtained as a result of traction calculations;
- analytical, based on the assessment of the components of the energy balance;
- empirical, based on the analysis of experimental data obtained under basic conditions.

At the same time, Safonau (2012) [6], believes that these methods do not take into account random factors (intervals between trolleybuses, interference with passing vehicles, passenger compartment occupancy, road conditions, meteorological factors, etc.), but deterministic factors (acceleration, inclines, resistance to movement, etc.) are taken into account by averaged values. Calculations by these methods can be taken as approximate with errors of up to 30%, and as a method with a greater degree of accuracy, the thrust calculation should be used, since in it the main factors are taken into account in a more rigorous mathematical model. Safonau (2012) [6], concludes that the most accurate determination of energy consumption is possible only on the basis of statistical probabilistic methods, which requires a number of experimental studies [6].

However, the fuel consumption of the bus is the best indicator of the energy consumption for the transportation of passengers. Therefore, it is of practical interest to determine the energy consumption for the transportation of passengers on the route according to the fuel consumption of the bus, as well as to calculate the required battery capacity of battery trolleybuses - this is the purpose of this work. The proposed method for calculating the power of the trolleybus battery when replacing buses on city routes is illustrated with a specific example.

2. Use of battery-powered trolleybuses in the mun. Chisinau

In the municipality of Chisinau since June 2017 on the route number 30, from the center of Chisinau to the International Airport of the Moldovan capital. started using hybrid battery trolleybuses instead of Ikarus 260 buses These trolleybuses model RTEC 62321 were purchased in Belarus and assembled in Chisinau [7].

The production of these trolleybuses, including battery ones, was organized by the Moldavian production holding “Informbusiness”, which produces power and low-voltage electrical equipment for trams and trolleybuses in cooperation with the Belarusian plant “Belkomunmash”. Trolleybuses assembled in Moldova on the basis of the electronics of the "Informbusiness" holding and Belarusian bodies and chassis for BKM-321 cars were named

RTEC model after the name of the municipal transport company of the capital of Moldova - "Regia Transport Electric Chișinău". The low-floor urban RTEC 62321 has a microprocessor control system, and a braking energy recovery mode is provided. The battery trolleybus is equipped with two lithium-iron-phosphate battery sections, 2x80 LiFePO4 (LFP) cells each. LFP cells have a nominal voltage of 3.2 V, a nominal capacity of 40 Ah [9], that is, *Ccell* = 128 Wh. Therefore, one section is capable of storing a charge of electrical energy:

$$\begin{aligned} &Cstored\ ,\ one\ section = Ccell \cdot Ncell \\ &Cstored, one\ section\ = 128 \cdot 160 \\ &Cstored\ ,\ one\ section = 20\ 480\ Wh = \ 20.5\ kWh \end{aligned} \quad (1)$$

The section output voltage is *Unom* = 512 V DC. Section weight - 300 kg. The holding "Informbusiness" informs that the batteries installed on RTEC 62321 trolleybuses provide the total number of discharge/charge cycles *EFK* = 20 000 (by Depth of Discharge *DoD* = 51% see figure 1) These indicators are in good agreement with the data of PowerTech Systems [8]. The expected service life is 6 -7 years at 10 charge cycles per day. The "Informbusiness" holding claims that the RTEC 62321 battery trolleybus can travel up to 50 km without being connected to a power source.

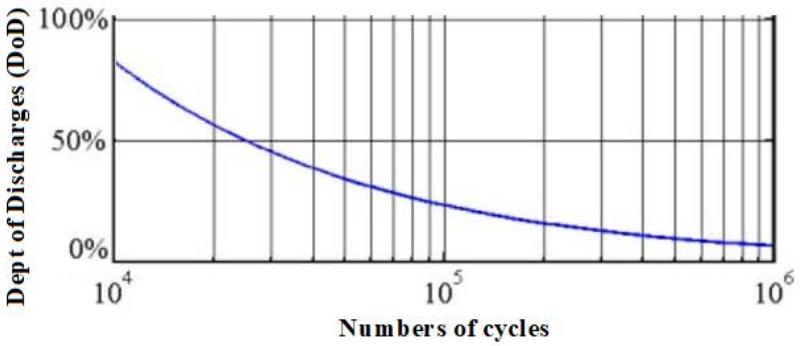

Figure 1. Life Cycle chart of new LiFePO4 cell generation [8].

After the appearance of route Nr. 30 in Chisinau, several more new trolleybus lines to the suburbs of the capital were launched to the airport (see Table 1).

The Directorate of Electric Transport of Chisinau municipality noted the positive effect of using the RTEC 62321 battery trolleybuses; they are three times more economical on municipal routes than diesel buses. Therefore, it is of practical interest to investigate bus routes in Chisinau, which partially coincide with the routes of trolley buses, for the use of battery trolley buses.

Analyzing the routes given in table 1 should be noted:

- all routes, with the exception of Nr. 30, are new and during their development the length of the autonomous run was chosen equal on average to 50% of the total length of the route;
- the routes are served by trolleybuses with an autonomous running reserve of 50 km, at the same time this cruising range is used by less than 47% (see Table 1);
- battery trolleybuses replaced minibuses on commuter routes and reduced air pollution from minibus diesels.

Table 1

Routes served by battery trolleybuses in mun. Chisinau

Route	Round trip route length, km	Autonomous mileage, km	Autonomous mileage from the entire route, %	Power reserve utilization, %
Nr. 30 - to airport	28.9	15.0	51.9	30.0
Nr. 31 - to Singhera	36.5	23.2	63.6	46.4
Nr. 32 - to Stauceni	24.0	11.2	46.6	22.4
Nr. 34 - to Trusheni	31.6	17.1	54.1	34.2
Nr. 35 - to Durlesti (circular route)	19.3	10.4	53.7	20.8
Nr. 36 - to Ialoveni	28.4	14.4	50.7	28.8
Nr. 37 - to Bubuieci	21.7	9.2	42.5	18.4

Based on data on routes served by RTEC 62321 battery trolleybuses in mun. In Chisinau, we can conclude that the autonomous running range declared by the "Informbusiness" holding is more than twice the autonomous mileage on the routes.

Determination of the required capacity of trolleybus batteries when replacing buses on city routes is the goal of this work. The proposed method for calculating the power of the trolleybus battery is illustrated with a specific example.

3. Methodology for calculating the energy consumed by trolleybuses on bus routes

The thermal energy of the diesel fuel, Q_{TEF}, in joules, can be expressed in W_{EEF} kilowatts. The useful work produced by the bus engine and spent for the transport of passengers by the W_{UWB} can be determined through the efficiency coefficient η_{TOTB} of the engine, transmission and other systems of the bus.

This energy will be spent by a trolleybus of equal weight to perform for useful work. The total energy consumption W_{CET} of a trolleybus can be determined through the efficiency coefficient η_{TOTT} of the battery, electric motor, transmission and other trolleybus systems.

When driving outside the contact network, the trolleybus covers the full energy consumption W_{CET} with the energy stored in the battery.

The application of the methodology is demonstrated by solving a specific problem: calculating the required battery capacity for the RTEC 62321 trolleybus when replacing the Ikarus 260 bus on bus route Nr. 23 (see Figure 2).

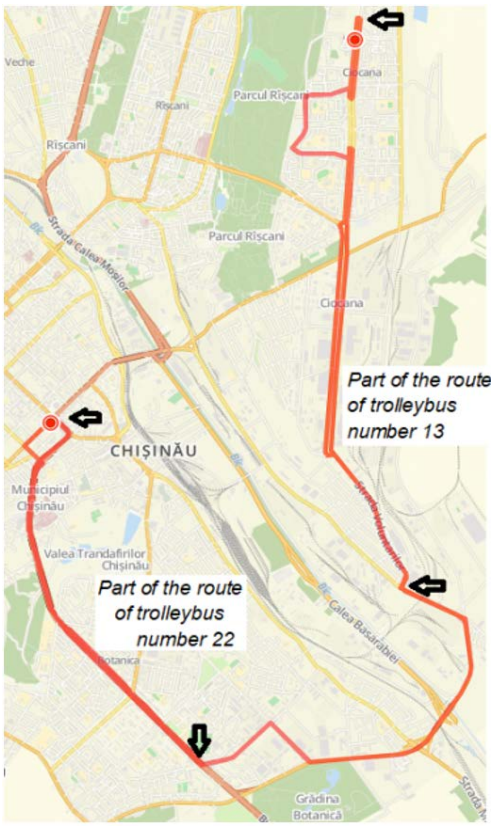

Figure 2. Diagram of connecting public transport lines of bus number 23 and trolleybus numbers 22 and 13 in Chisinau (source: own development based on OpenStreetMap [10]).

4. Approximate calculation of the energy consumed by the trolleybus on the bus route

Bus route Nr. 23 str. Izmail - bvd. Mircea cel Batrîn passes under the contact wires of the trolleybus route Nr. 13 – 5.75 km, and under the contact wires of the trolleybus route Nr. 22 – 6.0 km, that is 11.75 km from the length of the route L_R = 19.45 km, and in the autonomous total mileage L_A = 7.70 km (1.95 + 5.75) (see Figure 1).

Table 2

Technical characteristics of rolling stock

Bus Ikarus 260.01 release 1980 [8]	**Trolleybus RTEC 62321 (AKSM-32100M) release of 2017**
High floor city bus, single link, three door	Low-floor, city trolleybus single-link, three-door
Diesel engine - RABA-MAN D2156HM6U, Power - 250 HP at 2200 rpm	Asynchronous traction motor Power - 180 kW
Maximum speed - 66 km/h	Maximum speed - 70 km/h
Gross mass of the bus – 16 000 kg The mass of the equipped bus – 9 000 kg	The total mass of the trolleybus – 18 000 kg Weight of the equipped trolleybus - 11 100 kg
Total capacity: 102 - 107 passengers	Total capacity: 115 passengers

A bus of the Ikarus 260 type on the bus route Nr. 23 in Chisinau, when performing the transportation of passengers, consumes fuel: 7.6 L of diesel fuel [11].

Let's calculate the energy of the combustion heat of diesel fuel used by a bus of the Ikarus 250 type for a run of L_R = 19.45 km of route Nr. 23 and find the equivalent of this energy in kilowatt hours of battery charge required for a trolleybus with the same weight and number of passengers carried.

According to the current GOST [12], for summer diesel fuel at a temperature of 20°C, the specific gravity must be within γ_F = 860 kg/m^3, which means that the specific gravity of one liter will be γ_{Fl} =0.86 kg/dm^3, and, accordingly, the weight is 7.6 L fuel: G_F =6.54 kg. Specific heat of combustion for diesel fuel is in the range of Qy = 43 000 kJ/kg [13]. Therefore, therefore for G_F = 6.54 kg the thermal energy of the fuel Q_{TEF}:

$$\begin{gathered} Q_{TEF} = G_F \cdot Qy \\ Q_{TEF} = 6.54 \cdot 43\,000 \\ Q_{TEF} = 281\,220 \text{ kJ} \end{gathered} \quad (2)$$

Let's convert the thermal energy of the fuel in joules Q_{TEF} into the electric equivalent of fuel energy Q_{TEF} in watt-hours based on the ratio 1 Wh = 3 600 J, the conversion factor will be equal to kp = 1 Wh / 3 600 kJ = 0.28 Wh/kJ.

The electric equivalent of diesel fuel energy W_{EEF} will be equal to:

$$\begin{gathered} W_{EEF} = Q_{TEF} \cdot kp \\ W_{EEF} = 281\,220 \cdot 0.28 = 78\,742.60 \text{ Wh} \\ W_{EEF} \approx 78.74 \text{ kWh} \end{gathered} \quad (3)$$

To determine the amount of energy used to perform the useful work of the bus W_{UWB}, we use the efficiency of the engine, gearbox and other systems of the bus η_{TOTB} = 0.26 [14]:

$$\begin{gathered} W_{UWB} = W_{EEF} \cdot \eta_{TOTB} \\ W_{UWB} = 78.74 \cdot 0.26 \\ W_{UWB} = 20.47 \text{ kWh} \end{gathered} \quad (4)$$

The bus has a gross weight of 16 tons: G_B = 2 841 N, and the RTEC 62321 trolleybus has a gross weight of 18 tons: G_T = 3 196 N, that is, 2 tons more. The consumption of useful energy will be larger, in proportion to the power expended on rolling the additional mass. Let us determine the power P_f spent on overcoming the rolling resistance on a flat road surface (we take the elevation angle of the road $\alpha = 0^o$), at a speed of 60 km/h within the city limits, that is, v = 16.67 m/s according to the "Eq. (5)" [15]:

$$\begin{gathered} P_f = (G \cdot f \cdot v \cdot \cos(\alpha)) /1000 \\ \text{where: } f = fc\,(1+ v^2/1500) \\ f = 0.025\,(1 +16.672^2/1500) = 0.030 \end{gathered} \tag{5}$$

For the bus: $P_{fB} = (2\,840.97 \cdot 0.030 \cdot 16.67 \cdot 1) / 1000 = 1.420$ kW
For a trolleybus: $P_{fT} = (3\,196.10 \cdot 0.030 \cdot 16.67 \cdot 1) / 1000 = 1.598$ kW

The coefficient of increasing the consumption of useful energy of the trolleybus for rolling additional mass km will be equal to the ratio of the power spent to overcome the rolling forces of the trolleybus to the power to overcome the rolling forces of the bus:

$$\begin{gathered} kf = P_{fT} / P_{fB} \\ kf = 1.598 / 1.420 \\ kf = 1.13 \end{gathered} \tag{6}$$

For a run on bus route Nr. 23 with a length of L_R = 19.45 km, a battery trolleybus with an efficiency η_{TOTT} = 0.65 [14] and a useful weight 2 tons more than the bus will consume energy W_{CET} equal to:

$$\begin{gathered} W_{CET} = W_{UWB} / \eta_{TOTT} \cdot kf \\ W_{CET} = 20.47 / 0.65 \cdot 1.13 \\ W_{CET} = 35.59 \text{ (kWh)} \end{gathered} \tag{7}$$

At the same time, only on the section of the bus route between trolleybus routes Nr. 13 and Nr. 22 there will be a long autonomous mileage L_A = 5.75 km on battery energy with energy consumption in proportion to the energy consumption for the full length L_R:

$$\begin{gathered} W_{CETA} = W_{CET} \cdot L_A / L_R \\ W_{CETA} = 35.59 \cdot 5.75 / 19.45 \\ W_{CETA} = 10.52 \text{ kWh} \end{gathered} \tag{8}$$

RTEC 62321 trolleybuses are equipped with an LFP battery of 2 sections with a capacity of *Cstored* each, one section – 20.5 kWh, therefore, when operating a trolleybus with one section on route Nr. 23, the battery discharge with an autonomous run of the L_A = 5.75 km section will be *DoD*:

$$\begin{gathered} DoD = W_{CETA} / Cstored, \text{ one section} \cdot 100\% \\ DoD = 10.52 / 20.5 \cdot 100\% \\ DoD = 51\% \end{gathered} \tag{9}$$

According to the data of PowerTech Systems [8], at a battery discharge rate of 1C and a depth of discharge *DoD* = 51%, the expected number of discharge/charge cycles is *EFK* = 20 000 cycles. If the trolleybus is operated for *Ndpy* = 340 days per year and charge/discharge cycles *Cdc* = 16 per day battery life per year will be *Bl*:

$$Bl = EFK / (Ndpy \cdot Cdc)$$
$$Bl = 20\,000 / (340 \cdot 16) \quad (10)$$
$$Bl = 3.67 \text{ years}$$

the LFP battery will last 3.67 years.

Then you can replace this section with a second one and get the same service life of the LFP battery as 7.3 years announced by holding "Informbusiness".

The calculation showed that on bus route Nr. 23, an RTEC 62321 trolleybus with one LFP battery section can be used. Therefore, the cost of a trolleybus when installing one section will be 3 000 USD cheaper. In addition, the trolleybus's curb weight will be less by 300 kg.

5. Conclusions

The proposed method makes it possible to calculate the power of a trolleybus battery required to serve a bus route, based on the technical characteristics of the bus running along this route and data on fuel consumption for passenger transportation.

The proposed method improves accuracy and facilitates feasibility studies for replacing buses on urban routes.

The application of the proposed method allows you to choose the optimal power of batteries for autonomous operation of trolleybuses and reduce the cost of purchasing trolleybuses.

The application of the methodology is shown on a specific example of replacing a bus with a battery trolleybus on the city route Nr. 23 in the municipality of Chisinau. The calculation shows that on the bus route Nr. 23, it is possible to use the RTEC 62321 trolleybus with just one LFP battery section. Consequently, the cost of a trolleybus when using one section instead of two regular ones will be cheaper by 3,000 US dollars, at the same time, the curb weight of the trolleybus will decrease by 300 kg.

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Conflict of interest. The author declares no conflicts of interest.

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REPUBLIC OF MOLDOVA: ASSESSMENT OF ENERGY POVERTY

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Abstract. Energy poverty is a topic addressed every time when it comes to supplying residential customers with energy - either from traditional or from renewable sources. In the context of the preparations of the Republic of Moldova for the accession to the EU, it is relevant to evaluate the structure of energy consumption of households in the country, the level of related costs, as well as the level of energy poverty. The paper presents data on the evolution of household energy consumption for the period 2010-2020. For a reference year (2019), the level of poverty in the country was assessed under different aspects (by living environment – urban and rural, by socio-economic status (5 categories), by household size (5 cat.) etc.). From the calculations, the average value of the level of energy poverty, characteristic to the Republic of Moldova, as a whole, for the year 2019, was equal to 15.7 % and a slightly higher value for the urban area. The paper also presents the new government initiative to support energy-vulnerable households - the "Help at the meter" program.

Keywords: *energy poverty, energy poverty rate, energy vulnerability, vulnerable energy consumer.*

Rezumat: Sărăcia energetică este un subiect abordat de fiecare dată când e vorba de furnizarea de energie clienților rezidențiali – fie din surse tradiționale, fie din surse regenerabile. În contextul pregătirilor Republicii Moldova pentru aderarea la UE, este relevant să se evalueze structura consumului de energie al gospodăriilor casnice din țară, nivelul costurilor aferente, precum și nivelul sărăciei energetice. În lucrare sunt prezentate date cu privire la evoluția consumului casnic de energie pentru perioada anilor 2010-2020. Pentru un an de referință (2019) a fost evaluat nivelul sărăciei în țară sub diferite aspecte (după mediul de trai – urban și rural, după statutul socio-economic (5 categorii), după dimensiunea gospodăriei (5 categorii) etc.). Din calculele realizate a rezultat valoarea medie a nivelului sărăciei energetice, caracteristice Republicii Moldova, în ansamblu, pentru anul 2019, egală cu 15,7 % și o valoare un pic mai mare pentru zona urbană. În lucrare este prezentată și noua inițiativa guvernamentală de sprijin a gospodăriilor vulnerabile energetic - programul „Ajutor la contor".

Cuvinte-cheie: *sărăcia energetică, rata sărăciei energetice, vulnerabilitate energetică, consumator energetic vulnerabil.*

1. Introduction

In modern society ***energy*** has great economic, social and political value. The lack of energy has a strong impact on our daily lives.

In the second half of 2021 as the world economy recovered after the restrictions related to COVID-19 were lifted - in Europe, as in the rest of the world, the prices of natural gas and electricity began to rise rapidly. Later, in 2022, Russia's invasion of Ukraine intensified this phenomenon, causing great anxiety regarding energy security in our country - the Republic of Moldova, as well as in the most European states. Russia's decision to suspend gas supplies to some states, as well as to cut supply to many other states, has further worsened the situation. During this period, the price of natural gas in Europe reached record values - about 2500-3000 Euro/th.m^3.

The sudden increase in the price of gas naturally led to the increase in the price of electricity. In a short time, the majority of the country's population (about 80-90%) became vulnerable. In these circumstances the government comes up with compensations for households to reduce the burden of high energy costs.

The European Green Deal (EGD), which is a package of policy initiatives, launched the EU's goal of achieving climate neutrality by 2050 and aims to put the EU on the transition path to a fair and prosperous society with a modern and competitive economy. The EGD mentions the need to alleviate energy poverty and support the just energy transition for all, so that no one is excluded [1].

2. Legal aspects regarding the approach to energy poverty in the Republic of Moldova

In general perception, the term *energy poverty of households*, refers to a situation created by the combined presence of three unfavorable factors:

- low household income,
- low energy efficiency of the housing stock and
- high energy prices (for natural gas, electricity and thermal energy),

when a person or a household cannot afford to heat or cool the home to the preset thermal comfort level.

According to [2] - *the state is obliged to take measures so that every person has a decent standard of living, which ensures the health and well-being of him and his family, including food, clothing, housing, medical care, as well as the necessary social services.*

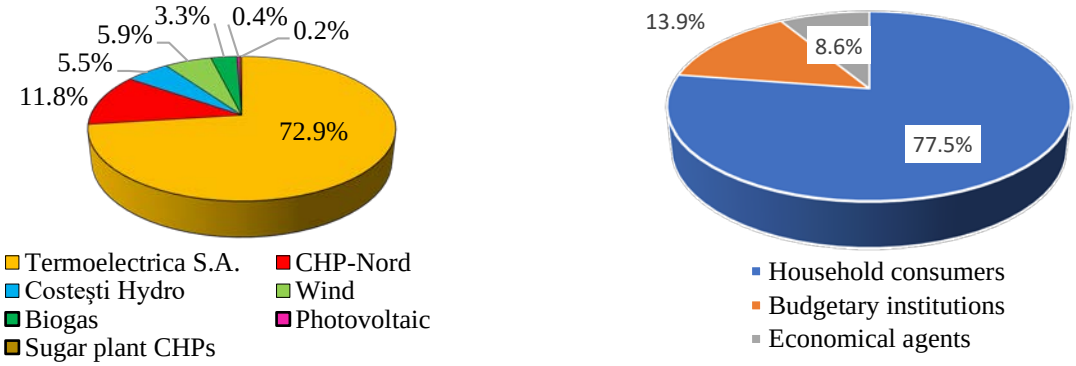
In the two "sister" laws - the Law on Electricity [3] and the Law on Natural Gas [4], the definition of the term *vulnerable consumer can be found: the household consumer who, in accordance with the normative acts in the field of social protection, is considered a disadvantaged person or disadvantaged family member*. Again, in the Law on Energy efficiency [5] *energy poverty* is defined as *a situation characterized by the final consumer's lack of access to modern sources of energy and technologies and/or by the reduced purchasing power of consumers in relation to (the cost of) energy resources, especially fuels for food preparation, electricity and/or thermal energy, and/or due to the lack of thermal comfort in the home or building.* A successful definition of energy poverty is proposed by *the Convention of Mayors for Climate and Energy, later taken up by* the European Committee of the Regions [6]. According to this source - ***energy poverty*** is "a *situation where, due to the combination of low income, high energy costs and low energy efficiency of the home, a person or a household cannot afford basic energy services (heating, cooling, lighting, mobility and electricity supply), which guarantees a decent standard of living*".

In the Republic of Moldova, the National Bureau of Statistics (NBS), the central state body in the field of national statistics, annually determines a set of poverty indicators, unfortunately, without separately presenting the phenomenon of energy poverty.

3. Developments in the energy supply of households in the period 2010-2020

In the last decade in the Republic of Moldova, there was an evolution of the total energy consumption, in weak growth, at an average rate of about 2%/year, while the practical household consumption held fairly stable values at the level of 1200-1300 thousand tons oil equivalent per year. The variation of annual energy consumption at the level of household consumers is mainly determined by the variation of the climate from year to year.

Figures 1-4 illustrate the evolution over time of the total energy consumption in the country, consumption of electricity, thermal energy, natural gas and energy losses, as well as the evolution of energy delivery tariffs to residential sector. Part of this information has been received from the National Bureau of Statistics, and another part from the National Energy Regulatory Agency (ANRE). The presented consumption curves indicate that residential consumers have the largest share in all three forms of energy consumption (electricity, heat and fuels). In 2020, the share of the population in electricity consumption was 46% and in heat consumption – 78.7%. As a result of the significant increase in the prices of energy and energy resources, residential consumers incur enormous expenses just for the supply of energy.



a) b)

Figure 1. Structure of domestic electricity production (a) and thermal energy supplies by consumer categories (b) in 2020 [7, 8].

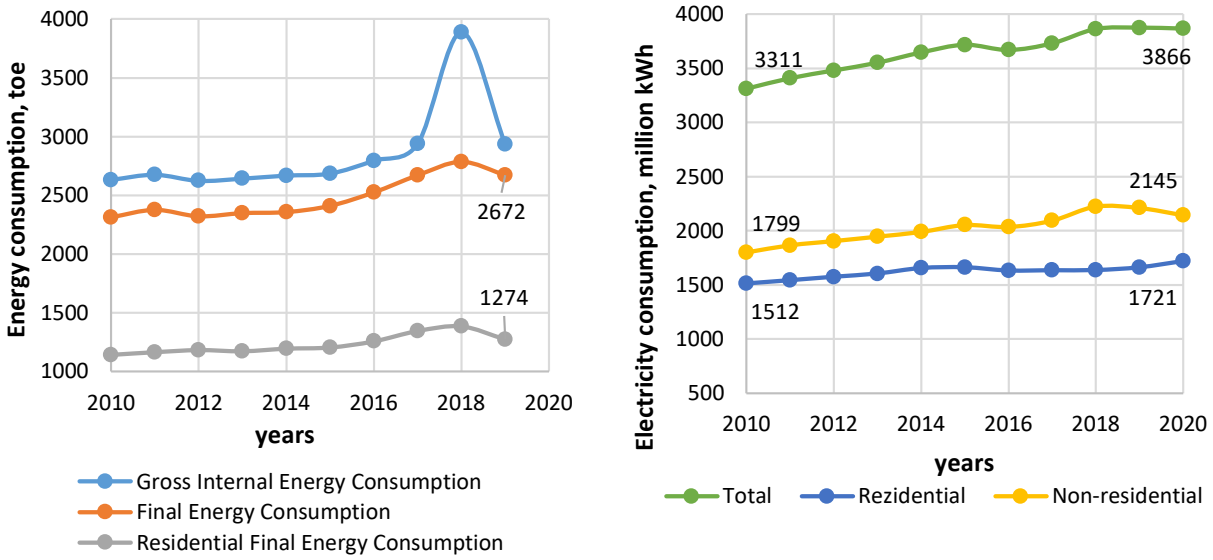
4. Assessment of the poverty level in the country. General aspects

In the Republic of Moldova*, the standard of living of the population* is determined annually by the National Bureau of Statistics based on a special study known as the *Household Budget Research* (CBGC).

By the notion of *household* (GC), hereinafter - *household*, is meant a group of two or more people who live together habitually, generally having family ties and having a common budget, participating fully or partially in generating income and spending it, or a person who lives and manages separately and does not belong to another household.

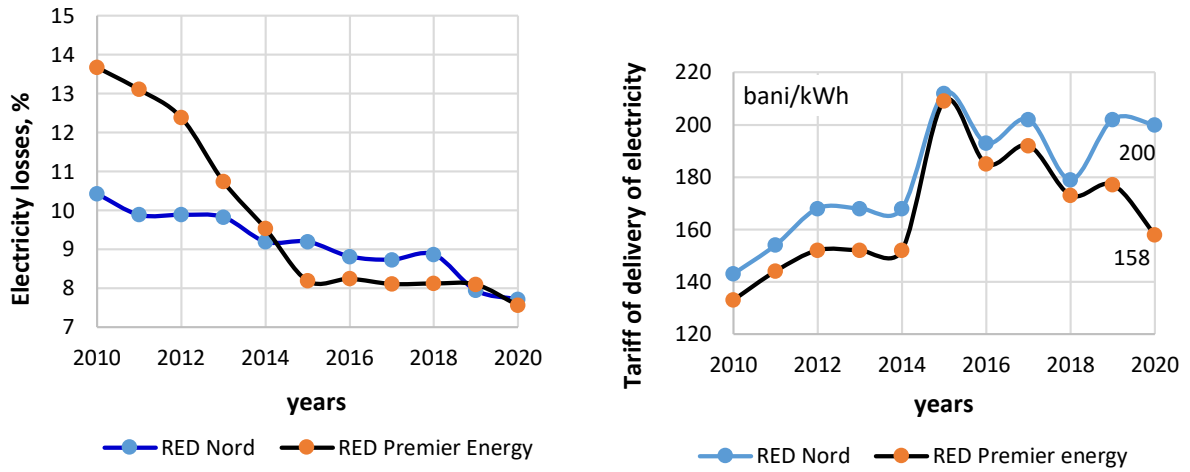
As a rule, household poverty is measured on several dimensions, among them:

- by residence environments – urban, rural;
- by groups of quintiles (1, 2, ..., 5);
- according to the socio-economic status of households;
- according to household size – 1, 2, 3, 4 and ⩾ 5 persons, etc.



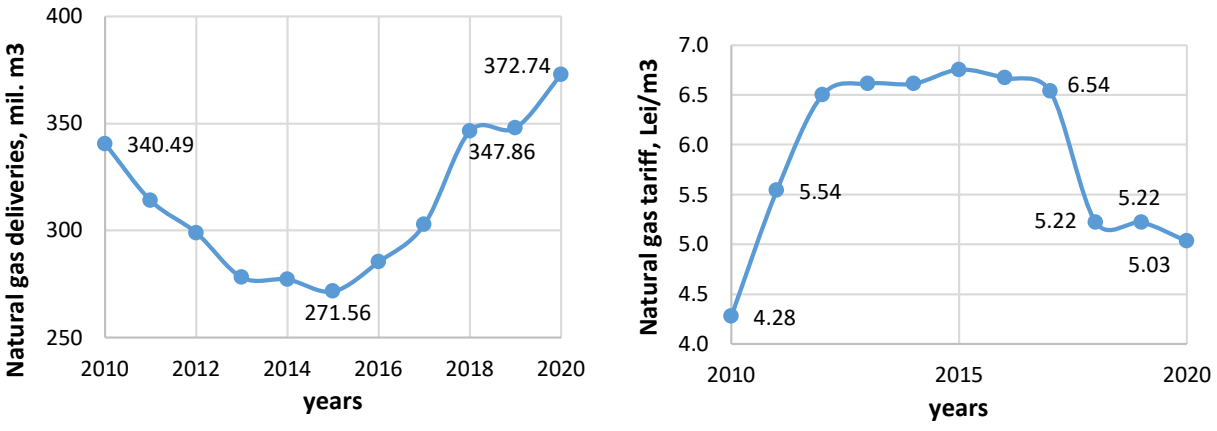
a) b)

Figure 2. Evolution of total energy consumption (a) and electricity consumption (b) [7, 8].



a) b)

Figure 3. The evolution of electricity losses in distribution networks (a) and the tariff of delivery of electricity to consumers (b) [7].



a) b)

Figure 4. Evolution of natural gas deliveries to household consumers (a) and the average tariff (b) [7].

The determination of energy poverty is based on the following indicators, which result from the CBGC:

- disposable income;
- expenses for the maintenance and furnishing of the home.

The average monthly disposable income of the household represents the totality of monetary and in-kind incomes from salary activity and on own account, various social benefits, from the realization of agricultural production from the auxiliary household, income from property, other current transfers (including goods and monetary sums received for free).

Disposable income are classified into six groups:

- salary activity,
- individual agricultural activity,
- individual non-agricultural activity,
- property income,
- social benefits,
- other incomes.

Monthly disposable income per person, in the country in 2019, they constituted 2880.6 lei, the main source of their formation being the salary activity in a proportion of 50.2%, followed by income from social benefits with 18.7% (of which 14.4% pensions) and income from individual agricultural activity (8.9%). Transfers from outside the country contribute to the formation of disposable income by 12.4%. The level of available revenues related to 2020 are presented in Figure 5.

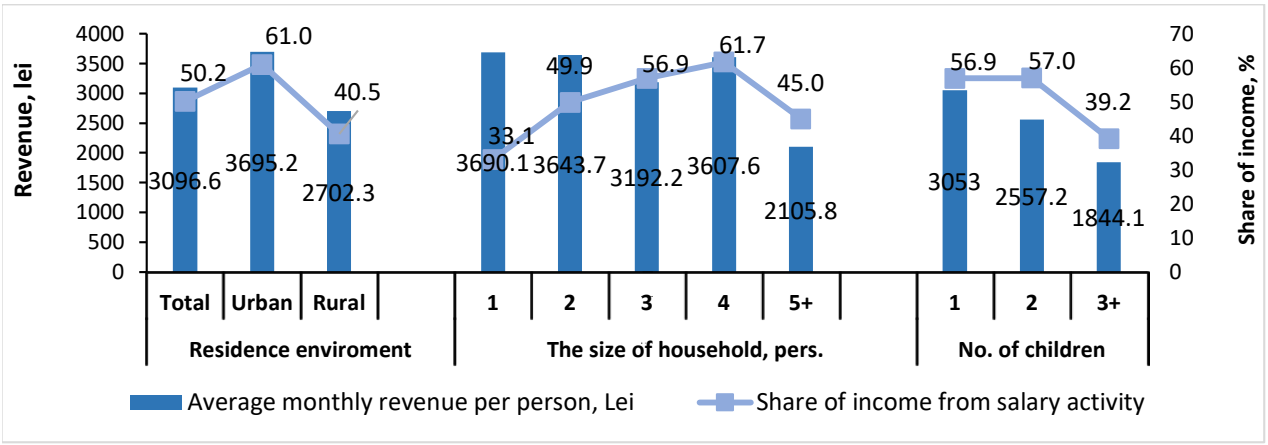


Figure 5. Monthly disposable income by main household characteristics (2020) [9].

***Average monthly consumption expenses* of the population** is divided into expenditures for:

- **food,**
- **alcoholic beverages,**
- **clothing and footwear,**
- **home maintenance,**
- **home furnishing,**
- **health,**
- **transport,**
- **communications,**
- **others.**

Housing maintenance expenses include all expenses incurred for rent, energy, water and other communal services, as well as expenses related to the arrangement and repair of the home.

Expenses for furnishing the home represents the totality of the expenses incurred for equipping and furnishing the home with various durable goods, household items, as well as the payment of services related to their maintenance.

Quintile is a term from the field of statistics, she represents *any of the five equal groups into which a population can be divided according to the distribution of the values of a certain variable (income, expenditure)*. The distribution of the population into quintiles is carried out according to income/expenditure per person, separately for each group of the population [9]. Within a category, the population is first ordered according to the values of average consumption income/expenditure per person, then it is divided into 5 equal groups, each comprising 20% of the population. As a result, the *first quintile* represents the least insured group, the second quintile – the next 20%, etc., and the *fifth quintile* - the best insured group - 20% of the population with the highest incomes/consumption expenses per person.

The socio-economic status of the household, in poverty studies, is established according to the main source of income of the household head. In this context, when assessing poverty, the following categories are used:

- *Employees* - households for which the main source of income of the head of the household is paid work.
- *Self-employed workers in agriculture* (farmers) – households for which the main source of income of the head of the household is the individual agricultural activity.
- *Self-employed workers in non-agricultural activities* – households for which the main source of income of the head of the household is income obtained from various self-employed activities in the non-agricultural sector (trade, business, crafts, etc.).
- *Pensioners* – households for which the main source of income of the head of the household is the pension.
- *Others* – households for which the main source of income of the household head is various social benefits, income from property, remittances and other income.

Figure 6 illustrates the weight distribution of households in the Republic of Moldova according to their socio -economic status.

Main indicator for measuring *poverty* is ***the poverty rate***, which represents the proportion of people whose consumption expenses are below an ***established poverty threshold*** (absolute and extreme) and is determined by the availability of the population's means that would allow them to ensure the minimum basic needs, acceptable at national level.

In 2019, *the absolute poverty threshold* in the country was on average per month for one person – 2095.1 lei, and *the absolute poverty rate* – **25.2%** (SDG indicator 1.2.1 , Table 1).

At the same time, *the extreme poverty threshold* was on average 1689.7 lei per month per person, and *the extreme poverty rate* was **10.7%.**

Another indicator used to measure poverty is *the poverty depth index*, which represents the average consumption deficit of the population needed to exceed the poverty threshold. In 2019, this indicator was 3.68%, which means that in order to overcome poverty,

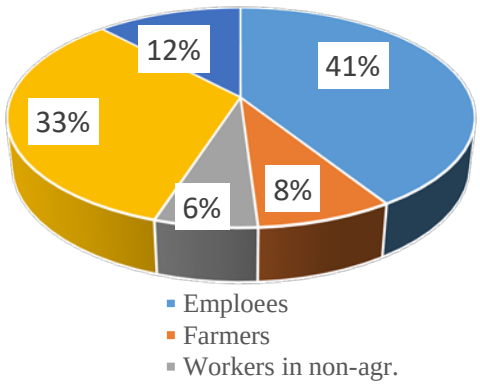


Figure 6. Distribution of households according to their socio-economic status (2019) [9].

under the conditions of maintaining or reducing the current level of inequality, it is necessary to increase the consumption of the population on average by 3.68% of the value of the absolute poverty threshold. The degree of inequality among the poor is measured by *the poverty severity index*, which represents the distribution of the level of well-being among the poor relative to the poverty line. In 2019, the *severity of poverty* constituted **1.02%.**

Table 1

The dynamics of the absolute poverty rate in the Republic of Moldova [10]

Year	2014	2015	2016	2017	2018	2019
Absolute poverty rate, %	29.5	25.5	26.4	27.7	23.0	25.2

The uneven distribution of income/expenditure on equal population groups is characterized by ***the Gini coefficient***. The statistical magnitude of the Gini coefficient varies from 0 to 1, the value 0 refers to absolute equality (uniform distribution) and 1 - absolute inequality (only one person gets all the income). The higher the value of this indicator, the less homogeneous the distribution of the population's income in society.

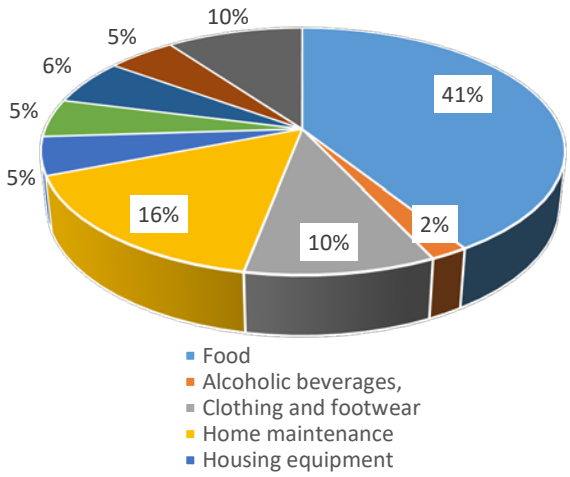


Figure 7. Structure of consumer spending (2019) [9].

In 2019, the value of the Gini coefficient, related to available income, was **-0.315**, or 14.0% more than the inequality after consumption expenses, which was **0.276**, which indicates a more uniform distribution of expenses than incomes, this being explained by the availability of stocks of consumer products of GC members.

It should be noted that the ratio between the incomes of the population in quintile V (the best insured group) compared to those of the population in quintile I (the least insured group) in 2019 was 5.1.

Table 2 describes the level of amenities present in our homes. In 2019, the average monthly consumption expenses per person constituted 2786.5 lei (in the urban area – 3469.2, and in the rural area -2335.7 lei). The distribution of expenses in quintiles I and V is presented in Figure 8.

Figure 8. The structure of consumption expenditure by quintile groups (2019) [9].

Table 2

Equipping homes with amenities by residence environment, in % (2019) [9]

Convenience	Total per country	Urban	Rural
Electric lighting	100.0	100.0	100.0
Aqueduct inside the house	70.6	93.5	55.3
Aqueduct outside the home	10.5	3.5	15.3
Water source - public network	68.8	93.2	52.5
Water source - spring well	30.7	6.5	46.9
Hot water - public network	7.3	18.1	0.0
Hot water - own system	51.8	69.4	40.1
Central heating system	14.6	35.8	0.4
Own thermal heating system	24.5	44.8	10.8
Other type of heating (stove, fireplace, etc.)	61.0	19.4	88.8
Natural gas from the network	59.2	86.3	41.0
Sanitary group with water inside the house	54.2	86.2	32.7
Sewage system - public network	33.0	78.0	2.8
Sewage system - own system	38.4	16.8	53.0
Bathroom or shower inside the home	61.1	88.9	42.5
Phone	79.2	74.3	82.5
Internet connection	60.8	74.8	51.3

5. Assessment of energy poverty

The level of energy poverty (EP) in the Republic of Moldova is determined by relating the ***expenses for home maintenance to the value of the household's available income***.

Below are presented the results of the calculation of the poverty level, characteristic of the Republic of Moldova for 2019, by place of residence (urban, rural), by socio-economic categories of households, by household size and by quintile groups (see Tables 3-7 and Figures 9-10).

a) Determination of energy poverty according to the environment of residence

Table 3

Level of energy poverty by residence environments (2019) [10]

Indicator type	Total per country	Urban	Rural
Available income, lei/pers.	2881	3522	2457
Home maintenance, lei/pers.	451	547	388
Level of energy poverty, %	15.7	15.5	15.8

Figure 9 shows the share of the population with average monthly expenses for home maintenance that exceed 30% of monthly disposable income, 2020 (SDG indicator 1.2.1).

b) Determination of energy poverty according to socio-economic status

Table 4 shows the values of available income, expenses for home maintenance and the level of energy poverty, resulting for each category of households.

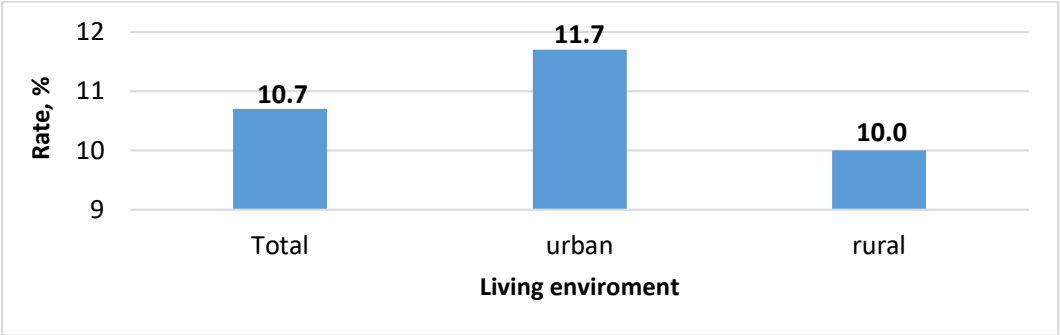


Figure 9. Energy poverty rate by living environment (2020) (housing expenditure ⩾ 0.3 disposable income) [9-10].

Table 4

Level of energy poverty by socio-economic categories of households and on average by country

Categories of households according to socio - economic status of the household head	The share held	Revenue available	The maintenance costs of the place	Energy poverty level
	%	Lei / pers.	Lei / pers.	%
Employee	41	3478	470	**13.5**
Self employed in agriculture (farmers)	8	1828	321	**17.6**
Self employed in non-agricultural activities	6	2837	380	**13.4**
Retirees	33	2444	475	**19.4**
Others	12	2399	482	**20.1**
Total per country	**100**	**2881**	**451**	**15.7**

Table 4 shows that the lowest level of energy poverty of 13.4% is observed in the *Self-employed category in non-agricultural activities*. The highest level of poverty of 20.1% - refers to the category *Others*; here incomes depend on social benefits, remittances (money received from those who work abroad), income from property (from rent; most often, in the urban environment, housing is rented, and in the rural environment - agricultural land).

c) Determination of energy poverty according to socio-economic status and residence environment

Table 5

Level of energy poverty (EP) by socio-economic categories of households and residence environments [9-10]

Categories of households	Urban			Rural		
	Disposable income	Maintenance expenses	EP level	Disposable income	Maintenance expenses	EP level
	Lei / pers.	Lei / pers.	%	Lei / pers.	Lei / pers.	%
Employee	3998.2	541.6	**13.5**	2898.3	390	**13.5**
Self employed in agriculture (farmers)	1659.0	412.7	**24.9**	1838.4	315	**17.1**

Continuation Table 5

Self employed in non-agricultural activities	3351.0	484.1	**14.4**	2509	313.8	**12.5**
Retirees	2718.6	556.5	**20.5**	2308.8	434.7	**18.8**
Others	2693.9	620.4	**23.0**	2255.5	413.0	**18.3**

From Table 5 it can be observed that the level of poverty in the urban area is higher than in the rural area.

d) Determining energy poverty according to household size and residence environment

Table 6

Level of energy poverty (EP) according to household size and residence environments

Type road sign	Total per country						Urban					Rural				
	1 pers.	2 pers.	3 pers.	4 pers.	⩾ 5 peopl e	1 perso n	2 pers.	3 pers.	4 pers.	⩾ 5 people	1 person	2 pers.	3 pers.	4 pers.	⩾ 5 peopl e
Revenues, lei/pers	3664	3303	3014	2444	1859	4520	4010	3576	2918	2280	3101	2866	2544	2060	1706
Maintenance expenses, lei/pers	733	531	424	345	257	891	653	487	391	355	630	455	371	307	221
EP level, %	20.0	16.1	14.1	14.1	13.8	19.7	16.3	13.6	13.4	15.6	20.3	15.9	14.6	14.9	12.9

e) Determining energy poverty according to quintile groups and residential environments

Table 7

Level of energy poverty (EP) by quintile groups and residential environments [9-10]

Indicator type	Total per country					Urban					Rural				
	I	II	III	IV	V	I	II	III	IV	V	I	II	III	IV	V
Revenues, lei/pers	1560	2150	2541	3172	4980	1648	2129	2536	3186	5365	1545	2158	2544	3158	4201
Maintenance expenses, lei/pers	216	323	415	512	790	291	355	451	516	766	203	309	393	508	838
EP level, %	13.9	15.0	16.3	16.1	15.9	17.6	16.7	17.8	16.2	14.3	13.2	14.3	15.4	16.1	19.9

Previously applied energy poverty policies and measures

The national policy related to social protection, including energy poverty is governed by a series of laws [11-15]. These laws provide for a series of measures dedicated to the social protection of low-income households, including in cases of energy price increases.

The Government of the Republic of Moldova, based on Law 133/2008, currently uses two social assistance programs (cash allowances), known as the *Social Assistance (AS) program* and the *Cold Period Allowance (APR***)** *program of the year*. Social aid is a monthly cash payment granted to the disadvantaged family, and APR – a fixed monthly cash payment granted to the disadvantaged family for the months of January-March and November-December of the year. The responsibility for meeting these objectives rests with the Ministry of Health, Labor and Social Protection.

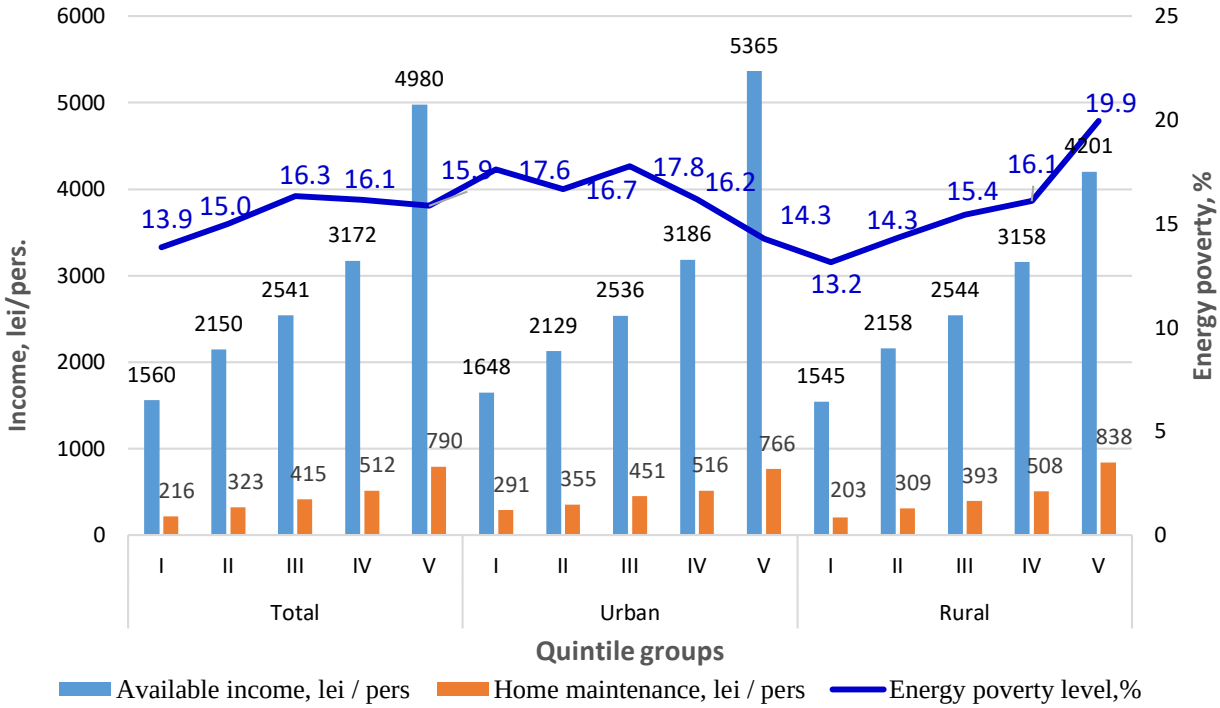


Figure 10. Level of energy poverty according to quintile groups and residential environments [9].

In addition to the national programs to support the vulnerable population, the authorities of the municipalities of Chisinau and Balti used to come with help for heating.

Budgetary allocations for social support programs varied from year to year and ranged from 1-3% of Gross Domestic Product (GDP). The effective coverage of social assistance programs was modest: between 3-10% of the total population.

Government initiative on household energy vulnerability

In order to improve the energy vulnerability of the population in 2022 in the Republic of Moldova, a new program was introduced, called "Ajutor la contor", and the so-called Energy Vulnerability Reduction Fund was established and the Energy Vulnerability Register. Shortly after, the Government approved *a new method regarding the assignment of categories of energy vulnerability to households and the payment of compensations for the payment of energy bills* [16]. The approved regulation provides for five categories of energy vulnerability of household consumers, determined according to the value of the poverty rate R (Table 8).

Table 8

Energy vulnerability categories of consumers

No.	Vulnerability category	The value of the poverty rate R, %
1.	Very high	R ⩾ 90
2.	High	35 ⩽ R < 90
3.	Average	20 ⩽ R < 35
4.	Low	10 ⩽ R < 20
5.	Non-vulnerable	R < 10

Household consumers in the first four categories of vulnerability can benefit from compensation for the cold period of the year (01.11-31.12 and 01.01-31.03).

According to Regulation [16], the energy poverty rate R is determined with the formula:

$$R = C_{RE} / V, \% \quad (1)$$

where: C_{RE} represents expenses for energy resources or energy used in the cold period of the year;
V - the income available to pay the cost of the energy consumed.

C_{RE} energy resources used to heat the residence comprise the cumulative expenses due to the average monthly consumption of fuel or energy (natural gas, thermal energy, electricity and solid fuels).

The expenses for the consumption of natural gas/thermal energy/electricity are determined with the formula:

$$C_{GN/ET/EE} = E_{med} \cdot c_{en}, Lei, \quad (2)$$

where: E_{med} is the average monthly consumption of fuel or energy in the previous cold period of the year within the limit of the eligible ceiling (Table 9);
c_{en} - the tariff/price in force on November 1 of the current year.

Table 9

The eligible ceiling for fuel or energy consumption used to heat the residence

Fuel/energy used for heating	Unity	M.U.
Natural gases	250	m^3/month
Heat	1.5	Gcal/month
Electricity – for heating	2500	kWh/month
Electricity – for other needs (lighting, etc.)	250	kWh/month

For consumers who do not have data on individual energy consumption for heating, the consumed volume is accepted at the level of 50% of the eligible consumption ceiling (Table 9). In the situation where the monthly consumption is higher than the eligible ceiling, the compensation is granted at the limit of the capped energy volume.

The monthly income available to pay for the energy $V_{disp.en}$ related to the household is calculated with the formula:

$$V_{disp.en} = V_{GL} - M_{CMI} - R_{CI}, lei \quad (3)$$

where: V_{GL} represents the global monthly income of the household, equal to the average value of the global monthly income for the last 6 months;
M_{CMI} - the minimum monthly expenditure level of the household, which represents the sum of the amounts of individual minimum expenditure;
R_{CI} - the monthly rate of the real estate loan, is considered the last rate paid for the registered property, but not higher than half of the household's minimum expenditure level.

The amount of minimum individual expenses for each member of the household is determined as follows:

a) consumption expenditure for the 4th quarter of the previous year, total per country, published by the National Bureau of Statistics, excluding expenditure on "housing, water, electricity and gas", increased by the rate of increase in consumer prices in September of the current year compared to December of the previous year, published by the NBS;
b) 70% of the value of p. a) for each other member of the household.

If the income available to pay energy bills is less than or equal to zero, the household consumer is assigned vulnerability category 1 (very high).

6. Conclusions

1. In recent years, energy poverty has been subject to increased attention within the policies of the European Union (EU). Alleviating energy poverty is treated as a key precondition for achieving equitable transitions to sustainability.
2. The accessibility of the population to energy is a constant concern of the government. Over the years there have been social assistance programs in the country. Recently, a new program was introduced, called "Ajutor la contor"**,** devoted to the support of energy-vulnerable households.
3. The period 2010-2020 was a difficult one for the country's economy and the well-being of the population, being marked by the mismanagement of the legally empowered verification and control bodies.
4. In the Republic of Moldova, measures focused on the energy poverty of the population, related to the energy efficiency policies of the housing stock, are to be developed and implemented.

Conflicts of Interest: The authors declare no conflict of interest.

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A MATERIAL FULL OF PROMISES: $Hg_{1-x}Cd_xTe$ - MERCURY CADMIUM TELLURIDE

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Abstract. In recent decades' doctors and scientists have intensively researched the effect of infrared applications. The rays of infrared devices penetrate the body to a depth of about 5 cm and provide a pleasant warmth, stimulating blood circulation and reducing joint pain. Long-wave infrared light exerts a beneficial effect on nerve cells. These nerve cells are responsible for transmitting the sensation of pain to the brain. Infrared light treatment increases the release of endogenous analgesic substances from the brain and adrenal glands, such as enkephalins and endorphins. The infrared range of the electromagnetic spectrum extends from about 0.75 μm to 1000 μm. The article presents a review of HgCdTe infrared detectors, which have been intensively developed in the last forty years since the first synthesis of this compound semiconductor in 1958.

Key words: *infrared detectors, trichromats, ROIC, FPA, Sofradir, CEA-Leti, stimulating blood circulation, infrared applications.*

Rezumat. În ultimele decenii, medicii și oamenii de știință au cercetat intens efectul aplicațiilor în infraroșu. Razele infraroșii pătrund in corp pana la o adâncime de aproximativ 5 cm si oferă o căldura plăcută, stimulând circulația sângelui si reducând durerile articulare. Lumina infraroșie cu undă lungă exercită un efect benefic asupra celulelor nervoase. Aceste celule nervoase sunt responsabile de transmiterea senzației de durere către creier. Tratamentul cu lumina în infraroșu creste eliberarea de substanțe analgezice endogene din creier si glandele suprarenale, cum ar fi encefalinele si endorfinele. Intervalul infraroșu al spectrului electromagnetic se extinde de la aproximativ 0,75 μm la 1000 μm. Articolul prezintă o trecere în revistă a detectoarelor cu infraroșu HgCdTe, care au fost dezvoltate intens în ultimii patruzeci de ani de la prima sinteză a acestui semiconductor compus în 1958.

Cuvinte cheie: *detectoare în infraroșu, tricromate, ROIC, FPA, Sofradir, CEA-Leti, stimularea circulației sanguine, aplicații în infraroșu.*

1. Introduction

Light is electromagnetic radiation (EM), but not all EM radiation is light. EM radiation is characterised by its wavelength, and visible is the range from just below 400 nm to just above 700 nm wavelength. In the near infrared range, green vegetation has about six times

higher reflectance than in the visible spectral range because the fresh leaf tissue has good reflectance for IR rays and the other wavelengths are absorbed by the chlorophyll and accompanying carotenoids.

Without a doubt, one of the most interesting developments of World War 2 were the infrared devices, which were then called ultra-red devices. By shifting the battle into the night, it was hoped to make up for the material inferiority of the German army. Before the discovery of German developments in this field, the USA had tried without success to convert infrared into visible light. Not only had the Germans managed to do this, but they had already successfully used infrared devices for military purposes.

Infrared detectors are devices that react to infrared light. Infrared waves cannot be seen with the human eye. The eye can see a basic spectrum of color - everything that can be seen in a rainbow of color. However, there are colors that range outside of a rainbow in the electromagnetic spectrum. Humans are called “trichromats,” meaning that we can see red, green, and blue and everything in between. Technically interesting is also the possibility to penetrate light haze (fog) with IR devices. When it snows, however, the IR rays are reflected by the snowflakes and IR devices cannot be used. After the end of the war, the Allies captured the German inventions in this field and used them to build their "own" infrared devices. The devices were also used, for example, in the Korean War and the Indochina War.

Infrared science has played a revolutionary role in the development of the modern technology age. The infrared range of the electromagnetic spectrum spans from approximately 0.75 μm to 1000 μm [1,2]. The discovery of infrared radiation is credited to the British Royal Astronomer, Sir William Herschel who demonstrated this radiation in 1800 by using sunlight dispersed through a prism and detecting it with a sensitive thermometer [3]. This work laid the foundation of the field of infrared spectroscopy. For more than forty years, the enormous potential of this new form of radiation was not realized until the intervention of more sensitive detectors such as the radiation thermocouple and the diffraction grating spectrometer. Since then, there has been phenomenal progress in both basic and applied research in infrared science and technology [4]. Infrared spectroscopy has played a leading role in the achievement of this progress.

The article analyzes the evolution of HgCdTe infrared detectors, which have been intensively developed in the last forty years, as well as future trends in this field.

2. The evolution of manufacturing technology

Studies of the mechanical properties of CdZnTe and HgCdTe materials and the impact of plastic deformation on the electrical performance of infrared photodiodes have been published [5,6]. The works carried out has allowed the determination of the mechanical properties of Cd_{1-y} Zn_yTe and $Hg_{1-x}Cd_xTe$ materials. The modulus of elasticity and hardness are lower than those of elemental semiconductors such as Germanium and Silicon. The fracture toughness, cracking threshold and toughness of these two materials were examined in detail as a function of the compositions, x and y, in ranges used for the design of infrared detectors. Nano- and micro-indentation methods were used to determine these mechanical data at room temperature [7].

As HgCdTe and CdZnTe materials are used at cryogenic temperatures, a micro-indentation tool was developed at liquid nitrogen temperature. These measurements determined an increase in the hardness, cracking threshold and toughness of HgCdTe and CdZnTe. Indentation generates plastic deformation marked by the presence of a footprint and

dislocations that are revealed by chemical etching [8,9]. The study of these dislocations was part of a second part of the study on understanding the nature of these dislocations and their electrical impact on the photodiodes.

The development of the indentation method as a tool for localised injection of dislocations into photodiodes was addressed. Tools such as chemical dislocation revelation and scanning and transmission electron imaging have revealed the presence of these dislocations with particular orientations dictated by the crystal structure of HgCdTe and CdZnTe materials [10]. A comparison was made between the nature of the injected dislocations and those present natively in the bulk materials, as well as their electro-optical impacts.

The third part of the study was the study of the electrical properties of HgCdTe-based infrared photodiodes [11,12]. These photodiodes are designed as arrays in order to produce high performance infrared images and videos [13-15]. However, sometimes pixels are missing from the image. The presumed origin was the presence of dislocations. This work has verified this hypothesis [16]. Using the micro-indentation technique, dislocations were injected into the photodiodes. Electrical measurements of current versus voltage and current versus time at fixed bias showed degradation caused by the presence of dislocations in the diodes. This degradation is mainly characterised by excess noise [17].

For comparison, HgCdTe materials have also been grown on GaAs and CdZnTe substrates (Figure 1). In the case of GaAs substrates, due to higher lattice mismatch than GaSb, a low temperature ZnTe nucleation technique was introduced to prevent twin generation (Figure 1c). A non-optimized HgCdTe/CdTe/GaAs structure was also grown for comparison (Figure 1b).

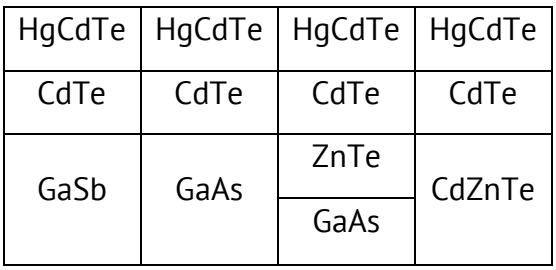

Figure 1. Growth structure for different substrates: *a)* GaSb substrate with 5 μm buffer layer; *b)* GaAs substrate with the same structure of GaSb for compare; *c)* GaAs substrate with nucleation technology and 5 μm buffer; *d)* CdZnTe substrate with 50 nm thin buffer layer [17].

Moreover, any kind of anneal process of HgCdTe involved in junction formation is associated with an impurity redistribution process and a change in Hg vacancy content. The formation of photovoltaic junctions in $Hg_{1-x}Cd_xTe$ is still an open research task [18]. Today, the best results for research and production, and the best products quality, are obtained with molecular beam epitaxy (MBE) – for the great majority – and less with liquid phase epitaxy (LPE) (Figures 2 and 3).

3. CEA-*Leti (*Laboratory of Electronics and Information Technologies)

Research and development is necessary for the technology company to provide the innovation needed to succeed in its markets.

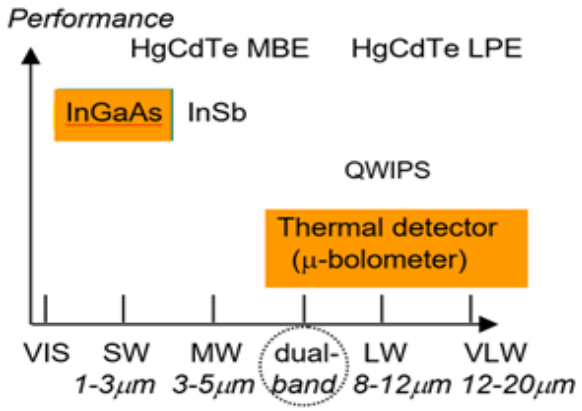

Figure 2. HgCdTe detectors grown by MBE and LPE deliver better object identification capability than thermal detectors, such as μ-bolometers and those based on InGaAs and InSb [13].

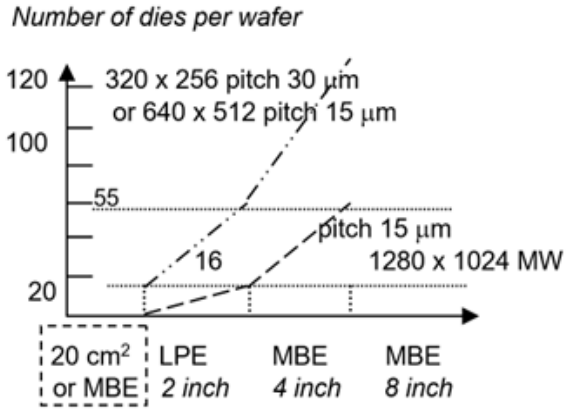

Figure 3. Switching from CdZnTe substrates to those made from Ge can substantially boots the number of dies per wafer [26].

The choice to collaborate with a partner can become crucial to achieve the expected growth. *Leti* brings together 2,000 people who are passionate about innovation in the service of industry. Experienced researchers, applications engineers, business managers, administrative support, a large majority of them have business experience [19-22]. A hundred or so scientific experts are internationally recognised and are members of learned societies. Around 400 PhD students and post-doctoral fellows bring the resourcefulness of youth every year [23-25].

Over the years, *Leti* has invested heavily in laboratory and manufacturing facilities that place it among the world's leading research institutes. In addition to high-tech microelectronics clean rooms, *Leti*'s facilities include advanced characterisation tools that are often unique in the world, state-of-the-art test benches and unparalleled pre-clinical and clinical research platforms [26-28].

The essence of *Leti*'s business model is its intellectual property policy and the objective of systematically protecting all new discoveries with a patent [29]. *Leti* relies on dedicated in-house resources and a renowned network of experts in the field to intelligently manage one of the world's largest patent portfolios [30-33]. This is a necessary and imperative cost, in order to offer future partners a competitive advantage and full protection in their markets.

Along with the patent policy, the other pillar of the business model is *Leti*'s willingness to collaborate as closely as possible with its partners' strategies and needs. *Leti* is committed to building a tailor-made research programme, on an exclusive bilateral basis, adapted to the roadmaps and resources proposed. *Leti*'s objective is to enable its customers to rapidly industrialize and bring to market the innovations it develops [34].

No research institute, however well endowed, can prosper without a network of related networks. Universities, engineering schools, other institutes, investors, companies... in France, Europe and abroad, *Leti* has patiently woven close relationships with a galaxy of players that it makes available to its partners in order to help innovations grow in an ecosystem that is conducive to their development.

Leti is a recognised player on the European scene and maintains close ties with its institutions. It is one of the institutes that receives the most funding from the for large-scale

research programmes. It is a sought-after partner in the constitution of consortia, with a success rate of projects submitted of over 30% [35-39]. *Leti* is one of the spearheads in terms of ambitious partnerships between Europe and Asia (Japan, South Korea, Taiwan).

4. Future tendencies

Pixel sizes of the order of 10 μm have been proven in hybrid systems. However, the practice of reducing pixel sizes may continue in future.

Reducing pixel size is essential for SWaP and cost reduction since the diameter of the optics goes down, and the size and weight of the dewar follow suit, and cooler power falls, but its lifetime and reliability improve. The pitch of 15 μm is in production today at Sofradir (France) and pitches of 10 μm and less are expected within a few years. There is a similar tendency to reduce the pixel size of microbolometer arrays to achieve several potential benefits.

Multispectral IR provides target identification under conditions where one wavelength is unable to identify the target. Multispectral colour display helps in object recognition. Four colours may be maximum number of bands that can be stacked in a single pixel. However, future trends and demands necessitate attempting almost all combinations of bands in short wave (SW), mid wave (MW) and long wave (LW).

5. Conclusions

It may be predicted that HOT HgCdTe technology will remain in the game because of its established fabrication houses and favorable and tunable properties. Since its spectral wavelengths can be tuned, this material will have its presence in almost all the spectral bands from short to very long wavelength bands. The technology will also keep on reducing the pitch of the detector arrays. In this context, uncooled microbolometers are being developed down to 5 to 10 μm pitch in LWIR. For achieving more integration times, for the same pixel area, signal or well capacity per unit area are required to be improved by innovations in integrating capacitor designs or else in fabrication technological capabilities. The foundry houses which can provide low manufacturing costs will continue to exist because of huge demand. Application for next generation of IRFPAs will include manportable sensors, micro UAVs, ground/wall penetration, missile warning, missile seekers, multispectral Surveillance will keep the technology pushing to its limits.

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NEW APPROACHES TO MISSING BIOMEDICAL DATA RECOVERY FOR MACHINE LEARNING

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Abstract. Missing data is a common problem for medical data sets, especially large ones. This issue is of major importance since it can influence the analysis and further use of the data, e.g., for machine learning purposes. There are various methods for recovering missing data. One such method is to remove observations with missing values, but this is not very useful given the limited amount of data available. Another commonly used approach is the Last Observation Carried Forward (LOCF). But most such methods are not universal and may need adjustments to the data set at hand. This article describes the possibility of solving this problem in the case of multimodal time series of biomedical data coming from patients with sepsis. It describes and compares three approaches tailored to a sepsis dataset, which is analyzed and finally used to build a sepsis prediction system based on clinical data routinely recorded in an intensive care unit.

Keywords: *multimodal biomedical time series data; missing values; data recovery; sepsis; machine learning.*

Rezumat. Datele lipsă sunt o problemă comună pentru seturile de date medicale, în special pentru cele mari. Această problemă este de o importanță majoră, deoarece poate influența analiza și utilizarea ulterioară a datelor, de exemplu, în scopuri de învățare automată. Există abordări diferite pentru a trata datele lipsă. Una obișnuită este ștergerea observațiilor care conțin astfel de date, însă ea nu este aplicabilă atunci când volumul datelor este limitat. O altă abordare frecvent utilizată este "Last Observation Carried Forward (LOCF)". Dar majoritatea acestor metode nu sunt universale și pot necesita ajustări la setul de date la îndemână. Această lucrare descrie posibilitatea abordării acestei probleme în cazul seriilor temporale multimodale de date biomedicale provenite de la pacienții cu sepsis. Ea descrie și compară trei abordări adaptate setului de date care este analizat și utilizat în cele din urmă pentru construirea unui sistem de predicție a sepsisului bazat pe date clinice înregistrate în mod obișnuit într-o unitate de terapie intensivă.

Cuvinte cheie: *serii temporale de date biomedicale multimodale; valori lipsă; recuperare date; sepsis; învățare automată.*

1. Introduction

In research, missing data are frequently inevitable, but their ability to affect the findings is rarely explored. According to recent systematic reviews [1,2] many healthcare data sets are found to be incomplete, with missing values, and require cleaning and missing values imputation to enhance the effectiveness and accuracy of the data analysis. Along with an overview of the situation in the field, these articles present a review of methods for using machine learning to impute missing data.

The nature of "missingness" in this context - random vs nonrandom - is important to note. However, using observable data, it is sometimes impossible to tell apart between missing at random and missing not at random. As the data set employed in this study lacks a justification for the nature of the missingness, it is believed that the missing data are absent at random (during the time the patient is undergoing a medical procedure that requires the sensors used for data collection to be removed, human errors, equipment malfunction, etc.). The bias imposed by the recovery technique is thought to be less in the situation of data missing at random, even though data recovery may be achievable regardless of the kind of missingness [3].

When missing values occur in data, there are several ways to handle them. A lesser number of tools are useful for continuous data, such as time series, while the majority of these techniques are acceptable for static data. Complete case analysis (CCA) [4] is the simplest method, which involves deleting observations with missing values, but in many situations, especially when there is a limited amount of data, this technique may not be practical. In imbalanced sets, where each observation in the minority class is significant, this problem is of particular significance when using the data for machine learning techniques.

Data recovery techniques may often be classified into:

1. Based on single imputation - replace a missing data point with a single value using a single imputation approach, often using the Last Observation Carried Forward (LOCF), Baseline Observation Carried Forward (BOCF), and Next Observation Carried Backward (NOCB) procedures or data from other sources (e.g., mean value imputation, regression imputation, etc.).

2. Based on multiple imputations - using many plausible imputed data sets and properly integrating the findings from each, multiple recovery methods create plausible imputed data sets. There are several statistical software available for this (e.g., Amelia, FURIA, MICE in R programming language (R), etc.)

The Guideline on Missing Data in Confirmatory Clinical Trials [5] states that "if missing values are handled by simply excluding any patients with missing values from the analysis, this will result in a reduction in the number of cases available for analysis and consequently typically result in a reduction of the statistical power." Obviously, the likelihood of a power drop increases with the number of missing data. Thus, it is imperative to make every effort to reduce the quantity of missing data. Unluckily, there isn't a methodical technique to handle missing data that works in every circumstance. As a result, while preparing a trial, it is crucial to take into account how to reduce the quantity of missing data and how missing data will be treated in the analysis.

Three data recovery techniques are presented in the current work, each of which involves a number of steps and components: (a) conventional techniques (such as LOCF and NOCB); (b) a less popular Kalman filtering-based approach; and (c) regression imputation, which substitutes the predictions from a regression of the missing variables on the observed

variables. The idea of seeing the human body as a complex system in which the many characteristics that define its functioning (in health or sickness) are associated and missing data may be generated from existing data using approximated correlation is one of the underlying principles for the final technique.

This paper's research contribution specifically relates to the presentation of several approaches for missing value recovery in connection to the objectives of future usage of the recovered data.

As part of a bigger research project aimed at developing a machine learning-based software application for sepsis prediction, the data recovered via a variety of ways are eventually being used to build a machine learning system.

2. Research Data and Processing Methods

2.1. Data

The "Early Prediction of Sepsis from Clinical Data: the PhysioNet/Computing in Cardiology Challenge 2019" [6] public database provided the information utilized in this study. The public portion of the data was sourced from two different US hospitals: Emory University Hospital (set A) and Beth Israel Deaconess Medical Center (set B). With the necessary Institutional Review Boards' consent, these data were gathered over the previous ten years, de-identified, and classified using Sepsis-3 clinical criteria. They include 8 vital sign variables, 26 laboratory variables, and 6 demographic factors. They are made up of hourly summaries of vital signs, lab results, and static patient descriptions for 40,336 patients. Each patient's characteristics were distilled into hourly bins (e.g., multiple heart rate measurements in an hourly time window were summarized as the median heart rate measurement).

The data in set B presents more than 80% of missing values. Thus, set A is selected for further study because it had fewer missing data (i.e., 79,4%) and a greater prevalence of sepsis (8,80% vs. 5,71% in set B). There are 1790 septic patients among the 20336 patients in this set, and 502 of those subsets have all the missing values for at least one parameter (out of 6 parameters of interest). Following the application of the initial selection criteria (such as the presence of at least 7 hourly observations prior to the diagnosis of sepsis, the lack of artifacts, etc.), there are 211 subsets that have missing data but may be able to have them recovered.

Table 1 depicts the look of an original sepsis file with one parameter (i.e., DBP) having all-missing values (NA) and other physiological parameters having some of their values missing. It describes observations on seven parameters of interest chosen for additional study, including age and labeling. These parameters include heart rate, peripheral blood oxygen saturation, temperature, systolic blood pressure, diastolic blood pressure, respiratory rate, patient's age, and the label of the observation.

Table 1

A fragment of an original sepsis file

HR	O_2Sat	Temp	SBP	DBP	Resp	Age	Sepsis label
NA	**NA**	**NA**	**NA**	**NA**	**NA**	43.55	0
83	99	**NA**	109	**NA**	13	43.55	0
89	99	**NA**	102	**NA**	22	43.55	0
82	98	36.56	108	**NA**	20	43.55	0
91	98	**NA**	108	**NA**	16	43.55	0

Continuation Table 1

93	99	37.1	106	**NA**	20	43.55	1
95	100	**NA**	130	**NA**	15	43.55	1
96	98	37.2	121	**NA**	18	43.55	1

Note. HR - heart rate, O2Sat - peripheral blood oxygen saturation, Temp - temperature, SBP - systolic blood pressure, DBP - diastolic blood pressure, Resp - respiratory rate. Sepsis label - the label of the observation (0 – for non-sepsis observations and 1 – for sepsis). NA – not available (missing value).

2.2. Missing Values Recovery Methods

Data recovery performed throughout this research is based on several simple common algorithms/methods, including their combination as well as less common techniques tailored to the available data. The first method is commonly used for similar data, while the next two methods are specifically designed for the data recovery task concerning the data at hand.

2.2.1 LOCF and NOCB

The last observation carried forward (LOCF) [7] is a missing value recovery method that uses the last measured value (per column) to fill in the next missing one(s). The next observation carried backward (NOCB) [8] is a "reversed version" of LOCF, by which the missing values are filled in backward. Examples of when these approaches can be applied are columns "HR", "O_2Sat", "Temp", "SBP" and "Resp" in Table 1. These techniques can evidently not be used for columns with all values missing (e.g., the "DBP" column in Table 1)

2.2.2 A custom technique

This approach was designed to take care of both cases: for columns with some values missing as well as for columns with all missing values.

The following procedures are included in this method when there is at least one value in each column: (a) each column is assessed for missing data (NA); (b) the first and last values (per column) are "recovered" in accordance with the value in the closest cell in the same column; (c) interpolation is completed, with the calculation of the values between two present values taking the trend into consideration (increase or decrease). For interpolation, the "zoo" package in R [9] (i.e., "na.approx()" function) is utilized (see, for instance, the "Temp" column in Table 1).

When all values in a column are missing, the recovery procedure is as follows: (a) from the complete cases set, the present values were extracted for each parameter/column separately by class (e.g., septic patients from set A). (b) the number of "non-missing" values (n) was determined and the mean (mean) and standard deviation (sd) were calculated for these values. Using the {rnorm()} function in R, and "n", "mean" and "sd" as arguments to it, Gaussian distributions were generated for each of the 6 parameters. The missing values in the original data are replaced with values extracted from generated distributions.

2.2.3 A technique with the use of Kalman filtering and machine learning algorithms

This approach uses Kalman filtering for columns with at least three non-missing values and Generalized Linear Models for data recovery in case of all missing values in a column.

The Kalman filter, which first appeared in [10], uses a discrete filtering model based on the dynamic and measurements models as linear Gaussian. The following is a description of the basics of this approach with elements of optimal control and dynamic linear models as in [11].

The Kalman filtering technique is used to estimate states based on linear dynamical systems in state space format and offers estimates of unknown variables given the observations over time. According to this model, the state is evolving as follows from time $t-1$ to time t:

$$x_t = Fx_{t-1} + Bu_{t-1} + w_{t-1}, \quad (1)$$

where F is the state transition matrix estimated using the previous state vector x_{t-1}, B is the control-input matrix applied to the control vector u_{t-1}, and w_{t-1} is the process noise vector that is assumed to be zero-mean Gaussian with the covariance Q, i.e., $w_{t-1} \sim N(0, Q)$.

The link between the state and the measurement at the current time step t is described by the process model in conjunction with the measurement model as:

$$z_t = Hx_t + v_t, \quad (2)$$

where z_t is the measurement vector, H is the measurement matrix, and v_t is the measurement noise vector that is assumed to be zero-mean Gaussian with the covariance C, i.e., $v_t \sim N(0, C)$.

Given the initial estimate of x_0, the sequence of measurements, $z_1, z_2, \ldots, z_t$, and the details of the system defined by F, B, H, Q and C, the Kalman filter's job is to offer an estimate of x_t at time t. Typically, Q and C are tuned parameters that the user may change to get the desired performance.

Kalman filter algorithm consists of two steps: (1) prediction and (2) update, and can be described as follows:

Prediction (step 1):

Estimating predicted state $\hat{x}_t^- = F\hat{x}_{t-1}^+ + Bu_{t-1}$ (3)

Calculating predicted error covariance $P_t^- = FP_{t-1}^+ + F^T + Q$ (4)

Update (step 2):

Estimating measurement residual $\tilde{y}_t = z_t - H\hat{x}_t^-$ (5)

Calculating Kalman gain $K_t = P_t^- H^T (R + HP_t^- H^T)^{-1}$ (6)

Updating state estimate $\hat{x}_t^+ = \hat{x}_t^- + K_t\tilde{y}$ (7)

Updating error covariance $P_t^+ = (I - K_t H)P_t^-$, (8)

where the „hat" operator denotes an estimate of a variable. Thus, $\hat{x}$ is an estimate of x. The superscripts "-" and "+" denote predicted (prior) and updated (posterior) estimates, respectively.

The software implementation used for the data recovery purpose in this research is "imputeTS" package in R [12] and represents an extended version of the algorithm described above (i.e., Eq. 1-8) with Kalman smoothing on structural time series models.

The algorithm used for data recovery purposes in columns with all values missing represents a Generalized Linear Model (GLM) [13] available on the H_2O platform [14].

The dependence between the response variable y and the covariates vector x is modelled as a linear function by the Gaussian technique (behind GLM):

$$y = x^T\beta + \beta_0 + \epsilon, \quad (9)$$

where, β is the parameter vector, β_0 denotes the intercept and ϵ is a gaussian random variable representing the noise in the model, $\epsilon \sim \mathcal{N}(0, \sigma^2)$.

By maximizing the log-likelihood over the parameter vector for the observed data, the model's estimation is achieved. By resolving the following likelihood optimization with parameter regularization, the GLM [13] employed in this study fits the model:

$$\max_{\beta,\beta_0} (GLM\ Log \cdot likelihood - \ Regularization\ Penalty). \tag{10}$$

The weighted sum of the ℓ_1 (least absolute shrinkage parameter) and ℓ_2 (ridge regression) norms of the coefficients vector is the regularization penalty, and it is expressed as follows:

$$\lambda P_\alpha(\beta) = \lambda \left(\alpha \|\beta\|_1 + \frac{1}{2}(1-\alpha)\|\beta\|_2^2 \right), \tag{11}$$

where α is the elastic net parameter, $\alpha \in [0, 1]$ and is λ a tuning parameter, and there is no penalty for the intercept.

The optimization task concerning observations can be described as follows:

$$\max_{\beta\beta_0} \sum_{i=1}^{N} \log f\,(y_i;\ \beta, \beta_0) - \lambda \left(\alpha \|\beta\|_1 + \frac{1}{2}(1-\alpha)\|\beta\|_2^2 \right). \tag{12}$$

The Gradient Boosting Machine (GBM) [15], offered by the same H2O platform, turned out to be the top performing algorithm at the final machine learning (ML) stage.

R [16] is the programming language employed in the current study, and a number of packages from the same environment are used for a variety of tasks throughout the study. Plotting and interacting with the H_2O ML platform are done in the same language and environment.

3. Data Processing and Results

This study's data processing cycle includes several processes, such as missing value recovery, and tries to provide datasets appropriate for machine learning.

Machine learning algorithms are used in this research at different stages for two distinct purposes: (a) for missing values recovery (i.e., GLMs), and (b) for building the final sepsis prediction model (at this stage it was experimented with several algorithms and this is described in coming sections). The following is a description of the main processing steps through a Consolidated Standards of Reporting Trials (CONSORT)-like diagram.

3.1. Preprocessing Stage

At this stage files containing artifacts like human errors, equipment malfunction or failure, etc. were excluded. Due to the study design and the goal of building a sepsis prediction system with a prediction horizon of at least four hours (and three-hour observations needed to get the first prediction), sepsis files with less than seven observations were also excluded. A similar approach was used for non-sepsis subsets keeping only the files with seven and more consecutive observations without missing values concerning the parameters of interest. This is illustrated in Figure 1.

502 sepsis subsets are initially lacking all values for at least one important parameter, such as heart rate, peripheral blood oxygen saturation, temperature, systolic blood pressure, diastolic blood pressure, and respiratory rate.

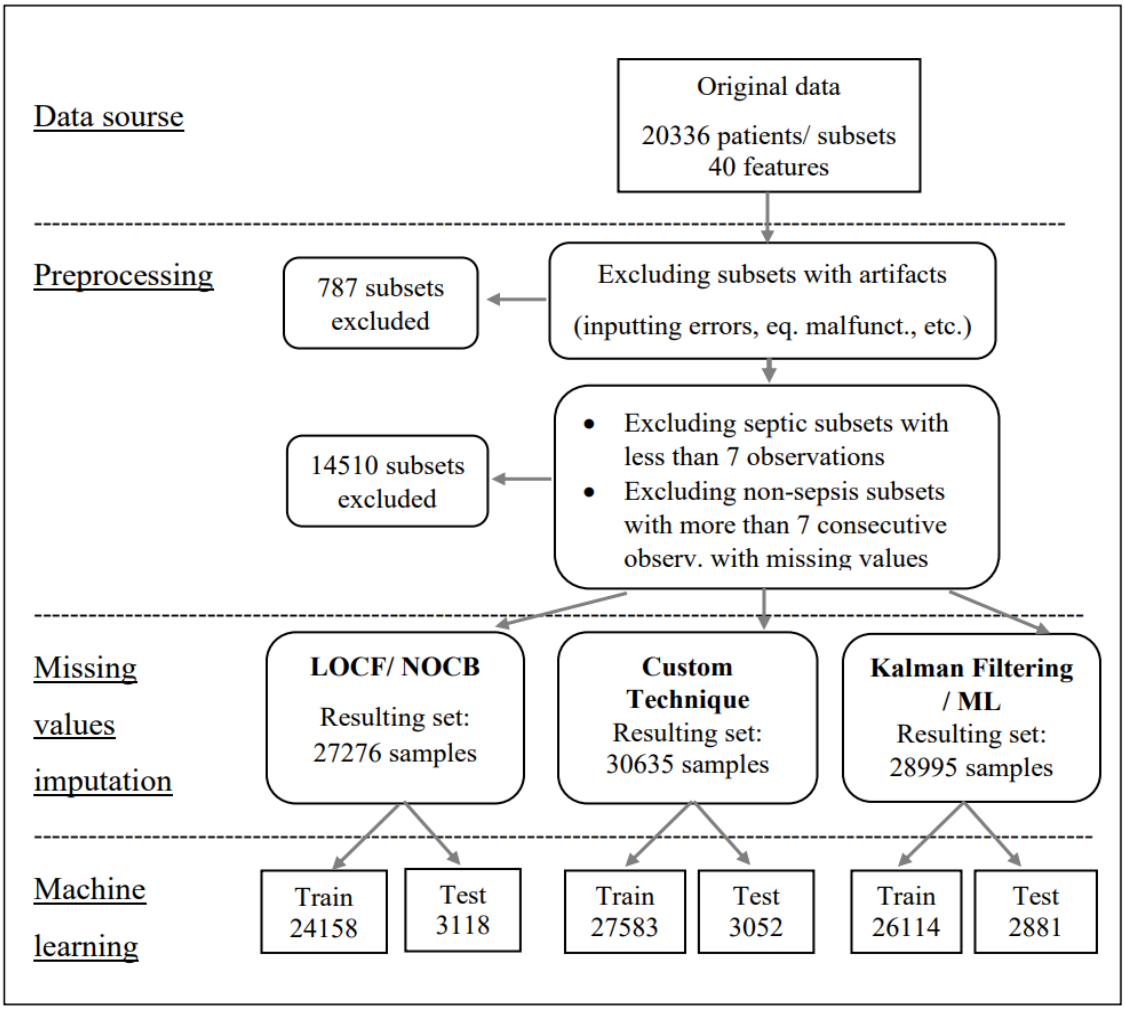


Figure 1. Data processing flow in the current research (CONSORT-like diagram).

Some of these files were reconstructed at the next stage with the custom approach described above or through ML algorithms used for data recovery purposes as part of the third method based on Kalman filtering.

3.2. Sepsis Data Reconstruction via Missing Values Recovery

3.2.1 Applying LOCF/NOCB

The first method (i.e., LOCF/NOCB) for data recovery in this research is LOCF (Last Observation Carried Forward, by "ImputeTS" package, R). The same package is used for NOCB as the second step. This is appropriate for columns in which some of the values are missing. It will not work for columns with all missing values, but it will recover lost data in columns when some of the values are missing.

3.2.2. Data recovery using the custom approach

Since this approach can deal with partially as well as totally (in a column) missing values it provides a final set of a larger size (i.e., 30635 samples) to be used for building the prediction system.

3.2.3 Kalman Filtering coupled with ML for data recovery

This approach also takes care of columns with partially missing values, on which Kalman filtering for data recovery can be used, should there be three and more non-missing values in the respective column.

The correlation between the six important factors listed above and the age was looked at in order to handle the all-missing values scenarios. The age has no missing data and exhibits a moderate correlation with some important metrics.

For each of the six parameters, the three most correlated parameters were chosen based on the correlation coefficients (e.g., for temperature the most correlated parameters are heart rate, systolic blood pressure, and age).

The correlation coefficients for seven parameters are shown in Table 2. The highest correlation coefficients are indicated by bold type.

Table 2

Correlation Coefficients

	HR	**O_2Sat**	**Temp**	**SBP**	**DBP**	**Resp**	**Age**
HR	1.00	-0.12	0.18	-0.02	**0.24**	**0.18**	**-0.18**
O_2Sat	**-0.12**	1.00	0.02	**0.06**	0.02	**-0.19**	-0.02
Temp	**0.18**	0.02	1.00	**0.09**	0.03	0.08	**-0.16**
SBP	-0.02	0.06	**0.09**	1.00	**0.53**	**0.07**	-0.01
DBP	**0.24**	0.02	0.03	**0.53**	1.00	0.06	**-0.33**
Resp	**0.18**	**-0.19**	**0.08**	0.07	0.06	1.00	0.07
Age	-0.18	-0.02	-0.16	-0.01	-0.33	0.07	1.00

Note. HR - heart rate, O2Sat - peripheral blood oxygen saturation, Temp - temperature, SBP - systolic blood pressure, DBP - diastolic blood pressure, Resp - respiratory rate. Sepsis label - the label of the observation (0 – for non-sepsis observations and 1 – for sepsis).

A series of GLMs were trained using this correlation data, and the models that performed the best were chosen for additional study. The primary traits of these models are displayed in Table 3.

Table 3

Logistic Regression Coefficients for Parameters of Interest (normalized)

Parameter for recovery	**Intercept**	**Coefficient (Parameter)**		
HR	89.4392	3.2658 (DBP)	3.2980 (Resp)	-2.3973 (Age)
O_2Sat	97.4894	-0.2305 (HR)	0.1840 (SBP)	-0.4954 (Resp)
Temp	37.2479	0.1233 (HR)	0.0720 (SBP)	-0.1001 (Age)
SBP	123.6418	1.6593 (Temp)	11.7255 (DBP)	0.6840 (Resp)
DBP	61.4999	2.5176 (HR)	6.8117 (SBP)	-3.7355 (Age)
Resp	20.3789	0.9001 (HR)	-1.0138 (O_2Sat)	0.3220 (Temp)

Note. HR - heart rate, O2Sat - peripheral blood oxygen saturation, Temp - temperature, SBP - systolic blood pressure, DBP - diastolic blood pressure, Resp - respiratory rate.

Together with Kalman filtering, these models are incorporated into the data recovery pipeline that reconstructs the missing value sepsis files. The look of a recovered file using this method is shown in Table 4. Bold values indicate recovered values. The resulting recovered subset is the one shown in Table 1 above.

Table 4

The recovered sepsis subset

HR	**O_2Sat**	**Temp**	**SBP**	**DBP**	**Resp**	**Age**	**Sepsis label**
83.37	**98.75**	**36.56**	**108.33**	**60.22**	**17.12**	43.55	0
83	99	**36.56**	109	**60.37**	13	43.55	0
89	99	**36.56**	102	**59.09**	22	43.55	0

Continuation Table 4

82	98	36.56	108	**59.93**	20	43.55	0
91	98	**36.83**	108	**61.2**	16	43.55	0
93	99	37.1	106	**60.87**	20	43.55	1
95	100	**37.15**	130	**68.45**	15	43.55	1
96	98	37.2	121	**65.86**	18	43.55	1

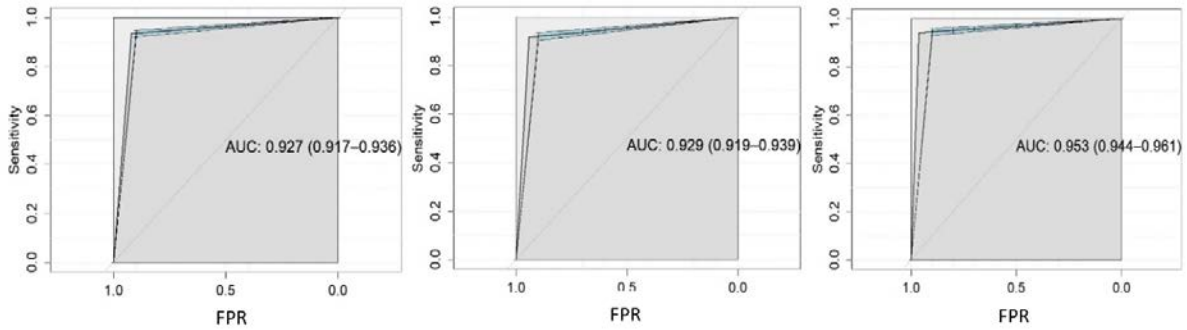
Note. HR - heart rate, O2Sat - peripheral blood oxygen saturation, Temp - temperature, SBP - systolic blood pressure, DBP - diastolic blood pressure, Resp - respiratory rate. Sepsis label - the label of the observation (0 – for non-sepsis observations and 1 – for sepsis).

3.3. Preparing Data Sets for Machine Learning

After being recovered, the data are divided into a training set (85–90% of the final samples) and a test set (10–15%). A sliding window method is used on each file (or subset) to aggregate observations into three-value-long chunks. Lastly, the algorithmic complexity (using the Block Decomposition Method) on each of the two 3x3 matrices is calculated, along with the difference between the parameter's value in three successive hourly samples [17]. The format of the data to be provided to the ML algorithm is represented by the 14L vector that is produced for each sample. The size of the final data sets is more than the number of initially selected files/subsets since each file comprises at least seven hourly observations of each of the six parameters of interest on which the sliding window approach is used. This procedure was applied to each of the final sets recovered through the approaches described earlier. The size of the final sets and train/test splits are presented in Figure 1.

3.4. Machine Learning Stage

A series of machine learning models are trained using the H2O platform with 10-fold cross-validation utilizing the training sets for ML produced with each of the three methods mentioned above. Gradient Boosting Machine (GBM), Generalized Linear Model (GLM), Distributed Random Forest (DRF), Stacked Ensemble (SE), and Deep Learning (DL) are the techniques utilized at this stage. Although GBM and SE had the best results, the GBM model was chosen for more study for explainability grounds.



a) b) c)

Figure 2. Classification performance by AUC of three GBM models built using the data recovered through three approaches: a) LOCF/NOCB (0.927); b) Custom method (0.929); c) Kalman filtering and ML (0.953).

Figure 2 displays the area under the ROC curve (AUC) for the classification (sepsis vs. non-sepsis) performance of these models on the test set of samples that did not take part in model training.

As one can see in the figure above the best performing model (i.e., AUC equal to 0.953) is model (c), or the model based on Kalman filtering for partially missing values coupled with ML approach through GLM for data recovery in columns with all-missing values. Table 5 summarizes further facts about the top-performing GBM.

Table 5

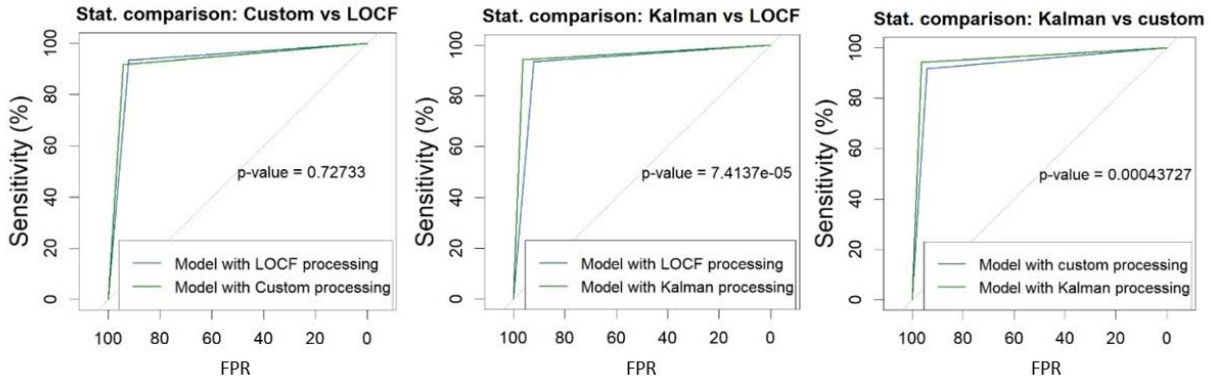
Confusion Matrices and Performance Statistics for Three Data Recovery Methods

		Reference (LOCF-NOCB)		Reference (Custom)		Reference (Kalman)	
		0	1	0	1	0	1
Prediction	0	1830	75	1874	89	1917	52
	1	159	1054	115	974	72	840

Accuracy	0.9250	0.9332	0.9570
95% CI	0.9151 - 0.9340	0.9237 - 0.9418	0.9489 – 0.9641
P-Value	< 2.2e-16	< 2.2e-16	< 2.2e-16
Cohen's Kappa	0.8401	0.8536	0.8999
Mcnemar's Test P-Value	5.767e-08	0.08006	0.08796
Sensitivity	0.9201	0.9422	0.9638
Specificity	0.9336	0.9163	0.9417

4. Discussion

It is possible to somewhat diminish the amount of missing data with thoughtful planning. This is significant because incomplete data might introduce bias into data analysis. This work uses a well-known viewpoint to handle the difficulty of recovering missing data during model construction. As far as we are aware, this is the first time the data recovery strategy based on the amalgamation of Kalman filtering and ML has been used for such or comparable datasets. One of key components of this method is the Kalman filter, used here in a less common way (in contrast to its more traditional application [11], e.g., for car cruise control, autopilot, dynamic positioning, target tracking, etc.). The second main component of this method is represented by six GLMs used to impute the values in columns with all-missing data. The latter is described in more details in [18].



a) b) c)

Figure 3. Statistical comparison of the performance of three ML models (by AUC): a) Custom method vs LOCF, b) Kalman vs LOCF, c) Kalman vs Custom method.

When used for missing values recovery, this approach provides the highest performance (AUC 0.953) of the sepsis prediction model and the difference is statistically

significant when compared with the other two approaches (p-values of 7.4137e-05 (b) and 4.3727e-04 (c) respectively). Figure 3 presents more details of the statistical comparison of the three methods described in the current work.

The suggested approach has some drawbacks. First off, it has not been evaluated on a variety of datasets, including datasets with categorical variables and those produced by other diseases (other than sepsis), among others. Additionally, it disregards data in which there is no association between the features and disregards the kind of variable distribution (normal, log-normal, logarithmic, etc.). So, identical datasets with continuous features and outcomes and a similar correlation between features could take into account our technique. Future research may have the opportunity to evaluate the method's resilience across various datasets.

Using the methods outlined in this study on sufficiently big and comparable data sets would be one of the future research paths. When analyzing various strategies for missing data recovery, particularly when evaluating the performance of classification ML models in differentiating between septic and non-septic cases, might serve as metrics of the method adequacy and dependability (e.g., comparing the results of the full set analysis to those of the complete case analysis).

5. Conclusions

The missing values in research data may be an issue, especially in case of large data sets with multiple observations and features. There are a number of methods for dealing with such issues, but a universally accepted approach is lacking, particularly when the data are used for machine learning purposes.

This paper tackles the missing value problem in a medical data set coming from patients in the intensive care unit. After recovery through three distinct approaches, these data are used to build a sepsis prediction system.

The authors' missing value imputation strategy, which is based on ML and Kalman filtering, offers the best classification performance (AUC 0.953) for the specific data utilized in this study.

As the missing values imputation method may have an impact on how well an ML model discriminates, it is worthwhile to test out several approaches before settling on the most appropriate one for the given set of data. It can result in a better diagnosis and course of therapy in some circumstances, potentially saving the patient's life (like septic patients in the current study).

Conflicts of Interest: The authors declare no conflict of interest.

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ANALYSIS OF THE USE OF GEOTHERMAL HEAT PUMPS FOR HEATING AND COOLING OF INDIVIDUAL RESIDENTIAL BUILDINGS

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Abstract. Today, humanity is beginning to realize the problem of the growing shortage of natural energy sources. The prices of these sources are rising uncontrollably and will continue to rise in the future. As the Republic of Moldova does not have its own fossil fuels fields and is totally dependent on foreign imports, the implementation of renewable energy sources technologies becomes vital. In this sense, the usage of closed type geothermal heat pumps with direct heat exchange in new and reconstructed residential buildings to replace traditional heating boilers is beneficial. They can be especially effective in areas where there are no gas supply pipelines. The purpose of the paper is to determine the perspectives of geothermal heat pumps using in residential buildings in the Republic of Moldova climatic conditions. Examples with implemented geothermal heat pumps and project solutions for heating/cooling and hot water supply systems for three individual residential buildings in the southern region of the Republic of Moldova were analyzed for task implementation. During the 2020-2021 heating season, it was not necessary to use the additional reserve heat source for the examined objects.

Keywords: Heating *system, warm floor, direct heat exchange, alternative energy source.*

Rezumat. Astăzi omenirea începe să conștientizeze problema deficitului tot mai mare de surse de energie naturale. Prețurile pentru acestea cresc necontrolat și vor continua să crească în viitor. Deoarece R. Moldova nu dispune de zăcăminte proprii de combustibili fosili şi totalmente depinde de importurile din exterior, implementarea tehnologiilor cu utilizarea surselor de energie regenerabile devine vitală. În acest sens este benefică, utilizarea pompelor de căldură geotermale tip închis cu schimb direct de căldură, în locuințe noi și reconstruite pentru a înlocui cazanele tradiționale de încălzire. Acestea pot fi deosebit de eficiente din punct de vedere al costurilor în zonele în care rețelele cu gaze naturale nu sunt disponibile. Scopul lucrării este de a determina perspectivele utilizării pompelor de căldură geotermale în clădirile rezidențiale în condițiile climatice ale R. Moldova. Pentru realizarea scopului propus au fost analizate exemple cu pompe de căldură geotermale implementate şi soluțiile de proiect de sisteme pentru încălzire/răcire şi alimentarea cu apă caldă pentru trei clădiri individuale de locuit din regiunea de sud a R. Moldova. Pe perioada sezonului de

încălzire 2020-2021, la obiectele examinate nu a fost necesară utilizarea sursei de căldură de rezervă adițională.

Cuvinte cheie: *Sistem de încălzire, podea caldă, schimb direct de căldură, sursă alternativă de energie.*

1. Introduction

According to statistics [1], the annual increase in the construction of individual residential houses was 30% in the period 2017-2019 in the Republic of Moldova. In 2021 it increased by 18 % compared to 2020 and amounted to 288.9 thousand m^2 (about 2 thousand of houses). But, despite the increase in the volume of construction of individual housing, the designers of engineering systems pay little attention to the provision of a comfort microclimate of a residential house using energy-efficient technologies, limiting themselves to classic solutions. The Republic of Moldova does not have energy resources. And after the gas crisis in the fall of 2021-2022, it became even more clear that it is necessary to implement alternative energy sources. In this sense, heat pumps that work on electricity and are safe, automated and reliable equipment offer great hope [2-7].

The purpose of this work is to analyze the already operational geothermal heat pumps (GHPs) in residential individual houses to understand the feasibility of using them in the conditions of the Republic of Moldova since the experience of using heat pumps in our country is very little. In this regard, for the analysis of the effectiveness of the use of GHPs, three residential houses in the southern regions of the Republic of Moldova were selected, in which the geothermal heat pumps were installed and used for heating, cooling, and supplying the house with hot water.

GHPs use the relatively constant temperature of the earth as the exchange medium. Some models of geothermal systems are available with two-speed compressors and variable fans for more comfort and energy savings. Compared to air-source heat pumps, they are quieter, last longer, need little maintenance, and do not depend on the temperature of the outside air [8].

The biggest benefit of GHPs is that they use 25 %–50 % less electricity than conventional heating or cooling systems. According to the Environmental Protection Agency, geothermal heat pumps can reduce energy consumption and corresponding emissions by up to 44 % compared to air-source heat pumps and up to 72 % compared to electric resistance heating with standard air-conditioning equipment [9].

2. Examples of practical solutions for the use of geothermal heat pumps in the conditions of the Republic of Moldova

2.1 General information

In this paper, closed-type GHPs with direct heat exchange (DX - "direct exchange"). Unlike other types of heat pumps, the refrigerant takes heat directly from the ground, without the use of intermediate heat exchangers and thermal agents, copper pipes are used as probes through which refrigerant R 407C circulates, taking heat from the soil. One of the benefits of the DX geothermal system is the copper ground loop, which is a more effective means of transferring heat than the plastic ground loop [10].

Among the advantages of this technology, a higher temperature difference can be noted, which increases heat transfer, this advantage is partially neutralized by a smaller area of contact with the ground. A significant advantage of this technology is the small diameter

of wells during drilling, which significantly reduces the cost of installation work. At the same time, they require more refrigerant and their piping systems are more expensive.

The ground loop system can be installed in several different configurations: vertical, diagonal, and horizontal. In the examples considered, diagonal systems are used, which usually take up very little space, the probes are located at an angle of 45 degrees (figure 1).

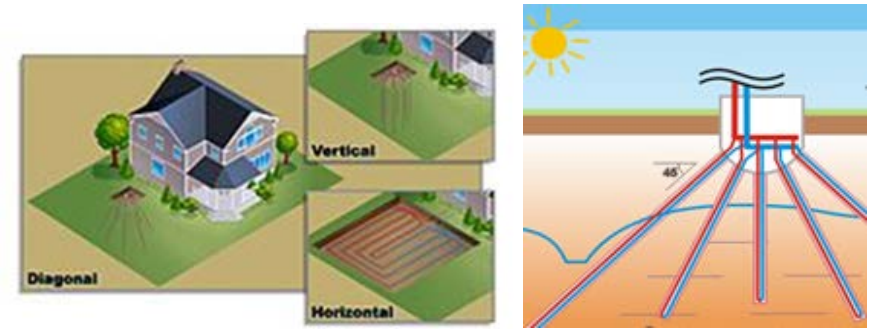

Figure 1. Configurations of the ground loop system and geothermal heat pumps with direct heat exchange [11].

High energy efficiency is ensured by combining a heat pump with a radiant floor heating system ("warm floor"). Low-temperature radiant floor heating system "warm floor" allows getting a heat flow of 50-150 W/m^2, at a heat transfer fluid temperature of 35-55 ºC. At the same time, there are restrictions imposed on interior elements, in the general case, the maximum area for laying a "warm floor" is 60-70 % of the heated area [12].

2.2 Application of a geothermal heat pump in a residential building located in the village of Cania, Cantemir district

The main indicators of objects and heat pumps are presented in (table 1). Calculation of heat losses for this building was made for two boundary conditions of outdoor temperature -16 ºC and 3 ºC and at an indoor air temperature of 22 ºC [13, 14]. The -16 ºC/22 ºC mode is selected to determine the heat pump capacity, the 3 ºC/22 ºC mode is selected to estimate the amount of heat required for the entire heating season to maintain the set indoor temperature.

Figure 2. Geothermal circuit of the heat pump in the village of Cania.
(*SRL "Climatehnic" photo*)

The temperature of 3 °C corresponds to the average temperature of the 2020-2021 heating season for Cantemir, calculated according to the data of the State hydro meteorological service [15], the duration of the heating period is 164 days [13, 14].

Estimated heat loss in -16°C/22°C mode is 4.2 kW and, respectively, in 3 °C/22 °C mode, 2.4 kW. A geothermal heat pump used for heating and cooling the house was installed by SRL "Climatehnic" in November 2018. The heat pump is built using direct evaporation technology. The geothermal circuit is made in the form of 5 probes with a total length of 120 m installed at an angle of 45 degrees, structurally the probes are made in the form of a single U-shaped connection of two copper pipes with a diameter of ¼ and ½ inch. Distribution collectors are located in the ground below the freezing depth (figure 2).

During the installation of the geothermal circuit and the analysis of the groundwater level, it was determined that approximately 60 % of the total length of the probes was located in water-saturated soil, which positively affects the performance of the system. Periodic monitoring of heat pump operation (figure 3), showed that the average boiling point of refrigerant (freon) at this facility during operation changed from -7 °C in the first year of operation (2018-2019) to -3 °C for the period (2020-2021). The measurements were carried out during periods of cooling in the second half of winter, while the continuous operation time of the compressor was at least 60 minutes. A digital manifold TESTO 550 was used as a measuring device. The increase in the average boiling point during the heating season can be associated with the degree of soil compaction around the walls of the probe, the complete shrinkage of which occurs over several years, and stabilizes, based on observations of objects, in the third year heat pump operation.

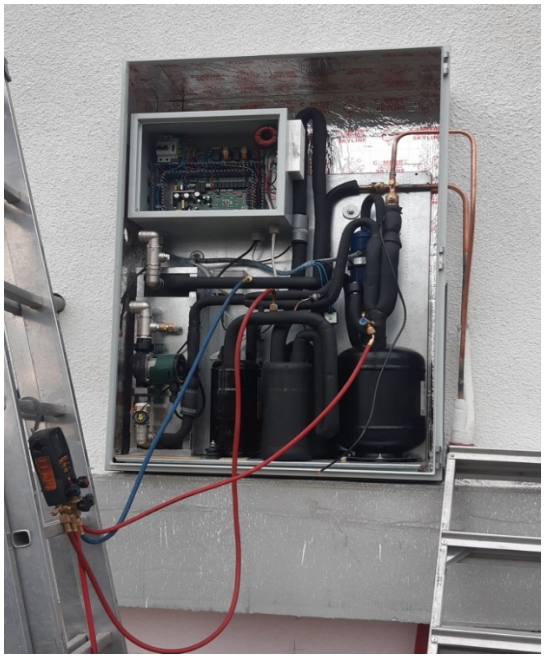

Figure 3. A heat pump implemented in the village of Cania.
(*SRL "Climatehnic" photo*)

This heat pump has a compressor, Copeland, Emerson Climate, the main parameters of the refrigeration circuit (boiling point of Freon R407C -3 °C, Freon condensation temperature 35 °C) in the selection program from the manufacturer, the compressor capacity is 5.07 kW (*Qc*), [16].

The operation of a heat pump is characterized by the performance coefficient (*COP*), defined as the ratio between the useful effect produced (thermal energy supplied, *Qc*) and the energy consumed to obtain it (actuation energy, *Qp*). To find out the heat pump coefficient performance (*COP*), the *Qc* is divided by the electric power consumption of the compressor, control unit, and circulation pump (*Qp*).

$$COP = \frac{Qc}{Qp} \tag{1}$$

$$COP = \frac{5.07}{1.11 + 0.045 + 0.03} = 4.2$$

The cooling of this residential building is also carried out by floors. The temperature of the heat carrier at the inlet to the HP heat exchanger, due to the limitations of the

controller used, cannot be set above 18 °C, which turned out to be too low in practice, therefore, to solve this problem, a room thermostat was installed that turns off the cooling when the set room temperature is reached. In this mode, according to the results of several measurements, over the summer temperature of the refrigerant, it was: boiling point t_o=8 °C, condensation temperature t_c=30 °C.

The demand for maintaining the indoor temperature all year round and covering the housing supply with domestic hot water is on average 4700 kW per year (a separate meter is installed to measure the electricity consumption of the heat pump).

2.3. Application of a geothermal heat pump in a residential building and a dental clinic in one separate building in the city of Comrat

The special feature of this object is that it is divided into 2 parts, one half of the building is a residential area, and the second is a dental clinic. The building size and thermal characteristics are presented in (table 1).

The estimated heat losses of the building in the -16°C/22°C mode are 15.1 kW, and in the average temperature mode for the heating season 2020-2021 3°C/22°C, they are 7.6 kW. For heating and cooling a house with an area of about 600 m^2, a heat pump with a rated capacity of 18 kW is used, taking into account the expansion of the area. This heat pump was manufactured and installed by SRL "Climatehnic" in April 2020. The heat pump is also built based on direct evaporation technology, compressor control is the inverter, and the total length of geothermal probes is 320 m (figure 4).

Figure 4. Geothermal circuit of the heat pump in the city of Comrat.
(*SRL "Climatehnic" photo*)

The GHPs are the main source for heating and cooling the building. A condensate gas boiler with a capacity of 35 kW is used as a backup (reserve) for heating and hot water supply. Radiant underfloor heating is used as a heat distribution system, to increase the efficiency of passive cooling, heat carrier pipes are also laid above the floor slab of the second floor under thermal insulation. The building has a supply and exhaust ventilation system with heat recovery.

The hot water supply at this facility is implemented according to the scheme: two indirect heating are used as storage tanks, the storage tanks of which are connected in series, the first boiler is heated directly from the heat pump, the second boiler heat exchanger is connected to a gas boiler. In case of insufficient heating of the water in the first boiler and to ensure a stable temperature in the hot water supply system the second boiler is an auxiliary source of energy to maintain the required hot water temperature (figure 5).

Figure 5. Gas boiler and hot water boilers.
(*SRL "Climatehnic" photo*)

In the heating mode, floor heating is used, and the heating working fluid is also supplied to the heating coils installed in the ventilation unit.

In the premises of the dental clinic, cooling in the warm season is hybrid, the ceiling of the second floor is used as a cooling panel, and fan coil units and a water cooler section are used in the supply ventilation system. It should be noted that in the first year of operation, the cooling of the building, except the water cooler of the supply ventilation system, was performed only using cooling panels (floors and the ceiling of the second floor). Analysis of the data obtained during this observation period allows us to draw the following conclusions:

- panel cooling system uses cold water at 14/18 °C temperature, higher than air type cooling system, 7/12 °C mode for fan coil units. Panel cooling is a very good alternative to standard air cooling systems;
- in the part of the building where the dental clinic is located, there was a problem with high relative humidity. The client required that the room temperature should not exceed 22°C. The optimum indoor air temperature is within 25-26 °C, when the indoor air temperature drops to 22 °C, the relative humidity in the room rises to 70 % at an outside air temperature of 35 °C and a relative humidity of 32 %, the operation of the ventilation system does not reduce the humidity. The indoor air humidity rises to 70 % because at least 15 people are constantly in the room, after each patient the rooms are processed, and wet cleaning is carried out at least 4 times per working day. All this led to the transition to fan coil cooling. It should be noted that the panel cooling system coped with maintaining the set temperature, but the high relative humidity (70-80 %) prompted a switch to a hybrid cooling system Due to the different requirements for the water temperature in the cooling circuits, the heat pump supply temperature is maintained in the range of 4 -7 °C, and water is supplied to the ceiling circuit using a mixing unit with a temperature of at least 14 °C.

The temperature of the coolant at the outlet of the heat exchanger for the heating season 2020-2021, was in the range of 32-37 °C, the boiling point of Freon was in the range of (-3 °C) – (-5 °C), the temperature difference in the heat exchanger of the heating circuit was about 3K, thus the average operating mode of the compressor was -4/38 °C. According to the manufacturer's data sheet for the compressor Mitsubishi LNB42FSAM [16] installed in this heat pump and after some extrapolation, the average calculated heat pump COP for the

heating season was 4.6. In cooling mode, the average operating mode is 2/35 °C, respectively, EER, according to [16], will be 5.18. During the past heating season, there was no need to connect a backup heat source.

2.4. Application of a geothermal heat pump in a residential building located in the city of Cahul

The building size and thermal characteristics are presented in (table 1). The estimated heat loss of a residential building in the city of Cahul in the -16 °C / 22 °C mode is 5.8 kW, in the average temperature mode for the heating season, 2020-2021 is 3.5 °C/22 °C they are 3.4 kW. The facility has a geothermal heat pump with a rated capacity of 12.5 kW. This heat pump was manufactured and installed by SRL "Climatehnic" in November 2020.

Heating and cooling of the building take place with the help of pipes embedded in the floor structure, as well as in the walls. In the building under consideration, the Multilevel^{tm} technology proposed by the Swedish company Thermotech was applied. This technology is described in [17]. In this building, the floor heating on the first floor is made according to standard technology, with insulation under the pipe, to avoid heat loss to the ground, on the second floor, the floor heating piping is located directly on the floor slab. The thermal calculation of the heating system was performed using the Valtec calculation program. The power of the warm floor was insufficient, therefore, pipes with a heat carrier were additionally installed in the wall panels placed under the windows of the first floor (figure 6).

Figure 6. Location of pipes with coolant in the walls.
(*SRL "Climatehnic" photo*)

Operation during 2020-2021 showed a high level of comfort in both heating and cooling modes. A gas condensate boiler was installed as a backup heat source, but it was not used during the heating season 2020-2021.

This heat pump is equipped with a Mitsubishi LNB42FSAMC compressor. The main parameters of the refrigeration circuit as of December 15, 2021 were: pressure in the circuit 6.14 Bar; boiling point of the Freon R410C -3.4 °C; Freon condensation temperature 33.6 °C; outdoor air temperature 1.3 °C, compressor frequency 30 Hz. Under these conditions, the compressor capacity was 5.5 kW. Taking into account the consumption of the compressor, circulation pump, and control unit, the calculated *COP* of the heat pump is:

$$COP = \frac{5.5}{(1.2+0.045+0.035)} = 4.23 \quad (2)$$

Table 1

Main indicators of objects

Indicators of objects	Residential building in the village of Cania	Residential building and a dental clinic in the city of Comrat	Residential building in the city of
Number of levels	1	3	2
Surface, m^2	118 $м^2$	600 $м^2$	250 $м^2$
Exterior walls Ceiling	400 mm limestone 200 mm clay	400 mm limestone, 160 mm reinforced concrete	400 mm limestone, 160 mm reinforced concrete
Thermal insulation [18]: - exterior walls - ceiling - floors	100 mm foam 100 mm mineral wool 50 mm polystyrene	100 mm mineral wool basalt 300 mm foam 50 mm polystyrene	100 mm mineral wool basalt 150 mm mineral wool 30 mm PIR panels
Heat pump capacity	5 kW	18 kW	12.5 кW
Heat pump technology	GHPs with direct heat exchange	GHPs with direct heat exchange	GHPs with direct heat exchange
Total probe length	120 m	300 m	250 m
Technology geothermal circuit	Diagonal loop pipe material - copper	Diagonal loop pipe material - copper	Diagonal loop pipe material - copper
Soil	Clayey water-saturated	Clayey water-saturated	Clayey water-saturated
Backup heat generator	Wood burning stove	Gas condensing boiler	Gas condensing boiler
Heating/cooling system	Warm floor	Warm floor, fan coil units	Warm floor, wall panels
Ventilation system	Natural	Mechanical supply and exhaust with heat recovery	Natural
Hot water supply	Indirect heating boiler 150 L	2 consecutive indirect heating boilers of 200 L each	Indirect heating boiler 200 L
Calculated average COP* of a heat pump for heating	4.28	4.6	4.23
Initial investment**, EUR	3225	6550	5200
Electricity consumption for the heating season, kWh	2463	7256	3146

Note. *- calculated COP of the system, based on the actual, operational, parameters of the heat pump; **- as an initial investment for heat pumps, we take the cost of a heat pump together with a geothermal circuit.

3. Conclusions and Recommendations

Having considered practical examples of the implementation of geothermal heat pumps, the following **conclusions** can be made:

- heating f residential individual buildings using gas boilers is by far the most common option, but more and more factors are forcing us to find out alternative, reliable, and sustainable energy sources. These factors are: the depletion of world hydrocarbon resources, the rising price of natural gas, the unpredictability of natural gas supplies; the lack of widespread gasification; and the need for air-conditioning housing in the warm season;
- the use of heat pumps in residential buildings is in many cases an energy-efficient and economically justified solution, leading both to saving of non-renewable energy resources and to protecting the environment by reducing CO_2 and other harmful greenhouse gas emissions into the atmosphere;
- operating experience of geothermal heat pumps shows that they can act as an efficient generator of heat and cold in the conditions of the Republic of Moldova and are most efficient when used in both heating, cooling, and hot water modes;
- in the conditions of Moldova, where clay soils prevail, it is reasonable to install a vertical heat exchanger for a geothermal heat pump;
- the use of a geothermal heat pump and radiant heating/cooling system (walls, floor, ceiling) ensures indoor comfort throughout the year;
- considering that the envelope of the examined buildings was thermally insulated and the real average outdoor air temperature for the heating period is 2-3 ºC, no auxiliary heating source was needed.

Recommendations for the use of heat pumps:

- considering the rather high building density in the Republic of Moldova and the relatively small areas of land for individual buildings, it is usually difficult to allocate space for the location of the geothermal circuit, one of the solutions to this problem is to use the diagonal loop method of installing geothermal probes, the essence of which is drilling probes from one receiver at an angle, this allows you to cover a large amount of soil without occupying a large area and without carrying out bulk earthworks, which reduces the cost of developing of the circuit (loop);
- taking into account the growth in electricity and gas tariffs and the rate of inflation in the Republic of Moldova, the demand for the installation of heat pumps for heating residential buildings will increase.

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A NEW CONCEPT REGARDING THE SELECTION OF SEWERAGE SYSTEMS AND NATURAL TREATMENT OF MUNICIPAL WASTEWATERS

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Abstract. The article contains a review of methods and procedures of the municipal wastewater treatment, with the discussion of their specifics. A new concept is proposed related to the selection of municipal sewerage and wastewater treatment systems, considering the local/decentralized, semicentralized or centralized systems, especially those suitable to rural and suburban localities, in dependence on the advantages and disadvantages of these systems and local specifics. The concept of phytofilters is proposed for the biological treatment of wastewater in small towns. This technology is simple, inexpensive and requires relatively little maintenance. Biological ponds in the Republic of Moldova have proven to be very suitable for advanced wastewater treatment, being a cheap and natural purification system with a good potential for implementation. When choosing a sewer system, priority must be given to its functionality and practical considerations.

Keywords: *sewerage systems, wastewater treatment, biological ponds, phytofilters, suspended microflora, fixed microflora.*

Rezumat. Articolul conține o trecere în revistă a metodelor și procedeelor de tratare a apelor uzate municipale, cu analiza specificului acestora. Se propune un nou concept legat de selectare a sistemelor municipale de canalizare si tratare a apelor uzate, având in vedere sistemele locale/descentralizate, semi-centralizate sau centralizate, in special cele adecvate localităților rurale si suburbane, in funcție de avantajele si dezavantajele acestor sisteme si de specificul local. Conceptul de fitofiltre este propus pentru tratarea biologică a apelor uzate din localitățile mici. Această tehnologie este simplă, relativ ieftină și necesită o întreținere relativ nesemnificativă. Iazurile biologice din Republica Moldova s-au dovedit a fi foarte potrivite pentru tratarea avansată a apelor uzate, fiind un sistem de epurare ieftin și natural, cu un bun potențial de implementare. Pentru alegerea unui sistem de canalizare, prioritate trebuie acordată funcționalității acestuia și considerațiilor practice.

Cuvinte cheie: *sisteme de canalizare, epurare a apelor uzate, iazuri biologice, fitofiltre, microfloră în suspensie, microfloră fixă.*

1. Introduction

Nowadays, from the point of view of social development, water supply and sanitation systems which have been applied mainly in the rural area and will be further developed, gain the special importance considering the association of the Republic of Moldova to the EU [1]. This fact is one of the beneficial consequences of association, and, therefore, there is still time to pay attention to one of the most important aspects – sewerage and waste waters treatment. First of all, the attention should be paid to the domestic wastewaters resulted from water using in sanitary and household scopes.

In addition to the high quality potable water, used by the people in houses or apartments for drinking and food preparation, the domestic water is also used in the toilets, forming the so-called *brown water* with the contents in urine and feces, evacuated with the closets flash water, and the so-called *grey water* used for corporal hygiene, kitchens and washing machines. In dependence on the toilet type, a person consumes from 10 to 25 thousand litres of water per year (brown wastewater), whereas in dependence on the condition of other sanitary objects and water savings in the households, from 25 to 100 thousands litres of waste water per person are formed annually.

In a settlement may be functioning the economic entities as well, which may be sources of the industrial waste waters resulted from the technological processes. In dependence on their character, different quantities of water are consumed and evacuated. One can imagine the situation when the waste waters formed in the significant amounts would not be collected and evacuated in the sewage system and further discharged into the different receiving bodies, most often the surface waters, without any treatment.

Therefore, while designing and constructing the water supply systems for the people, the collection, evacuation, treatment and eventually, reuse of the waste waters and sludge treatment should be obligatory envisaged. There are many relevant technical approaches which, however, require both the different investments and the operation costs [2].

2. Sewerage systems

In many countries, including the Republic of Moldova, centralized management of waste waters is one of the most common solutions. This imply the collection and evacuation of wastewaters through the centralized sewerage system, up to the central treatment station, where the waste waters and the sludge are treated and depolluted in the controlled conditions (Figure 1).

Figure 1. Reservoir from which the water treated at the Orhei treatment plant is discharged into the Raut river [3].

The advantages of this concept imply the lower investment and operation costs for the large treatment plant, as compared to the several smaller treatment plants, considering the more efficient control of both the treated water and sludge quality, and plant operation processes. However, this approach is not universal, especially in case of the less populated regions.

The ratio between the costs and advantages of centralized systems can be less favorable when the big and long-term expenses for the construction and maintenance of sewerage system are taken into account. Provided the sewerage system is not properly maintained, the leaks can appear which may cause the soil and underground waters pollution. The centralized sewerage systems, as a rule, need many pumping stations which must be operated and maintained properly. In addition, the centralized treatment plants reduce the possibility of the waste waters, nutrition substances and sludge reuse, because of the pollution with harmful substances such as chemicals, heavy metals and pathogenic microorganisms, especially in the combined sewerage system where the industrial waste waters are collected as well.

In this situation, the selection of a sustainable public sewerage system is not easy univocal, especially due to the fact that there are decentralized (local), semicentralized (with many treatment plants) and combined (local and centralized) systems available. In the last years the more and more attention is paid to the modern decentralized or semicentralized concepts of local management of waste water, which are already applied in many countries, especially in the rural and suburban zones.

3. New concepts of the waste waters sewerage and treatment

During the las 20 years it became obvious that the existing centralized systems for the waste waters treatment have a series of disadvantages. They often do not meet the conditions of durability.

The durability implies the following 5 aspects:

1) *Sanitation and hygiene*: includes the risk of exposure to pathogens and harmful substances, which can affect the public health at all the stages of sewerage system, starting from the toilets, the collection, evacuation, transportation and treatment system, up to the reuse or discharge points into the transmitters/receivers and downstream settlements.

2) *Natural environment and resources*: involve the energy, water and other natural resources necessary to construct, operate and maintain the system, as well as their eventual emissions in the environment resulted from their usage; it also implies their recycling and reuse leve and their effects (such as nutrients and organic substances reuse in agriculture), protection of other fossil / non-renewable sources through the production of renewable energy (such as biogas).

3) *Technology and exploitation*: involve the functionality and easiness with which the entire system, including the wastewater collection, transportation, treatment, sludge treatment, reuse and/or storage, can be constructed, exploited and controlled by the communities and/or technical teams of the utilities' suppliers. In addition, the system resistance, vulnerability with regard to the power outages, water shortage, floods, as well as the flexibility and adaptation of technical components to the existent infrastructure and demographic and socio-economic evolution are the important aspects that need to be evaluated.

4) *Financial and economic aspects*: they are related to the ability of households and communities to pay for the sewerage, including for the construction, operation exploitation, maintenance and necessary reinvestments for the system.

5) *Socio-cultural and institutional aspects*: the criteria belonging to this category evaluate the socio-cultural acceptability, how appropriate and how convenient is the system, its impact on human dignity, conformity with the legislative framework, as well as with the stable and efficient institutional framework.

Even there are wastewater treatment systems already known and the indisputable improvements in the public health and natural environment, the quality of many surface and underground waters remains to be affected by the nutrients, microorganisms and harmful substances resulted from the discharged and treated waste waters.

The need for the nutrients recovery from the waste waters, especially phosphorus – a non-renewable disappearing source, is highlighted by the need of the new concepts that would allow the safe use of nutrients. The management of the centralized sewerage systems and waste water treatment plants is not a right solution for adapting to climate changes, because it requires a lot of energy and does not include the local water circuit. High investment and operation costs, due to the related conditions, obligations and inflexibility, make the centralized systems inadmissibly costly and inefficient.

The conclusion can be made that the sewerage systems should be modified in such a way that they would allow decentralizing, including at the level of households or the group of households. Water circuit must be closed up locally, and the nutrients coming from the households must be available for the reuse in agriculture.

Fundamental principles of the new concepts regarding the canalization and waste water treatment are as follows: (a) on-site waste water treatment; (b) water and nutrients recycling/reuse and (c) decentralization.

To be mentioned that the trend towards the dry sanitation makes part of the new concepts. Specifically, the modern toilets have been elaborated for the rural zones and installed for the compost and separate evacuation of urine. Certain practical examples demonstrate that the dry sanitation combined with the simple filtration of grey waters is an accessible solution from the economic point of view and technically secure for the zones without the secure water supply.

The other trend is the biogas and organic fertilizer collection from toilets, according to the sanitary concepts for urban zones. Domestic wastewaters (from their toilets, grey water, stormwaters) are separated on-site. Vacuum toilets only discharge 5 litres of the domestic wastewater per capita and per day, therefore, the domestic water consumption for potable scopes is very low - below 80 L/pers.·day [4]. The grey waters are treated with filters planted with reed or in the constructed wetlands and are infiltrated locally into the soil, as well as the stormwaters, especially rainwaters [5].

These concepts involve the collection, evacuation, treatment and discharge / reuse of the wastewaters, storage, treatment and using of the sludge from small communities (from the households to the parts of localities) integrated in the locality/village/town development projects. Such systems involve the numerous small-scale wastewater purification equipment, designed and manufactured locally.

The decentralized systems maintain a variety of pollution sources, having both the liquid phase and solid fraction, thus reducing the wastewater collection and disposal network and, respectively, offering a high degree of flexibility allowing to modify the design and the way of the sewage system operation, according to different local conditions and scenarios.

The decentralized and semi-centralized systems offer the following advantages: (a) low investment, operation and maintenance costs for the sewage system with the lower

length network; (b) better protection of water sources, with less damage in case of deflections (risk minimization); (c) offer the solutions corresponding to the individual pollution level; (d) are flexible (allow extension) and adaptable to the changes in conditions, population, tourism, industry; (e) permit taking the decisions in dependence on the real needs of sensible environmental zones, they can be implemented when needed; (f) they can be harmoniously framed into the landscape; (g) the treated water and nitrition substances (N and P) can be reused easily.

The main disadvantages of decentralized or semi-centralized wastewater management are as follows: (a) potentially lower wastewater treatment efficiency (especially for the nutrients N and P); (b) need for the training and correct using; (c) the presence of qualified personnel for operation and management is necessary; (d) monitoring can be insufficient; (e) legislation and institutional environment could become an obstacle.

These factors must be considered when selecting the sewage and wastewater treatment system.

4. Wastewater treatment technologies

The technology applied for the wastewater treatment is relatively independent of the collection and disposal system for the localities with up to 10 thousand population connected to sewage system. Although any intensive and extensive technology is applicable both locally and on the larger, centralized scale, the technologies have the different advantages and disadvantages. The intensive biological processes are the most highly developed and broadly used technologies on the level of domestic and communal/municipal wastewaters treatment plants [6]. The principle consists in exploiting on a small space the intensified natural biodegradation of the organic pollutants along with the elimination of nutrients (N and P) [7].

The most developed and widely implemented technology is the system with active sludge (with the suspended microflora in the form of very fragile flakes) with mainly pneumatic aeration with the compressed air using the blowers [8]. This technology needs the permanent electric energy supply as well as the qualified personnel for the operation and maintenance. There are also the biological treatment systems with microflora fixed on the solid support (package) in the form of biological film (biofilm). These systems are well known around the world and are often defined as a standard ones, according to some experts.

Figure 2. Water pumping into the filtration platform [3].

The anaerobic technology is an innovation for the communal wastewaters treatment. Their principal advantage is that the anaerobic system does not need aeration, at the same time producing an energy in the form of biogas. This system represents an intensive biological treatment which needs technical, technological, biochemical knowledge and other obligatory conditions (heat, further aerobic treatment, semi-centralization, etc.) [9].

To the extensive biological purification are related most often the biologic ponds and filters artificially planted with macrophytes – the so-called phyto-purification systems (Figure 2). The extensive technologies have the considerable advantages with regard to both the investment and operation costs [10].

The common feature of extensive technologies is that they can be exploited without electricity (apart from artificially aerated biological ponds). For these reasons, the extensive options for aerobic biological treatment as well as the anaerobic treatment are considered for the rural areas more durable than the intensive ones.

5. Biological ponds for the wastewaters treatment

The communal wastewaters treatment in the biological ponds (lagoons) is a well-known and broadly spread technology in the Republic of Moldova. The extensive treatment is based on the natural self-purification processes with the bacterial cultures and it realized with the long-term retention of wastewaters, which needs more extended space then in case of the intensive systems. The treatment in ponds has a high performance, reduced costs and low energy consumption (sometimes equal to zero), representing a process with low maintenance costs and is very suitable for a hot climate or hot seasons [11].

The treatment in biological ponds with natural aeration is done in several dammed ponds, usually artificial, arranged consecutively [12-15]. The system is usually composed of three ponds connected in series: one optional pond and two maturation ponds. The serial placement of the three ponds allows the efficient removal of insoluble pollutants (suspended matter), biodegradable organic substances (BOD or COD) and nutrients (N and P), as well as partial disinfection. Additional ponds (with up to 6 ponds in series) are required for safe nitrogen removal or disinfection. Prior to the first pond, it is useful to consider removal of solid large size particles (usually larger than 16 mm), both sedimentable and floating.

The first pond, having a depth of 1÷2 m, has the role of removing the most of the sedimentable suspended matter, of both mineral and organic origin, as well as partial removal of biodegradable soluble organic pollutants (BOD). It can be anaerobic and may be deeper than 3 m. To avoid the methane emissions, this pond must be covered and the biogas produced should be collected.

The maturation ponds 2 and 3 are designed for the complete removal of soluble biodegradable organic pollutants (BOD), the nutrients (N and P) and pathogenic agents. Their depth is usually up to 1 m, in order to ensure the aerobic conditions (presence in water of free dissolved oxygen). The ponds should be designed in such a way that to be harmoniously incorporated in the landscape.

The efficiency of the disposal of organic matter is over 75% COD, which ensures a COD concentration in the effluent purified of less than 125 mg/L, which corresponds to the requirements of the EU Directive on the treatment of communal wastewater. Nitrogen concentration can meet the standards for areas sensitive to eutrophication in the summer, but due to the low temperature in winter the results are less good, but this is also observed in intensive procedures. Phosphorus is reduced by over 60% due to its accumulation in

sedimentary sludge. Disinfection is especially important during the summer, when evacuating in small surface water receivers. The result obtained is better than in the case of intensive systems due to the long retention time and the impact of the ultraviolet solar rays.

The efficiency of the organic matter removal is over 75% chemical oxygen demand (COD), which ensures the concentration of COD in the treated effluent below 125 mg/L, which corresponds to the requirements of the EU Directive on municipal wastewater treatment. Nitrogen concentration may meet the standards for the areas sensitive to eutrophication in summer, but due to the low temperature in winter the results are not as good, but this is also observed in case of intensive procedures. Phosphorus is reduced by over 60% due to its accumulation in sedimented sludge. Disinfection is especially important in summer, when treated water is discharged into the small surface water receptors. The result obtained is better than in the case of intensive systems due to the long retention time and the impact of ultraviolet sunlight.

In order to improve the natural purification method (self-purification), it is practiced to introduce in the biological pond system an artificial aeration through the surface aerators (mechanical aeration) or blowers (pneumatic aeration). Thus, the system becomes closer to the intensive one, being similar to the aeration basins with activated sludge without recirculation. It should be noted that energy consumption can be as high as in case of the intensive sludge systems. This system usually has a total of three ponds: the first aerated pond (the first stage) and two settling / decant ponds (the second stage) connected in parallel.

The treatment in the aerated (main) pond takes place by artificial aeration and is similar to the intensive treatment, but the concentration of microflora (biomass) is much lower and the retention time is longer - about 20÷30 days. The depth of the aerated ponds is 2÷3 m if aeration with the compressed air is used.

The subsequent decant ponds in the second stage are used for the advanced treatment and secondary clarification, to ensure the sedimentation of suspended solids. The decanted sludge is periodically evacuated by pumping. The decant ponds are made in the form of rectangular basins in the ratio length: width equal to 3÷1. It is advisable to connect these ponds in parallel to evacuate the sludge. The removal efficiency of biodegradable organic pollutants (CBO) in aerated ponds is over 80%. For the efficient elimination of nitrogen, a recirculation of treated wastewater is necessary, otherwise only the nitrification is achieved. The elimination of phosphorus is limited, but can be ensured by the addition of precipitating salts (mineral coagulants).

6. Filters planted with artificial macrophytes / artificial wetlands

Constructed wetlands (phytofilters) are artificially created natural ecosystems for biological and physical treatment in which wastewater is introduced into the sand gravel filters on which aquatic vegetation grows [16 - 19]. Usually, the technology includes several stages (Figure 1). The filter bed can be filled with filter materials such as sand and / or gravel and is tightly insulated with natural soil (i.e. clay) or plastics. Wastewater treatment is realized through the activity of bacteria in the layer of biofilm and physical filter, and by the adsorption effects. To accelerate the treatment process, water plants are usually planted and grown, such as reed or cane, for which reason they are called reed / cane bed filters [20, 21].

Reed planted filters have been used for the first time in Germany and their use for wastewater treatment has been continued for more than 40 years, especially in the rural areas in Austria, France, Italy, Greece, Canada and other countries, for example, the Republic of Moldova (Figure 3).

Figure 3. Zone of water filtration through the reed, and water storage tanks [3].

Different types of systems are known; however, the superficial system is used more often, where water level is maintained below the level of the reed-planted filter surface. Depending on the mode of the wastewater flow running through the filtering layer, these systems are subdivided in two categories - with vertical flow movement (Figure 4) and with horizontal flow movement (Figure 5).

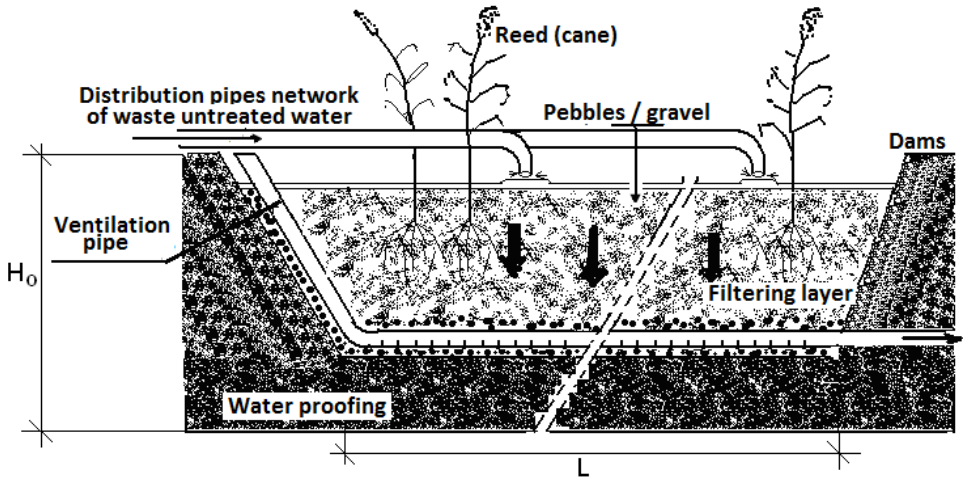

Figure 4. Scheme of phytofilter with vertical flow [22].

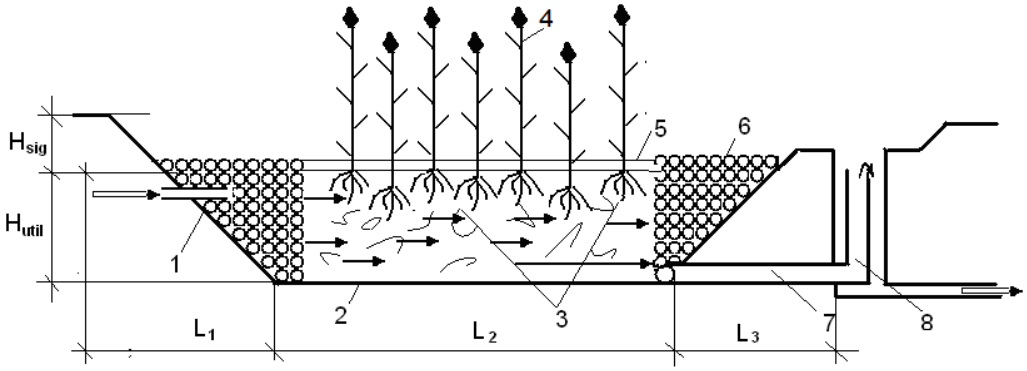

Figure 4. Scheme of the phytofilter with horizontal flow [22]: 1 - structure for uniform distribution of raw wastewater (made of boulders) - gabion; 2 - waterproofing; 3 - filter layer combined with the root system of plants; 4 - emergent macrophytes (reeds); 5 - wastewater level; 6 - gabion / structure for uniform collection of treated wastewater (made of boulders); 7 - exhaust pipe; 8 - flexible hose for regulating the drained water level.

Generally, the reed planted filters are used after a pre-treatment to remove, usually by sedimentation, the organic solids in order to avoid the clogging the pores of the filter layer (Figure 5).

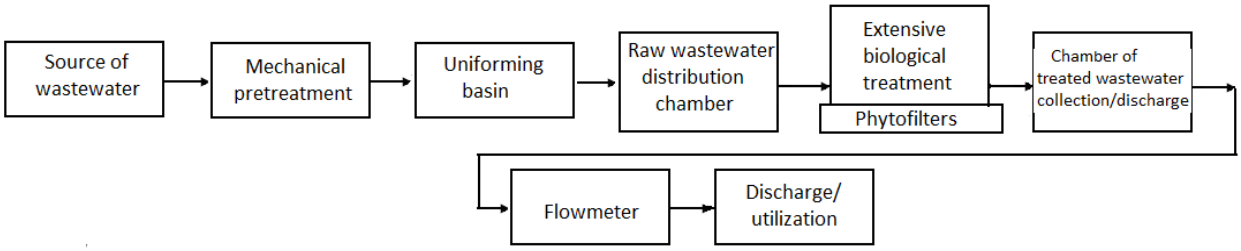

Figure 5. Flow sheet of the extensive biological treatment of waste waters in phytofilters (filters planted with macrophytes).

If there is no mechanical pre-treatment, the sludge can be accumulated in the in the discharge points, that produce an unpleasant odor, clogging of filter layer or even blockages of the pipes and infiltration nozzles. Pre-treatment can be carried out by passing of the raw wastewater through the grids or rare sieves and the subsequent sedimentation in decanters. For the small treatment plants, the septic tanks are used as decanters, from which the sludge is discharged, for example, once a year. For the larger treatment plants, sedimentation in the Imhoff-type multi-layer decanters is used.

An alternative pretreatment can also be performed in biological ponds. But there is a model of filters planted with reeds that do not require a pretreatment of raw wastewater, for example, in France. This is how the largest treatment plant in Orhei, Republic of Moldova, is designed. Phytofilters can be made in one, two or more steps, which allows to increase both the degree of wastewater treatment and the operational safety of the respective installations (Figures 6 and 7).

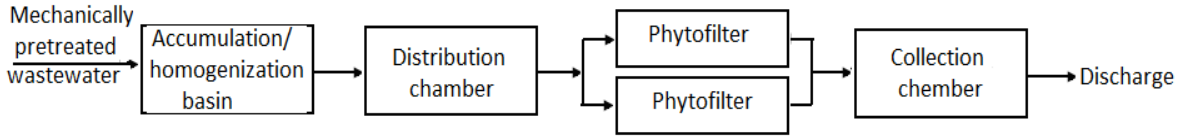

Figure 6. Flow sheet of natural/extensive biological treatment in the single-step phytofilters.

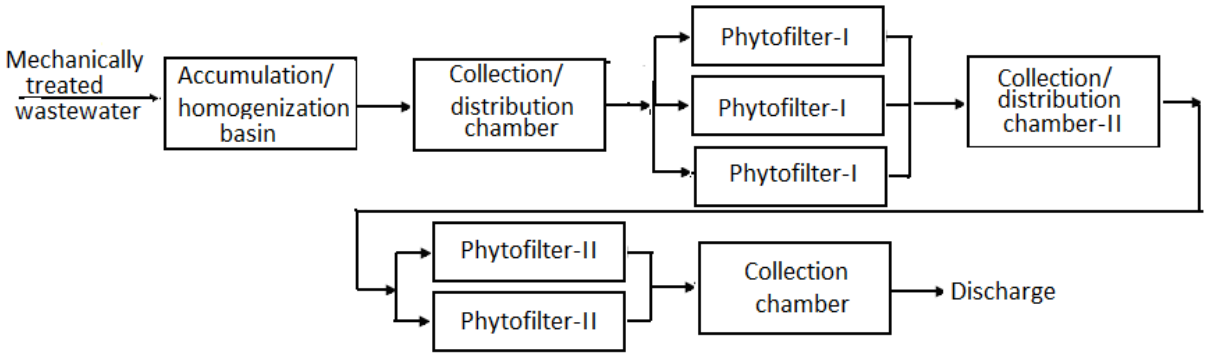

Figure 7. Flow-sheet of natural/extensive biological treatment in the two-step phytofilters.

Reed-planted filters applied after the pre-treatment can be a single-stage, with vertical-flow or horizontal process. The wastewater is supplied intermittently, with the sufficient pause to ensure the aerobic conditions in the filter layer, due to the oxygen-containing air penetrating into the pores. The design parameters of the reed-planted filters with horizontal flow are a necessary surface of up to 5 m^2 per resident connected to the sewerage system and a daily hydraulic load of maximum 40 mm; the depth of the filter bed is between 0.5 and 1.0 m. The filter body is made of the gravel and sand filling.

The vertical flow filters are dimensioned based on a specific surface area of up to 4 m^2 for an equivalent resident and a daily hydraulic load of 80 mm. The depth of the filter bed is 0.5 ÷ 1.0 m and it is also made of a sand gravel. A drainage system with the perforated plastic tubes is placed in the lower layer of the filter body only made up of gravel. The efficiency of the reed-planted filters with the mechanical pretreatment in the elimination of organic matter exceeds 80% expressed in COD (chemical oxygen demand). The aerobic conditions in the filters with the water level below the filter bed surface allow reaching a good nitrification capacity, although the denitrification process is limited. Only in the two-stage filters nitrogen is eliminated efficiently and the conditions for the treated wastewater discharges into the eutrophication-sensitive surface waters ("flowering" of water rich in nutrients - N and P) are observed. Phosphorus reduction depends on the absorption capacity of the filter medium, but is generally limited. Instead, it is important to eliminate pathogens, especially in the hot period.

The so-called "French method does not require the pre-treatment but the filters are designed in two stages. The wastewater supply into the filters is carried out intermittently, in case of the vertical flow, with a flow rate higher than the infiltration speed, in order to ensure a more uniform distribution of the wastewater layer on the filter bed's surface. In case of the horizontal flow the wastewater is distributed over the entire surface of the cross section of filter bed and is fed constantly. Thus, the "French system" comprises two stages, each of them using the filters connected in parallel. The first stage usually consists of three filters. Whereas the one is supplied with treated water (active), the others are passive or inactive (in a hydraulic sense). For the first stage, the area of 1.2 ÷ 1.5 m^2 is provided for an equivalent resident. In the upper layer of the filter bed the coarse sand is used to avoid the clogging, and the depth of the filter layer is around 80 cm. In the second stage, no less than two filters are used, which are also fed with treated water intermittently. The surface of the filters is 0.8 m^2 per resident, and the depth of the filters is also around 80 cm. The two-stage reed-planted filters constructed according to the "French system" ensure the elimination of organic matter by over 80% COD, allow the efficient removal of nitrogen and meet the conditions of wastewater treatment in sensitive areas. The nitrogen reduction in them is limited, whereas the elimination of pathogenic bacteria reaches 100%, being similar to that of the intensive wastewater treatment systems.

7. Conclusions

Analysis of the municipal wastewater treatment technologies and processes has shown that the three basic functions of sewage and water treatment comprise: protection of public health, reuse of nutrients and protection of the environment. For the system to be sustainable, the technical, socio-cultural and economic considerations must be balanced.

When selecting a sewerage system, the focus must be directed on the system operation as well as practical considerations; technology is a way to achieve the goals pursued, along with the presence of qualified staff.

The concept of phytofilters is proposed for the biological treatment of wastewater from small settlements, as shown on the examples of the Republic of Moldova. This technology is simple, relatively inexpensive and requires relatively insignificant maintenance. Biological ponds in the Republic of Moldova have shown to be very suitable for the advanced wastewater treatment, being a cheap and natural treatment system, demonstrating a good implementation potential.

This paper draws attention to a serious concept on how to radically increase an access to the basic sewerage and sanitation system through the technology that meets the principles of economic efficiency, social equality and environmental sustainability. This is the beginning of an integrated and sustainable management of Europe's water resources. For sewerage water convey and the treatment of communal wastewater, a new selection concept is proposed for practical implementation, especially in the rural and suburban localities, local/decentralized, semi-decentralized and centralized systems. To reach the scopes of environmentally-friendly and economically justified water treatment, the more suitable systems for the given locality must be chosen primarily, taking into account the particularity of the settlement, in terms of the treated wastewater and sludge reuse in agriculture, the advantages and disadvantages of the systems.

In the wastewater treatment, a priority should be given to the natural biological treatment processes, along with the intensive biological treatment processes, especially when treating the industrial wastewater containing the products, which would cause damage to agriculture. In this case, priority should be given to the fixed or hybrid microflora.

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REDUCING THE RISK OF SPOILAGE CAUSED BY *BACILLUS CEREUS* IN COW'S AND GOAT'S MILK YOGURT WITH BERRIES PUREE

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Abstract. The objective of this study was to investigate the impact of adding aronia (*Aronia melenocarpa*), raspberry (*Rubus idaeus*), and strawberry (*Fragaria xananassa*) in the form of 10% puree to a mixture of cow's and goat's milk in order to reduce the risk of spoilage caused by activity of *Bacillus cereus* in yoghurt made from a mixture of cow's and goat's milk. During the fermentation process (360 min.), changes in water activity, pH, moisture content, bacterial growth curve were monitored. The results showed a decrease in water activity, pH, and moisture content. Adding aronia puree to yoghurt yielded the most significant results for water activity modification (0.971-0.868), pH (5.31-4.28), moisture content (85.12-81.55 %), and optical density (0.19-0.34). Also, the investigation of the kinetics of the *Bacillus cereus* grows indicated that the stationary phase was reached at 360 minutes, resulting in a total population of $5.5 \cdot 10^{13}$ c.f.u./g. Microscopic examination revealed Gram-positive strains of lactic acid bacteria, arranged in chains of varying lengths, in an amount of $139 \cdot 10^{2}$ c.f.u./g. Antimicrobial activity showed a zone of inhibition with a diameter of 18.5±0.1 mm in aronia yoghurt, a zone of inhibition with a diameter of 16.2±0.2 mm in raspberry yoghurt and a zone of inhibition with a diameter of 15.2±0.1 mm in strawberry yoghurt compared to classic yoghurt which showed a zone of inhibition with a diameter of 12.1±0.2 mm.

Keywords: *lactic acid bacteria, quality, contamination, fermentation, spoilage, inhibition.*

Rezumat. Scopul lucrării a fost de a studia influiența adaosului de pomușoare de aronia (*Aronia melenocarpa*), zmeură (*Rubus idaeus*) și căpșună (*Fragaria xananassa*) sub formă de piureu în concentrație de 10% în vederea diminuării riscului de alterare produse de *Bacillus cereus* în iaurtul din amestec de lapte de vacă și de capră. În timpul procesului de fermentare (360 min.) au fost monitorizate modificările activității apei, pH-ului, conținutului de umiditate și a curbei de creștere a bacteriei. Rezultatele au arătat o scădere a activității apei, a pH-ului

și a conținutului de umiditate. Adaosul piureului de aronia în iaurt a dat cele mai semnificative rezultate ale modificării activității apei (0.971-0.868), pH (5.31–4.28), conținutului de umiditate (85.12-81.55 %) și densității optice (0.19-0.34). De asemenea, rezultatele studiului cineticii creșterii bacteriilor *Bacillus cereus* au arătat că creșterea a ajuns la faza staționară la 360 min., dezvoltând o populație totală de $5.5 \cdot 10^{13}$ u.f.c./g. Examinarea microscopică a evidențiat tulpini gram-pozitive de bacterii lactice poziționate în lanțuri de diferite lungimi în număr de $139 \cdot 10^{2}$ u.f.c./g. Activitatea antimicrobiană a evidențiat o zonă de inhibiție cu diametrul de 18.5±0.1 mm în iaurtul cu aronia, o zonă de inhibiție cu diametrul de 16.2±0.2 mm în iaurtul cu zmeură și o zonă de inhibiție cu diametrul de 15.2±0.1 mm în iaurtul cu căpșună în raport cu iaurtul clasic care a evidențiat o zonă de inhibiție cu diametrul de 12.1±0.2 mm.

Cuvinte-cheie: *bacterii lactice, calitate, contaminare, fermentare, alterare, inhibare.*

1. Introduction

The quality of yogurt is a top priority in the Moldovan economy, and the dairy industry is facing increasing pressure to maintain impeccable sanitary standards in order to prevent economic losses [1]. A high-quality yogurt must be made from milk and starter cultures of exceptional quality, with strict adherence to technological conditions, as milk is a perishable product. Milk, which is rich in proteins, carbohydrates, fats, minerals, and vitamins, provides an ideal environment for the growth and development of microorganisms and can be preferentially altered by lipase-producing microorganisms such as *Pseudomonas, Bacillus, Candida, Geotrichum, Aspergillus, Rhizopus*, among others [2].

Bacteria are known for their metabolic complexity and adaptability, which allows them to thrive in diverse environments by producing enzymes that enable them to use macromolecular organic compounds as a source of nutrition. Bacterial growth is dependent on temperature and can occur over a wide range between 10°C and 90°C, with most food spoilage caused by mesophilic bacteria that can grow at room temperature. Bacteria in their vegetative form can be thermally inactivated at pasteurization temperatures, while endospores can be inactivated at sterilization temperatures [3].

To accurately identify a bacterial species, a variety of tests and criteria must be considered. These may include factors such as dye affinity, family as a taxonomic unit, and content of the same type of bacteria (Gram-positive or Gram-negative). Additionally, physiological characteristics such as assimilation or fermentation of carbohydrates, relationship to oxygen, temperature, pH, and resistance to inhibitors must also be evaluated. These criteria collectively provide a comprehensive understanding of the bacterium being identified and allow for accurate classification within the bacterial taxonomy system.

Representatives of certain genus of Gram-positive bacteria, such as *Bacillus cereus*, have the ability to form highly resistant, dormant structures named endospores. These spore-forming species are referred to as sporulated bacteria that develop within the cell cytoplasm [4]. Bacillus cereus is a Gram-positive, facultatively anaerobic, toxin-producing bacterium that can grow in a moderate temperature range. Most strains are considered mesophilic, with optimal growth temperature at 37°C and survival below 10°C, which makes them easily isolated from food even in cold temperatures. *Bacillus cereus* is associated with gastrointestinal syndrome (GS), which can cause diarrheal disease without significant upper intestinal symptoms, and a predominantly upper GS with nausea and vomiting states without diarrhea [5].

It is well known that pH and water activity (a_w) are important parameters that influence to the replication of bacteria and low-pH foods guarantee bacterial stability. Water activity influences the rates of chemical spoilage reactions because water acts as a solvent, which can change mobility in the environment. Microorganisms can grow in a wide a_w range between 0.62-0.99 depending on their adaptation to the a_w limits that allow them to grow. Thus, for the development of xerophytic microorganisms, the water activity must be within 0.68±0.5, with the development of g. *Xeromyces* and *Aspergillus* moulds, osmotolerant yeasts and halotolerant bacteria; for mesophytes - 0.80±0.4, with the development of fungi and bacteria; for hydrophytes - 0.92±0.5, with the development of bacteria, including *Bacillus cereus*, whose optimum value of water activity for development is 0.93. It is known the behavior of cells in relation to a_w as an intrinsic factor which is conditioned by the amount of free water accessible to carry out vital processes [6].

Lactic acid bacteria are known for their ability to synthesize organic acids and bacteriocins, but the potential of these compounds against them spans a wide variety of genera, including a considerable number of species. The composition of starter cultures for obtaining fermented dairy products includes both lactic acid bacteria in the form of bacilli, represented by the genus *Lactobacillus*, and in the form of cocci represented by the genus *Streptococcus* [7,8].

In the study by Radmehr B. et al [9], the potential growth capacity of *Bacillus cereus* strains in dairy products was evaluated, where it was observed that pasteurized milk is an optimal substrate for its growth due to the inactivation of microorganisms and enzymes. After 5 days of storage, no growth of *Bacillus cereus* was detected in raw milk (<0.5 c.f.u./g) due to the action of natural microflora (mainly formed by lactic acid bacteria), which together with the acidification of the substrate made a remarkable contribution. A similar trend was observed in classic yoghurt, where after 5 days of storage, a very limited growth of *Bacillus cereus* was observed (<1 c.f.u /g) due to the low pH. However, as the authors of the study note, the growth in pasteurised milk after 5 days of storage was 3.08-3.11 c.f.u /g was observed [9].

Effective control of microbial growth in food products is of utmost importance in the agri-food sector. Following studies by Cowan M. [10] and Savoia D. [11], berries were found to possess antimicrobial activity due to the presence of various compounds such as terpenoids, essential oils, alkaloids, phenolic acids, quinones, flavones, flavonoids, tannins and coumarins. Phenolic compounds are the most abundant antimicrobial compounds in berries and each plant species has its own phenolic complex [12]. The effectiveness of phenolic compounds in inhibiting microbial growth is pH-dependent [13] and is caused by organic acids. Aronia [14], raspberry and strawberry [15] fruits are particularly rich in antimicrobial compounds due to their high content of vitamin C, anthocyanins, polyphenols, etc., forming a high antioxidant potential. In this context, aronia shows a polyphenol content of 719±5.71 mg/100 g, while strawberry and raspberry have an almost identical polyphenol content between them, but much lower than aronia: 295.0±8.50 and 288.9±8.84 mg/100 g. Talking about vitamin C content, strawberry contains 46.6±0.30 mg/100 g, raspberry 34.2±0.64 and aronia 40.2±0.61 mg/100 g. Concerning anthocyanin content, aronia is superior: 357±22 mg/100 g, while raspberry and strawberry contain 33.3±0.5 and 35.7±0.5 mg/100 g. These compounds form an antioxidant potential with maximum value in aronia 26.4±0.45, followed by strawberry 15.4±0.45 and raspberry 3.78±0.17 mg AA/g [16].

Biologically active substances are concentrated in various plants, including leaves, fruits, seeds or roots, which provide wellness benefits when consumed continuously. Some

research on the incorporation of biologically active substances from fruits, juices or extracts into dairy matrices offers positive effects, as milk is a good medium for their incorporation, thus reducing the use of synthetic additives [17-19]. In yoghurt, the addition of bioactive compounds from fruits has the potential to improve the structure, in addition to being appreciated by consumers [20-24].

The Food and Agriculture Organization (FAO) [25] has issued a report stating that the most common cause of body ailments is the consumption of is contaminated food, and it is also an important cause of the economic decline. The possibility of using berries as a natural bactericide in yoghurt allows the shelf-life to be extended due to their chemical composition, more specifically their content of compounds with enhanced biological value [26]. It is known that compounds with enhanced biological value in an optimal concentration have a strong impact on pathogenic bacteria and their use is a complete option due to their antimicrobial properties. Thus, on the antimicrobial properties of berries influences the diameter of the growth inhibition zones of *Bacillus cereus*, which in aronia can be 17.4...18.6 mm, in raspberry 15.6...16.4 mm and in strawberry 14.5...15.05 mm [27].

Taking into consideration the aspects described, this research aims to investigate the impact of adding aronia (*Aronia melenocarpa*), raspberry (*Rubus idaeus*), and strawberry (*Fragaria xananassa*) in the form of puree to yoghurt made from a mixture of cow's and goat's milk for reduce the risk of spoilage produced by *Bacillus cereus*. In order to achieve this, a number of indicators have to be studied during the fermentation process: changes in water activity, pH, moisture content, bacterial growth dynamics as well as antimicrobial activity.

2. Materials and methods

2.1. Materials

The yoghurt was obtained in the laboratory of the Food Technology Department of the Technical University of Moldova, where the following ingredients were used: cow's milk purchased from the farm ”Ferma cu Origini” SRL from the village of Horăști, district of Ialoveni [28], goat's milk purchased from the farm ”Vilador” SRL from the village of Slobozia-Măgura, district of Sângerei [29], starter culture Lyofast YAB 205 *(Streptococcus thermophillus*, *Lactobacillus delb. Bulgaricus*) purchased from ”Ingreda” SRL [30], aronia berries (collected from plantations in the village of Cuizăuca, Rezina district), raspberry (collected from plantations in the village of Elizavetovca, Donduseni district), strawberry (collected from plantations in the village of Sadova, district of Călărași) [31], sugar (purchased from the ”Suedzucker Moldova” company) [32], nutrient agar medium M001 (HiMedia Laboratories) and the bacterial culture *Bacillus cereus* M091 (HiMedia Laboratories) [33]. During the yogurt production, the consecutiveness of all steps, the technological process regimes (by thermostat method) and hygienic conditions were respected [34].

2.2. Preparation of berries puree

The berries puree was obtained according to the technology described by [16].

2.3. Preparation of yogurt with addition of berries puree

The yoghurt with added berries puree was obtained according to the technology described by [16]. Coding of yogurt is: P1 (control sample), P2 (yogurt with aronia puree), P3 (yogurt with raspberry puree), and P4 (yogurt with strawberry puree).

2.4. Methods

The physico-chemical parameters of the yoghurt were determined during fermentation for 360 min at 120 min intervals. The growth dynamics of *Bacillus cereus* in the

yoghurt were examined for 900 min to determine the number of cells during the different growth periods in order to determine the optimum growth point of the culture.

2.4.1. Determination of physico-chemical indices of berries yogurt

pH. The pH of yoghurt samples was determined by the method described by [35] with a TESTO 205 portable pH meter.

Water activity. The water activity was determined according to the method described by [36] using the Novasin LabSwift.

Moisture content. This parameter was determined by the method of AOAC [37].

2.4.2. Determination of microbiological indices yogurt with addition of berries puree

Number of bacteria. Inoculation of the diluted samples of the finished product on a nutrient agar medium was performed to determine the number of bacteria. The dilution method was used in order to count more clearly the colonies that will grow after noculation. The results were expressed in colony-forming units per gram (c.f.u./g) [38].

Monitoring of lactobacilli growth. For the determination of growth of the population of lactic acid bacteria, diluted (10^{-2}) yogurt samples were inoculated on a nutrient agar medium. To monitor this growth in the fermentation medium, a colorimetric determination was made on a Heidolf spectrophotometer (Ʌ = 600 nm) after prior dilution with distilled water. For this purpose, 1 ml of yogurt is diluted with 9 ml of distilled water, shaken and the extinction read on the spectrophotometer in a 1 cm cuvette with distilled water. The growth of lactobacilli was studied twice by measuring optical density (OD) at λ= 600 nm. The method is described according to [39].

Growth Rate of bacteria *Bacillus cereus species*. The methodology for this experiment was based on the work of Lambert et al [40]. The sequence of growth phases of a periodic culture of *Bacillus cereus* was investigated to study the growth and die-off patterns and to determine the duration of each phase: lag, exponential, stationary and die-off phases. The studies were carried out over a 24-hour period.

Antimicrobial activity of yogurt samples was performed using the disk diffusion method [41]. 15 mL of nutrient agar medium was added to the Petri plate. After solidification, 3 indentations were created in each Petri plate using a sterile tube of 5 mm diameter. The medium was intentionally contaminated with *Bacillus cereus* culture. 1 g of each sample was introduced under sterile conditions into the recesses, with subsequent thermostatted at 37° C for 72 h. The zone of inhibition that appeared as a transparent area around the disk was measured using the vernier caliper.

2.5. Statistical analysis

The analysis of the variance of the results was performed by applying the Student test and the version of the Microsoft Office Excel 2010 program. All tests were performed in triplicate. Experimental results are expressed as mean ± SD.

3. Results and Discussion

3.1. Modification of some physicochemical indices during the fermentation of yogurt with addition of berries puree

Amplification of the microbiota is due to the presence of free water, which acts as a solvent, as a reaction medium for cellular enzymes, and for the bidirectional transport of metabolic products. Water activity (a_w) has a direct influence on the growth of the microorganisms, as it accelerates the growth of yeasts, molds, and bacteria; it favors their

production of toxins and participates in various chemical and biochemical reactions that can destroy: texture, color, odor, appearance and nutritional value of yogurt on storage [42]. Figure 1 represents the aw variation during fermentation, where a decrease is observed in all samples, and the values that were recorded in P1 (0.971-0.868), P2 (0.975-0.875), P3 (0.974-0.873), P4 (0.973-0, 871).

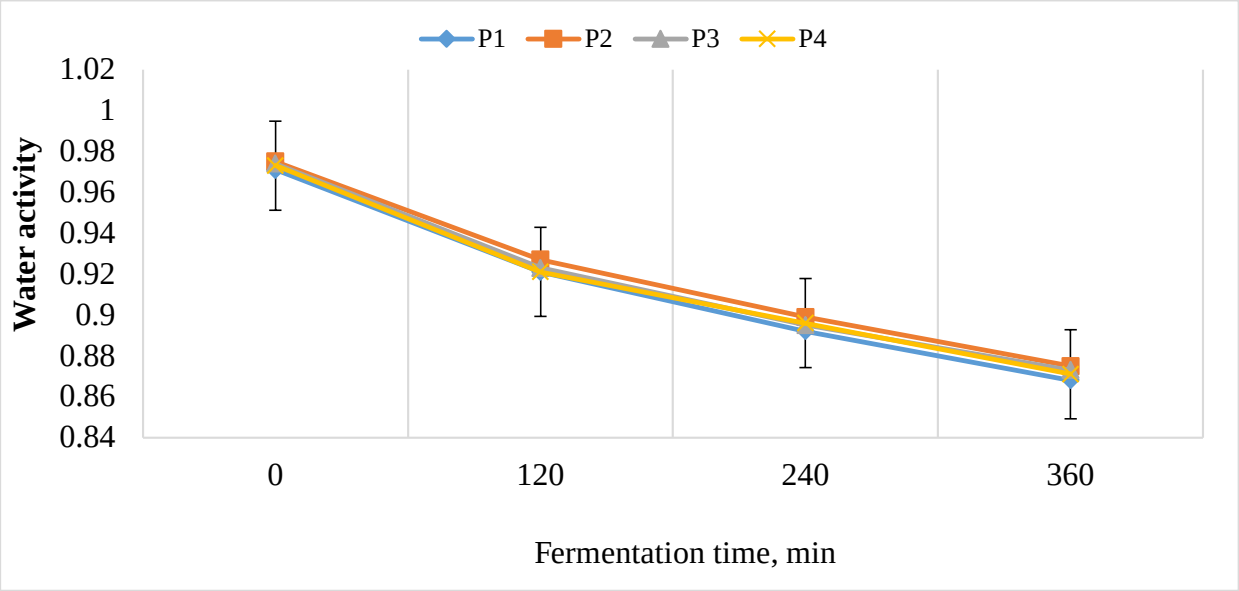

Figure 1. Modification of water activity of yogurt samples during fermentation: P1-control sample, P2-aronia yoghurt, P3-raspberry yoghurt and P4-strawberry yoghurt.

The obtained data support the hypothesis of [43] that water was so tightly bound to a protein molecule that it could not participate in the hydrolysis reaction, thus the amount of water was reduced and the fermentation process contributed to the preservation of the yoghurt.

Table 1 represents the results of the pH evolution of the yoghurt sample during fermentation, where it can be seen that the pH decreasing trend was attributed to the activity of the microorganisms which was due to sugar consumption and organic acid production. Berries contain several acidic compounds, such as citric, malic, acetic, tartaric, succinic and phosphoric, hence these acids contributed to lower pH values in samples with berries [44].

Table 1

pH evolution of yoghurt samples during fermentation

Sample	Time, min.				Correlation coefficients pH-time
	0	120	240	360	
P1	5.63±0.03	5.22±0.02	5.09±0.01	4.38±0.02	R^2= 0.8554
P2	5.31±0.02	5.18±0.01	5.01±0.02	4.28±0.03	R^2= 0.9964
P3	5.27±0.03	5.16±0.03	4.98±0.02	4.25±0.01	R^2= 0.9938
P4	5.19±0.02	5.10±0.01	4.95±0.03	4.27±0.03	R^2= 0.9725

Note: P1-control sample, P2-aronia yogurt, P3-raspberry yogurt, and P4-strawberry yogurt. Results are expressed as mean ± standard deviation, insignificant ($p > 0.05$).

The recorded values of the samples are P2 (5.31-4.28), P3 (5.27-4.25), P4 (5.19-4.27) in comparison with control sample P1 (5.63-4.38). The observations of yogurt in the present study are in agreement with the results of similar studies investigated by Fitratullah et al.

[45] on the development of yogurt incorporated with red dragon fruit. A decrease in the pH of yogurt was also obtained in his study, where it is observed that the addition of fruit showed a pH value ranging from 5.21 to 4.28.

Moisture is an important aspect of food, present in various vegetal and animal products as a cellular and extracellular component, as a dispersion medium and solvent that determines texture and structure, but also affects appearance, taste, and stability [46]. Figure 2 indicates the modification of the moisture content during fermentation.

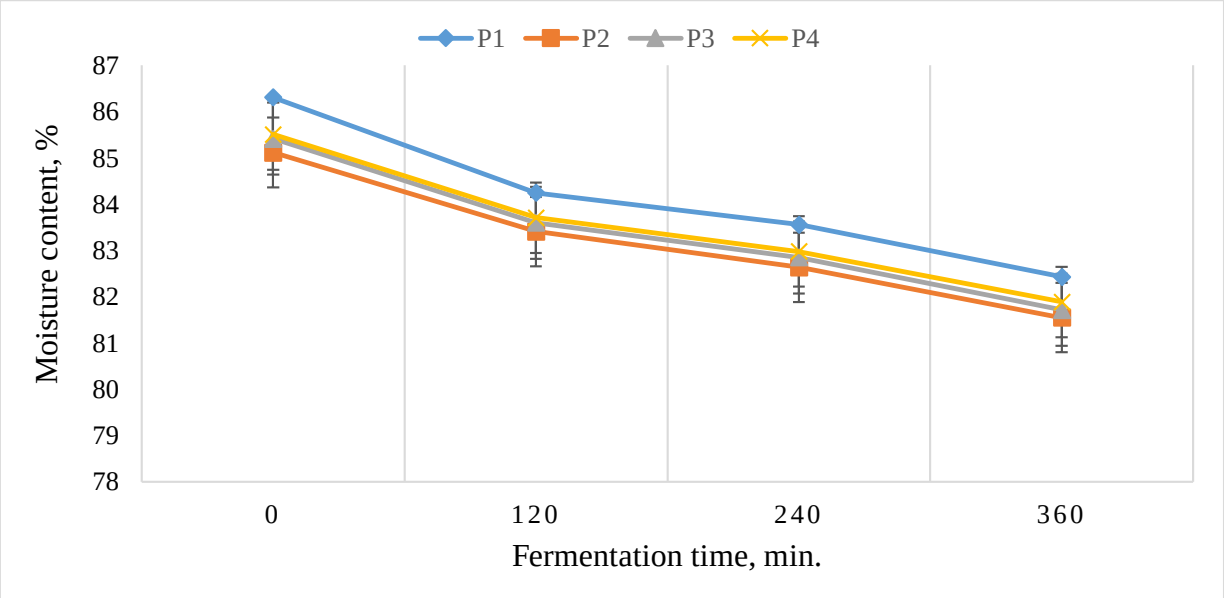

Figure 2. Reducing of moisture content or yogurt samples during fermentation: P1-control sample, P2-aronia yoghurt, P3-raspberry yoghurt and P4-strawberry yoghurt.

The results obtained for all samples show a reduction in moisture content and have the following values: P2 - 85.12-81.55%, P3 - 85.42-81.72%, P4 - 85.51-81.89% in comparison with control sample P1 - 86.31- 82.43%. This decrease in moisture content is due to casein argumentation was in the isoelectric state in which the activity of water particles decreased, not affecting the hydrolysis efficiency. These results are in agreement with those of Suriasih K. [47], who reported that the moisture content of yogurt resulted in acceleration of starter culture to fermentation. However, the results of the present study are consistent with the results of De Silva and Rathnayaka [48], where he reported that the moisture content of fruit yoghurt ranged between 79.18% and 81.15%, respectively.

3.2. Investigation of the dynamics of *Bacillus cereus* growth in yogurt with addition of berries puree

Contamination of food with *Bacillus cereus* can be attributed to the presence of persistent spores that can be transferred via soil particles or dust and can survive in extreme conditions such as heat [49]. Despite the fact that initial contamination is usually low, spores can germinate under improper storage conditions and bacteria can subsequently proliferate. The growth range of *Bacillus cereus* is between 7 and 40 °C, but *Bacillus cereus* may contain thermotolerant spores capable of growing even at higher temperatures, but at lower temperatures, microbial growth is, however, significantly slower [50]. Heat treatment, such as pasteurisation (at least 70°C for 2 minutes), is necessary to inhibit vegetative forms of *Bacillus cereus* [51,52]. Figure 3 represents the investigation of the Bacillus cereus growth curve on the number of colonies grown.

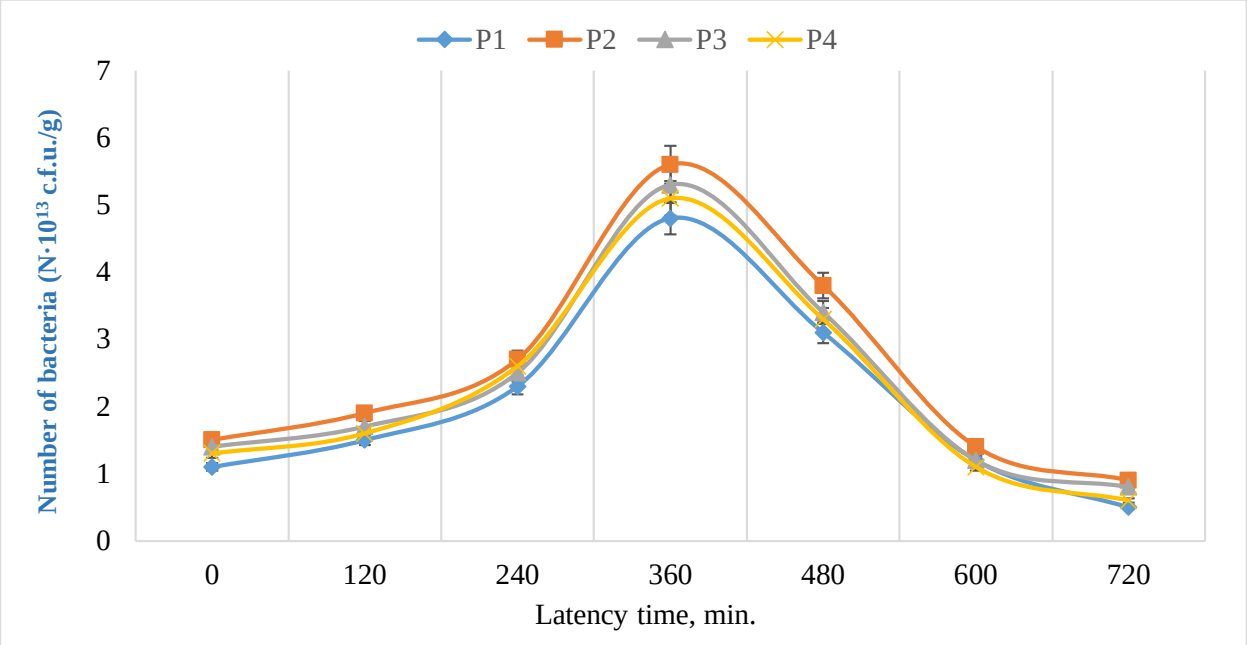

Figure 3. Growth curve of *Bacillus cereus* in yogurt samples during fermentation: P1-control sample, P2-aronia yoghurt, P3-raspberry yoghurt and P4-strawberry yoghurt.

The results showed that in all samples the growth of bacteria reached the stationary phase at 360 min of fermentation of yogurt, reaching a total population of 5.5-10^{13} c.f.u./g in P2; 5.3-10^{13} c.f.u.//g in P3; 5.1-10^{13} c.f.u.//g in P4, compared to the control sample P1 with a total population of 4.8-10^{13} c.f.u.//g.

Lactic acid bacteria are a specialized group of microorganisms that catalyze the process of acid lactic fermentation by metabolizing carbohydrates to lactic acid [53]. These bacteria have a high nutritional demand and thrive in chemically complex environments [54,55]. The findings depicted in Figure 4 demonstrate that the addition of berry puree (i.e., aronia, raspberry, and strawberry) in combination with lactic acid bacteria had a comprehensive effect on mitigating the risk of spoilage associated with *Bacillus cereus*, as anticipated.

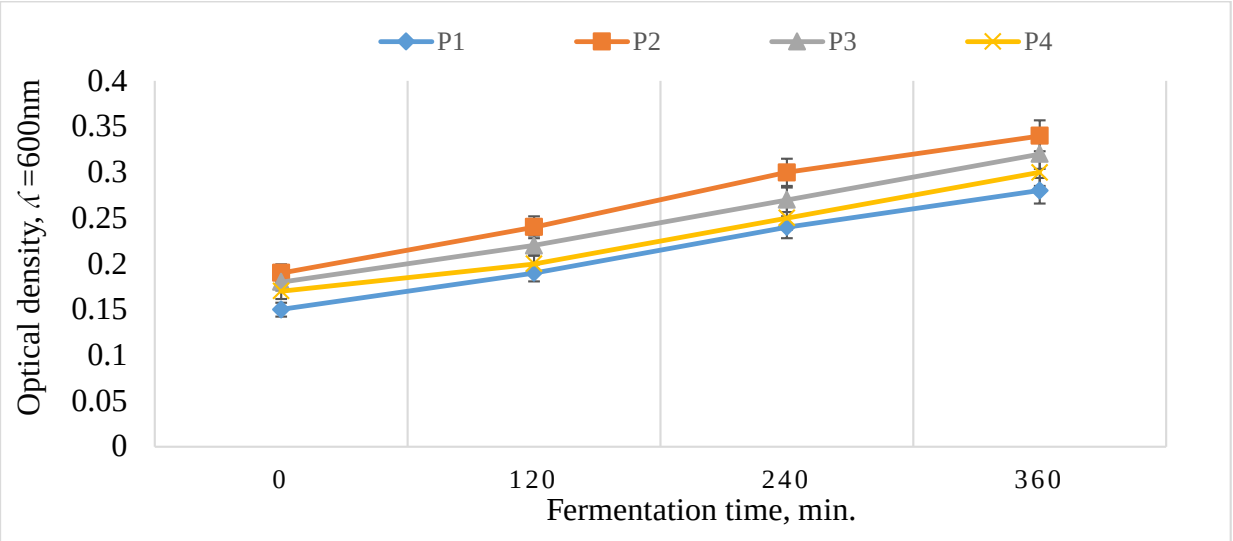

Figure 4. Variation of optical density in yogurt samples during fermentation P1-control sample, P2-aronia yoghurt, P3-raspberry yoghurt and P4-strawberry yoghurt

When fermenting yoghurt, the optical density increased in all yoghurt samples because a synergism was formed between the lactic acid bacteria and the chemical composition of the added, which kept the risk of spoilage associated with of *Bacillus cereus* under control. The decline of pH was due to the activity of lactic acid bacteria to produce energy through the fermentation process and by breaking the substrate into simpler components. At the same time, the intensive growth of bacteria did not lead to excessive lactic acid accumulation, favorably influenced the physico-chemical parameters of yogurt. The highest proportion of optical density increase was observed in P2-0.34, followed by P3-0.32, and P4-0.30, in comparison with control sample P1-0.28. These findings are also reflected in Mantzourani's research [56] suggesting that pomegranate juice is an effective natural preservative in yogurt puree because lactic acid bacteria can alter nutrient compounds and bioavailability through their metabolism and interactions with gut microbiota and the immune system. Furthermore, lactic acid fermentation can increase the antioxidant activity of phenolic derivatives beyond that of their precursors [57,58]. In Terpou [59] and Di Cagno's [60] study it is reported that lactic acid fermentation phenolic compounds provide higher antioxidant activity than its predecessors. Thus, when bioconverting phenolic compounds, lactic acid fermentation can positively transform food components that have a strong influence on consumer welfare. In this context, it has been shown that fruits have a rich content of biologically active substances, which simultaneously grant enhanced bioavailability when fermenting milk by lactic acid with *Lactobacillus spp.* [61-63].

Microscopic examination of the prepared dried and fixed Gram stained smears revealed Gram-positive strains of lactic acid bacteria arranged in different chain lengths of bacilliform (*Lactobacillus lactis*) and cocciform (*Streptococcus thermophilus*) microorganisms. The most representative sample was P2, with a colony count of $139 \cdot 10^2$ c.f.u./g. The mechanisms regulating the number, type, and metabolic activity of bacteria are highly complex. However, some bacteria (of the *Lactobacillus* and *Streptococcus* genus) act antagonistically towards pathogenic bacteria. Both bacterial species are found in the microbiota of the gastrointestinal tract, but their numbers decrease with age, alcohol consumption, antibiotic administration, stress, and other factors [64,65]. The study by Kim K. H. et al. have shown that the addition of cherry blossoms to yogurt enhances the growth of lactic acid bacteria [66], but the study by Oh H. et al. [67] revealed that the addition of acanthopanax powder to yogurt inhibits the growth of lactic acid bacteria.

3.3. Analysis of the bactericidal potential of yogurt with addition of berries puree

As microbial resistance to antibiotics continues to increase and interest in eco-friendly lifestyles grows, there is a growing focus on natural antimicrobial compounds [68]. Inhibition of microbial growth has been discovered in a wide range of food plants, including various berries and fruits [69,70]. One of the functional properties of yogurt is its antimicrobial activity, which is produced during the fermentation process. The presence of antimicrobial activity, as indicated by the diameter of the inhibition zone, indicates that the tested bacteria cannot grow around the indentations. Inhibiting the growth of pathogenic and conditionally pathogenic microorganisms is an important microbiological property for ensuring the quality and safety of yogurt [71,72]. In Nohynek L.J.'s study it is reported that there is a direct correlation between the phenolic content of fruits and their antimicrobial effects [73].

The results obtained are in agreement with those of Naidu et al. [74] which confirm that the antibacterial activity of yogurt increased with decreasing pH value, as the unbound

lactic acid penetrated the cell membranes and cytoplasm. The antibacterial mechanism is mediated through several pathways, such as disruption of cell wall formation, reaction with cell membranes, and inhibiting enzyme activity that causes disrupting cellular metabolism and bioactive components that interfere with the nucleic acid formation, damaging genetic material and disrupting the cell's cleavage process. The ability of antimicrobial compounds to inhibit microbial growth in the food system can be influenced by physical factors such as: acidity, pH, oxygen availability, temperature as well as the interaction between these factors [75].

The different zones of inhibition (Figure 5) of samples P2 (18.5±0.1 mm), P3 (16.2±0.2 mm), and P4 (15.2±0.1 mm) in comparison with the control sample (12.1±0.2 mm) can be explained by the chemical composition of the aronia [76], raspberry or strawberry berries [77], being representative for the content of antioxidants, polyphenols, vitamins, anthocyanins, organic acids, etc. and based on their beneficial effects on cytoplasmic membrane destabilization, cell membrane permeability, enzyme inhibition, direct action on microbial metabolism or inhibition of microbial growth of the substrate, especially mineral substances.

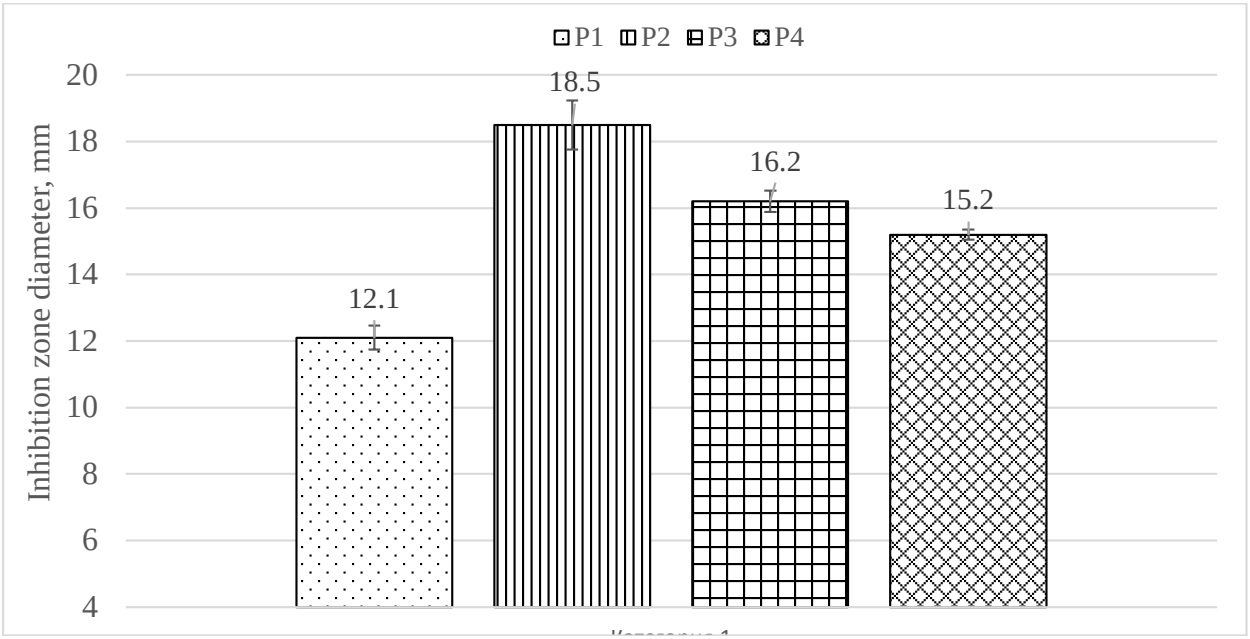

Figure 5. Antimicrobial activity of yogurt samples

P1-control sample, P2-aronia yoghurt, P3-raspberry yoghurt and P4-strawberry yoghurt.

In the study conducted by Vicenssuto et.al. [78], it was observed that the addition of fruit to yogurt resulted in an increase in its antioxidant activity. Furthermore, the presence of phenolic compounds in the fruit helped in inhibiting the oxidation of lipids, which is responsible for the development of unpleasant flavors in yogurt. This is due to the ability of phenolic compounds to donate electrons to neutralize the chain reaction initiated by free radicals, thereby extending the shelf life of yogurt. Additionally, the acidic environment of yogurt with a pH of 4.6 facilitated the interaction of phenolic compounds with yogurt, making it an excellent carrier of these compounds. Hence, the incorporation of phenolic compounds from fruits had a positive impact on the antioxidant properties of yogurt.

4. Conclusions

This study indicated that berries could be applicable in food as a source of antibacterial products. The incorporation of 10% berries puree to yogurt, derived from cow and goat milk, exhibited promising functional properties through its antimicrobial activity.

The findings suggest that pH was not the only determining factor for the antimicrobial activity observed in the puree. While organic acids are known for their strong antimicrobial effect, the whole complex of biologically active compounds present in the puree was found to play an important role in providing the observed antimicrobial properties. Aronia puree, in particular, demonstrated exceptional potential as a natural preservative due to the presence of several antimicrobial compounds that act as a barrier against harmful bacteria, thereby prolonging the shelf life of yogurt. Fermenting lactic acid bacteria with aronia and incorporating it into yoghurt increases aronia's polyphenolic and antioxidant capacity, creating a blend of prebiotic and probiotic compounds with enhanced benefits. The microbiological analysis of yogurt revealed the significant potential of berries to mitigate the risk of spoilage caused by *Bacillus cereus* activity. Overall, this study highlights the potential of Moldovan berries as a natural source of antimicrobial compounds for enhancing the safety and shelf life of dairy products.

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Conflicts of Interest: The authors declare no conflict of interest.

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DRYING OF PEARS IN CO_2 MODIFIED ATMOSPHERE

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Abstract. One of the biggest problem encountered in drying area of food processing are the losses in food quality. While drying process is held, there is an important damage done to vitamins, polyphenols and other important nutriments. Being easily affected by high temperature and oxygen exposure, our concern was to find out what will be the effect of convective drying in air flow and CO_2 modified atmosphere upon pears, "Conference" variety quality. Testing took place with temperatures between 60 and 100°C for both drying methods, one also used three different CO_2 concentration regimes for the modified atmosphere approach, namely 30, 60, and 80%. The usage of carbon dioxide instead of air inside the drying chamber is expected to reduce oxygen exposure of the product during drying process, thus reducing oxidative reactions. Using CO_2 as air substituent for convective drying showed good results from the organoleptic point of view by preserving a more natural pear color closer to the row material one, reduced damage done to ascorbic acid and total polyphenols concentration presumably thanks to reducing oxygen concentration and a slight drying duration reduction. There was deducted and established a mathematical model for the convective modified CO_2 drying atmosphere as well as a pilot drying installation was designed for combined dying methods equipped with a CO_2 recycling system.

Keywords: *pears, experimental drying plant, convection, drying kinetic curves, ascorbic acid, polyphenols.*

Rezumat. Una din cele mai grave probleme întâlnite la procesarea produselor alimentare și anume în domeniul uscării, este pierderea calității. În funcție de durata procesului de uscare pot fi grav denaturate vitaminele, polifenolii și alte nutrimente. Astfel cum, toate aceste substanțe, sunt mult afectate de expunerea la temperaturi înalte și oxigen, noi am avut ca scop să determinăm care va fi efectul uscării convective cu aer și în mediu modificat de CO_2 asupra calității perelor de soi „Conferința". Pentru ambele metode de uscare, testările au avut loc la temperaturi cuprinse între 60 și 100°C, iar pentru metoda de uscare cu CO_2 au fost utilizate și trei regimuri de concentrații 30, 60 și 80%. Prin utilizarea dioxidului de carbon în camera de uscare, ca substituent al aerului, se așteaptă o reducere considerabilă a proceselor oxidative prin reducerea concentrației de oxigen. Folosirea CO_2 ca substituent pentru uscarea convectivă a arătat rezultate bune din punct de vedere organoleptic și anume prin păstrarea unei culori a perelor aproape de cea a perelor proaspete, a redus nivelul de denaturare a acidului ascorbic și a conținutului total de polifenoli, fapt care probabil se datorează reducerii

concentrației de oxigen și unei micșorării ușoare a duratei de uscare. A fost dedus și stabilit modelul matematic pentru uscarea convectivă în atmosferă modificată de CO_2 și proiectată instalația experimentală pentru uscarea combinată cu sistem de reciclare a CO_2.

Cuvinte cheie: *pere, instalația de uscare experimentală, convecție, curbele vitezei de uscare, acid ascorbic, polifenoli*.

1. Introduction

The human diet consists in a high percentage of fruits and vegetables. Pears, bring us a delicate taste and a sweet aroma as well as being characterized by a high digestibility, making them very popular [1]. The popularity of pears is due to their composition, containing polyphenols, minerals, vitamins, amino acids, sugars as well as an important quantity of water [2, 3].

Drying is the oldest method of food preservation and is used till our days as it brings a large gamma of benefits as reducing storage and transportation space as well as energy consumption. Through the time there were lots of scientist and researches that developed this conservation method introducing new drying types and regimes, that were meant to reduce food treatment time and assure an overall better final product quality. Such drying methods as microwave, vacuum, freeze were introduced for the food industry. As each method has its own advantages and disadvantages, there's a good decision to combine those and use their strong qualities to create new hybrid drying methods as convection with microwave, vacuum with microwave drying, etc.

One of the recent drying methods that was highlighted by researchers is modified atmosphere drying, in which the conventional drying agent – the air, is changed or mixed with an inert gas (carbon dioxide, nitrogen, etc.).

Using the modified atmosphere drying method is a potential way to reduce oxidative processes during drying course. Reducing oxygen concentration inside the drying chamber, or even fully eliminating it, being replaced by another gas (carbon dioxide, nitrogen, etc.) has already proved to be a promising drying method. Several studies [4-6] were conducted in this context using as experimental material vegetal products (ginger, apples, strawberry, carrot, etc.) for whom were determined some important submitted to oxidative reactions components, such as gingerol, acid ascorbic, carotedoids, etc.

A group of scientists [4] experimented with different drying methods (freeze, vacuum, conventional and modified atmosphere convection) on ginger, namely they analyzed the effect of those specific drying methods upon 6-gingerol content preservation in dried ginger. For this goal the researchers had designed a closed circuit heat pump drying installation, adjusted for modified atmosphere drying. The results of the study represent the comparison between different drying methods dried ginger 6-gingerol content. As such, the highest content of gingerol was characteristic for vacuum (11 mg/g) drying method whilst modified atmosphere (carbon dioxide and nitrogen) was close enough to the same result (9.5 mg/g). The lowest 6-gingerol content was shown for conventional air drying (6 mg/g) [4].

The next study [5] was concentrated on analyzing the effect of freeze, conventional and modified atmosphere convection drying on ascorbic acid content in dried strawberries. The researchers have designed as well a close circuit drying installation, that allows the use of modified atmosphere. Analyzing the results, we can conclude that the highest losses of ascorbic acid were found to be in air dried strawberry samples (28 %), while the lowest were in freeze dried one (4 %). In terms of ascorbic acid losses, good result had also shown the modified atmosphere dried strawberry samples (6 %) [5].

The influence of drying atmosphere oxygen concentration on carotenoid and ascorbic acid retention ratio in dried carrot samples was researched [6] using a designed closed circuit experimental tunnel drier. The researchers experimented with different (5%, 10%, 15%, 20.9%) oxygen concentrations and established that retention ratio of ascorbic acid and carotene in dried carrot samples (70°C conventional and modified atmosphere convection) is inversely proportional to oxygen concentration, namely it increases 1.8 times for carotene and 1.7 times for ascorbic acid retention ratio.

The most undesirable drying results are the effect of browning of vegetal food, that is visible right away at the end of the process and important nutriments losses as a result of oxidation effects in general that happens throughout the drying procedure. This effect has been spotted and analyzed by diverse plants breeders, plants physiologists and food scientists. Some browning reaction are useful but their majority is not, as they lead to food quality diminution as result of organoleptic and nutritional properties alteration. The food browning of enzymatic nature brought by polyphenol oxidases has a significant economic effect on products like cereals, fruits and vegetables that should be well controlled [7-9].

The main goal of the study was to create a technology of drying vegetal food, namely "Conference" pears, in CO_2 modified atmosphere as well as designing a pilot drying installation for the same purpose. To accomplish that goal one formed the following objectives: optimizing the process of drying pears in CO_2 modified atmosphere, by mathematical modeling; elaboration of the experimental installation for drying pears in a CO_2 modified atmosphere; analysis of the quality parameters of dried pear fruits in a CO_2 controlled atmosphere in order to develop recommendations.

2. Materials and methods

2.1 Samples preparation

"Conference" variety pears belong to the family *Rosaceae*, genus *Pyrus*, species *Communis*, were selected from Republic of Moldova marketplaces according to [10] and prepared for the experiment.

The "Conference" pears were washed and cut in half circles (Figure 1) with a 0.005±0.0005 m thickness and a total pieces' weight of 100 ± 0.2 g. The drying was performed by two convective methods: in air flow and CO_2 modified atmosphere.

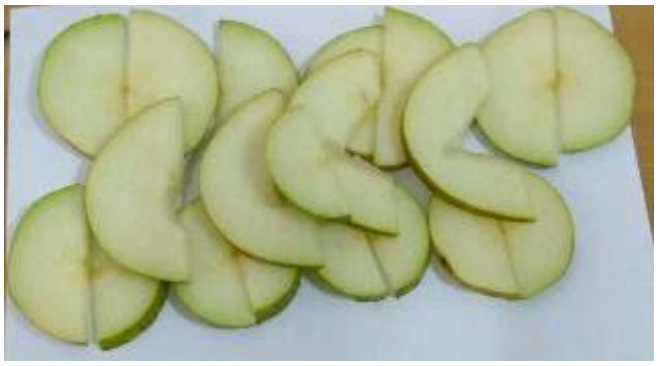


Figure 1. Preparation of half circles sliced "Conference" pears for drying.

There were chosen several temperature regimes between 60°C and 100°C, drying agent velocity of 1.5±0.13 m/s for both drying methods and three concentrations for modified CO_2 atmosphere, namely 30%, 60% and 80% of CO_2.

2.2 Experimental drying installation

For the experimental part, one has designed and elaborated an experimental laboratory drying installation (Figure 2), that allows drying to take place through different methods, including conventional convection – using air, microwave drying and their combination, as well as the use of modified atmosphere by replacing air with different concentrations of carbon dioxide.

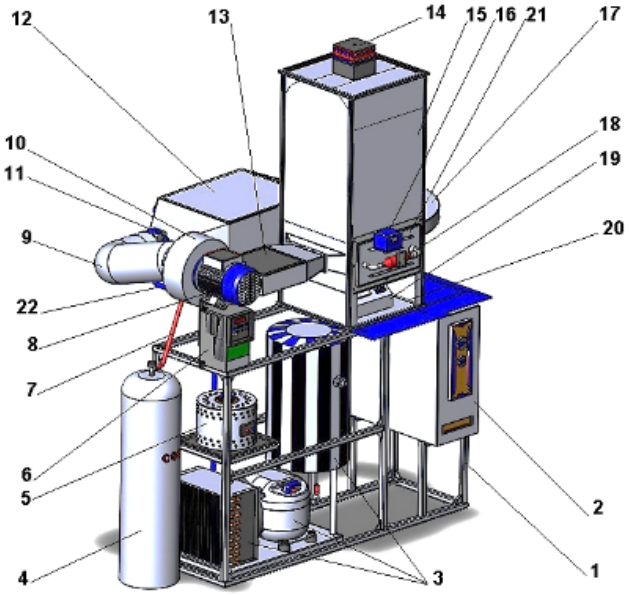


Figure 2. Experimental laboratory drying installation.
1 – carcass; 2 – control panel; 3 – cooling installation; 4 – CO_2 recipient; 5 – temperature controller; 6 – fan inverter; 7 – CO_2 income hose; 8 – electrical motor; 9 – intermediate pipe; 10 – centrifugal fan; 11 – pipe fastening; 12 – condenser; 13 – heat source; 14 – magnetron; 15 – drying chamber; 16 – CO_2 concentration indicator; 17 – drying agent recycling pipe; 18 – receiver; 19 – electronic scale; 20 – electronic scale space; 21 – lid.

The installation presents a drying chamber 15 which is installed on a metallic carcass 1 along with the heat source 13 and a centrifugal fan 10 which is driven by the electrical motor 8 and an inverter 6 which allows fan's velocity control. The gas, from the drying chamber may be recycled (Figure 3) through the recycling pipe 17, that is connected to the condenser 12, from which the gas is transferred into the drying chamber using the centrifugal fan 10 and the intermediate pipe 9. The installation allows drying using microwave energy. For this purpose, the installation is equipped with a magnetron 14 on the top of the drying chamber, that allows changing the height of the magnetron towards the product. For research purposes and data collection there is an electronic scale 19 installed under the working chamber 20. The drying chamber is hermetically closed using the lid 21 which holds the carbon dioxide concentration indicator 16 and receiver 18.

2.3 Total polyphenol content

The total polyphenol content was expressed in milligram of gallic acid equivalent (GAE) per 100 g of the researched product. Polyphenols content was established by optical density measurement of an extract that, in presence of the Folin-Ciocalteu reagent, absorbs at the wavelength of 765 nm. For the analysis 5 mL double distilled water, 1 mL of dried pears sample and 0.5 mL Folin-Ciocalteu reagent in a 10 mL volumetric flask were mixed.

After 3 minutes, 1.5 mL of 10% sodium carbonate was added and brought up to the mark with double-distilled water. The solutions are placed on the water bath at a temperature of 50°C for 16 min, after which it cools down to room temperature. Afterwards the absorbance is measured using a Hach Lange DR-5000 spectrophotometer [11].

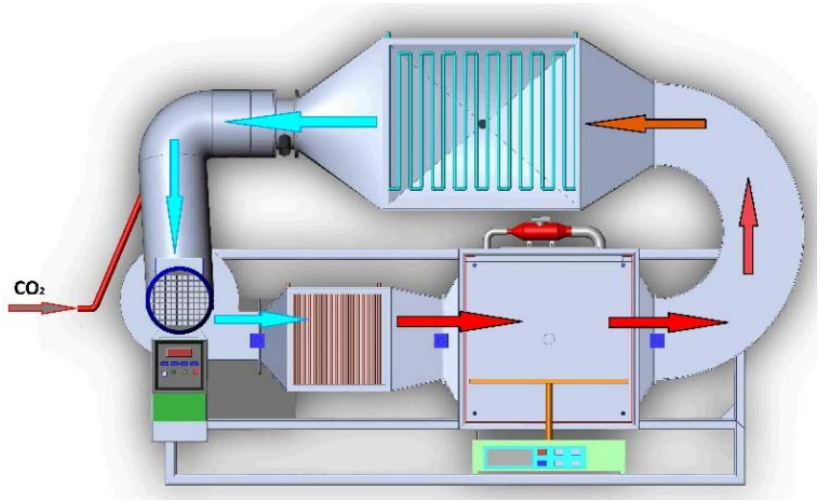


Figure 3. Experimental drying installation gas recycling system.

2.4 Vitamin C content

Using a mortar, 10 g of each analyzed "Conference" pear samples: fresh, convection-dried (air and CO_2), were separately crushed in the presence of 1% oxalic acid and quantitatively transferred to a 100 cm^3 volumetric flask and brought up to the mark with oxalic acid and mixed. The content of the flask was poured through filter material into a conical flask adding. 6 cm^3 of 2,6-dichlorophenolindophenol. The extinction is determined transferring the obtained solution to the cuvette and subjected to photocolorimetry at the wavelength 540 nm. For the second extinction: a few crystals of ascorbic acid are added to the cuvette with the analyzed solution (the color of 2,6-dichlorophenolindophenol disappears), the solution is stirred and photocolorimetry is performed again [12].

2.5 Mathematical modelling

For the drying process to be performed there was created a mathematical model which takes in account the changes of drying atmosphere by establishing boundary conditions adapted for carbon dioxide [13]:

$$(0{,}0008 \cdot t_a + 0.0149) \cdot \frac{\partial t(H,\tau)}{\partial \tau} + \left[\frac{Nu \cdot (0{,}0008 \cdot t_a + 0{,}0149)}{d}\right] \cdot [t_a - t(H,\tau)] -$$
$$-(1-\varepsilon) \cdot \grave{r} \cdot [0{,}167 \cdot \frac{0{,}13 \cdot 10^{-9} \cdot (-0{,}0004 \cdot t_a^2 + 0{,}8252 \cdot t_a + 163{,}69)}{d} \cdot \rho_{co_2} \cdot Re^{0.74} \cdot \quad (1)$$
$$\cdot Pr^{0.33} \cdot \left[\frac{l}{d}\right]^{-0.47}](\theta(H,\tau) - \theta_p) = 0$$

$$(0{,}0008 \cdot t_a + 0.0149) \cdot \frac{\partial \theta(H,\tau)}{\partial x} + \lambda_m \delta \cdot \frac{\partial t(H,\tau)}{\partial x} + [0{,}167 \cdot$$
$$\cdot \frac{0{,}13 \cdot 10^{-9} \cdot (-0{,}0004 \cdot t_a^2 + 0{,}8252 \cdot t_a + 163{,}69)}{d} \cdot \rho_{co_2} \cdot Re^{0.74} \cdot Pr^{0.33} \cdot \quad (2)$$
$$\cdot \left[\frac{l}{d}\right]^{-0.47}](\theta(H,\tau) - \theta_p) = 0$$

where t – moist body temperature, K; t_a – drying atmosphere temperature, K; τ – drying time, s; H – layer thickness, m; a_q, a_m – temperature and potential diffusion coefficients, m^2/s; ε – phase transformation criterion; r' – vaporization latent heat, kJ/kg; c'_T, c_q – specific mass, kg/kg·M and specific heat, J/kg·K capacities; ρ – moist body dry part density, kg/m^3; δ – moist body Sore coefficient, 1/K; ϑ – mass transfer potential (moisture), M potential units; λ_q, λ_m – thermal conductivity, W/m·K and mass conductivity, kg/m·s·M; Re – Reynolds criterion; Pr – Prandtl criterion; Nu – Nusselt criterion.

2.6 Statistical processing of the results

To determine the error of a series of successive measurements of experimental data (ascorbic acid concentration, polyphenol concentration, etc.) standard deviations were calculated [14]. All calculations were performed using Microsoft Office Excel 2007 (Microsoft, Redmond, WA, USA). Data obtained in this study are presented as mean values ± standard error of the mean calculated from three parallel experiments.

3. Results and discussions

The speed of the drying agent plays an important role in the process of diffusion of moisture evaporated from the surface of the product into the surrounding environment. In the given case, the mathematical description of this phenomenon is strictly necessary for more efficient optimization of the drying process. The correct choice of the speed of the heating agent leads to the reduction of the energy consumption of the fans that ensure the parameters of the given flow and the consumption of thermal energy in the case of convection drying. In order to determine the optimal drying speed, the mathematical model of the speed of the drying agent at the mass transfer between the product and the environment was built. After performing the calculus, the following product temperature and humidity, for CO_2 environment formulas were deducted:

$$T = C_1 + A_1 e^{B_1 \tau} \tag{3}$$

$$U = C_2 + A_2 e^{B_2 \tau} \tag{4}$$

A, B, C – deducted coefficients which take in account drying process conditions and product characteristics

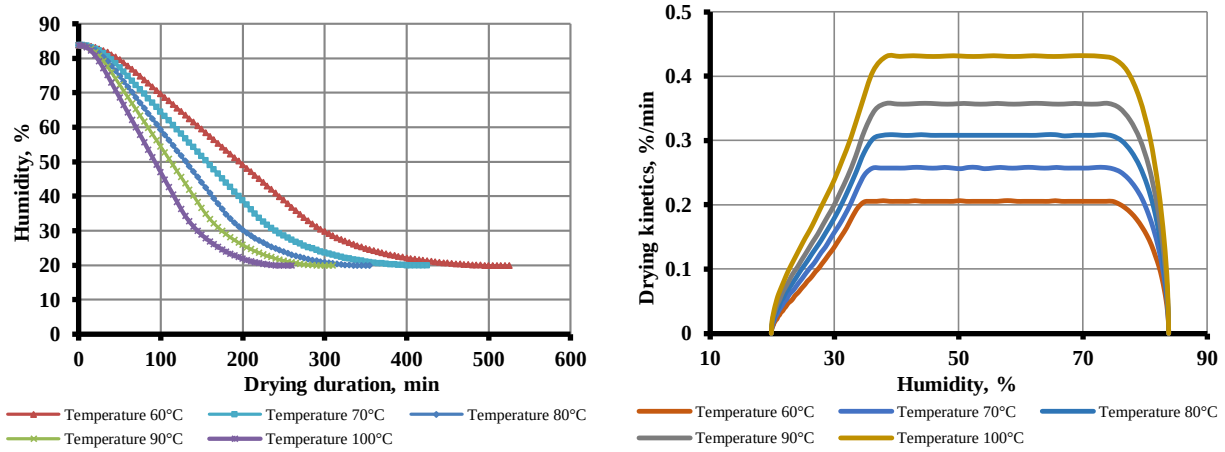
The mathematical model presented and the results of its verification for deviations, allows it to be used both for drying pears in a CO_2 modified environment and for air convection, more than that, the given model, after introducing some modifications, which would take into account thermophysical properties, would also find application in the determination of temperature and humidity during drying for other vegetable food products with a pear-like structure.

To carry out the experimental drying, the experimental drying installation with a modified CO_2 medium, with a closed cycle of the drying agent, with the possibility of changing the concentration of carbon dioxide inside the drying chamber and automatically taking over the experimental data during the drying process was designed and made (Figure 3).

In order to establish the influence of the environment modified by CO_2 on the drying process, experimental dryings of pears of the "Conferința" variety were carried out, both by the conventional method - with air, and in a modified environment. Drying took place at several thermal regimes and for CO_2 at several gas concentrations in the working chamber (30, 60 and 80%).

Based on the experiments drying process and drying kinetics curves were established for convective air drying (Figure 4) and convective 80% CO_2 modified atmosphere drying (Figure 5), from 60 to 100°C and 1.5±0.13 m/s drying agent velocity.

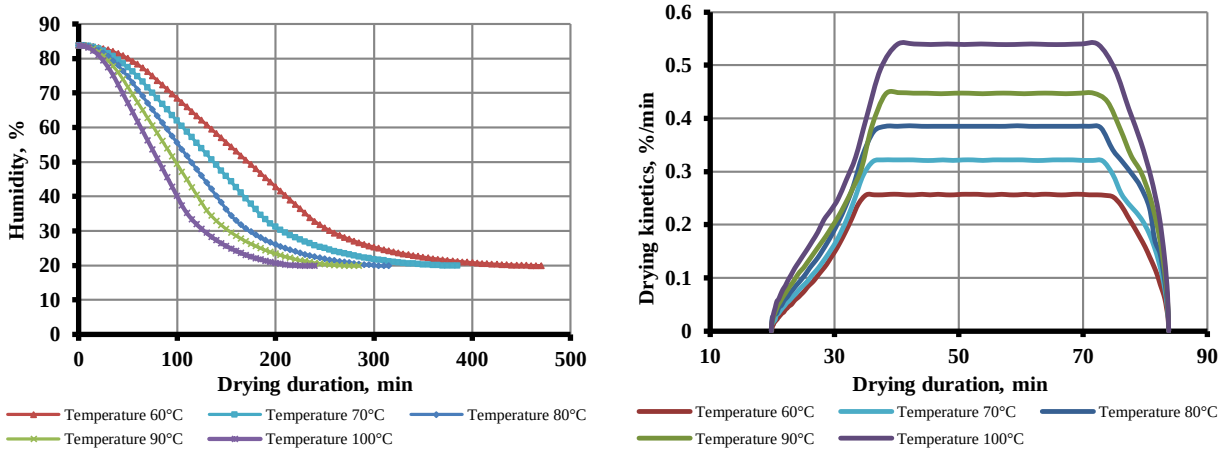
Analyzing Figure 4a and Figure 5a, an intensification of the drying process can be observed with the increase in the temperature of the drying agent. As a result of mass and heat transfer phenomena, at 60°C (air, convective regime), the drying time is 525 min, while at 100°C – 260 min, showing a 2.02 times diminution in drying duration. The same effect was reported by other researches [15-18].



a) b)

Figure 4. Drying process (a) and drying kinetics process (b) curves for dried "Conference" pears, by air flow method; drying agent air: 60, 70, 80, 90 and 100°C, drying agent velocity 1.5±0.13 m/s.

The drying kinetic curves for both methods (Figure 4b and Figure 5b) highlight all three stages of drying, in which the heating stage takes place up to 73-75% humidity, the constant drying stage – from 73-75% to 34 -38% and the speed reduction step – from 34-38% until equilibrium humidity is reached.



a) b)

Figure 5. Drying process (a) and drying kinetics process (b) curves for dried "Conference" pears, by CO_2 modified atmosphere method; drying agent CO_2: 60, 70, 80, 90 and 100°C; carbone dioxide concentration: 80%; drying agent velocity 1.5±0.13 m/s.

One can notice that temperature growth also shows an augmentation of drying process velocity, for example air drying constant drying stage velocity, for 60°C, 0.21±0.01 %/min, at 70°C – $dU/d\tau \approx 0.26\pm0.01$ %/min, at 80°C – $dU/d\tau \approx 0.31\pm0.02$ %/min, at 90°C – $dU/d\tau \approx 0.36\pm0.02$ %/min and at 100°C – $dU/d\tau \approx 0.43\pm0.02$ %/min, meaning an increase of 2.04 times from 60°C to 100°C. the same effect was mentioned by other authors [20, 21].

Drying kinetics curves for 80% CO_2 modified atmosphere (Figure 5 b.) has the same patterns as air drying one (Figure 4 b.) except higher values for the constant drying stage: 60°C, 0.25±0.01 %/min, at 70°C – $dU/d\tau \approx 0.32\pm0.02$ %/min, at 80°C – $dU/d\tau \approx 0.38\pm0.02$ %/min, at 90°C – $dU/d\tau \approx 0.43\pm0.02$ %/min and at 100°C – $dU/d\tau \approx 0.54\pm0.03$ %/min, showing an increase of 1.19 times for 60°C and 1.26 times for 100°C, that confirms the drying process acceleration namely while humidity is evaporated from the product surface.

The small reduction in drying time for the CO_2 modified atmosphere compared to air drying, which is most likely explained by an intensification of mass transfer from the product to the medium, and less by mass transfer within the product. This phenomenon can also be related to the reduction of the vapor pressure of the drying product while the CO_2 is washed, a fact noted by other researchers [6].

After performing the experiments there was determined the total polyphenols content and ascorbic acid concentration for dried "Conference" pears samples. Basing on the Figure 6. One can identify the effect of drying upon total content of polyphenol in dried "Conference" pears by both methods of air and CO_2 convection.

Analyzing the diagram from Figure 6., one can observe an augmentation of total polyphenols content with temperature increase. The same effect was mentioned by other scientists [15, 19, 22], and is presumably caused by shorter exposer of polyphenols to temperature action, as a result of reduced drying time at higher temperatures. identify an evolution of the polyphenol content as CO_2 concentration augments, if taking the same temperature of 60°C, we'll have 28.03±1.45 mg GAE/100 g of plant for air drying; 36.77±1.90 mg GAE/100 g of plant for 30% CO_2 drying; 40.73±2.11 mg GAE/100 g of plant for 60% CO_2 drying and 42.34±2.19 mg GAE/100 g of plant for 80% CO_2 drying respectively.

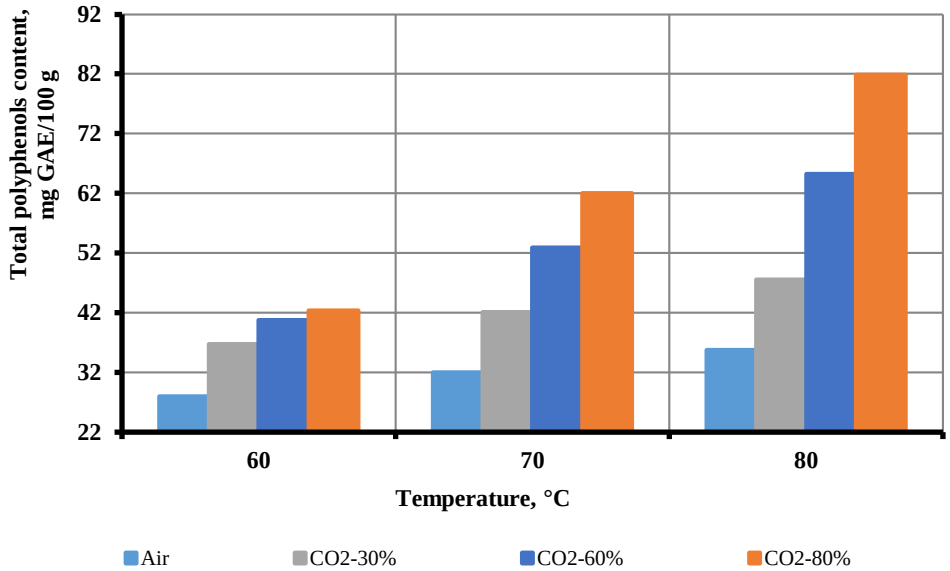


Figure 6. Total polyphenol content in dried pears, "Conference" variety, by air flow and CO_2 modified atmosphere methods. Drying agent temperature (air and CO_2): 60 and 80°C; Carbone dioxide concentration: 30, 60 and 80%.

If compared, the same CO_2 concentrations will show a boost for the temperature of 80°C: 35.79±1.85 mg GAE/100 g for air drying; 47.59±2.46 mg GAE/100 g for 30% CO_2 drying; 65.25±3.38 mg GAE/100 for 60% and 81.90±4.24 mg GAE/100 g for 80% CO_2 drying which shows an increase of total polyphenols preserved of 1.27 times for air drying environment and 1.93 times for 80% CO_2 drying atmosphere. The increase in total polyphenols content in CO_2 modified atmosphere, as noticed by other researchers [5], is due to the even more reduced drying time, as such decreased product temperature exposure, as well as the reduced concentration in oxygen, that presumably reduce the probability that oxidative reactions will occur.

From Figure 7 one can observe the degradation process of vitamin C which is easily affected by high temperature exposure, as well as oxygen presence. Researches also noticed that diminution in ascorbic acid is closely connected to moisture content of the product to be dried [15, 23], so lower temperatures are not recommended, for a rich vitamin C dried product. Beginning with a fresh "Conference" pear concentration in ascorbic acid of 44.05±2.47 mg/100 g DW (dried weight), for air convective drying, versus 43.86±2.41 mg/100 g DW, for CO_2 modified atmosphere drying, one can notice the deterioration process intensifying with drying process length.

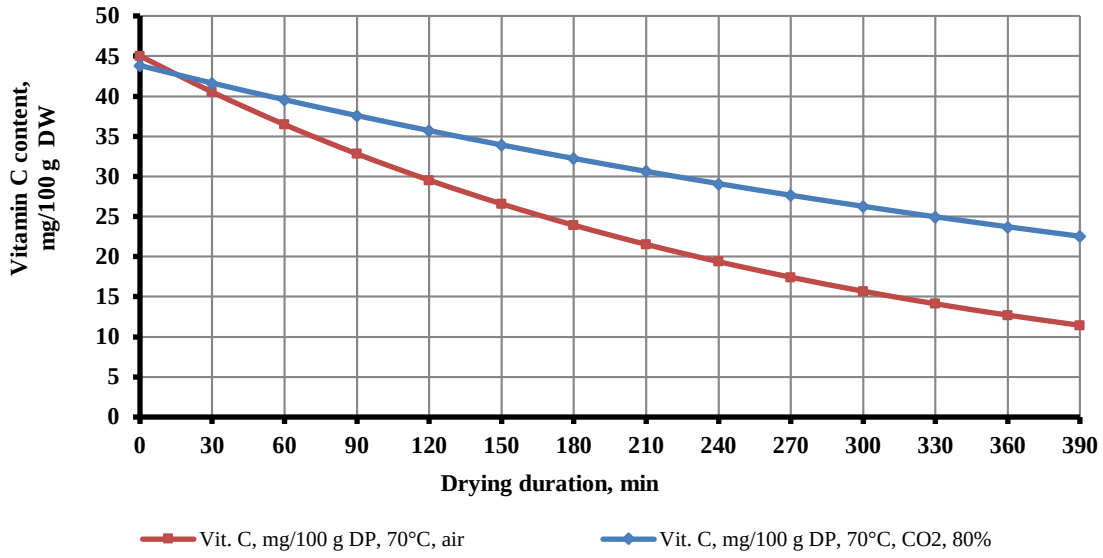


Figure 7. Ascorbic acid concentration for dried pears, "Conference" variety by air flow and CO_2 modified atmosphere methods (Carbone dioxide concentration: 80%; t= 70°C).

As such at 390 min the losses in Vitamin C represents 77 %, or 11.45±0.63 mg/100 g DW for air dried pears and 50%, or 22.74±1.24 mg/100 g DW for modified atmosphere one. There is a boost of 27%, or 1.98 times to preserved ascorbic acid. As mentioned by other sources [5, 15] that effect can be explained by the reduction of oxidative processes of ascorbic acid during drying process, that is possible to achieve with oxygen concertation reduction in the drying chamber when using CO_2 modified atmosphere.

4. Conclusions

This study was meant to investigate the effect of different types of drying agents, namely air and carbon dioxide for half-circle sliced pieces of "Conference" pears convective drying, with a temperature range of 60 – 100°C, and three CO_2 concentration: 30%, 60%, 80%.

The resulting data allowed to conclude that the above mentioned boost to polyphenols and ascorbic acid content can be explained as an effect of CO_2 modified atmosphere, as it allows to diminish oxygen presence thus reducing the oxidative action inside the drying chamber during heat treatment. There is as well a correlation between the augmentation of drying temperature and lower levels of damage to nutriments in dried products which is presumably due to the fact that drying temperature elevation means shorter drying duration which reduce polyphenols and Vitamin C temperature and oxygen exposure thus preserving them better.

In conclusion, one can recommend to maintain the quality of dried vegetable products, it is recommended to apply the drying method in a CO_2 modified environment, with the speed of the drying agent of 1.5 ± 0.13 m/s; temperature of the thermal agent of 70°C; concentration of carbon dioxide in the working chamber of 80%.

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MODEL OF STATISTICAL DATA ANALYSIS ON NITROGEN CONTENT IN SOYBEANS (GLICINE MAX MERRILL) IN CLAVERA VARIETY

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Abstract. Climate change, drought and high temperatures lately have led to the need to increase the adaptation capacities of plants to these changes. The purpose of the research is to gain knowledge regarding the influence of the biologically active substances *Reglalg* (compound of algal nature) and *Biovit* (compound of humic nature) on plant development, productivity and adaptation of plants to new climatic conditions. The research was based on decision support systems, machine learning and graph databases. These systems allow in-depth processing of unstructured data and making the necessary decisions. In this sense, an intelligent model was developed for the processing of biological data as part of a Decision Support System. For data analysis and knowledge generation, a graph database was developed to determine relationships and connections between entities, phenomena or events. Graphs allow the representation of complex information in a simple and intuitive way, which makes it easier to perform and analyze them. The use of Machine Learning methods allows the highlighting of laws and interactions between different elements, which can lead to the discovery of patterns and trends that can be easily identified. The paper presents the structure and functions of some components of the decision support system for the study of nitrogen content in soybean.

Keywords: *Decision Support Systems, biostatistics, Wolfram Mathematica, soy, Biovit, Reglalg.*

Rezumat. Schimbările climatice, seceta și temperaturile ridicate din ultima vreme au dus la necesitatea creșterii capacității de adaptare a plantelor pentru a face față acestor schimbări. Temperaturile ridicate au un impact semnificativ asupra proceselor fiziologice care au loc în plante. Problemele studierii influenței biostimulatorilor asupra compoziției chimice a boabelor unor culturi sunt slab structurate. Cercetarea s-a bazat pe sisteme de sprijinire a deciziilor, învățare automată și baze de date graf. Aceste sisteme permit prelucrarea în profunzime a datelor nestructurate și luarea deciziilor necesare. Printre problemele analizate se numără obținerea unei producții de înaltă calitate, care să satisfacă nevoile tot mai mari ale populației: problema mediului și cea a alimentelor. A fost dezvoltat un model inteligent pentru prelucrarea datelor biologice. Permite o înțelegere cuprinzătoare a mecanismelor de acțiune ale biostimulatorilor asupra calității boabelor de soia (*Glycine Max* Merrill). Scopul cercetării este de a dobândi cunoștințe privind influența substanțelor biologic active asupra

dezvoltării plantelor, productivității și adaptării plantelor la anumite condiții climatice. Lucrarea prezintă structura și funcțiile unor componente ale sistemului de suport decizional pentru studiul conținutului de azot din boabele de soia. Plantele au fost crescute în condiții de câmp prin administrarea de compuși obținuți din surse naturale.

Cuvinte cheie: SSD, biostatistică, *Wolfram Mathematica*, soia, *Biovi*, *Reglalg*.

1. Introduction

Agriculture is a field highly dependent on natural conditions, climate changes caused by increasing temperatures and reducing precipitation, factors with a significant role in obtaining high quality crops. One of the global problems at the present time is to provide the population with high quality food products and to a sufficient extent to ensure both the health of the population and the protection of the environment. The continuous growth of the population leads to an increase in consumption and, implicitly, in the quality of food products.

The main objective in agriculture is to obtain a high yield of agricultural crops, to adapt them to climate change and to develop their own responses as a result of adaptive reactions. This yield is due to several factors: the amount of precipitation, the temperature, the quality of the soil. Each of these factors contributes significantly to obtaining a high yield.

In addition to the mentioned factors, biologically active compounds play an essential role in the growth and development of plants, as well as obtaining high quality products. To determine the quantity and quality of agricultural production, the efficiency of biologically active compounds, we must take into account all the factors that interact with each other, each having a certain impact and influencing to a certain extent the quantity and quality of the products. In order to achieve the set objectives and make the necessary decisions, a decision support system was developed for the purpose of analyzing and solving problems through a trans-disciplinary approach on problem families.

The application of efficient and complex technologies to reduce the use of chemical fertilizers and their replacement with ecological compounds (biostimulants), optimizing production costs by optimizing the use of resources and obtaining consistent and stable incomes, as well as improving their quality and efficiency, obtaining a high production and quality soybean. Thus, it is necessary to implement advanced technologies for data processing and knowledge generation in order to solve decision-making problems.

A general definition of the problem is: a matter that presents unclear, debatable aspects, that requires clarification, that lends itself to discussions, an important matter that constitutes a task, a (major) concern and that requires an (immediate) solution, a difficulty that must be solved to achieve a certain result; weight, impasse, thing hard to understand, hard to solve or explain; mystery, enigma [1]. „A question proposed for solution; a matter stated for examination or proof; hence, a matter difficult of solution or settlement; a doubtful case; a question involving doubt" [1]. Research Problem is a situation or circumstance that requires a solution to be described, explained, or predicted [2].

The decision-making problems faced by managers from various fields of activity and research are: ***structured***, ***semi-structured*** or ***unstructured***.

A classification given by H. Simon and A. Newell, adapted by C. Gaindric reveals aspects of systems modeling and decision making [3].

1) ***Well-structured problems*** are formulated quantitatively, in which the essential dependencies are highlighted so well that they can be expressed by numbers and symbols, which ultimately receive numerical evaluations.

2) ***Unstructured problems*** or problems expressed qualitatively, are those problems that contain only the description of the most important resources, characteristics and properties, the quantitative dependencies between which are absolutely unknown.

3) ***Poorly structured problems*** are those problems, which contain both quantitative and qualitative elements. Qualitative moments tend to predominate [3, 4].

To solve these problems, Decision Support Systems (DSS) are developed and implemented. These systems can be used for all types of decision problems, but lend themselves best to loosely structured and unstructured ones.

The field of science, which deals with decision-making, is an interdisciplinary field, in training, in which methods of management science, optimization, information technologies, psychology, etc. are accumulated.

The decision-making process has the following components:

1) ***The object*** (system, process examined).

2) ***The subject*** (the decision maker) - the person or the intelligent system that makes the decision and determines that the system needs to be transformed to obtain new qualities and characteristics. The decision-maker formulates the objectives and establishes the criteria by which the degree of achievement of the objectives is measured, determines the internal parameters and restrictions, imposed by the technology and the operation of the system [5].

The problems researched in the doctoral project are loosely structured problems and can effectively be modeled within a *decision support system*.

An DSS is an interactive software system used to help decision makers extract useful information from a set of raw data, documents and knowledge, identify and solve problems in order to make optimized decisions.

The Academician Florin Gheorghe Filip defines the concept of DSS as "an anthropocentric, adaptive and evolving computer system intended to implement some of the functions of a possible "human support system" (or team) that would otherwise be needed to help the decision-maker overcome his limits and constraints they might face when approaching a problem of decision that matters" [5].

DSS integrates a knowledge base. The model materializes and harmonizes the decision concept with the user criteria and the user interface. The main advantages of using an DSS include examining more alternatives, better understanding of processes, identification of contingencies, improved communication, cost efficiency, and better use of data and resources [4].

The concept of decision is defined as "Decision taken after examining a problem, a situation, etc. adopted solution (among several possible)" [4, 6].

F. Gh. Filip defines the concept of "decision" as follows: "The decision represents the result of conscious activities of choosing a course of action and engaging in it, which usually involves the allocation of resources. The decision results from the processing of information

and knowledge and belongs to a person or a group of persons, who have the necessary authority and who are responsible for the effective use of resources in certain given situations" [5, 7].
Depending on the degree of structuring of problems and decisions, they can be classified into [7]:

1. **Structured decisions** are made following a known and explicit process that allows the processing of input information to choose alternatives for the adoption of which there are predetermined procedures.

2. **Unstructured (non-programmable) decisions** are those decisions whose elements are more qualitative, the aims and objectives are not precise and there is no known solution algorithm. They are important decisions, innovative and often atypical. There are no set procedures for their adoption.

3. **Semi-structural decisions** are those decisions in the adoption of which only partially known procedures can be used. The decision has predominantly quantitative elements and the objectives and goals are not precise and the solution algorithm does not cover all the elements of the problem.

In the field of biology and agriculture we often face unstructured problems. The application of DSS in agriculture and the environment has grown rapidly in recent times, which allows the rapid assessment of agricultural production systems, knowledge acquisition and decision-making both at the farm level and at the regional or national level.

One of the important applications of DSS in agriculture is the management of the use of compounds to stimulate the growth and development of plants, as well as to increase the quality of the fruit, the aim being to reduce or eliminate the use of chemical products in agriculture and to replace them with biological compounds.

Knowledge decisions are related to evaluating ideas for new information products and services, methods of communicating new knowledge, and disseminating information in the organization.

In order to solve the problems regarding the quality assurance of food products, an DSS was developed. Its purpose is to assist research to determine:

(a) the influence of certain biostimulants on plants and

(b) determining the degrees of influence of these biostimulators.

The goals of DSS are:

a) Research assistance to determine the influence of certain biostimulants on plants and their degrees of influence.

b) Complex data analysis and extraction of information/knowledge/opinions with applicability in the field of biology and agriculture, starting from the model made on soybean plants (*Glicine Max* Merrill) and processing them for the discovery of patterns, correlations, classifications, groupings, or new predictive models as well as data mining using data processing techniques based on biostatistics.

c) *Graph database* development to improve data access by providing customized search services, normalization and distributed access to content and multiple data sources. Information technologies equipped with graph databases make it possible to store relationships and connections as first-class entities. The architecture of graph databases is based on graph theory. A graph database can be defined as a database that uses semantic query graph structures with nodes, relationships, and properties to represent and store data [8,9]. This type of database presents data as it is conceptually visualized. This ability is achieved by transferring data in nodes and the relationships

between them in edges, being an optimized solution for modelling and querying large volumes of closely related data, representable by graph-type structures, which allows a high degree of adaptability to real models. Graph databases demonstrate the advantages of efficiently storing relationships between data points and are flexible in adding new types of relationships or adapting new data models for new research requirements. Stakeholders can use graph databases to generate competitive insights and meaningful value from connected data. These databases are that technology solution that allows data professionals at all levels to exploit the potential of their data relationships rather than just individual data points and the imagination of the database is the only limitation of how these relationships could be harnessed by the user [9]. A subgraph reflecting the content of *Nitrogen*, *Phosphorus* and *Protein* in the samples untreated and treated with compound *Prep1* and *Prep2* at soil *S1* is represented in figure 1.

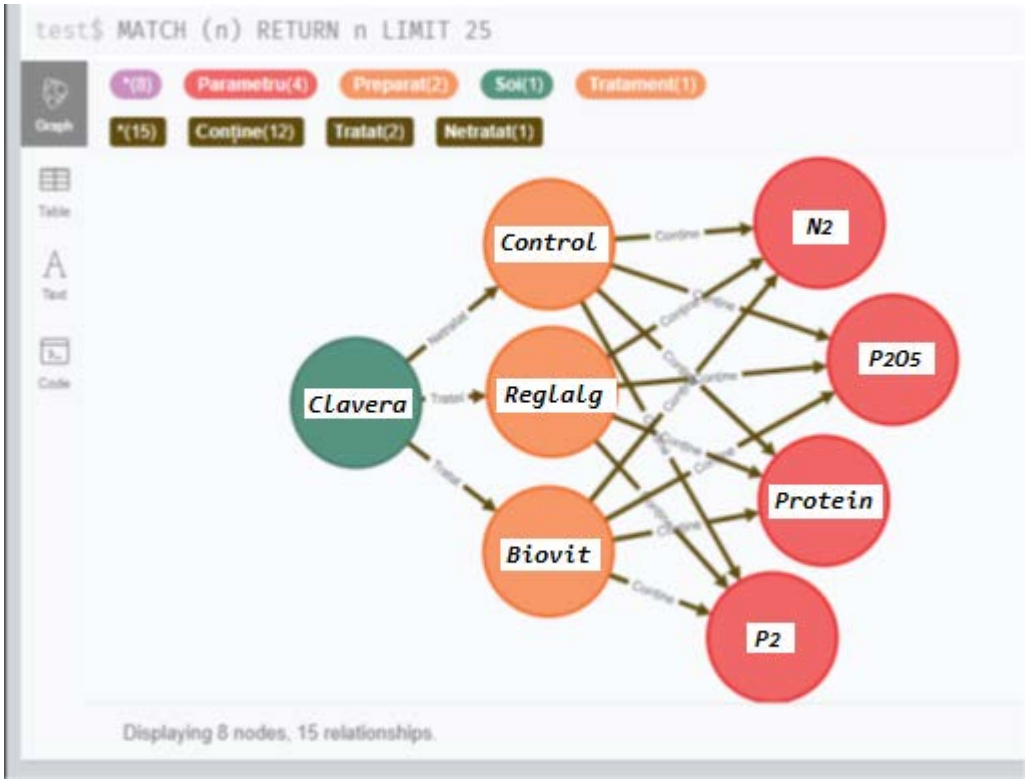

Figure 1. Subgraph content of elements.

The created model allows determining the influence of humic (Biovit) and algal (Reglalg) biostimulant compounds on the quality of soybeans. Research can help researchers and agricultural producers strengthen their efforts in order to mitigate the consequences of climate change and increase the adaptability of crops to new development conditions [10]. The research was carried out on several soybean genotypes. In this work, the results obtained on the Clavera variety are reproduced.

The Clavera variety is an indigenous variety obtained by hybridization and selection of the combination Timpurie × Nordic 138. Grain production within the limits of 22.3 - 32.5 q/ha. The protein content in the grains is 36.9% and 20.5% oil. The mass of 1000 grains (MMB) is 161 g. The vegetation period is 122 days. The plant has a height of 80-90 cm. The medium-sized grain has an oval-elongate shape, a thin yellow skin, with an elongated, light yellow hilum. The variety is resistant to falling, shaking and drought, with tolerance to diseases and pests [11].

2. Materials and Methods

The biostatistics method was used in our research [12]. The objectives of the software components, carried out at the moment, were to assist research to determine the degrees of influence of the biostimulators *Reglalg* (compound of algal nature) and *Biovit* (compound of humic nature) on the quality of soybeans. The results of the statistical processing of the data with this model are presented.

The main problem of the research is the verification of the statistical hypothesis regarding the difference of means. Eq. (1), [13]:

$$h_0 : \bar{d} = 0 \text{ or } h_a : \bar{d} \neq 0, \tag{1}$$

where: h_0 - null hypothesis.

h_a - alternatival hypothesis.

$\bar{d}$ - the difference of means.

The meaning of the first two concepts is as follows:

- ***Null hypothesis h_o*** - determines the probability distribution of one or more variables by which it finds that there is no difference or relationship between two measured phenomena or association between two groups. Thus, a fact is assumed to be true until proven otherwise [14].
- ***Alternative hypothesis - h_a -*** the data are not related to each other, the compared values differ from each other.

One of the parameters for statistical analysis are the *degrees of freedom*. The degrees of freedom (*df*) in statistics indicate the number of independent values that can vary in an analysis without breaking any constraints. It is an essential idea that appears in many contexts throughout statistics including hypothesis tests, probability distributions, and linear regression [14-17].

To determine the degree of influence on the researched parameters based on a small sample, the *t test* (*Student)* was used.

We note, that the data sets are independent, with different dispersions Eq. (2):

$$(\sigma_1^2 \neq \sigma_2^2), \tag{2}$$

where: σ_1^2 – the dispersion of the first sample.

σ_2^2 – the dispersion of the second sample.

and equal number of repetitions Eq. (3):

$$(n_1 = n_2 = 3), \tag{3}$$

where: n_1 – the number of items in the first sample.

n_2 - the number of items in the second sample.

Thus the difference of the means will be calculated [13].

2.1. Data processing

The component's model former realized using the biostatistics method [12].

Testing stages/ In the current research we have different dispersions ($\sigma^2 \neq \sigma^2$) and the number of repetitions is equal ($n_1 = n_2$) , the mean of the differences will be calculated [17].

a) Functions have been developed to calculate ***the mean's difference*** **.** Eq. (4):

$$\bar{d} = |\bar{x}_1 - \bar{x}_2|, \text{ where} \quad (4)$$

$\bar{d}$ - the mean's difference;
$\bar{x_1}$ – the mean of the first sample;
$\bar{x_2}$ – the mean of the second sample.

Example of a function made in Wolfram Mathematica:

medCN2MR = Abs[Mean [cN2M]] – Abs[Mean[cN2R]], where:

- *medCN2MR* - The variable that determines the difference in the average *nitrogen* content between the sample treated with *Reglalg* and *Control* in the *Clavera* variety;
- *Abs[Mean [cN2M]]* - The absolute value of the average nitrogen content in the control sample of the Clavera variety;
- *Abs[Mean[cN2R]]*- The absolute value of the average nitrogen content in the sample treated with *Reglalg* of the *Clavera* variety.

b) Degrees of freedom (*df*) for the independent test are determined according to the following formula Eq. (5):

$$df = n_1 + n_2 - 2 \quad (5)$$

c) The error of the average of the differences is calculated according to the formula Eq. (6):

$$s_{\bar{d}} = \sqrt{s_{\bar{x}_1}^2 + s_{\bar{x}_2}^2}, \quad (6)$$

where: $s_{\bar{d}}$ - The error of the mean of the differences.
$s_{\bar{x}_1}^2$ - Standard error of the first sample.
$s_{\bar{x}_2}^2$ - Standard error of the second sample.

Having 3 repetitions in each sample, we have *df = 3 + 3 – 2 = 4* (degrees of freedom).

d) *t -test (Student)* is determined as the ratio between the mean of the differences and the error of the mean of the differences according to the formula Eq. (15,16):

$$t = \frac{|x_1 - x_2|}{s_{\bar{d}} = \sqrt{s_{\bar{x}_1}^2 + s_{\bar{x}_2}^2}}. \quad (7)$$

The elements of this formula being exposed above.

If the experimental value is greater than the theoretical value ($t_{exp} \geqslant t_{teor}$), the null hypothesis of no significant differences is accepted, the differences are within the confidence interval.

Example: The theoretical *t*-value (t_{teor}) for 4 degrees of freedom at a significance threshold of $t_{0.05}$ is 2.13 and at a significance threshold of $t_{0.01}$ is 3.75 for the one-sided *t*-test. The *t*-value obtained is 34.2, therefore the null hypothesis is rejected and a significant positive influence of the treatment on grain quality is found.

The result can also be confirmed by using analysis ***lsd*** - *Least Significant Difference* Eq. (8), Eq. (9) [15, 18]:

$$lsd_{0.05} = t_{0.05} * \bar{d} \quad (8)$$

$$lsd_{0.01} = t_{0.01} * \bar{d} \quad (9)$$

When the difference of means ($\bar{d}$) is greater than the value *lsd* calculated, the null hypothesis is rejected.

Examples:

$$lsd_{0.05} = t_{0.05} * \bar{d} = 2.13 * 0.657 = 0.0409;$$
$$lsd_{0.01} = t_{0.01} * \bar{d} = 3.75 * 0.657 = 0.072.$$

difference of means represents $\bar{d} = 0.657$, which is higher than the *lsd value* obtained, therefore *confirms* the previous result.

An alternative to the point of rejecting the null hypothesis (H_0) is the *p - value*, which provides the lowest significance threshold below which the alternative hypothesis (H_a) is proven that there is sufficient evidence to reject the null hypothesis (H_0). It is a measure of statistical significance. The result *p* of the test, provided as a number between 0 and 1, and represents *the probability of error* if we reject the hypothesis H_0 . If *p* is lower than the significance threshold α chosen (usually $\alpha = 0.05$), we reject the hypothesis H_0 and accept as true the hypothesis H_a [19]. The interpretation of *p* values is done in most statistical tests as follows:

- ✓ $p < 0.05$ *(5%)*, the statistical link is significant (*S*, 95% confidence).
- ✓ $p < 0.01$ *(1%)*, the statistical link is significant (*S*, 99% confidence).
- ✓ $p < 0.001$ *(0.1%)*, the statistical link is highly significant (*HS*, 99.9% confidence).
- ✓ $p \geqslant 0.05$, the statistical relationship is not significant (*NS*).

2.2. Statistical analysis

The statistical analysis and the results obtained are presented below. The exposed tasks were carried out by means of the Wolfram Mathematica software system [20]. This is a high-level language that allows automation of the software development process.

To create and use the calculation functions, the Wolfram Mathematica libraries are imported:

- **Needs["Hypothesis Testing`"]** is a hypothesis testing package. The package contains functions for computing confidence intervals from data, *p-values* and confidence intervals for distributions related to the normal distribution.
- **Needs["ComputerArithmetic`"]** represents an arithmetic calculation package.

The experimental data are presented in Table 1.

Table 1

Nitrogen content (experimental data)

	Control	***Reglalg***	***Biovit***
N_2 (%)	5.35	6.0	6.17
	5.39	6.05	6.19
	5.37	6.03	6.26
$\bar{x}$	**5.37**	**6. 02**	**6.20**

Note. N_2 **–** nitrogen; $\bar{x}$ - values' mean.

3. Results and Discussion

3.1. Nitrogen content (N_2)

Functions were developed to create the diagram that determines the mean nitrogen content with the standard error based on the experimentally obtained data. The resulting diagram is shown in figure 2.

The *MeanAround* function provides an Around object that describes the mean of x_i and its uncertainty. By means of this function, the mean of the analyzed values and the standard error are calculated which will be indicated on the bar.

The chart is made with the *BarChart* function with formatting parameters such as style, labels, legend, appearance, etc.

ChartElementFunction is an option for chart functions. In the present case *BarChart* provides a function to use to generate the rendering primitives of each chart element.

"GlassRectangle", "Pastel" is the display style of the chart and bars.

ChartStyle - option for chart functions to specify styles in which chart elements should be drawn.

ImageSize - the size of the chart.

ChartLabels - the labels of each bar.

ChartLegends - chart legend. Specifies the legends used for chart elements.

Comments are shown between symbols: (* *Comment* *).

ClaveraN2 (*Declare the variable used in the calculation*).
={ MeanAround [{5.35,5.39,5.37}],
MeanAround [{6,6.05,6.03}],
MeanAround [{6.17, 6.19, 6.26}]};
BarChart [ClaveraN2,
ChartElementFunction → "GlassRectangle",
ChartStyle → "Pastel",
ImageSize → 400,
ChartLabels →{"1","2","3"},
ChartLegends → {"Control", " Reglalg ", " Biovit "}].

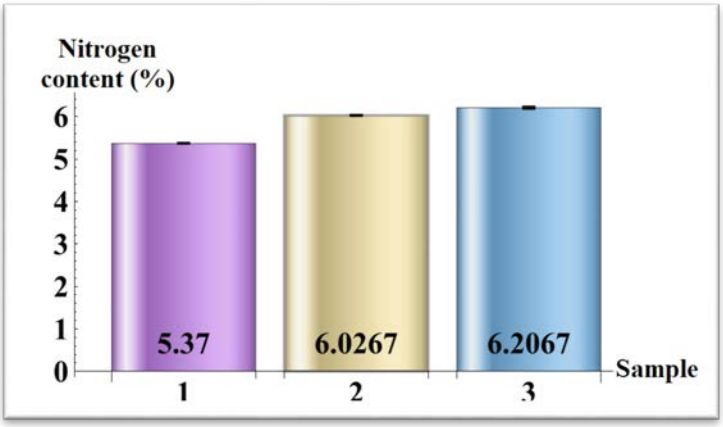

Figure 2. Variation of Nitrogen Content: 1– control, 2 – reglalg, 3 – biovit.

3.2. Variation of nitrogen content (N_2)

Functions have been developed to analyze the variation in nitrogen content. They materialize in a table, using the following elements:

- *Grid* function - is an object that is formatted with $_{an}$ *expression* arranged in a two-dimensional grid.

The statistical functions for each parameter (*Control* , biostimulators *Reglalg* and *Biovit*):

1) *Sample mean* with standard error - *MeanAround* (described previously).

2) *Dispersion - Variance* (- σ_2).

3) *The standard deviation - StandardDeviation* (σ).

4) *The coefficient of variation* expressed as a percentage, which is calculated as the ratio between *the standard deviation* and *the mean of the sample values* * 100, according to the formula Eq.(10):

$$\frac{\sigma}{\bar{x}} * 100, \quad (10)$$

where: σ - *standard deviation.*

$\bar{x}$ - *the mean of the sample values.*

5) ***Confidence Interval*** - *MeanCI*. A confidence interval provides boundaries within which the value of a parameter is expected to lie with a certain probability. Interval estimation of a parameter is often useful in observing the accuracy of an estimator as well as making statistical inferences about the parameter in question [16]. The *MeanCI* function provides confidence intervals of means and differences of means based on the central limit theorem.

The functions receive as parameters the variables declared for each studied parameter (*Control, Reglalg , Biovit*). The results are presented in table 2.

*Grid[{{"Parameters", " $\bar{x}$(%)", " σ^2 ", " σ ", "CV(%) * ", "C I * * "},*
{"Witness", MeanAround [cN2M],
*Variance [cN2M], StandardDeviation [cN2M], StandardDeviation [cN2M]/ Mean [cN2M]*100, MeanCI [cN2M]},{ " Regallg ",*
MeanAround [cN2R],
Variance [cN2R],
Standard Deviation [cN2R],
*StandardDeviation [cN2R]/ Mean [cN2R]*100,*
MeanCI [cN2R]},
{ " Biovit ",
MeanAround [cN2B],
Variance [cN2B],
Standard Deviation [cN2B],
*StandardDeviation [cN2B]/ Mean [cN2B]*100,*
MeanCI [cN2B]}} //N]]

Table 2

Variation of nitrogen content (N_2)

Parameters	$\bar{x}$ (%)	σ^2	σ	Coefficient of variation (%)	Interval trustworthy
Control	5.37 ± 0.012	0.0004	0.02	0.372	{5.32, 5.42}
Reglalg	6.027 ± 0.015	0.000633	0.025	0.418	{5.96, 6.09}
Biovit	6.207 ± 0.027	0.00223	0.047	0.761	{6.09, 6.32}

Notes. $\bar{x}$ - mean's differences; σ^2 – sample's dispersion; σ – sample's standard deviation.

3.3. Results of treatment influence on nitrogen content (N_2)

Functions were developed to analyze the influence of treatment on nitrogen content. The influence of a compound is compared with the control sample (control) and we find:

The difference in the values of the samples expressed in percentage (Δ) according to the formula Eq. (11):

$$dif = 100\ \frac{Mean[para_{m_1}]}{Mean[para_{m_2}]}, \tag{11}$$

where: *dif* is the difference between the mean values expressed as a percentage

Mean [ ] is the function for determining the average of the first parameter [*Control*] and the second parameter the group treated with the biostimulator [*Reglalg*] or [*Biovit*]:

1) Difference of sample means ($\bar{d}$).
2) Standard error of differences ($s_{\bar{d}}$).
3) The result of the *t*-test (student).
4) Least significant difference (*lsd*).

The formulas used [2-5] were previously presented in the paper. The results are presented in table 3.

Grid [{{" Comparison ", " Δ (%)", "$\bar{d}$", "s $\bar{d}$", "t", " lsd 0.05 ", " lsd 0.0 1 "},
*{"Witness vs Reglalg ", dif =10 0 -(Mean [cN2M]*100/ Mean [cN2R], medCN2MR = Abs [Mean [cN2M] – Mean[cN2R]], ercN2MR=√ 0.12 ^{2} +0.15 ^{2} , t=(medCN2MR/ erCN2MR) * , lsd 0.05 =t 0.05 * erCN2MR * ,*
*lsd 0.01 = t 0.01 * erCN2MR * },*
*{"Witness vs Biovit ", dif =10 0 -(Mean [cN2M]*100/ Mean [cN2B], medCN2MB = Abs [Mean [cN2M] – Mean [cN2B]], ercN2MB=√ 0.12 ^{2} +0.27 ^{2} , t=(medCN2MB/ erCN2MB) * , lsd 0.05 =t 0.05 * erCN2MB * ,*
*lsd 0.01 = t 0.01 * erCN2MB * }]*

Table 3

Results of treatment influence on nitrogen content (N_2)

Comparison	**Δ *(%)***	$\bar{d}$	$S_{\bar{d}}$	***t***	$lsd_{0.05}$	$lsd_{0.01}$
Control vs Reglalg	10.9	0.657	0.0192	34.2 *	0.0409 *	0.072 **
Control vs Biovit	13.5	0.837	0.0295	28.3 *	0.0629 *	0.111 **

Notes. * Significant influence at the 95% level. ** Significant influence at 99% level. **Δ** - the absolute difference in percentages; $\bar{d}$ - the mean's differences of samples; $s_{\bar{d}}$ - the standard error of differences; ***t*** – rezult of test ***t*** (Student); ***lsd*** – least significant diffenences.

The influence of biostimulators on protein content is determined. Table 3 shows that *the* t_{exp} value obtained from the data analysis is 34.2 when using *Reglalg* and 28.3 when using *Biovit*, which is higher than the theoretical value which is 2.13 at the 95% confidence level and 3.75 at the 99% confidence level. Thus, **the null hypothesis is rejected**.

The result can also be confirmed by using least significant difference analysis. The differences of means $\bar{d}_{reglalg}$ = 0.657, $\bar{d}_{biovit}$ = 0.837 are greater than the *lsd values* obtained according to table 2.3 ($lsd_{0.05}$ =0.04 and $lsd_{0.01}$ = 0.072 when using *Reglalg* and $lsd_{0.05}$ =0.0629 and $lsd_{0.01}$ = 0.111 when using *Biovit*), therefore the previous result **is confirmed** , the null hypothesis is rejected.

An additional confirmation for rejecting the null hypothesis is the ***p***-value [16] is used:

Wolfram Mathematica function is used for this purpose *StudentTPValue* which has as parameters the value of the test ***t*** and the degrees of freedom *(df)*:

StudentTPValue [34.2, 4] → $\boldsymbol{2.1843*10^{-6}}$

StudentTPValue [28.3, 4]→ $\boldsymbol{4.6273*10^{-6}}$

The result of this test is less than the significance threshold. Thus, the result obtained by the ***t*** and ***lsd*** tests is confirmed.

4. Conclusions

The evaluation of the quantity and quality of agricultural production, the efficiency of the compounds involved is done by analyzing their interaction and the impact on plant development. The model helps solve the problems of eliminating synthetic chemicals and using ecological products, which will subsequently contribute to obtaining high-quality products and increasing production volumes.

Wolfram Mathematica systems and graph databases. Representing linked data is simple. Data analysis is done quickly across a large number of entities. No complex connections are required to retrieve connected data for analysis. Solutions to complex problems can be obtained quickly. Any type of problem can be solved: structured, semi-structured and unstructured.

The statistical analysis of the data shows that the experimental preparations substantially influence the chemical composition of soybeans. The biostimulants used influence the nitrogen content, the values of the researched parameters increase substantially in the Clavera variety, the results demonstrating significant influence both at the 95% and 99% level of veracity. Thus, these biostimulants are recommended to be widely used in agriculture to increase plant resilience. This system helps researchers, manufacturers of plant preparations and agricultural producers to solve their research and activity problems aimed at obtaining high-yielding soybean crops and plant adaptation to climate change.

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THE ROLE OF BASIL, THYME AND TARRAGON IN REDUCING THE CONTENT OF NITRITE IN MEAT PRODUCTS

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Abstract. Reducing the content of nitrites and nitrates in food, including meat and meat products is a current issue. More and more studies are being done to reduce these synthetic food additives by using vegetative additives. This paper examines the issue of reducing nitrite content in meat products. The role of the basil, thyme and tarragon on nitrites and nitrates content in meat products is presented. The study showed the possibility of reducing the content of nitrites and nitrates in Lacta sausages, by using basil extract (BE 0,1%) by 0.4-0.94%, (BE 0.2%) by 0.80-1.88%. (BE 0.3%) by 1.20-2.82%; by thyme extract (ThE 0.1%) by 0.56-071%, (ThE 0.2%) by 1.12-1.42%, (ThE 0.3%) by 1.68-2.13%; by tarragon extract (TE 0.1%) by 0,08-0.66%, (TE 0.2%) by 1.16-1.32. (TE 0.3%) by 0.24-1.98%, maintaining the quality and safety of meat products.

Keywords: *nitrite, nitrate, basil, thyme, tarragon, meat products*.

Rezumat. Reducerea conținutului de nitriți și nitrați din alimente, inclusiv din carne și produse din carne este o problemă actuală. Numărul studiilor consacrate procedeelor tehnologice pentru reducerea acestor aditivi alimentari sintetici prin utilizarea aditivilor de origine vegetală este în creștere continuă. Această lucrare analizează problema diminuării conținutului de nitriți în produse din carne. Este prezentat rolul adaosurilor de busuioc, cimbru și tarhon asupra conținutului de nitriți și nitrați din produsele din carne. Studiul de caz a demonstrat posibilitatea reducerii conținutului de nitriți și nitrați din cârnații Lacta, prin utilizarea extractului de busuioc (BE 0,1%) cu 0,4-0,94%, (BE 0,2%) cu 0,80-1,88% (BE 0,3%) cu 1,20-2,82%; prin extract de cimbru (ThE 0,1%) cu 0,56-071%, (ThE 0,2%) cu 1,12-1,42%, (ThE 0,3%) cu 1,68-2,13%; prin extract de tarhon (TE 0,1%) cu 0,08-0,66%, (TE 0,2%) cu 1,16-1,32. (TE 0,3%) cu 0,24-1,98%, menținând calitatea și siguranța produselor din carne.

Cuvinte cheie: *nitrit, nitrat, busuioc, cimbru, tarhon, produse din carne*.

1. Introduction

Different spices and herbs, in different concentrations, are used to produced meat products [1]. Basil, thyme and tarragon are currently widely used in various food industries,

including the meat industry. Their antioxidant and antimicrobial properties are increasingly being the subject of international research [2-5].

The microbial properties of these plants have been reported in numerous scientific papers: the authors of the studies [6-8] report antimicrobial activity of basil, authors [4, 9, 10] report antimicrobial activity of thyme, authors [11-13] report antimicrobial activity of tarragon. The chemical composition and antioxidant properties are also reflected in many scientific papers, for example: basil [14], thyme [15, 16], tarragon [17].

Nowadays, cured meat products are widely produced using nitrate and nitrite salts [18]. Nitrites and nitrates are used in the meat industry due to their beneficial effect on the quality and meat products microbiological safety [19-21]. Nitrates (sodium nitrate - E251, potassium nitrate - E252) and nitrites (sodium nitrite - E249, potassium nitrite - E250) are food additives listed as official preservatives according to Commission regulation (EC) No. 1129/2011 [22]. Nitrates and nitrites legal limits are reported in Regulation (EC) No. 601/2014 [23]. Sodium nitrite permissible dose according to GD No. 229/2013 [24]. The content of nitrates and nitrites in meat and meat products in the Republic of Moldova is regulated in [25]. But lately it is increasingly mentioned that these substances in meat products form carcinogenic N-nitrosogenic compounds, which pose a major risk to consumers [26-28]. Nitrite plays a distinct role in human physiology. In acidic environments or under oxidative stress conditions it may be converted to a number of reactive nitrogen species [29], such as nitric oxide (NO), nitrogen dioxide (NO_2) and peroxynitrite ($ONOO^-$) [30].

In living systems, they are involved in a variety of biological functions and their uncontrolled intracellular presence produces significant toxicity, as they can target a variety of biomolecules including proteins, DNA, lipids and carbohydrates [31]. Reducing the nitrite / nitrate content of meat is a global problem [32]. There are many studies that determine the content of nitrite in meat and meat products [33].

The benefits of aromatic plants (basil, thyme, tarragon) on the food stability, including meat products [8, 11, 16], and on the consumer's health [33-35] have been demonstrated and argued in various scientific papers. Nitrites are used in the production of various meat products, with the role of printing and stabilizing their color and flavor, as well as maintaining the products microbiological stability [36]. Currently, more and more international research is aimed at the use of various plant sources in order to reduce the content of nitrites / nitrates in meat products [35-37]. The stability of the meat and meat products color, quality and safety can also be achieved by using natural antioxidants that are able to regenerate Met-Mb to MbO_2 [18, 38], and have microbiostatic and microbicidal properties [11, 39].

In this work we have tried to reflect another property of basil, thyme and tarragon that of providing the opportunity to reduce the content of nitrites / nitrates in meat products.

2. Materials and methods

2.1. Sampling

The sausage samples were prepared in laboratory conditions (semi-industrial) according to classic technology of manufacturing “Lacta” sausages, included in the group of boiled sausages. In the control sample a mixture of salts was introduced, according to the classic recipe (NaCl salt and sodium nitrite $NaNO_2$ are introduced separately).

The research samples were prepared with extracts of aromatic plants (basil – SBE, basil, thyme SThE, tarragon STE) 0.1%, 0.2%, 0,3% concentration. Table 1 shows the recipes of the researched samples.

Table 1

Sausage recipes "Lacta"

Raw materials and ingredients	Unit	"Lacta" sausages		
		The classic recipe	Control	With an addition of 0.1% aromatic plants (SBE/ SThE/ STE)
Consumption rate for 100 kg of unsalted raw material				
Beef, high quality	kg	35	35	35
Pork, semi-fat	kg	60	60	60
Powdered milk	kg	2	2	2
Eggs mixture	kg		3	3
Ice	%	25	25	25
Consumption rate of spices and materials, g (per 100 kg of unsalted raw material)				
Food salt	g	2090	1870	1870
Sodium nitrite	g	7.1		
SBE/SThE/STE*	g	-	-	100
Granulated sugar	g	120	120	120
Ground black pepper	g	120	120	120
Nutmeg	g	40	40	40

*The sausages were prepared with extracts of aromatic plants (basil – SBE, basil, thyme - SThE, tarragon - STE).

2.2. Methods

2.2.1. Sensory Analysis of Sausages was determinate exterior appearance, color in section, taste, odor, and consistency using the 5-point system by an expert panel of eleven trained food technologists. The 5-point assessment system includes the following scores characteristics: 5 - very good; 4 - good, 3 - satisfactory, 2 - poor, 1 - bad, having as reference the sensory characteristics of the classic product according to GD 624 of 19-09-2020 on the approval of the Quality Requirements for meat preparations and products [26].

2.2.2. Moisture content was determined according to gravimetric method, based on the weight loss of the analyzed sample to constant mass, due to water evaporation by heating in an oven at a temperature of up to 130 °C [40].

2.2.3. Determination of the meat pH made with the pH meter Titroline 5000 at 20°C.

2.2.4. Determination of water activity was performed by the express method using the LabSwift-a_w device (Novasina AG, Lachen, Switzerland).

2.2.5. Determination of nitrites and nitrates content (predictive method) based on bibliographic sources, regarding their content in aromatic plants.

2.3. Statistical analysis

All calculations were performed using Microsoft Office Excel 2007 (Microsoft, Redmond, WA, USA). Data obtained in this study are presented as mean values ± the standard error of the mean, calculated from three parallel experiments. The comparison of average values was based on the one-way analysis of variance (ANOVA), according to Tukey's test, at a significance level of $p \leqslant 0.05$, using the Staturphics program, Centurion XVI 16.1.17 (Statgraphics Technologies, Inc., The Plains, VA, USA).

3. Results and Discussion

Reducing food additives, especially nitrates used in the manufacture of meat products, is one of the most important problems facing the meat industry. Consumers prefer natural additives instead of chemicals used in meat products because of the health risks of nitrous compounds. Therefore, studies on the use of natural compounds as nitrites / nitrate alternatives have increased in recent years.

Processed meat producers have begun to use "natural" sources of nitrates, such as celery juice, beet extract or spinach, where the nitrates present are reduced to bacterial nitrites and as a result contribute to the formation of nitrosamine [41]. Nitrate reduction in nitrites is mainly caused by bacteria possessing nitrate reductase activity (*staphylococcus* and *micrococcus*), naturally contained in the raw material or in the case of addition to manufacture [42].

Most scientific papers mention the antimicrobial and antioxidant properties of herbs (basil, thyme and tarragon) and their use in various foods. There are insufficient studies on the possibility of using these plants in order to reduce the content of nitrates / nitrites in the food processing. In this research we conducted a reliability study in this direction.

The reduction in the salt amount introduced in the samples did not diminish the products quality and stability, Table 2.

Table 2

Physicochemical indicators and sensory characteristics of "Lacta" sausages

Tested samples	Quality indicators						
	Physicochemical			Sensory			
	Moisture content, %	Active acidity, pH	Water activity a_w	Color in section	Odor	Taste	Consistency
Control sample	64.37± 0.09 ^{a}	6.38± 0.06 ^{c,d}	0.875± 0.001 ^{e,f}	5.00± 0.00 ^{e}	5.00± 0.00 ^{g}	5.00± 0.00 ^{h}	5.00± 0.00 ^{d}
„Lacta" sausages with basil extract (SBE)							
SBE 0.1%	67.38± 0.06 ^{b}	6.15± 0.02 ^{b}	0.873± 0.001 ^{c,d}	5.00± 0.00 ^{e}	5.00± 0.00 ^{g}	4.75± 0.11 ^{f,g}	4.99± 0.01 ^{d}
SBE 0.2%	69.07± 0.06 ^{c}	6.13± 0.06 ^{b}	0.873± 0.001 ^{c,d}	4.75± 0.02 ^{d}	4.87± 0.04 ^{f}	3.83± 0.05 ^{c}	4.98± 0.02 ^{d}
SBE 0.3%	69.16± 0.05 ^{c}	6.12± 0.06 ^{b}	0.873± 0.001 ^{c,d}	4.45± 0.01 ^{b}	3.83± 0.01 ^{b}	3.46± 0.04 ^{b}	4.98± 0.01 ^{d}
„Lacta" sausages with thyme extract (SThE)							
SThE0.1 %	69.33± 0.09 ^{c}	6.16± 0.08 ^{b,c}	0.875± 0.001 ^{e,f}	5.00± 0.00 ^{e}	5.00± 0.00 ^{g}	4.95± 0.02 ^{h}	4.99± 0.01 ^{d}
SThE0.2 %	69.44± 0.06 ^{c}	6.12± 0.03 ^{b}	0.875± 0.001 ^{e,f}	4.75± 0.02 ^{d}	4.37± 0.02 ^{d}	4.27± 0.08 ^{d,e}	4.95± 0.02 ^{c,d}
SThE0.3 %	71.48± 0.12 ^{e}	6.10± 0.05 ^{b}	0.873± 0.001 ^{c,d}	4.60± 0.04 ^{c}	4.00± 0.01 ^{c}	3.35± 0.01 ^{b}	4.87± 0.07 ^{b,c}
„Lacta" sausages with tarragon extract (STE)							
STE 0.1%	69.48± 0.11 ^{c}	6.29± 0.04 ^{c}	0.874± 0.001 ^{d,e}	5.00± 0.00 ^{e}	4.75± 0.02 ^{e}	4.70± 0.10 ^{f,g}	4.99± 0.01 ^{d}
STE 0.2%	69.56± 0.08 ^{c,d}	6.14± 0.03 ^{b}	0.870± 0.001 ^{b}	4.50± 0.02 ^{b,c}	3.83± 0.01 ^{b}	4.33± 0.05 ^{d,e}	4.98± 0.02 ^{d}
STE 0.3%	69.64± 0.06 ^{c,d}	5.12± 0.03 ^{a}	0.867± 0.001 ^{a}	3.75± 0.00 ^{a}	3.63± 0.02 ^{a}	3.25± 0.04 ^{a}	4.45± 0.03 ^{a}

Values in the table represent the means of three replicated trials ± standard deviation. Different letters ($^{a-h}$) designate statistically different results ($p \leqslant 0.05$).

Probably this effect was achieved by introducing aromatic herbs, with remarkable antioxidant and microbiological properties, which were mentioned in another study [23]. Other authors also report that herbs control microbiological risk and do not affect color, and flavor of products [38, 43].

Levels of nitrite and nitrate in vegetable are dependent on several factors [44 - 46]: type of soil, temperature, humidity, light intensity, plant maturity, genetic, harvesting time, storage time and source of nitrogen [47 - 49]; method of plant cultivation and the early stage of their vegetative development [50]. Jolanta Molas says that according to the susceptibility degree to nitrate accumulation in plants, they are arranged as follows: lettuce> spinach> basil> mint> oregano> thyme [50].

Currently, great attention is being paid to the determination of nitrate / nitrate content in food, including meat products [53, 54], in the context that no substance has yet been found which would completely replace the functions of nitrites or nitrates. Positive effect of nitrites / nitrates on meat products are related to the improvement of color, the development of the typical meat flavor, the antimicrobial role and the antioxidant effect [55]. The reaction of nitric oxide with myoglobin, contributes to the formation of the nitrosylmioglobin complex, which imprints the meat color's characteristics. Following the interaction of nitrates / nitrites with meat lipids and proteins [56], several compounds are formed that influence the aroma of the meat product. Also the antimicrobial effect of nitrites which is related to the inhibition of bacteria metabolic enzymes, limiting oxygen absorption and breaking the proton gradient [30]. However, some plant origin raw materials can replace nitrates / nitrites due to their increased nutritional and biological value as well as their microbiological stability.

The estimated percentage reduction in nitrite content in the analyzed samples was based on the nitrite content reported in the bibliographic sources, Table 3.

Table 3

Estimation of the probability to reduce the nitrite / nitrate content in the examined sausages samples

Concentration of extract / Evaluated parameters	**Classic recipe**	**Control**	**SBE**	**SThE**	**STE**	**Levels of nitrite, nitrate, mg/100g / Bibliographic sources***
The amount of salts, nitrites	2097.1	1870				
percentage reduction, Δ%		6.09				
			0.1%			
percentage reduction NO_2^-, Δ%			0.22 - 0.54	0.52 - 0.64	0.07 - 0.64	154 - 381 (B) 369 - 453 (Th) 50.4 - 450 (T) [47, 51, 52]
percentage reduction NO_3^-, Δ%			0.18 - 0.40	0.04 - 0.07	0.01 - 0.02	1872 - 3972 (B) 369 - 702 (Th) 83 - 139 (T) [47, 51, 52]
NO_2^- + NO_3^-, Δ%			**0.40 - 0.94**	**0.56 - 071**	**0,08 - 0.66**	
			0.2%			

Continuation Table 3

percentage reduction NO_2^-, Δ%	0.44 - 1.08	1.04 - 1.28	0.14 - 1,28	[47, 51, 52]
percentage reduction NO_3^-, Δ%	0.36 - 0.80	0.08 - 0.14	0.02 - 0.04	
NO_2^- + NO_3^-, Δ%	**0.80 - 1.88**	**1.12 - 1.42**	**1.16 - 1.32**	
	0.3%			
percentage reduction NO_2^-, Δ%	0.66 - 1.62	1.56 - 1.92	0.21 - 1.92	[47, 51, 52]
percentage reduction NO_3^-, Δ%	0.54 - 1.20	0.12 - 0.21	0.03 - 0.06	
NO_2^- + NO_3^-, Δ%	**1.20 - 2.82**	**1.68 - 2.13**	**0.24 - 1.98**	

* The nitrate / nitrite content taken into account is the average value reported in the target bibliographic sources. B- basil, Th- thyme, T- tarragon.

In the 0.1% SBE samples, the NO_2 - reduction percentage are of 0.22% to 0.54%. If we take into account the level of nitrates reported in the bibliographic sources, this percentage would be higher (0.40 - 0.94%).

The quality and microbiological stability of the examined samples were achieved due to their antioxidant, antimicrobial properties and the nitrite / nitrate content of the aromatic plants, although the amount of salt and nitrites in the samples was reduced by 6.09% compared to the classic recipe.

4. Conclusions

Herbs (basil, thyme and tarragon) with remarkable antioxidant and antimicrobial properties are recommended ingredients for use in the meat products manufacture. In the context of the bibliographic and experimental study, it was found that these plants could reduce the consumption of nitrites and salts that we use in the meat products manufacture.

So it is possible to replace sodium nitrite with basil, thyme or tarragon (plant extracts, powders or pears) which result in the nitrite content elimination / reduction of the end product. Herbal extracts appear to be a suitable alternative to synthetic nitrite, may prevent meat products discoloration and, in appropriate quantities, shall not impair the flavor, texture and consistency of the product.

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EFFECTS OF DEFATTED WALNUT MEAL AS A POTENTIAL INGREDIENT IN BREAD: PHYSICOCHEMICAL, RHEOLOGICAL, FUNCTIONAL AND SENSORY PROPERTIES

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Abstract. Potential functional ingredients, resulting after partial oil extraction by cold pressing, present a promising direction with perspective for the nutritional improvement of traditional bakery products and may enhance their health-promoting properties. The current study sought to determine the effect of wheat flour substitution with walnut (*Juglans regia L.*) meal by 0, 2, 4, and 6% of the total amount. The influence of partially defatted walnut meal (BWF) incorporation on dough physicochemical, and rheological properties, as well as the final sensory properties of the bread was investigated. Mixolab test results indicated an increase in dough development time and stability, a reduction of hydration capacity, free water content, enzymatic activity as well as a reduction of the shelf life of the enriched bread. Physical and sensory analyses showed that substitution of wheat flour with partially defatted walnut meal below 6% (on a flour basis) in bread manufacturing recipes yielded products with an enhanced porosity (72.2 to 74.5%), titratable acidity (1.4 to 2.3 degrees), freshness (2.0 to 7.8%) and polyphenol content (0.09 to 2.20 µg GAE/100 g product). All samples show specific positive characteristics, well defined, without defects, with a total acceptability of 4.54 - 4.88. The samples with 2% and 4% BWF show better quality indicators, therefore they can be recommended to consumers as products with high nutritional value.

Keywords: *flour, walnut meal, dough, Mixolab, baking quality, bread.*

Abstract. Ingredientele funcționale potențiale, rezultate după extracția parțială a uleiului prin presare la rece, prezintă o direcție promițătoare cu perspectivă pentru îmbunătățirea nutrițională a produselor de panificație tradiționale și le pot îmbunătăți proprietățile de promovare a sănătății. Studiul actual a urmărit să determine efectul înlocuirii făinii de grâu cu șrot de nucă *(Juglans regia L.),* cu 0, 2, 4 și 6% din cantitatea totală. A fost investigată influența încorporării șrotului de nucă parțial degresat (BWF) asupra proprietăților fizico-chimice și reologice al aluatului, precum și asupra proprietăților senzoriale finale ale pâinii. Rezultatele testului Mixolab au indicat o creștere a timpului de dezvoltare și a stabilității aluatului, o reducere a capacității de hidratare, a conținutului de apă liberă, a activității enzimatice precum și o reducere a termenului de valabilitate al pâinii îmbogățite. Analizele fizice și senzoriale au arătat că înlocuirea făinii de grâu cu șrot de nucă parțial degresat sub

6% (pe bază de făină) în rețetele de fabricare a pâinii a dat produse cu o porozitate sporită (72.2 până la 74.5%), aciditate titrabilă (1.4 până la 2.3 grade), prospețime (2.0 până la 7.8%) și conținut de polifenoli (0.09 până la 2.20 μg GAE/100 g produs). Toate probele prezintă caracteristici pozitive specifice, bine definite, fără defecte, cu o acceptabilitate totală de 4.54 - 4.88. Probele cu 2% și 4% BWF prezintă indicatori de calitate mai buni, prin urmare pot fi recomandate consumatorilor ca produse cu valoare nutritivă ridicată.

Cuvinte cheie: *făină, șrot de nucă, aluat, Mixolab, calitatea coacerii, pâine*.

1. Introduction

The transformation of industrial by-products into high-quality food ingredients is a trend to combat the problem of food safety. Millions of tons of agricultural by-products are produced each year along agricultural and food processing procedures. It is necessary to take further steps to explore the internal potential of agri-food waste to stand out as a food ingredient to partially or completely replace the composition of other food products [1].

Currently, there is a multitude of plant sources of perspective in the view of researchers for which classification was made by genesis, processing, product, and production stage, and information on their effect in the industry was also systematized [2]. Some agricultural waste contains the most valuable nutrients, which combine a range of vitamins and minerals, and other important components: dietary fiber, phospholipids, and biologically active substances of natural origin with protective or stimulating action on physiological systems and body functions [2]. Potential ingredients obtained from industrial by-products can be a remedy for nutritional improvement of traditional bakery products, intensification of the technological process, fortification of flour [3], creating of new products with treatment effect and prophylaxis [4-7].

Nowadays, research is being done to obtain functional bakery products with the addition of protein preparations from defatted, deodorizing soybean flour [8], cotton [9], sunflower flour [10-11], pinus [12] rapeseed, black sesame, hazelnut [13, 14], which are also beneficial supplements that increase the quality bakery products [2]. For example, defatted, deodorizing soybean flour has very wide use: in the USA, bakery products and baby food are manufactured (2-6% is added to ordinary bread and 10-15% to special varieties); in France, Germany, the Netherlands - is added to diet bread [8].

For the preparation of bakery products (buns, baguettes, croissants, muffins) it is interesting to use flour enriched with „grits", partially defatted, from which can be obtained products with high nutritional value, intended for both healthy people and people with health problems (overweight, sports, vegetarians, etc.) [13, 15-18].

Partially defatted walnut meal is a secondary product that remains after nuts pressing [19, 20] and oil extraction. Extremely rich in proteins, essential amino acids, minerals [21], vitamins, and polyphenols with antioxidant activity [22], these by-product has attracted the attention of scientists [19, 23-27]. Characteristics of partially defatted walnut meal indicate that it could have applications as a food additive with nutritional benefits in the manufacture of food for consumption [1]. Due to its high protein content and partial solubility, partially defatted walnut meal *(Juglans regia L.)* has satisfactory functional properties and can be a good source of protein and a functional ingredient in heterogeneous food systems (emulsions, foams, and suspensions) [28, 29]. In addition, the partially defatted walnut meal is used in the confectionery industry in the production of fillings, cakes, candies, etc. [30-38].

The experimental results obtained by Blessing showed that the substitution of wheat flour with a walnut meal (in proportions of 0-50%) significantly increases the bread's content of proteins and fats (respectively 12.17% - 25.70% and 2.40% - 37.57%) and decreases the level of carbohydrates (63% - 19.4%).

As the degree of substitution of wheat flour with walnut meal increases, the volumetric density and hydration capacity decrease insignificantly, but the assimilation capacity of the composite flour increases [39]. Another study conducted by Almoraie demonstrates the effect of improving bread by adding walnut meal that was prepared by soaking, shelling, oven drying, and sifting. As a result, substitution with 30% walnut flour provided the best bread quality [40]. The presence of walnut meal, peanut meal, and membrane between the kernel of the nut, also significantly improves the organoleptic qualities of bakery and confectionery products [10, 14, 40, 41].

In this study, the purpose of the experiments was to establish compositions using a functional ingredient - partially defatted walnut meal to obtain products with high nutritional value. The effects of adding 2 to 6% BWF (on a flour basis) to bread formulation were compared. Emphasis was placed on its effect on the physicochemical, and rheological properties, as well as the properties of the final products. Rheological parameters were estimated using an empirical method, the Mixolab instrument/device that measures both protein (gluten matrix) and starch characteristics and can also provide information on dough development time, protein breakdown, starch gelatinization, enzyme activity, and gel strength.

By applying these methods, those skilled in the art can obtain key information regarding the performance characteristics of wheat flour when measuring the rheological properties of a dough sample. The initial configuration of the Chopin system offers 16 profiles for the following products: bread, biscuits, pizza, pasta, baklava, etc. If the flour does not meet the parameters of a configured profile, Mixolab suggests changes [42].

2. Methods and materials

2.1. Research materials

The main ingredients for the bakery products were first-grade wheat flour „Beatrice-Com" [43] and walnuts *(Juglans regia L.)* [44]. After walnut cold pressing in laboratory conditions, partially defatted walnut meal was obtained.

The manufacturing recipes include other ingredients as well: compressed yeast *(Saccharomyces Cerevisiae)*, salt [45], refined sunflower vegetable oil [46], water [47] and ascorbic acid (E300) [48].

2.2. Determination of the quality and technological properties of wheat flour and walnut meal

To determine the quality of wheat flour, sensory analysis methods and physicochemical methods were used according to international standard methods [49], namely: total ash content [50], moisture [51], titratable acidity [52], quantity [53] and quality of wet gluten [54].

In addition, it was rated the quality of the partially defatted walnut meal, following the characteristics: sensory analysis [55], physicochemical: moisture [51], crude fat [56], total ash content [50], peroxide value [57] and acidity [58].

To assess the physicochemical indicators of the dough, titratable acidity and moisture were determined before and after fermentation [59].

2.3. Evaluation of rheological properties

The dough rheological characteristics were tested by means of the Chopin Mixolab using the standard „Chopin+" protocol; the running parameters of the device are depicted in Table 1. The Mixolab analyzes the quality of the proteins during the dough's kneading (formation time, hydration capacity, stability, elasticity, softening), heating behavior when protein denaturation, starch gelatinization (gelatinization and gelatinization temperature), enzymatic activity (proteolytic), the behavior of the starch when cooling (jellification and relegation).

A typical curve recorded by Mixolab (Figure 1) illuminates the following parameters: C1 - maximum torque during mixing, Nm; C2 - measures the protein weakening based on the mechanical work and temperature, Nm; C3 - expresses the starch gelatinization, Nm; C4 - indicates the stability of the formed starch gel, Nm; C5 - measures the starch retrogradation during the cooling stage, Nm; *α* - represents the slope of the curve between the end of the period of 30 °C and C2 (gives an indication about the rate of the proteins thermal weakening); *ß* - represents the slope of the curve between C2 and C3 (gives indications about the gelatinization rate); *γ* - represents the slope of the curve between C3 and C4 (gives indications about the rate of enzymatic hydrolysis) [42, 60, 61].

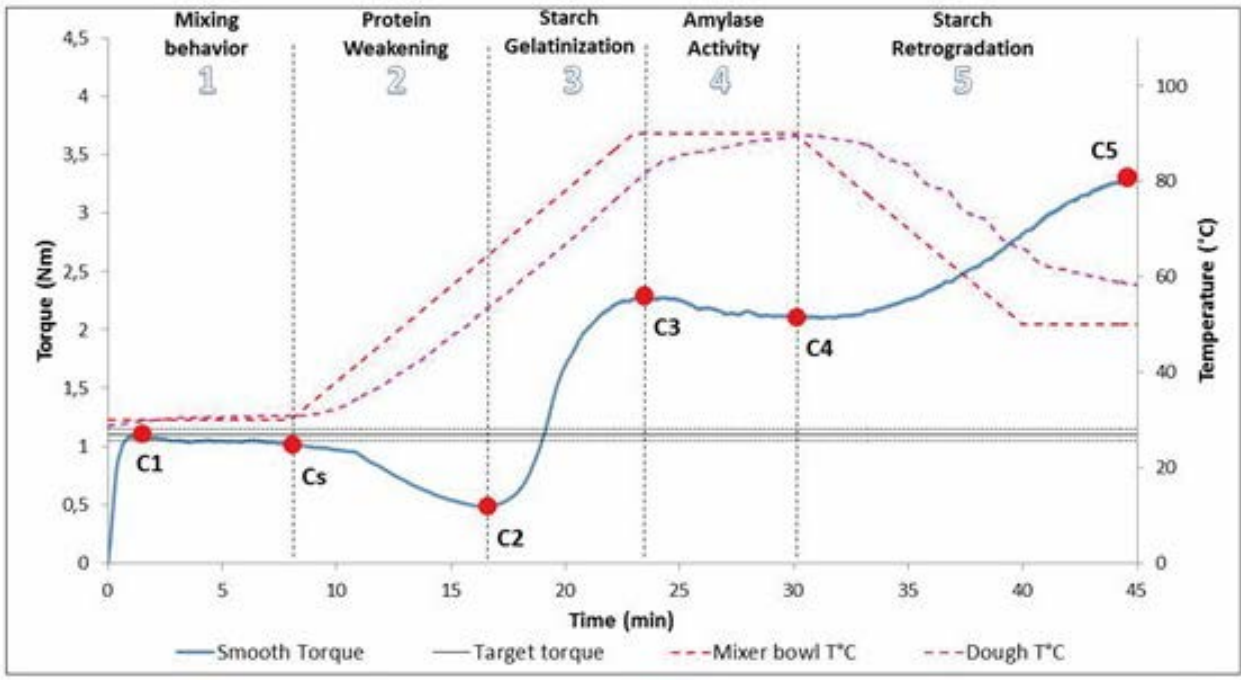


Figure 1. Typical curve recorded by Mixolab [60].

Table 1

Settings of the Mixolab [61]

Parameter	Value
Mixing rate, rpm	80
Dough weight, g	75
Tank temperature, °C	30
Temperature of the first plateau, °C	30
Duration of the first plateau, min.	8
Temperature of the second plateau, °C	90
First temperature gradient, °C/min.	4

Continuation Table 1

Duration of the second plateau, min.	7
Second temperature gradient, °C/min.	4
Temperature of the third plateau, °C	50
Duration of the third plateau, min.	5
Total analysis time, min.	45

The determinations were made in the laboratory of the Department of Food Technology, the Technical University of Moldova, Republic of Moldova and in research laboratory of the University „Dunarea de Jos", Galati, Romania.

2.4. Preparation of bread

Dough preparation is a crucial stage in the technological process of bread making. The dough was prepared using first-grade wheat flour, with or without the addition of walnut meal. The recipes for the different variants are as follows: a control sample without any addition (CS), and samples with 2, 4 and 6% partially defatted walnut meal (2% BWF, 4% BWF and 6% BWF). The control sample was made solely with first-grade wheat flour. Salt and baker's compressed yeast were added in doses of 1.5% and 3%, respectively, based on the weight of the flour mixture. The amount of water was calculated beforehand and adjusted based on the hydration capacity values determined using the Mixolab. After mixing the ingredients with a laboratory mixer (Mesko-AGD, Poland), the dough left to ferment for 60 min at a temperature of 31 ± 1 °C, with a puncture made after 30 minutes. The dough was then divided into pieces weighing 0.400 ± 0.010 kg and placed into molds. The final dough fermentation lasted 30 minutes. The bread was baked in an electric modular oven (Forni Mini-Rotor, Italy) at 240 ± 10 °C for 22 ± 2 min [8]. The obtained samples were analyzed 12 hours after baking.

2.5. Determination of the quality of the experimental samples

To determine the quality of the experimental samples, the following standardized physicochemical methods were used [62, 63]: porosity, freshness, the specific volume of bread, acidity titratable, polyphenol content [64], the water activity (Rotronic Hygro Palm) [65] and microbiological characteristics [66].

Sensory evaluation was performed using 9 panelists trained comprising of graduate students and staff members of the Department of Food Technology, UTM. Samples were randomly assigned to each panelist. The panelists were asked to evaluate each loaf for appearance, color, consistency, taste, smell and total score on organoleptic. A 5-point scoring scale was used [67]. The individual score was given in accordance with the table, which represents the magnitude of the deviation from the sensory requirements provided by the technical documents in force (Table 2) [68].

Table 2

The scoring scale that represents the magnitude of the deviation from the sensory requirements provided by the technical documents in force

Scoring	Description of the evaluation step
5	No deviation from sensory quality requirements
4	Minimal non-conformities from sensory quality requirements
3	Visible non-conformities from sensory quality requirements
2	Obvious/considerable non-conformities from sensory quality requirements

Continuation Table 2

1	Very obvious/considerable non-conformities from the sensory quality requirements
0	The product cannot be analyzed from the sensory point of view

The score awarded by the evaluators was recorded in the sensory analysis sheet.

2.5.1. Methodology for determining the peroxide value

The peroxide value is a physicochemical index that characterizes the degree of freshness of oils. But not only oils but also other products that contain fat can be affected by the rancidity process. In the present research study on the utilization of a secondary product of walnuts - defatted walnut meal *(Juglans regia L.)* in bakery products, we concluded that the quality of the proposed product may be affected by the oxidation of fats in defatted walnut meal, which is about 40%. To receive truthful results, methods of analysis approved on the territory of other countries were studied. Thus, to determine the peroxide value in food products containing flour, the methodology [69] was applied. The method consists in extracting the fat from 15 ± 0.1 g of the sample to be analyzed, with 100 ml of chloroform and treating a volume of 10 ± 0.1 mL of the chloroform extract in the medium of 15 ± 0.1 mL acetic acid with 1 ± 0.1 mL potassium iodide solution with a concentration of 50-55%. The released iodine is titrated with a solution of sodium thiosulfate, 0.01 n solution, in the presence of 1 mL of starch solution with a concentration of 0.5%.

2.5.2. Determination of total polyphenols content (TPC)

The evaluation of the total polyphenol content in the experimental samples was carried out according to the Folin-Ciocalteu method [70], with some non-essential modifications. The amount of sample, 0.2 ± 0.01 g, was dissolved in an amount of 15 ± 0.1 mL of methanol: deionized water (6:4, v/v) and sonicated (ISOLAB Laborgeräte GmbH) at 28 ± 2 °C, for 30 min and at maximum power (frequency 20 kHz, and power 130 W). Then the extracts were centrifuged (10 min, 2500 rpm) and the supernatants were collected. An aliquot (0.1 mL) of the aqueous methanolic phase was diluted with water to a total volume of 6.5 mL, to which 0.5 mL of Folin-Ciocalteu reagent was then added. After 8 min, 3 mL of sodium carbonate solution (10%) was added to the mixture. The reaction mixture was incubated at 40 ± 2 °C in a water bath for 30 min The spectra of the preparation extracts were recorded at spectrophotometer DR 5000 (HACH-Lange GmbH, USA-Germany) in the range of 200...1000 Nm. Results were expressed in μg gallic acid equivalents (GAE)/ 100 g product. The experiments were performed in 3 replications.

2.6. Statistical analysis

Statistical analysis of the experimental data was performed [71] through variance analysis (one-way ANOVA), by comparison at a significance level of 95% ($p \leqslant 0.05$). All tests were performed in triplicate and all results have been presented as average ± standard deviation. All calculations were made using IBM SPSS Statistics 23 and Microsoft Excel 2010.

3. Results and discussion

3.1. Evaluation of the raw material

3.1.1. Evaluation of wheat flour

Wheat flour was characterized from the point of view of the most important specific parameters that determine the baking quality.

The flour used in the study met the sensory quality requirements [43]. Following the physicochemical determinations, it was established that the registered parameters for the used flours fall within the permissible limits. The moisture of first-grade wheat flour was 14.4 ± 0.2%, the titratable acidity 2.2 ± 0.1 degrees and the ash content - 0.750 ± 0.001%, the content of wet gluten is 24.4 ± 0.2%, wet gluten quality at appliance IDC-1 60 ± 5 c.u., which demonstrates a high quality of gluten.

3.1.2. Evaluation of walnut meal

The partially defatted walnut meal *(Juglans regia L.)* was obtained under laboratory conditions, treated by mixing with ascorbic acid (1% by weight of flour mixture used) [72] and stored under vacuum conditions to prevent the fat oxidation [73], thus favoring the preservation of their organoleptic characteristics - color, taste and aroma.

Partially defatted walnut meal presents a fine-grained powder, light brown in color, with the taste and smell characteristic of nuts. The physicochemical characteristics indicate particles' size of 220 ± 10 μm [28], moisture content 5.8 ± 0.2%, crude fat 40.0 ± 0.1%, the ash content 4.57 ± 0.03%, peroxide value 9.2 ± 0.1 mmol/kg oil, acidity value 3.85 ± 0.10 mg KOH/ g oil.

According to USDA (2013), dry matter, crude fat and ash content of walnut meal are 95.3, 49.42 and 2.99, respectively [74]. The peroxide and acidity index of edible walnut oil should not exceed 10 mmol/kg oil and 4.0 mg KOH/g oil respectively [30].

3.2. Evaluation of the semi-finished product

Characterization of dough is an essential task to ensure good technological quality.

The inclusion in the technological recipe of different raw materials usually affects the properties of the dough and the quality of the bread. The properties of the dough depend directly on the state of the protein-proteinase complex, which is characterized by the quantity and quality of gluten [75].

Walnuts contain up to 11-26% protein (essential amino acids, especially lysine) [30]. The composition of the addition contributed to the intensification of microbiological processes, as a result of the vital activity of bacteria [22].

Lactic, acetic and propionic acid, accumulated in the fermentation process, have antagonistic activity against sporulating bacteria and molds, which would increase the microbiological purity of bakery products, given the high microbiological contamination of walnut meal [75]. In this case, it increases the gas formation capacity and the enzymatic, amylolytic activity, and the biochemical and microbiological processes are activated which will possibly reduce the fermentation time of the dough. The maximum value of titratable acidity was observed after fermentation of the sample 6% BWF, reaching the value of 3.3 degrees (Table 3).

Table 3

Physicochemical indices of quality wheat flour dough with the addition of secondary product of walnuts - partially defatted walnut meal

Characteristics / The product	Titratable Acidity, degrees		Moisture content, %	
	(before fermentation)	(after fermentation)	(before fermentation)	(after fermentation)
CS	1.9 ± 0.2	2.9 ± 0.2	40.0 ± 0.1	36.0 ± 0.2
2% BWF	2.0 ± 0.2	3.0 ± 0.1	38.8 ± 0.2	34.0 ± 0.2

Continuation Table 3

4% BWF	2.3 ± 0.1	3.2 ± 0.1	33.7 ± 0.1	33.0 ± 0.2
6% BWF	2.8 ± 0.1	3.3 ± 0.1	32.6 ± 0.2	32.0 ± 0.2

Note. Results are expressed as mean ± standard deviation. CS - control sample; BWF - sample with addition of partially defatted walnut meal.

It was shown that the added amounts of partially defatted walnut meal influence greatly moisture during fermentation dough fermentation. In the control sample, CS, the moisture values are the highest (40.0 ± 0.1% before and 36.0 ± 0.2 after fermentation) as a consequence of the significant content of carbohydrates in wheat flour [40]. According to our research, the dough moisture with the addition of 2% BWF before fermentation was reduced to 38.8 ± 0.2% and after fermentation to 34.0 ± 0.2%. When introducing a maximum amount of 6% BWF, the moisture value before fermentation was reduced to 32.6 ± 0.2% and at the end of fermentation to 32.0 ± 0.2%. Partially defatted walnut flour added to wheat flour tended to bind moisture, thus reducing the moisture content of the composition. A decrease in moisture was also observed due to the lack of gluten and starch in wheat flour, which have the property of binding water in the dough [39].

Similar patterns were observed by Burbano, Tsyganova, Gomez and Aghamirzaei et al. [4, 16, 17, 75], who argued that the protein and fiber in walnut meal could bind water in the dough, causing moisture to decrease as addition concentration increases. As the percentage level of walnut meal increases (20-50%), the results obtained by Almoraie [40] indicated increased moisture values. The author Tsugkieva claims that the addition of 1% membrane the kernel of the nut does not influence the quality parameters of the semi-finished product [41].

3.3. Testing the rheological character of the semi-finished products with the addition of partially defatted walnut meal

The rheological characteristics are a determining factor for obtaining quality products. In the work, it was followed the influence of the elaborated technology on the properties of the dough with the addition of partially defatted walnut meal using the Mixolab Chopin. The Mixolab is a complex device that measures the rheological properties of the dough. Briefly, this device cumulates the farinographic, extensographic and amyloographic analysis in one [76-78].

One of the features that are evaluated in this device is the hydration capacity. The hydration capacity of flour depends on the quantity and quality of gluten (increases as the quantity is greater and the quality is better); the degree of flour extraction (in flours with increased cellulose content it is higher); the fineness of the flour (increases with finer ground flours, whose starch particles absorb more water). For widely consumed wheat flour, the hydration capacity is 54-64% [25, 79].

The high-water absorption capacity of the dough accounts for consistency, which is one of the attractive characteristics of bread making. In this study the, BWF was used to replace an amount of wheat flour. In the first stage, for the control sample were obtained higher values of the hydration capacity, of 60%.

With the increase in the amount of partially defatted walnut meal in the composition of the recipe, a decrease in the hydration capacity values was observed: for the 2% BWF sample - 58.4%, the 4% BWF sample - 57.0% and respectively the 6% BWF samples – 56.3% (Table 4).

This can be explained by the presence of compounds with hydrophobic properties, as well as the fatty acids contained in the partially defatted walnut meal. Although BWF is high in fiber [30], it contains a great quantity of oil (40%) and is considered an oily additive that obviously reduces water absorption in the dough. Thus, the high hydration rate of the fiber and protein in the walnut meal requires the inclusion of a pre-hydration step before it is added to the dough.

Table 4

Influence of the addition of BWF on dough hydration capacity

Parameters	CS	2% BWF	4% BWF	6% BWF
Hydration capacity, %	60.0 ± 0.4	58.4 ± 0.3	57.0 ± 0.2	56.3 ± 0.5

Note. Results are expressed as mean ± standard deviation. CS - control sample; BWF - sample with addition of defatted walnut meal.

The values of the increase of the dough moisture in the case of the previous determinations are argued by the calculation of the recipes, but the values obtained for this device (Mixolab) prove the opposite. A similar pattern was observed by Aghamirzaei et al. [75] when the effects of the incorporation of grape seed flour on the rheological properties of the dough were studied. Water absorption decreased significantly by increasing the additive content from 0 to 25%.

The decrease in hydration capacity values is explained by the content in the walnut meal of non-polar hydrophobic amino acids (alanine, phenylalanine, proline, valine, methionine), which repel water [30].

The partially defatted walnut meal does not have the property of binding water because it does not contain gluten and starch. The authors argue that this could be due to increased concentrations of chemical compounds with hydrophobic properties, such as fatty acids. Although the additive has fiber-rich fractions, still its oil content is high and it is considered an oily additive that obviously reduced the water-holding capacity of the flour through reduced water absorption [4, 8, 39, 75].

In addition, other research, by Pycia et al. [80] was characterized by low water absorption capacity, and this parameter decreased as the share of walnut flour in the system increased (from 5 to 15 %). The average value of this parameter was 47.9%.

Burbano et al. [4] claimed that the addition of walnut flour (WF) greatly affected the microstructural characteristics of the dough, leading to differential molecular mobility and rheological behavior. Likewise, the addition of WF improved the consistency of the dough, making it much easier to mold.

In contrast, other studies [40] showed that the addition of walnut flour in dough progressively ($p \leqslant 0.05$) significantly affected water absorption capacity, from 60% in the control to 65% in wheat flour supplemented with 50% flour of walnut. This increase, the author mentions, is due to the protein solubility and dough composition following the addition of nuts whose protein is characterized by high solubility and water absorption capacity. Furthermore, the addition of walnuts could lead to a structural change in the dough that may allow more water to be absorbed due to hydrogen bonding.

Parameters of the rheological evaluation of the dough with the addition of partially defatted walnut meal are presented in Table 5.

Significant development time values were observed for the flour mixture with the addition of 4% BWF, with values of 0.98 min. Following the addition of more than 6% BWF, an obvious decrease in C1 development time to 0.63 min was observed.

From the presented results, higher stability with a value of 1.73 min was observed in the flour mixture with the addition of 4% BWF, thus showing a positive influence of partially defatted walnut meal on this dough characteristic. The value of the dough development time also increased, from 0.92 to 0.98 min, compared to the control sample.

In the second stage with the heating of the dough (53-59 °C) and the mechanical action of the kneading paddles increases and the minimum consistency C2 (with the increase of the amount of partially defatted walnut meal has reduced the denaturation of proteins, therefore the free water content from the dough).

Table 5

The variation of the rheological characteristics of the dough in the Chopin Mixolab, for the samples with added partially defatted walnut meal walnut meal

Stages		CS	2% BWF	4% BWF	6% BWF
C1	Development time, min.	0.92 ± 0.02	0.95 ± 0.03	0.98 ± 0.02	0.63 ± 0.08
	Standard consistency, Nm	1.08 ± 0.12	1.13 ± 0.12	1.12 ± 0.12	1.13 ± 0.12
	Dough temperature, °C	29.90 ± 1.10	31.30 ± 1.30	31.10 ± 1.10	31.40 ± 1.40
	Standard consistency amplitude, Nm	0.09 ± 0.00	0.08 ± 0.01	0.07 ± 0.02	0.10 ± 0.00
	Stability, min.	1.47 ± 0.03	1.38 ± 0.02	1.73 ± 0.07	1.70 ± 0.10
C2	Development time, min.	17.12 ± 0.15	17.5 ± 0.16	17.62 ± 0.24	18.02 ± 0.37
	Standard consistency, Nm	0.35 ± 0.08	0.37 ± 0.07	0.36 ± 0.02	0.37 ± 0.07
	Dough temperature, °C	53.80 ± 1.20	58.9 ± 1.10	57.40 ± 0.90	58.60 ± 1.40
C3	Development time, min.	23.95 ± 0.20	23.5 ± 0.30	23.73 ± 0.27	23.73 ± 0.07
	Standard consistency, Nm	1.70 ± 0.02	1.69 ± 0.02	1.64 ± 0.02	1.61 ± 0.02
	Dough temperature, °C	77.50 ± 1.50	79.80 ± 0.20	78.80 ± 1.20	78.80 ± 1.20
C4	Development time, min.	33.58 ± 0.56	33.87 ± 0.34	33.60 ± 0.65	32.67 ± 0.30
	Standard consistency, Nm	1.28 ± 0.02	1.22 ± 0.02	1.21 ± 0.02	1.16 ± 0.02
	Dough temperature, °C	84.10 ± 0.90	83.80 ± 1.20	84.00 ± 1.00	85.30 ± 0.30
C5	Development time, min.	45.00 ± 0.00	45.00 ± 0.00	45.00 ± 0.00	45.00 ± 0.00
	Standard consistency, Nm	1.84 ± 0.02	1.85 ± 0.02	1.77 ± 0.02	1.74 ± 0.02
	Dough temperature, °C	58.30 ± 0.70	57.30 ± 1.70	58.40 ± 0.60	57.50 ± 1.50

Note: Results are expressed as mean ± standard deviation. CS - control sample; BWF - sample with addition defatted walnut meal.

Research by Almoraie et al. [40] showed that increasing the level of walnut addition significantly reduced dough development time. This value is an important indicator of the hydration capacity of the flour particles and therefore of the presence of a hydrophobic substance. Based on published reports, dough stability parameters decreased while the mixing tolerance index increased with increasing amounts of addition in the mixes. This hypothesis is also supported by other authors [61, 80, 81]. The reduction of hydration capacity could be due to the fact that the addition of nut constituents could disrupt the wheat gluten-starch network, competing with wheat flour proteins for water, and then decreasing its stability.

In the second stage with the heating of the dough (53-59 °C) and the mechanical action of the kneading paddles increases and the minimum consistency C2 (with the increase of the amount of partially defatted walnut meal has reduced the coagulation of proteins, therefore the water content free from the dough).

In third stage, the control sample showed the highest values of the maximum gelatinization C3 with a maximum value of 23.95 min, and the consistency of 1.7 Nm. Due to the increase in temperature (78-80 °C), the proteins denature and release water which becomes available for starch. Starch granules absorb water and as a result, increase the consistency of the dough.

In the 4th stage, with the increase of the amount of partially defatted walnut meal, the C4 consistency decreases, also the enzymatic activity (proteolytic, amylolytic) and the most stable gel formed is presented by the sample with 6% of partially defatted walnut meal with 1.16 Nm (by 9.4% compared to the control sample).

In the 5th stage, we have a more efficient downgrading of the starch in the sample with 2% of partially defatted walnut meal, with 0.54% compared to the control sample, which gives us a longer shelf life compared to the other samples. The addition of 6% BWF reduces the shelf life of the products by 5.4% compared to the control sample.

Our results agreed with other reports that indicated that the addition of ground walnut increased the gelatinization temperature values and led to a very noticeable reduction in the viscosity of such systems [82].

Conversely, other studies have shown that increases in peak viscosity and gelatinization temperature were observed in composite wheat flours [40]. The difference could be attributed to the variation in added materials. Some additives are free of sugars or starches, while others contain materials that may contain sugars and starches that increase viscosity and gelatinization temperature.

The authors Pycia ed Juszczak (2021, 2022) [80, 82] claim that the retrogradation enthalpy and degree of retrogradation increase significantly compared to the control and reduce the storage modulus values that characterize the tested doughs.

Based on the results obtained at Mixolab, was built the graph regarding the rheological evaluation of the dough with the addition of BWF (Figure 2).

It is possible to compare the obtained curves with the associated profiles. The profiler is a translation into six qualitative index measurements, shown in the graphical test result (Figure 3).

Based on the baking test results, Mixolab C2, C3 and C4 characteristics were positively correlated with porosity, while C5 was significantly correlated with bread freshness. The correlation coefficients recorded were in the range of 0.64-0.80 ($p < 0.001$) and - 0.88 ($p < 0.001$), respectively.

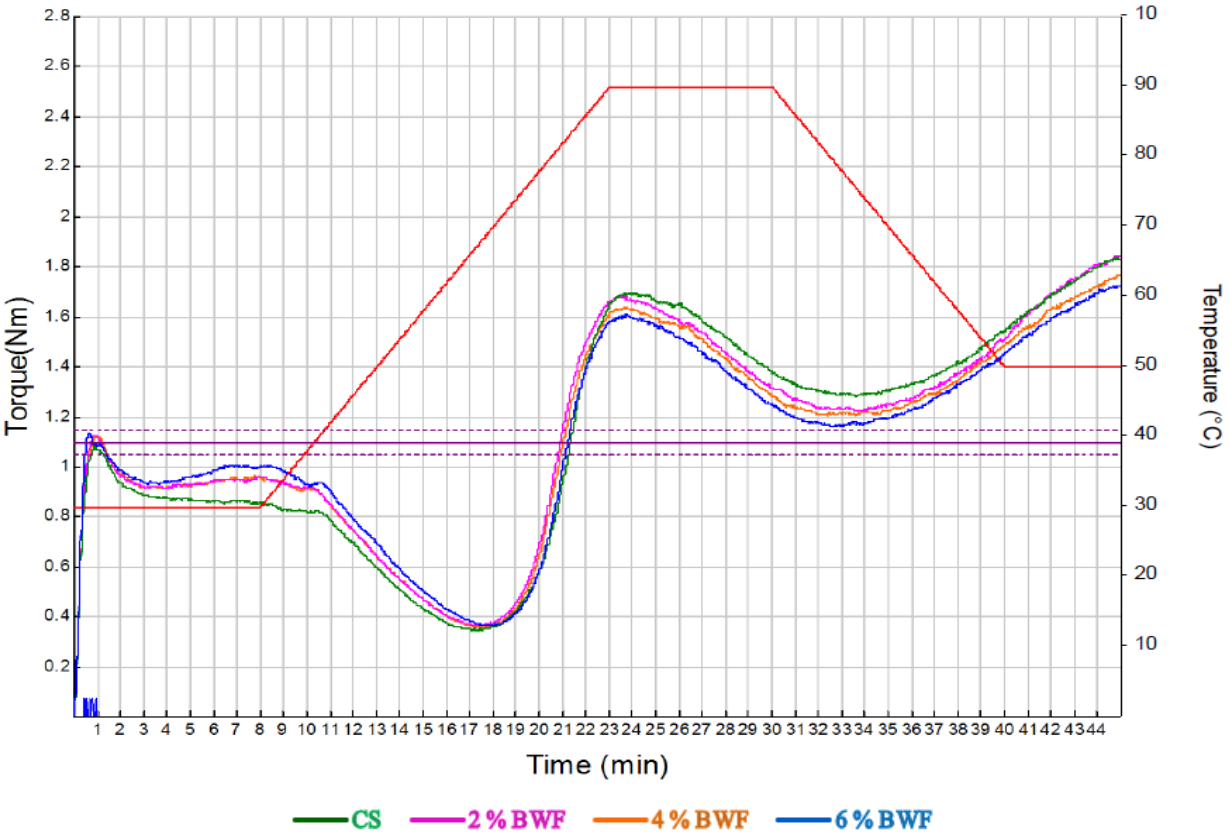


Figure 2. Rheological evaluation of the dough with the addition of BWF, in Mixolab (Done by author).

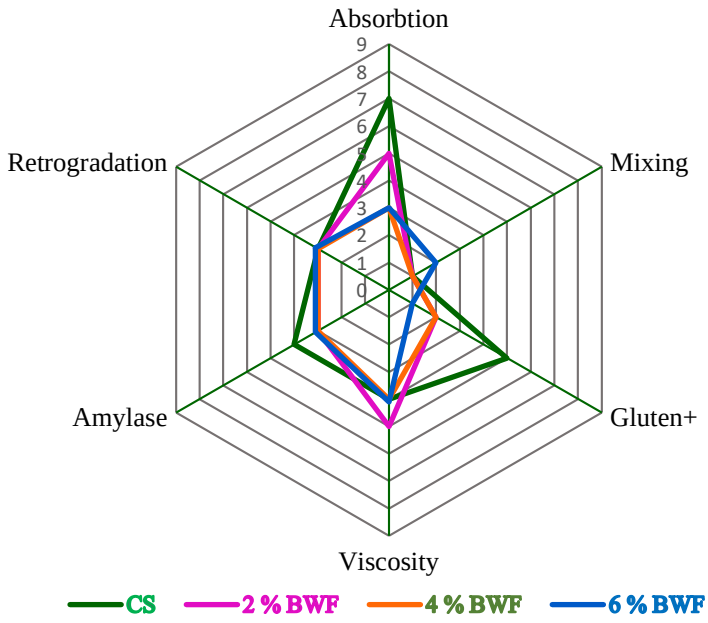


Figure 3. Graphic profile of overlapping experimental samples:
CS - control sample; BWF - sample with addition defatted walnut meal.

3.4. Testing the nutritional and functional characteristics of bread with the addition of walnut meal

The physicochemical quality indicators of the products obtained with the addition of partially defatted walnut meal and control are presented in Table 6.

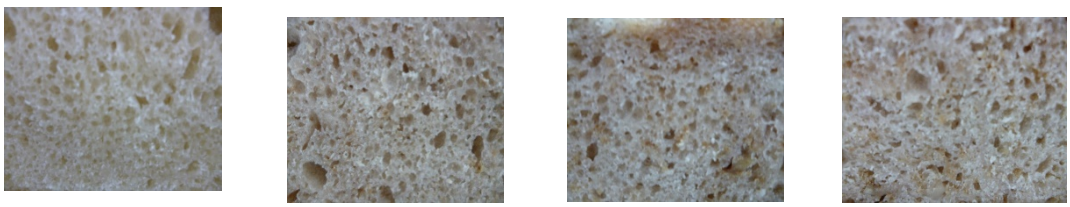
Table 6

Influence of the addition of BWF on wheat bread quality

Parameters	CS	2% BWF	4% BWF	6% BWF
Porosity, %	72.2 ± 1.4	72.8 ± 1.3	73.1 ± 1.2	74.5 ± 1.5
Specific volume of bread, cm^3/100 g	271 ± 12	268 ± 15	263 ± 10	261 ± 11
Acidity titratable, degrees	1.4 ± 0.2	1.8 ± 0.1	2.2 ± 0.1	2.3 ± 0.2
Freshness, %	2.0 ± 0.1	4.0 ± 0.1	6.0 ± 0.1	7.8 ± 0.1
Water activity, c.u.	0.227 ± 0.001	0.276 ± 0.003	0.301 ± 0.006	0.317 ± 0.003
Total polyphenol content, μg GAE/100 g product	0.09 ± 0.02	1.02 ± 0.05	1.44 ± 0.07	2.20 ± 0.08

Note. Results are expressed as mean ± standard deviation. CS - control sample; BWF - sample with addition partially defatted walnut meal.

The analysis of the results presented in Table 6 showed that the addition of partially defatted walnut meal influenced the bread quality parameters [68]. The porosity of bread increased linearly with the added concentration of partially defatted walnut meal, showing values of 72.8%, 73.1% and 74.5% in samples with 2%, 4% and 6% BWF, respectively, compared to control. This phenomenon is explained by the stimulation of the fermentation activity of baker's yeast by the components of the partially defatted walnut meal (Figure 4). Therefore, the porosity of products with the addition of walnut flour increased insignificantly, with a maximum of 3.09% compared to the control**.**



CS 2% BWF 4% BWF 6% BWF

Figure 4. Influence of partially defatted walnut meal addition on the porosity of experimental samples from wheat flour: CS - control sample; BWF - sample with addition partially defatted walnut meal.

In general, porosity is characterized by the uniformity, size and thickness of the pore walls. In this study the control sample is characterized by uniform, medium-sized pores with thin walls. With the increase of the amount of addition the pores have larger sizes and thicker wallswhich thus influencing the porosity results.

Increased values for porosity were also obtained by Chochkov [7] ed Sandulachi [83] for bread in the presence of defatted walnut meal. Pycia et al. (2020) state that the reduced and uneven porosity of the product enriched with walnut meal, over 20%, is probably due to the high amounts of fat that hinder the activity of the yeast and the retention of gas bubbles, and the reduced amount of gluten in the dough as a result of the replacement of wheat flour with walnut meal. Consequently, the support of the three-dimensional gluten network it's weaker [10].

On the contrary, the specific volume of bread was reduced by supplementing wheat flour with partially defatted walnut meal, where the specific volume was highest in the control (271 ± 12 cm3/100g) and lowest in the sample containing 6% BWF (261 ± 11 cm3/100g). The authors claim [61, 81] that these changes are due to the fact that the addition contributed to reducing the amount of gluten, but had a tonic effect on it. The amount of partially defatted walnut meal walnut meal increased the gas-forming capacity, but less the gas-holding capacity in the dough. Chochkov et al. [7] claim that the optimal addition of walnut meal to maintain the correct bread volume is 5-10%. Almoraie et al. [40] estimated that supplementing bread with walnut meal at a level higher than 20% has a very negative effect on its weight and volume. Following the interaction of the components in the recipe, the gluten network responsible for retaining the fermentation gases produced by the yeasts is weakened [17]. This is consistent with the results obtained in this study.

The values of titratable acidity and freshness of baked samples are important indicators in directing the evolution of physicochemical transformations in bread during the storage period. In this work, we observed that these parameters have changed depending on the amount of addition, manifesting an increasing trend. The bread samples with partially defatted walnut meal supplementation showed an increase in titratable acidity value within the range of 1.8 ± 0.1 to 2.3 ± 0.2 degrees compared to wheat flour (1.4 ± 0.2). This could be associated with the high percentage of fatty acids in the added supplement, which contributes to the intensification of biochemical and microbiological processes in the dough [40].

The freshness is due to the behavior of the starch during cooling (crystallization of amylopectin). The higher the index, the shorter the shelf life of bakery products [80]. According to our research, the freshness of the core in the sample with the addition of 2% BWF increased to 4.0% compared to 2.0% for control sample. Hydrophobic amino acids (non-polar) in the partially defatted walnut meal have the property of repelling water during the baking stage, significantly influencing the freshness of the bread core. Freshness increased to 6.0% and 7.8% in samples with 4% and 6% BWF. This can be explained by the fact that with a greater addition of BWF, the amount of free water will be greater [18, 40] and thus we will have greater decreases in baking losses.

Water activity is frequently used as a critical control point in HACCP programs aimed at controlling microbial stability or physicochemical and enzymatic degradation in products [65]. The tested samples showed increasing a_w values, from 0.227 c.u. (CS) at 0.317 c.u. (6% BWF).

According to the sources [65] it is considered that the values do not exceed the range determined for food quality and safety. Following the microbiological evaluation, the baked bread samples with the addition of partially defatted walnut meal showed no signs of mold contamination, having a color from golden yellow to dark yellow. Microbiological stability of work samples has been comparatively higher than those of control [83]**.** In the samples, 4% and 6% BWF were found to be a common microbiota, with the presence of *Streptococcus lactobacillus*, *Streptococcus lactis* and *Bacillus subtilis*.

According to the studies [6, 22, 84, 85], it can be stated unequivocally that walnuts (Juglans regia L.) are leaders in the content of phenolic substances compared to other nuts. Their value is 1.5-2.5 g gallic acid equivalents (GAE)/100 g fresh matter. In this study, the presence of bioactive compounds in partially defatted walnut meal increased the total content of phenolic compounds in bread. The highest results were recorded in the sample with 6% BWF, of 2.20 ± 0.02 μg GAE / 100 g product, compared to the control sample 0.09 ± 0.02 μg GAE / 100 g product.

The results of the sensory analysis of the wheat bread samples with the added partially defatted walnut meal are presented in Table 7.

Table 7

Sensory profiles of bread samples prepared with the addition of BWF

Sensory characteristics	CS	2% BWF	4% BWF	6% BWF
Exterior appearance	4.40 ± 0.03	5.00 ± 0.00	4.80 ± 0.00	5.00 ± 0.00
Color	4.40 ± 0.01	5.00 ± 0.00	4.80 ± 0.00	5.00 ± 0.00
Consistency	4.80 ± 0.00	5.00 ± 0.00	5.00 ± 0.00	5.00 ± 0.00
Taste	4.00 ± 0.02	4.40 ± 0.03	4.60 ± 0.04	4,80 ± 0.00
Smell	5.00 ± 0.00	4.60 ± 0.02	4.80 ± 0.00	4.80 ± 0.00
The total score on organoleptic	4.54 ± 0.06	4.71 ± 0.05	4.78 ± 0.04	4.88 ± 0.00

Note. Results are expressed as mean ± standard deviation. CS - control sample; BWF - sample with addition defatted walnut meal.

The table 7 shows the sensory attributes of the composite bread of different percentages of supplementation of defatted walnut meal added to wheat flour. The prepared bread was evaluated by the evaluators regarding the external appearance and color of the crust. The control sample, CS, has a specific color of first-grade wheat flour, and at the samples with addition of BWF an increase in crust color intensity was observed with a higher level of walnut meal. Probele CS, 2%, and 6% BWF au obținut un scor de 5.0. The 2% and 6% BWF samples have a more pleasant and more homogeneous shade, with a score of 5.0. Three analysts indicated skin surface color differences in the 4% BWF sample (4.80) expressed by irregular shape and uneven surface color. But these differences were described as moderately perceptible. The color change is explained by the content of polyphenols *(TCP)* existing in the partially defatted walnut meal which, when homogenized with other components in the recipe and after heat treatment, lead to a change in the color of the finished product. On the other hand, the inclusion of 2, 4, 6% BWF significantly increased the core consistency compared to the control, from 4.80 to 5.00.

Following the sensory analysis of the samples taken in the research, a pleasant smell was noticed, specific to freshly baked bread, with a slightly sweet taste. With the evaluation for the smell of the bread, the quality score ranged from 4.00 to 4.80. The results clearly show that bread made from 100% wheat flour had the highest score (5.00), followed by bread with 4% and 6% BWF (4.80), while bread with 2% BWF had the lowest value (4.60). A reason for this may be caused by the bitter taste of some inherent compounds of BWF, especially at high temperatures, as reported by Santos et al. [86].

The overall evaluation also shows that the degree of supplementation influences the overall approval of the bread samples. Bread made with 6% walnut flour had the highest score with 4.88 compared to the control (4.54) and other walnut flour supplements.

Similar patterns were observed by [13, 16-18, 83] in their tries of enhancing the nutritive and biological value of bread.

4. Conclusions

In this study, the effects of the incorporation of partially defatted walnut meal on the dough physicochemical and rheological properties, as well as properties of the final products were investigated. Increasing the incorporation of BWF from 2 to 6% (on a flour basis) led to increased final dough moisture after fermentation (32.0 to 36.0%). The composition of the

partially defatted walnut meal addition contributed to the intensification of microbiological processes, as a result of the vital activity of bacteria. The changes in the trend of the Mixolab curve depended on the doses of the walnut meal. The results demonstrate that increasing the amount of partially defatted walnut meal reduces the hydration capacity, the free water content of the dough, the enzymatic activity (amylolytic and proteolytic) as well as the shelf life of the bakery products. Significant correlations were observed between gluten quantity and C1, C3, C4, and C5 and also between gluten quality and C3 and C4. Stability is also correlated with wet gluten quantity and quality. Moreover, the parameters C2, C3 and C4 were positively correlated with porosity based on the results of baking tests, while C5 was correlated with bread freshness.

The addition of partially defatted *(Juglans regia L.)* walnut meal increased the bread final titratable acidity (1.4 to 2.3%) and freshness (2.0 to 7.8 %). The fiber content of the partially defatted walnut meal also hinders the leavening ability of the bread, as a result, the specific volume of the bread was progressively reduced, while the porosity of the bread increased (72.2 to 74.5%). The inclusion of bioactive compounds from partially defatted walnut meal in bread increased the overall amount of phenolic compounds, from 0.09 to 2.20 μg GAE/100 g product. Following the sensory analysis, all samples have specific positive characteristics, very well defined, without defects with a total acceptability of 4.54 - 4.88. The samples with 2% and 4% partially defatted walnut meal can be recommended to consumers as products with high nutritional value.

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