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## BIOLOGICAL ACTIVITY OF NEW INDOLE DERIVATIVES

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### Abstract:

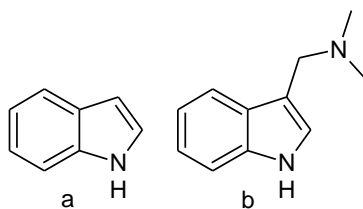
Three groups of indole derivatives were obtained. The first group are the conjugates containing indole and uracil moiety. These derivatives were synthesized by the reaction of indole alkaloid - gramine with appropriate uracil (uracil, 2-thiouracil, 6-methyl-2-thiouracil, thymine, 6-methyluracil and barbituric acid). The second group consisted of triazole-bearing indole derivatives, which were synthesized through a CuAAC procedure and the last group were indole dimers. All compounds were screened for their protective potency against oxidative haemolysis of human erythrocytes induced by free radicals generated from 2,2'-azobis(2-methylpropionamide) dihydrochloride (AAPH).

### Keywords:

*indole, gramine, click chemistry, antioxidant activity, haemolysis*

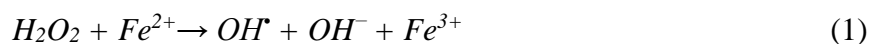
### Introduction

Indole (2,3-benzopyrrole) (Fig. 1), an organic chemical compound, is present in many natural compounds of plant origin (strychnine, lysergic acid). The structure of indole also occurs in one of an exogenous amino acid – tryptophan, which is a component of many proteins and precursor of important neurotransmitters serotonin and melatonin. Indol and its derivatives have various biological activity. For example, lysergic acid *N,N*-diethylamide (LSD), is a very famous psychotropic agent, while melatonin coordinates the circadian rhythm in mammals [1-3]. Indole compounds are also very effective antioxidants protecting lipids and proteins against oxidative stress, induced by an increased level of reactive oxygen species (ROS) [4].



**Fig. 1. The structure of indole (a) and gramine (b)**

Free radicals are very reactive species with unpaired electrons. They are intermediates in many oxidation chain reactions; for example, the reaction described by Fenton, where the hydroxyl radical is formed in the reaction of hydrogen peroxide with  $Fe^{2+}$ .



The  $Fe(III)$  ions, formed in the Fenton reaction, catalyzes the reaction of regeneration of  $Fe(II)$  ions.



Free radicals take part in many important chemical processes, including those in the human body. Under physiological conditions these processes are under the strict control of the organism, due to enzymatic and non-enzymatic defence mechanisms. The intensified generation of reactive oxygen species (ROS) in cells may lead to DNA damage or cell death through apoptosis or necrosis. There is more and more discussion about iron metabolism's in the formation of oxidative stress in the nervous system in the course of neurodegenerative diseases such as Parkinson's and Alzheimer's diseases. Studies indicate that excessive iron accumulation is associated with an increased risk of diabetes type 1 and type 2. Iron accumulation in metabolically active  $\beta$  cells of the pancreas is particularly harmful and leads to increased hydrogen peroxide production in the mitochondria. Hydrogen peroxide in reaction with iron ions gives reactive oxygen species formed directly in the Fenton reaction and cause the excessive secretion of insulin. The use of iron chelators could probably reduce the problem of excessive formation of free radicals in the body. The chelating compound must stabilize the ion not to be oxidized by hydrogen peroxide and reduced by common reducing agents [5, 6].

Gramine, 3-(dimethylaminomethyl)indole (Fig. 1) is a natural chemical compound belonging to the indole alkaloids. It occurs mainly in barley (*Hordeum vulgare*) and sugarcane. This alkaloid has broad physiological activity. It causes the relaxation of the bronchi's smooth muscles, increases blood pressure and relieves symptoms of bronchitis and asthma. It also plays an important role in the metabolism of amino acids. Due to its structure (mainly to the presence of an indole ring system), gramine is used to synthesize compounds with potential therapeutic properties, including antibacterial, antiviral, anticancer and inhibiting the work of protein kinases [2, 7, 8].

Uracil is one of the pyrimidine nitrogenous bases included in the RNA nucleotides. This compound and its derivatives exhibit a wide range of biological activities, such as antiviral and anticancer properties, which is why they are significant in drug discovery [9].

Click chemistry is highly effective chemoselective and the stereospecific method of synthesizing chemical compounds known as copper (I) - catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC). The reaction of azide and terminal alkyne, involving Cu (I) ions leads to the selective formation of di-substituted (at the N1 and C4 positions) triazoles. The click reaction takes place in a short time and under mild conditions, and the formation of the 1,2,3-triazole ring gives stability to the molecule of product. Reactions based on click chemistry can be a powerful tool for combining diverse molecular fragments [2, 10-14].



## Experimental

Gramine-uracil conjugates (compounds 2-8) were synthesized according to [9]. Triazole-bearing gramine derivatives (compounds 9-12) and compounds 21a and 21b were obtained according to [15].

### Synthesis of compounds 19 and 20

An appropriate azide (1 mmol of 21a; for compound 19 and 0.24 mmol of 22a, for compound 20) was dissolved in mixture of  $\text{CH}_2\text{Cl}_2$  /  $\text{H}_2\text{O}$  (1:1; 5 mL). Then I3C 3-propargyloxy ether (21b), (1.2 mmol; compound 19) or phenylacetylene (0.72 mmol; compound 20) was added. The mixture was stirred at room temperature for 15 minutes. Suspension of  $\text{CuSO}_4 \times 5\text{H}_2\text{O}$  (3 mg) and sodium ascorbate (9 mg) in distilled water was added to the mixture. The mixture was stirred at room temperature for 24 h. Upon completing the reaction, the mixture was extracted with diethyl ether (3 x 15 mL). The combined organic layer was washed with water (3 x 50 mL) and brine (100 mL), dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated under reduced pressure. The crude product was purified over column chromatography using gradient elution, starting from eluent toluene/ethyl acetate 100:1, finishing on a 5:1 ratio.

### Synthesis of compound 21a and 21b

Compound 21a was synthesized according to [15].

### Synthesis of compound 22a

Gramine (1 mmol) and phthalimide (1 mmol) was dissolved in dry DMF (10 mL). The mixture was heated at the reflux temperature for 18 h. On completion of the reaction, the mixture was extracted with diethyl ether (3 x 30 mL). The combined organic layer was washed with water (3 x 50 mL) and brine (100 mL), dried (KOH) and concentrated under reduced pressure. The obtained solid was crystallized from ethanol.

### Synthesis of compound 22b

Derivative 22a (0.54 mmol) was dissolved in toluene (5 mL). Then the Na OH (50% v/v, 1 mL) was added. After 15 minutes TBAB (0.6 mmol) and 1,3-dibromopropane (0.6 mmol) was added. The mixture was stirred at room temperature for 24 h. On completion of the reaction, the mixture was extracted with diethyl ether (3 x 30 mL). The combined organic layer was washed with water (3 x 50 mL) and brine (100 mL), dried (KOH) and concentrated under reduced pressure. Obtained products were separated over column chromatography using gradient elution, starting from eluent toluene/ethyl acetate 100:1, finishing on a 5:1 ratio.

### Synthesis of compound 22c

Compound 22b was dissolved in acetone (3 mL), then sodium azide, dissolved in 3 mL of distilled water was added. The mixture was stirred at room temperature for 24 h. On completion of the reaction, the mixture was extracted with diethyl ether (3 x 15 mL). The combined organic layer was washed with water (3 x 50 mL) and brine (100 mL), dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated under reduced pressure.



## Biological assay

### Fe<sup>3+</sup> reducing power assay

Reducing power was determined by the direct reduction of Fe<sup>3+</sup>(CN)<sub>6</sub><sup>-</sup> to Fe<sup>2+</sup>(CN)<sub>6</sub><sup>-</sup>, and determined by measuring absorbance resulted from the formation of the Perl's Prussian Blue complex following the addition of excess ferric ions (Fe<sup>3+</sup>). 0.05 mg/mL concentration of compounds tested in 0.06 mL of distilled water were gently mixed with 0.1 mL of 0.20 MPBS (pH 6.6) and 0.1 mL of 1% potassium ferricyanide [K<sub>3</sub>Fe(CN)<sub>6</sub>]. Trolox® and BHT were used as the reference compounds. The samples were vortexed and incubated for 20 min at 50 °C. Following incubation, 0.1 mL of 10% trichloroacetic acid was added to the samples to acidify the reaction medium. Finally, 0.040 mL 0.6M FeCl<sub>3</sub> was added to the medium and the absorbance (Abs) was measured at 700 nm in a spectrophotometer. The increase in the reaction medium's absorbance value corresponded to a more effective reduction capability of the compound tested. Each sample was made in triplicate, and three independent experiments were performed.

### Ferrous ions (Fe<sup>2+</sup>) chelating activity

Ferrous ions (Fe<sup>2+</sup>) chelating activity was evaluated by inhibition of the formation of Fe<sup>2+</sup>-ferrozine complex after incubation of the compounds tested with Fe<sup>2+</sup>. The Fe<sup>2+</sup>-chelating ability of compounds tested was determined by the ferrous ion-ferrozine complex's absorbance at 562 nm. In brief, 0.05 mg/mL concentration of the compounds tested in 0.2 mL ethyl alcohol were added to a solution of 0.6 mM FeCl<sub>2</sub> (0.05 mL). EDTA was used as the standard metal chelator. The reaction was started by adding 5mM ferrozine (0.05 mL) in ethyl alcohol and shaken vigorously immediately. The samples were stored for 10 min at room temperature. Following incubation, the absorbance (Abs) of the solutions was measured at 562 nm in a spectrophotometer. The percentage of inhibition of ferrozine Fe<sup>2+</sup> complex formation was calculated using the equation (3):

$$Fe^{2+} \text{ chelating effect (\%)} = [1 - (Abs_1) / Abs_0] \times 100 \quad (3)$$

where:

*Abs*<sub>0</sub> - the absorbance of the sample without the tested compound;

*Abs*<sub>1</sub> - the absorbance in the presence of compound tested.

Each sample was made in triplicate and three independent experiments were performed.

### DPPH<sup>•</sup> free radical scavenging activity

In brief, 0.1 Mm solution of DPPH<sup>•</sup> was prepared in ethyl alcohol and 0.2 mL of this solution was added to 0.2 mL of compound tested at 0.05 mg/mL concentration in ethyl alcohol and vortexed. Trolox® and BHT were used as the reference compounds. The samples were incubated in the dark for 30 min at room temperature. Following incubation, the absorbance (Abs) was measured at 517 nm in a spectrophotometer. The percent DPPH<sup>•</sup> scavenging effect was calculated using the equation (4):

$$DPPH\bullet \text{ scavenging activity (\%)} = [(Abs_0 - Abs_1) / Abs_0] \times 100 \quad (4)$$

where:

$Abs_0$  - the absorbance of the control reaction without compounds tested;

$Abs_1$  - the absorbance in the presence of compounds tested.

Each sample was made in triplicate and three independent experiments were performed.

### Erythrocyte preparation

Freshly human erythrocytes suspensions were obtained from the blood bank. The erythrocytes were washed three times (3000 rpm, 10 min, +4 °C) in 7.4 pH phosphate buffered saline (PBS-137 mM NaCl, 2.7 mM KCl, 10 mM NaHPO<sub>4</sub>, 1.76 mM KH<sub>2</sub>PO<sub>4</sub>) supplemented with 10mM glucose. After washing, cells were suspended in the buffer at  $1.65 \times 10^9$  cells/mL, stored at +4 °C and use within 5 h.

### Haemolysis assay

RBC ( $1.65 \times 10^8$  cells/mL, ~1.5% haematocrit) were incubated in PBS (7.4 pH) supplemented with 10 mM glucose and containing derivatives tested at concentration equal to 0.1 mg/mL for 60 min at 37 °C in a thermo-shaker. Samples with RBC incubated in PBS without compounds tested were taken as the controls. Each sample was repeated three times, and the experiments were repeated three times using RBC from different donors. After incubation, the RBC suspensions were centrifuged (3000 rpm, 10 min, 4 °C), and the degree of haemolysis was estimated by measuring the absorbance of the supernatant at 540 nm. The results were expressed as the percentage (%) of haemolysis. Haemolysis 0% was taken as the absorbance of the supernatant of erythrocyte suspensions in PBS only, while the total haemolysis (100%) was determined when PBS was replaced by distilled water.

### Inhibition of the free-radical-induced haemolysis

RBC ( $1.65 \times 10^8$  cells/mL, ~1.5% haematocrit) were pre-incubated in PBS buffer (pH 7.4) supplemented with 10 mM glucose, and containing derivatives at the concentration equal to 0.1 mg/mL for 20 minutes at 37 °C in a shaking water bath. After pre-incubation, the standard free radicals inducer 2,2'-azobis(2-methylpropionamide) dihydrochloride (AAPH) were added to get the final concentration equal to 60 mM. Samples were incubated for the next 4 hours at 37 °C in a thermo-shaker. RBC incubated in PBS only and in the presence of AAPH, were taken as a control. After incubation, the RBC suspensions were centrifuged (3000 rpm, 10 min, 4 °C), and the degree of haemolysis was determined by measuring the absorbance values (Ab) of the supernatants at 540 nm. The percentage of oxidative haemolysis inhibition was calculated using the following equation (5):

$$\text{Inhibition of haemolysis (\%)} = 100 - [(Abs_{\text{sample}} - Ab_{\text{blank}} / Ab_{\text{control}} - Ab_{\text{blank}})] \times 100 \quad (5)$$

where:

*Absample* - the absorbance value of supernatant obtained from samples incubated with compounds tested;

*Abblank* - the absorbance of the supernatant obtained from samples without compounds tested and without AAPH;

*Abcontrol* - the absorbance of the supernatant obtained from samples with AAPH and in the absence of compound tested.

Each sample was repeated three times, and the experiments were repeated three times using RBC from different donors.

## Results and discussion

### Antioxidant properties

The antioxidant properties of the gramine-uracil conjugates have been investigated by evaluation of the DPPH scavenging activity, ferrous ions ( $\text{Fe}^{2+}$ ) chelating activity and total reducing ability determination by  $\text{Fe}^{3+}/\text{Fe}^{2+}$  transformation. These methods are commonly used in antioxidant tests. DPPH• is a stable free radical with a delocalized electron which yields a strong absorption maximum at 517 nm. The absorption decreases after pairing the electron in the presence of a free radical scavenging antioxidant or hydrogen donor [16]. Among the all tested gramine-uracil conjugates, the best results in the DPPH test were obtained for compounds 3 (16.64 %), 4 (16.93 %) and 8 (21.79 %). For comparison, this activity for reference antioxidants was for Trolox® 52.57 % and BHT 38.85 %.  $\text{Fe}^{3+}$  reducing power of compounds relates to the electron donation capability. Compounds 3 and 4 exhibits the highest reducing power: 83% and 53% of Trolox®, respectively. As we mentioned before, there is a correlation between free radicals and iron ( $\text{Fe}^{2+}$ )-induced oxidative stress in the pathogenesis of Parkinson's and Alzheimer's diseases [17]. Therefore, chelating a metal ion inhibits the formation of ROS [18]. Compounds 3, 4, and 5 exhibited the highest chelating activity (23.52 %, 13.31 %, and 28.6 %, respectively).

### Protective activity of compounds on oxidative stress-induced haemolysis and their effects on the RBC membrane structure

AAPH (2,2'-azo-bis(amidinopropane) dihydrochloride) is the most commonly used source of free radicals in a hydrophilic environment. The cytoprotective effects of all compounds against (AAPH)-induced oxidative haemolysis of human erythrocytes were estimated *in vitro*. All gramine-uracil conjugates showed cytoprotective activity in the range of 73-93 %. Moreover, compounds 2 and 3 were more effective than Trolox®. This activity can be explained by the stabilizing effect of indole derivatives on the human erythrocyte membrane structure. Among the triazole derivatives, only compounds 9 and 11 showed protective properties against free radicals generated by AAPH. The cytoprotective activity of derivative 11 is comparable to the Trolox® and were approximately 80%, while derivative 9 exhibited a higher protective effect against oxidative

haemolysis than the standard and was over 90 %. Compounds 10 and 12 showed no protective activity. In diindole compounds, only compound 13 has a protective activity of ~60%.

Haemolysis is a degradation of red blood cells and release the hemoglobin from their inside. Normal erythrocytes are in the shape of a discocyte (biconcave disk). Discocyte, stomatocyte and echinocyte are considered to be the physiological shapes of erythrocytes. Erythrocytes' ability to transform between these shapes aims to protect them from being destroyed by echinocytogenic factors (e.g. high ionic strength, alkaline pH) or stomatocytogenic factors (e.g. hypotonic solution, acidic pH). These transformations take place in healthy red blood cells and are reversible [19, 20]. Erythrocytes shapes are presented in the Fig. 2.

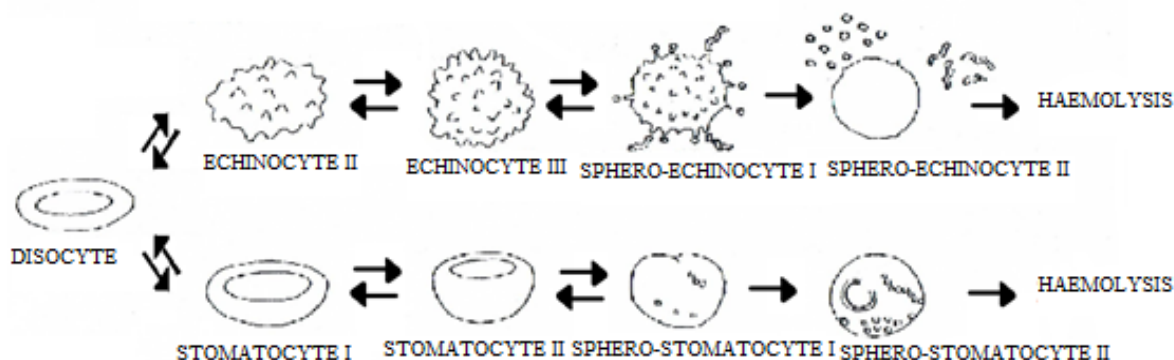
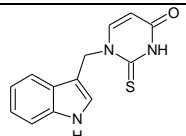
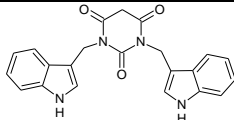
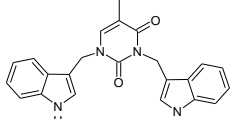
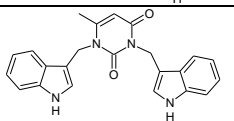
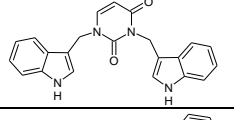
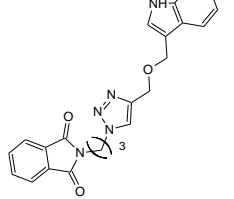
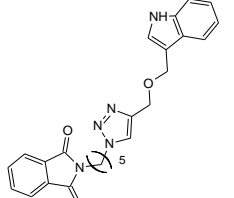
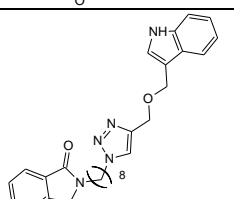
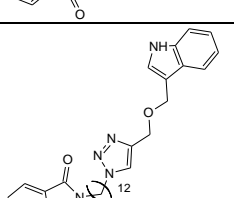
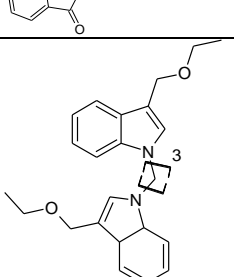


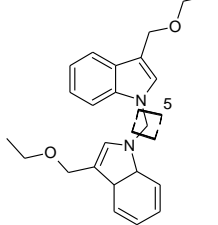
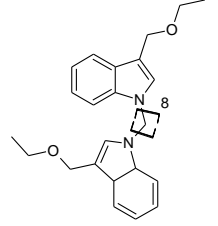
Fig. 2. Erythrocytes shapes  
Source: [2]

Gramine and its uracil derivatives did not involve modification in the RBC membrane permeability. Compounds 9 and 11 induce stomatocytosis and echinocytosis, after 60 min incubation/ Therefore their high protective effect may result from the specific penetration of these compounds into the erythrocyte membranes [9, 15]. All results are presented in Tab. 1.

Tab. 1 Antioxidant properties of compounds 1-17

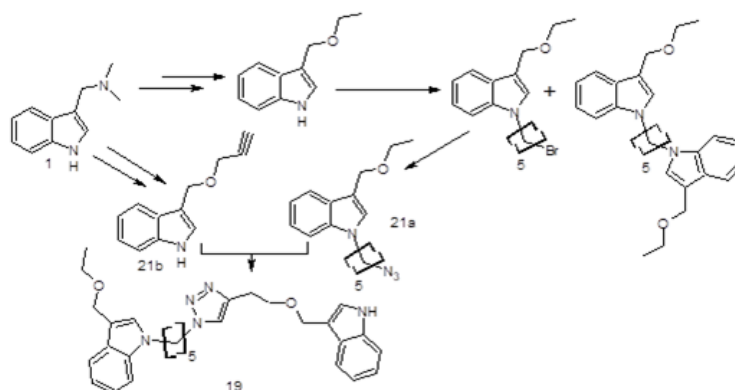
| Comp.         | The structure of compound | Haemolytic activity (%) 1h | Haemolytic activity (%) 24h | Dominate cell shape | Antiradical activity [AA%] | Reducing Power [Ab ] | Chelating activity [%] | Protective activity against AAPH [%] |
|---------------|---------------------------|----------------------------|-----------------------------|---------------------|----------------------------|----------------------|------------------------|--------------------------------------|
| Control (PBS) | -                         | 0-2                        | 2-3                         | D/DE                | 0.0                        | 0.622                | 0.0                    | 0.0                                  |
| 1             |                           | 0-2                        | 2-3                         | D/DE                | 3.75                       | 0.714                | 81                     | 47.14                                |
| 2             |                           | 0-2                        | 2-3                         | D/DE                | 0.0                        | 0.695                | 8.80                   | 93.5                                 |
| 3             |                           | 2-4                        | 3-5                         | S/DE                | 16.64                      | 1.830                | 23.52                  | 92.33                                |

|    |   |      |     |      |       |       |       |       |
|----|---|------|-----|------|-------|-------|-------|-------|
| 4  |    | 2-4  | 3-5 | S/DE | 16.93 | 1.177 | 13.31 | 89.5  |
| 5  |    | 2-4  | 5-7 | S/DE | 3.93  | 0.752 | 28.6  | 86.9  |
| 6  |    | 2-5  | 5-7 | S/DE | 0.0   | 0.782 | 4.43  | 85.5  |
| 7  |    | 2-3  | 3-5 | DE   | 0.0   | 0.832 | 0.0   | 82.00 |
| 8  |    | 2-5  | 5-7 | S/DE | 21.79 | 1.052 | 0.0   | 73.17 |
| 9  |   | 1.02 | -   | D/DE | -     | -     | -     | 93    |
| 10 |  | 1.38 | -   | DE/E | -     | -     | -     | -     |
| 11 |  | 1.26 | -   | S    | -     | -     | -     | 85    |
| 12 |  | 6.40 | -   | S    | -     | -     | -     | -     |
| 13 |  | 2.08 | -   | D/DE | -     | -     | -     | 57    |

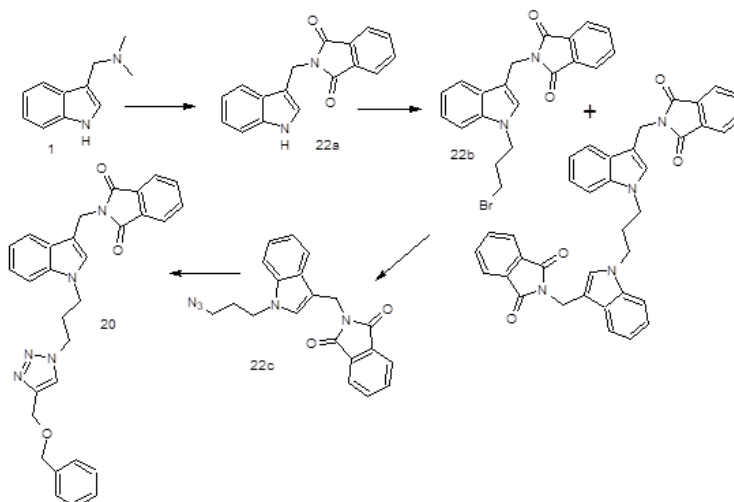
|    |   |      |   |      |       |       |       |       |
|----|---|------|---|------|-------|-------|-------|-------|
| 14 |  | 2.47 | - | D/DE | -     | -     | -     | 2,5   |
| 15 |  | 1.80 | - | D/DE | -     | -     | -     | 3     |
| 16 | Trolox®   | -    | S | D/DE | 52.57 | 2.209 | -     | 87.72 |
| 17 | BHT   | -    | S | D/DE | 38.85 | 1.242 | -     | 41.33 |
| 18 | EDTA  | -    | - | -    | -     | -     | 97.11 | -     |

Source: [9] compounds 1-8, [15] compounds 9-15

Schemes of synthesis compounds 19 and 20 are presented in Figs. 3 and 4.



**Fig. 3. Synthesis of derivative 19**



**Fig. 4. Synthesis of derivative 20**

## Conclusions

Most of newly obtained gramine derivatives exhibit good antioxidant and cytoprotective activity. High antioxidant potential displayed by compounds 3 and 4 can be explained due to the presence of the sulphur atom in their structures. Among the triazole derivatives, only compounds 9 and 11 show protective activity against free radicals generated by AAPH. All gramine-uracil conjugates and compounds 9 and 11 could be taken into account as the antioxidant and cytoprotective agents in the future studies.

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## TESTING THE OXIDATION STABILITY OF DIESEL FUELS

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### **Abstract:**

The paper discusses the issues related to the aging of diesel fuels during their storage. The aim of the research was the oxidation stability of diesel fuels taken at various stages of the fuel logistics chain: from refineries, through fuel bases to fuels and the consumer. Samples previously prepared for baseline parameters were subjected to tested tests for heat, water and anger for 16 weeks. The PetroOxy device was used to determine a significant parameter, i.e. oxidation stability, according to PN-EN 16091: 2011. The final result is the conclusion that fuel oxidation degrades fuel in-service testing.

### **Keywords:**

*oxidation stability, oxidation, PetroOxy*

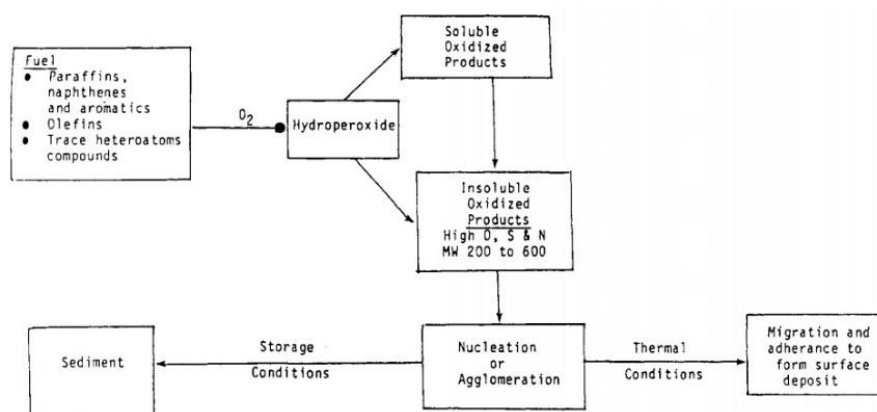
### **Introduction**

Another year in which we are dealing with the SARS-CoV-2 pandemic forces remote work. Due to the fact that people use passenger cars more often than public transport, more attention is paid to the quality of fuels. A recent event, which was the discussion forum "On monitoring and controlling the quality of fuels, biofuels, LPG and CNG" created by the Polish Chamber of Liquid Fuels, showed that we are still dealing with the problem of not meeting the quality requirements in terms of oxidation stability of diesel oils [1]. The Office of Competition and Consumer Protection (UOKiK), as an institution monitoring the quality of products, including fuels, operates on the basis of the Act of August 25, 2006 on the fuel quality monitoring and scrutinizing system. In the first half of 2020, compared to the first half of 2019, there was a deterioration in the quality of diesel oil at stations selected by the Office of Competition and Consumer Protection, as well as an increase in the number of diesel fuel samples whose requirements were not met by the parameter - oxidative stability (oxidation stability). The number of inspected diesel oil samples that do not meet the quality requirements in accordance with the Regulation of the Minister of Economy of October 9, 2015. on the quality requirements for liquid fuels in the first half of 2020 amounted to about 4% - which, compared to the results of engine gasoline, is a value four times higher.

Fuel aging is defined as any changes that have occurred in the fuel, as a result of which we deal with irreversible deterioration of its operational properties, mainly due to the action of oxygen from air, light and heat. There are many terms for aging, but the best definition is "change over time, which

reduces the performance of the fuel below the level usually called "usable" [2]. Fuel aging is a complex process. One of the elements of this process is the direct action of oxygen from the air. Additional elements determining the aging process are both internal factors directly related to the chemical composition of diesel fuels, as well as external factors, including: water content, heat, oxygen from the air, location of the tank, type of tank roof, weather conditions, stored fuel volume, antioxidant additives, multiple storage operations, catalytic action of metals, etc. [3].

A direct process related to the aging of fuels is the oxidation process, i.e. a chemical reaction consisting in the donation of an electron by an ion, atom or a group of atoms, as a result of which the degree of oxidation of the ion donating element is increased [4]. Thus, the term oxidation stability is a measure of the tendency of diesel fuel to react with oxygen at around room temperature. Each fuel has its own oxidation mechanism, however Taylor and Frankenfeld attempted to explain the general process of fuel stability [5] (Fig. 1).



**Fig. 1. The overall process of fuel stability**  
Source: [5]

Oxidation stability is very important from the point of view of the use of motor vehicles. This parameter has a significant impact on both the operation of the vehicle and the service life of its many components. Diesel fuel that does not meet the quality requirements in terms of oxidation stability during storage, especially when it takes place in the summer, undergoes rapid oxidation. During the oxidation of fuels, the following are formed: alcohols, organic acids, ethers, ketones, oligomers, and resins and sediments precipitate.

Contaminants and deposits in the fuel [Tab. 1] contribute to the accelerated wear of parts that come into contact with diesel fuel, and may even lead to their damage. First of all, they can block the injectors or the fuel filter, which leads to a deterioration in engine performance and the quality of the sprayed diesel fuel. An additional effect can be noisy engine operation, excessive exhaust emissions, poor driving characteristics. Due to the increasing number of problems with blocking fuel filters, a test determining the propensity of fuels to block the filter (ASTM D 2068) has been introduced. A measure of this trend is a dimensionless indicator called FBT. It is calculated according to the formulas included in the standard. They depend on the amount of filtered fuel and the pressure in the filtration system.

**Tab. 1. Diesel contaminations sources**

| Types of contamination  |   |   |  |
|---|---|---|--|
| Outside   |   |   | Inside   |
| Production  | Distributive  | Operating   |  |
| Petroleum (sulfur and sulfur compounds not removed in production) | Dust particles getting through the respiratory system from the air to storage tanks at fuel depots, cisterns and cars during their refueling and emptying |   | Self-oxidation products, thermal oxidation and pyrolysis of diesel fuel components |
| Coming from technological installations                           | From the outer surfaces of storage tanks  | Corrosion and wear products of tanks and diesel fuel supply system components |  |
|   | From the internal surfaces of railroad and road tankers, pipelines - corrosion products   |   |  |

Source: Own source

Tests aimed at checking the oxidation stability of various operating fluids and the conditions in which fuel can be stored for longer are still being carried out. The following tests were also aimed at checking the influence of various factors on the oxidation stability of the prepared samples.

## Research

Samples for testing (diesel oil) taken from various points in the fuel logistics chain were prepared for testing by filtering and removing water. Mixtures of base diesel fuel with biofuel (2%, 7% and 10%) were made (Fig. 2). The oxidation stability of both fresh and aged samples was tested under laboratory conditions. The aging was carried out by subjecting the samples to the action of oxygen by:

- 16 weeks of storage (Fig. 3),
- 16 weeks of storage in the presence of light and water (Fig. 4).

The following types of diesel fuel samples were tested:

- Base diesel fuel taken from a refinery (BON),
- Diesel oil taken from the fuel base (ON BP),
- Commercial diesel fuel from petrol stations (ON SP),
- Rapeseed oil fatty acid methyl esters (RME).



**Fig. 2. Fresh samples used for testing**

1 - BON, 2 - ON BP, 3 - ON SP, 4 - 98% BON + 2% RME, 5 - 93% BON + 7% RME, 6 - 90% BON + 10% RME

Source: Own source



**Fig. 3. Diesel and RME samples aged for 16 weeks**

7 – BON (16 weeks), 8 – ON BP (16 weeks), 9 – ON SP (16 weeks), 10 – 98% BON + 2% RME (16 weeks),  
11 – 93% BON + 7% RME (16 weeks), 12 – 90% BON + 10% RME (16 weeks)

Source: Own source



**Fig. 4 The appearance of samples aged with the action of light and the content of 2% water**

13 – BON (16 weeks + H<sub>2</sub>O + sun), 14 – ON BP (16 weeks + H<sub>2</sub>O + sun), 15 – ON SP (16 weeks + H<sub>2</sub>O + sun),  
16 – 98% BON + 2% RME (16 weeks + H<sub>2</sub>O + sun), 17 – 93% BON + 7% RME (16 weeks + H<sub>2</sub>O + sun),  
18 – 90% BON + 10% RME (16 weeks + H<sub>2</sub>O + sun)

Source: Own source

In order to check the changes in parameters that occurred during the forcing of the aging process, fresh (Tab. 2) and aged samples were tested in accordance with the standards of the following parameters:

- impurity content [6],
- kinematic viscosity at 40°C [7],
- flash point [10],
- density at 15°C [8],
- cloud point [11],
- cold filter plugging point [9],
- oxidative stability at 140°C.

**Tab. 2. Selected basic parameters of fuels used for research**

| Lp. | Parameter  | Unit               | BON    | ON BP  | ON SP             | RME    | According to the standard |
|-----|--|--------------------|--------|--------|-------------------|--------|---------------------------|
| 1.  | Content of fatty acid methyl esters                | %(m/m)             | < 7.0  | < 0.5  | < 7.0             | 97.1   | max. 7.0                  |
| 2.  | Total impurity content                             | mg/kg              | < 24   | < 12   | < 12              | 3.33   | max. 24                   |
| 3.  | Sulfur content                                     | mg/kg              | < 10.0 | 6.7    | 5.9               | < 10.0 | max. 10.0                 |
| 4.  | Cetane number                                      | -                  | > 51.0 | 51.4   | 51.5              | > 51   | min. 51.0                 |
| 5.  | Investigation of corrosive action on copper plates | class              | 1      | 1      | 1                 | 1      | max. 1                    |
| 6.  | Oxidative stability at 140 °C                      | min.               | 82.89  | 103.09 | 89.99             | 26.14  | -                         |
| 7.  | Density at 15 °C                                   | kg/m <sup>3</sup>  | 832.7  | 832.0  | According to Norm | 882.9  | 820.0 – 845.0             |
| 8.  | Kinematic viscosity at 40 °C                       | mm <sup>2</sup> /s | 2.67   | 2.618  | 2.505             | 4.42   | 2.000 – 4.500             |
| 9.  | Flash point closed cup method                      | °C                 | 64.7   | 64.0   | 63.5              | > 120  | min. 55                   |
| 10. | Cold Filter Plugging Point                         | °C                 | -4.5   | - 29   | -29               | -15    | max. -20                  |
| 11. | Cloud point  | °C                 | -4.1   | - 9    | -8                | -5     | -                         |

**Source: Laboratory decisions / own parameter tests**

## Findings

The oxidation stability test was carried out using the PetroOxy device according to PN-EN 16091: 2011 "Liquid petroleum products - Fuels and mixtures from middle petroleum distillates and fatty acid methyl esters (FAME) - Determination of oxidative stability by the method of fast oxidation on a small scale" [6]. A test sample of 5 ml is exposed to an elevated temperature of 140 °C and a pressure of 1000 kPa. The measuring chamber of the device with the tested sample is initially twice filled with oxygen to a pressure of 700 kPa, and then heating of the sample is started. The increase in temperature leads to the pressure increase to approx. 1000 kPa. The test continues until we notice a pressure drop of 10% in relation to the maximum value. The pressure reduction is directly related to the oxidation of the sample. The test result is the time in which the sample was exposed to the forcing factors until the pressure dropped by 10% of the maximum value. The result is given in minutes. During the test, a graph of pressure versus test time is created.

The parameter described in the Tab. 6 should be read as follows: the shorter the oxidation time of the samples in the PetroOxy device, the lower the oxidation stability and, therefore, the suitability of the fuel for storage.



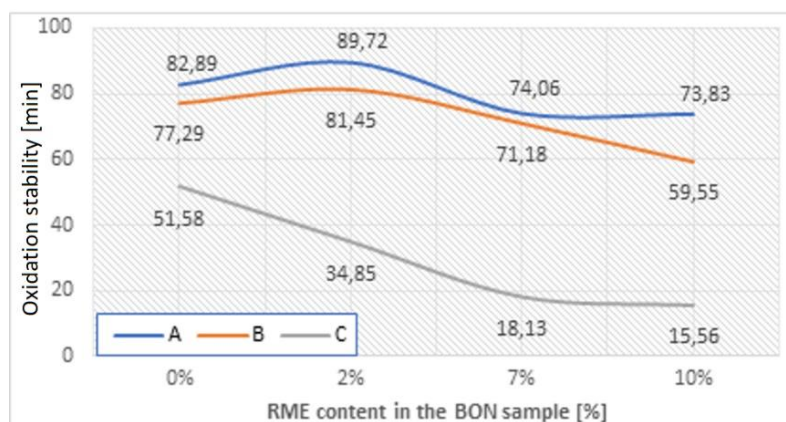
**Tab. 3. Test results of selected parameters of samples of tested fuels after 16 weeks of aging**

| Sample | Contaminants [mg/dm <sup>3</sup> ] | Oxidation stability [min] | Flash-Point [°C] | Cold Filter Plugging Point [°C] | Cloud Point [°C] | Kinematic viscosity 40°C [mm <sup>2</sup> /s] | Density 15°C [kg/m <sup>3</sup> ] |
|--------|------------------------------------|---------------------------|------------------|---------------------------------|------------------|---|-----------------------------------|
| 1.     | Contains no content                | 82.89                     | 64.7             | -4.5                            | -4.1             | 2.67  | 832.7                             |
| 2.     |                                    | 103.09                    | 65.3             | -28.5                           | -10.1            | 2.58  | 833.2                             |
| 3.     |                                    | 89.99                     | 62.7             | -29.0                           | -9.4             | 2.59  | 834.3                             |
| 4.     |                                    | 89.72                     | 64.7             | -8.0                            | -3.7             | 2.83  | 833.1                             |
| 5.     |                                    | 74.06                     | 65.3             | -8.5                            | -2.8             | 2.85  | 833.8                             |
| 6.     |                                    | 73.83                     | 65.7             | -8.0                            | -2.6             | 2.92  | 837.1                             |
| 7.     | 0.9                                | 77.29                     | 62.0             | -5.0                            | -4.5             | 2.69  | 828.2                             |
| 8.     | 4.2                                | 98.13                     | 64.0             | -27.0                           | -10.2            | 2.57  | 829.2                             |
| 9.     | 5.7                                | 89.56                     | 62.0             | -27.0                           | -9.8             | 2.59  | 830.4                             |
| 10.    | 5.6                                | 81.45                     | 63.5             | -8.0                            | -3.7             | 2.83  | 829.2                             |
| 11.    | 6.3                                | 71.18                     | 65.0             | -9.0                            | -3.1             | 2.90  | 831.7                             |
| 12.    | 7.3                                | 59.55                     | 65.5             | -8.0                            | -3.1             | 2.91  | 833.2                             |
| 13.    | 10.3                               | 51.58                     | 63.5             | -5.0                            | -4.4             | 2.72  | 828.5                             |
| 14.    | 18.1                               | 42.19                     | 64.0             | -27.0                           | -10.3            | 2.60  | 829.4                             |
| 15.    | 16.4                               | 21.46                     | 64.0             | -28.0                           | -9.1             | 2.63  | 830.7                             |
| 16.    | 20.1                               | 34.85                     | 64.0             | -6.0                            | -4.0             | 2.88  | 829.5                             |
| 17.    | 29.5                               | 18.13                     | 65.0             | -7.5                            | -3.7             | 2.93  | 832.0                             |
| 18.    | 32.9                               | 15.56                     | 64.5             | -8.0                            | -4.0             | 2.95  | 833.5                             |

Source: Own source

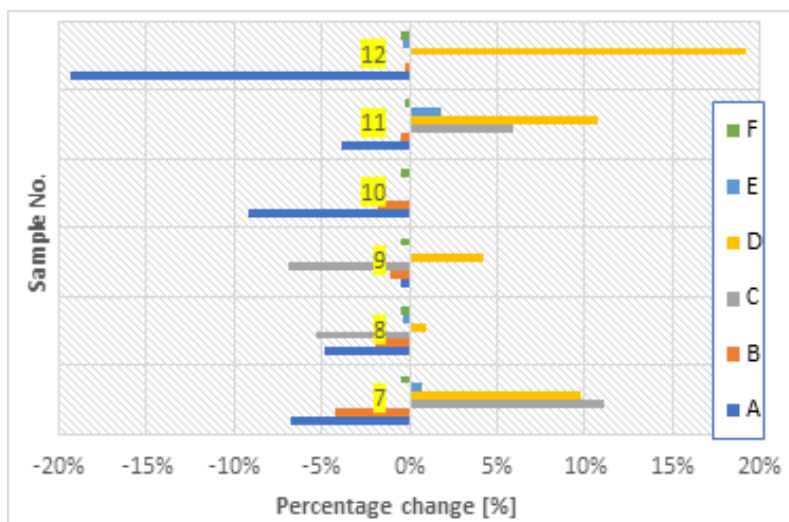
The tests of aging of fuel samples showed that the sample of diesel fuel taken from the fuel base had the highest oxidation stability and the smallest sample no. 18 (exposed to oxygen and containing 2% of water). The content of methyl esters of rapeseed oil fatty acids in a mixture with diesel fuel significantly deteriorates the oxidation stability.

As can be seen in the graph (Fig. 5) for the aged BON and BON samples, the 2% biofuel content slightly increases the oxidation stability. Increasing the RME content above 2% causes a significant decrease in the oxidation time of the samples.



**Fig. 5. Changes in oxidation stability depending on the RME content in the BON sample**  
A – Fresh BON samples, B – 16 weeks BON samples, C – 16 weeks BON samples + sun + 2% water  
Source: Own source

By analyzing the graph below (Fig. 6), for most of the samples, slight changes in parameters such as: flash point, density at 15 °C, kinematic viscosity at 40 °C are clearly visible. However, from samples subjected only to the aging process, sample no. 7 showed the largest percentage changes in the value of the density parameter. The differences in the cloud point between fresh and aged samples were the greatest for sample no. 12, and for sample no. 10. and 7, the aging considerably affected the deterioration of the low temperature parameter. It can therefore be concluded that in total, sample 12 showed the greatest percentage changes in parameters, but sample no.7 had slightly less.



**Fig. 6 Percentage change in the values of the tested parameters in aged samples (No. 7-12) in relation to fresh samples**

**A – Oxidation stability, B – Flash point, C – Cold filter plugging point, D – cloud point, E – kinematic viscosity, F – Density.**

**Source: Own source**

Samples exposed to light and with a water content of 2% for a period of 16 weeks show significantly greater changes in the parameters tested. As can be seen, the greatest cumulative percentage changes in parameters were seen for sample 18 (Fig. 7). When analyzing individual parameters, it can be seen that the density at 15 °C, the kinematic viscosity at 40 °C and the flash point changed slightly. Sample No. 18 showed the largest change in the cloud point parameter, and sample No. 15 the smallest.



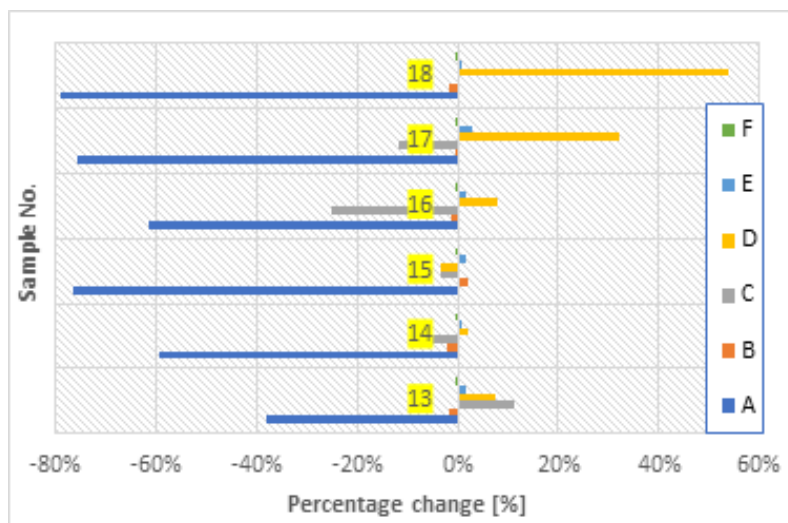


Fig. 7 Percentage change in the values of the tested parameters in aged samples (No. 13-18) in relation to fresh samples

A – Oxidation stability, B – Flash point, C – Cold filter plugging point, D – cloud point, E – kinematic viscosity, F – Density.

Source: Own source

## Conclusions

The obtained results confirm the research cited in the literature section. Based on the research carried out, the following conclusions can be drawn:

1. Light and water have a significant impact on the total amount of sediment produced and the decrease in oxidation stability, which has a negative impact on the stored fuel.
2. Under the influence of water and RME, microorganisms are formed in the sample.
3. Light greatly changes the color of the samples, those containing RME become lighter and the diesel samples darken.
4. The largest amount of sediments was contained in sample no. 18 with water content and access to light, and the least contained in BON placed in a dark place and without water.
5. The most oxidation stability fuel turned out to be the base diesel oil subjected to aging, the least of which was sample no. 18 with water content and access to light.
6. Forced aging does not significantly affect the density at 15 °C, the kinematic viscosity at 40 °C of the test specimens.
7. Forced aging of samples does not significantly affect the following parameters: ignition temperature, cold filter blocking temperature.

## Literature

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## OVERVIEW OF SELECTED PRODUCTION METHODS AND HYDROGEN STORAGE

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### **Abstract:**

Hydrogen economy is one of the important aspects related to the development of the global economy. Hydrogen due to its properties and global resources is a very promising energy carrier. However, the practical use of hydrogen is still underdeveloped. Although there are many methods of production and storage, many obstacles, both technological and administrative, are encountered. Additionally problematic is also the economic aspect, which limits efficient technologies in use because of the high investment costs for installation and subsequent use. The use of renewable energy sources both as a raw material for production and as an energy source in production and storage processes seems to be of key importance in the aspect of the hydrogen economy.

### **Keywords:**

*hydrogen, hydrogen economy, storage, production*

### **Introduction**

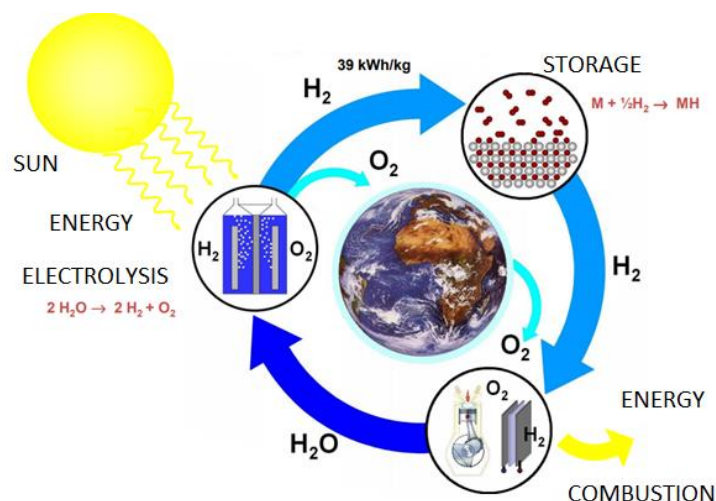
Hydrogen as a fuel is currently at the stage of research and initial introduction into operation in the economy. Yes, there are already technologies that allow the use of hydrogen to power motor vehicle engines, but petroleum fuels are still the main source of energy to power motor vehicle engines. Hydrogen can be a self-contained fuel, and be used as an additive to other types of fuels. It is assumed that the resources of non-renewable energy sources, such as crude oil, may one day run out completely, which forces the necessity to look for other resources allowing for the production of fuels that do not threaten the natural environment. In this case, hydrogen seems to be a perfect example of a medium that can become an energy carrier on a very large scale. It is puzzling, however, why, despite such positive opinions and, as the authors say, "clean energy carrier", hydrogen has not yet dominated the economy by using it as a fuel [1]. According to various sources, it is recognized that hydrogen as a fuel can be used to power road, rail, air and sea transport, but it requires appropriate investment, both technological and financial.

### **Characteristics of hydrogen**

Hydrogen is one of the basic chemical elements with an atomic number equal to 1 and is assigned the symbol "H". Hydrogen is the most abundant element on Earth. Unfortunately, it does not occur

singly, individually, and is practically always associated with other elements. Hydrogen can be obtained from various sources using various methods and techniques.

Hydrogen can exist in three physical states. Most often it is a gas, it is a colorless, odorless, tasteless, non-toxic and flammable gas. Hydrogen occurs on Earth in the form of chemical compounds, most often water and organic compounds. Combined with oxygen in the form of water, it is a non-flammable mixture, but when combined with carbon, it reacts with oxygen, which produces heat and water vapor.



**Fig. 1. Hydrogen life cycle**  
Source: Own study based on [2]

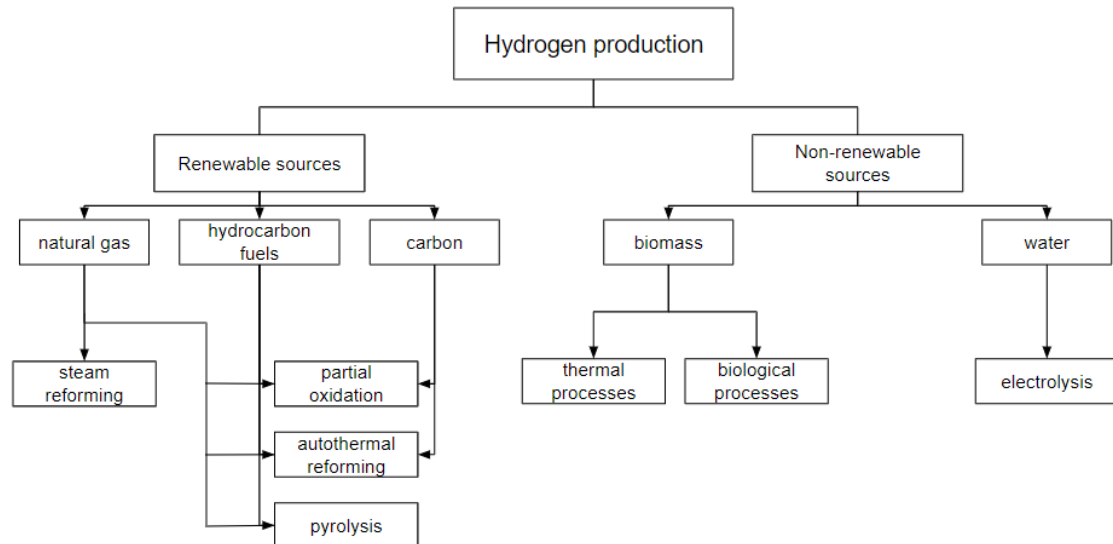
As shown in Fig. 1, the life cycle of hydrogen operates in a closed system. Hydrogen can be taken up from the water. Then, oxygen is separated from it, for example in the electrolysis process. If energy from renewable energy sources is used for the electrolysis process, then the hydrogen production process is ecological, if energy from non-renewable energy sources is used (e.g. burning coal), then hydrogen production cannot be treated as ecological, which translates into immediately to the fact that although the hydrogen itself is eco-friendly can not be so treated. Then the hydrogen is stored in an appropriate manner while maintaining the required environmental conditions. There are several ways to store hydrogen and they will be described below. In a further step, the hydrogen is used to generate energy, where it is combined with oxygen again in the combustion process. The energy is used for certain purposes, while the by-product in this case is water in the form of steam, which can be reused to produce hydrogen. As shown in the diagram in Fig. 1, hydrogen is a renewable energy source, and its resources on Earth are practically infinite.

## Hydrogen production

According to the current state of knowledge, hydrogen can be used in all areas of everyday life, starting from transport, industry, through households, reaching as far as outer space [3]. Its practical application is associated with many aspects and limitations, which to a greater or lesser extent translate into the profitability of using hydrogen in a given area.

Hydrogen production is quite common and there are several methods of greater or lesser-technology, which allow to produce hydrogen, which can then be used to power the engines of motor vehicles. Whether the production of hydrogen will be ecological or not results from the sources of energy to produce hydrogen, which energy is necessary to perform the appropriate production processes. Hydrogen itself should be treated as a renewable element in the entire ecosystem, however, if non-renewable energy sources are used to produce it, then such a product cannot ultimately be treated as an ecological energy source.

As shown in Fig. 2, the basic methods of hydrogen production can be divided into several groups, of which these methods should be first divided depending on whether the raw material used to produce hydrogen comes from fossil fuels or from renewable sources. Currently, the production of hydrogen is mainly made of fossil fuels such as natural gas, crude oil and coal. These fossil fuels account for more than 80% of the raw materials used to produce hydrogen, which proves that hydrogen produced from these raw materials is no longer a green fuel, as it uses non-renewable energy sources. Hydrogen from natural gas is obtained by steam reforming methane, also from crude oil by partial oxidation steam reforming, autothermal reforming and pyrolysis. On the other hand, hydrogen from coal is obtained in the process of coal gasification, which mainly comes from fossil energy sources, but can also come from renewable sources [4]. There are also other pathways for producing hydrogen. It is about the production of hydrogen from renewable sources, biomass and water. These methods are known, but their application is not common and generally used due to a number of technical and technological limitations.



**Fig. 2. Hydrogen production methods**  
Source: Own study

The most common method of producing hydrogen is natural gas steam reforming. This method of production is currently considered the cheapest and most efficient compared to other methods. Due to the fact that this method has been used for several decades, it is highly effective in obtaining hydrogen. Steam Methane Reforming (SMR) is the production of hydrogen and carbon dioxide by treating natural gas or other methane-rich hydrocarbon with steam in the presence of a suitable catalyst (usually nickel) [5]. The effectiveness of this method reported in the literature ranges from

74–85% [4, 6-8]. Obtaining hydrogen in the process of steam methane reforming involves a number of chemical transformations, as a result of which hydrogen, carbon monoxide, carbon dioxide and unreacted methane are obtained.

Another method in which the raw material is fossil fuel is the Partial Oxidation (POX) process. In this reaction, the raw material for hydrogen production may also be methane, as well as fuels, hydrocarbon oils and coal. In the case of this method, the partial oxidation process can be catalytic and non-catalytic, the difference is the temperature at which the process takes place. As a result, you can get 60-75% hydrogen along with carbon monoxide, carbon dioxide, and trace amounts of methane and nitrogen [4-6].

Another way to make hydrogen from fossil fuels is autothermal reforming (ATR). This method is to some extent a combination of SMR and POX processes, where heat is produced by partial oxidation, and steam reforming is responsible for the production of hydrogen, which in effect creates a thermal process from which hydrogen is generated [6]. The efficiency of this process is determined at the level of 60-75% [6, 7].

Another way of producing hydrogen is pyrolysis, in which the hydrocarbons are broken down into carbon and hydrogen. In this method, due to the lack of water and air, no carbon oxides are formed, which directly translates into a reduction in the emission of harmful substances generated in the hydrogen production processes with the previously described methods. Currently, this method is not very popular, although the main advantages include flexibility in the selection of raw materials, simplicity of the process and reduction of carbon oxide emissions. The main disadvantage of this method is the formation of soot and tar as a by-product [4, 7].

The production of hydrogen from renewable energy sources is based on the use of biomass and water as raw materials for production. In the case of biomass, thermal processes such as pyrolysis, gasification, combustion and liquefaction as well as biological processes, which include biophotolysis, dark fermentation and photofermentation, can be used. In the case of water as a raw material, processes such as electrolysis, thermolysis and photoelectrolysis can be used to produce hydrogen [7].

Biomass is nothing more than an organic substance of non-geological origin that can be used to generate energy. Biomass can be solid, liquid and gaseous. Biomass is considered to be wood, plant residues from industry, trade and agriculture, municipal organic waste, agricultural and forestry waste, and plants grown directly to generate energy [9]. One of the thermal processes of producing hydrogen from biomass is pyrolysis. It is defined as a thermochemical technology in which biomass is heated under appropriate pressure without oxygen, which results in obtaining a liquid phase (biofuel), a solid phase in the form of coal and gaseous compounds (including hydrogen). The resulting gas phase containing methane and other hydrocarbons can be steam reformed to obtain additional hydrogen. In addition, the resulting liquid phase, called pyrolysis oil, can be used to produce additional hydrogen, for which only the water-soluble fraction of the oil can be used [4, 7].

Another way of obtaining hydrogen from biomass is gassing. This process produces gas and charcoal by subjecting biomass to high temperatures. In this process, oxygen is necessary, and its main disadvantage is the low thermal efficiency resulting from the biomass moisture, which should be less than 35% for the gassing process to be feasible. Tar and ashes are produced as by-products,



which hinder the steam reforming process. The efficiency of this method is estimated at 35-50% [7, 10].

Biological methods, unlike those mentioned above, are conducted under ambient conditions, i.e. temperature and atmospheric pressure. Renewable energy sources are used as a raw material. Biophotolysis is based on the principles of the process of photosynthesis, adapting it to the production of hydrogen. We can distinguish between direct biophotolysis and indirect biophotolysis. Direct biophotolysis uses the photosynthesis process of microalgae by using solar energy and converting it into energy in the form of hydrogen. The direct biophotolysis process is based on two stages, the first one produces a reducing agent for carbon dioxide reduction, and the second one disperses water into hydrogen and oxygen. As a standard, plants do not have hydrogenase, which only reduces carbon dioxide, while microalgae have this enzyme, which allows them to produce hydrogen [4, 6, 7]. Indirect biophotolysis is based on 4 basic steps, such as: biomass production in photosynthesis, biomass thickening, oxygen dark fermentation and the conversion of acetates to hydrogen. In the intermediate biophotolysis as an organism they are often used cyanobacteria [4, 6, 7]. Photofermentation is another way to produce hydrogen using biological processes. This method uses solar energy to produce hydrogen and biomass or organic acids using the action of nitrogenase, appropriate bacteria that can photosynthesize lead to the production of hydrogen [6, 7].

Yet another method is dark fermentation, in which anaerobic bacteria and some microalgae are placed on a carbon-rich medium. The process takes place in the absence of oxygen, without solar energy, i.e. in "dark" conditions. In this method, in addition to hydrogen, the end product is also carbon dioxide and other toxic substances resulting from the input used in the fermentation process [6, 7, 11, 12].

Biological methods, although they are more environmentally friendly, because they cause less emission of carbon dioxide and other harmful substances to the atmosphere, and use renewable energy sources to produce hydrogen, do not give the appropriate level of hydrogen production efficiency. High hopes are placed on the method of dark fermentation, which does not require the presence of solar energy. However, the efficiency of biological methods is still relatively low, especially in relation to methods using fossil fuels for the production of hydrogen.

The production of hydrogen from water is considered the cleanest method of obtaining hydrogen, where electricity and an appropriate electrolyser consisting of a positive and negative electrode are needed to produce it. There are currently three essential technologies for water electrolysis, such as [17, 19]:

- alkaline electrolysis;
- electrolysis of solid oxides;
- electrolysis with proton exchange membrane.

The most developed of the mentioned technologies is the alkaline electrolysis, which results from the greatest maturity and the large number of installations installed all over the world. This technology allows for the production of hydrogen on a large scale. Proton exchange membrane electrolysis is a less mature technology and is used on a smaller scale. Unfortunately, this method is less competitive due to the shorter life of the membrane used in the electrolysis process. The solid oxide technology, on the other hand, is currently under development and research, but has a high potential for hydrogen production [17, 19]. Water electrolysis allows to obtain pure hydrogen that will not be contaminated with other components, as is the case with the other production methods described above.



Additionally, the efficiency of this method is estimated at 80-85%, which is a very good result [20]. Unfortunately, much more energy is needed to produce hydrogen by electrolysis of water than with other methods. An alternative to this is the use of electricity from renewable energy sources, such as solar energy, wind energy, hydropower or geothermal energy, in the process of water electrolysis to produce hydrogen.

## **Hydrogen storage**

In the natural environment, hydrogen occurs in a gaseous state, where under normal conditions of pressure and temperature it occupies a very large volume with a small mass, which results from the density of hydrogen in the gas state. Hydrogen in its natural form has a high gravimetric energy density and a low volumetric energy density. This aspect poses a serious problem in the context of hydrogen storage for energy use.

Hydrogen can be stored using several methods [13]:

- in the form of compressed gas;
- in liquid form;
- cryogenic storage of hydrogen;
- in solid form on various materials.

The storage method in the form of compressed gas and liquid hydrogen are currently the most popular due to the period of development and many years of technology that is constantly being developed. The use of these methods has some drawbacks, which causes the determination to look for other methods of hydrogen storage. One such way is to store hydrogen on materials. The technology of storing hydrogen on materials is relatively new, in the research and development phase. The main problem of faster development of this method is the aspect related to the search for suitable materials that must be affordable, have a relatively large storage capacity and provide a moderate operating temperature as well as ease of adsorption and desorption [14].

Hydrogen is stored as compressed gas under pressure in cylinders, tanks and underground chambers. This method is currently the most popular due to its simplicity and ease of performing various operations in the supply chain. When hydrogen is compressed, the pressure of the gas in the tank increases, and thus the density of the hydrogen also increases. Taking into account various factors, hydrogen gas is stored at a pressure of 35-70 (75) MPa [15]. Hydrogen in gaseous form can be stored in several types of pressure vessels. The first type is metal tanks, the second type of pressure vessels is based on the use of a thick internal metal band which is wrapped in a cylindrical part with a resin-based composite fiber. The third and fourth type of pressure vessels are fully composite tanks. They are marked with the abbreviation COPV and are most often made of a plastic, sometimes metal lining, which is wrapped with carbon fiber. If the fiber insert contributes to the improvement of mechanical resistance by more than 5%, then it is a third type tank, otherwise it is a fourth type tank [16].

Storing hydrogen in liquid form is based on bringing hydrogen from a gaseous state to a liquid state. The process consists in the first step of compressing the hydrogen under high pressure, then the pressurized hydrogen is cooled down in two steps, pre-cooling and final cooling, where heat is removed in both stages. The last step is to expand the hydrogen to a low pressure level [17].

Hydrogen in liquid form is a very promising energy carrier. Storing hydrogen in liquid form allows for high gravimetric and volumetric densities. Hydrogen in this form is stored under much lower pressure than in the case of gas storage, which in turn translates into lower costs associated with hydrogen compression. Liquid hydrogen storage tanks consist of two walls with special insulation between them. Insulation is a very important element of this type of tank due to the fact that it must prevent the absorption of heat from the outside by the liquid hydrogen. Liquid hydrogen tanks should be shaped in such a way as to minimize the ratio of the tank area to its volume. In this case, cylindrical tanks work best. Such a tank shape is advantageous for large-scale liquid hydrogen storage, while when cylindrical tanks are used in vehicles it creates the drawback of taking up a large space for such a tank and problems with adapting the shape of the tank to the vehicle structure [18].

Cryogenic hydrogen storage is based on creating appropriate cryogenic conditions for the storage of hydrogen. Under such conditions, hydrogen is stored under high pressure (350 MPa) and at cryogenic temperature (usually below 77 K). The use of cryogenic tanks for storing hydrogen allows the shelf life of liquid hydrogen to be extended, and heat absorption by the hydrogen becomes less of a problem. Ultimately, the method of cryogenic tanks allows it to be filled with gaseous, liquid and two-phase hydrogen [18].

The storage of solid hydrogen in materials is based on chemical processes. According to research, this method is much more efficient than storing hydrogen in gaseous or liquid form, as it allows the storage of large amounts of hydrogen in a relatively small volume. This method is based on the interaction of hydrogen with the storage material. The storage of solid hydrogen on materials involves the bonding of hydrogen atoms with other elements. This binding can be based on the principles of absorption or adsorption. When absorbed, the hydrogen reacts with metals and forms metal hydrides. The metals used are lithium, magnesium, sodium, beryllium, titanium, aluminum and intermetallic compounds. This method of storing hydrogen is very attractive due to its simple structure, safety, reliability, easy operation and the possibility of using the heat generated during the formation of metal hydrides and their release. An important aspect of hydrogen absorption is that related to the heat management that occurs when hydrogen is combined with a suitable material, or when hydrogen is subsequently separated from the material. In this case, it is very important to manage the generated heat, use it for other processes directly or indirectly related to the process of using metal hydrides. [13, 16]. In the case of adsorption, a hydrogen gas molecule interacts with atoms on the surface of a given material. The main problem of this process is the use of relatively light materials as an energy carrier, with a simultaneous large number of places to ensure bonding. The current state of knowledge allows the use of graphite, carbon nanotubes, fullerenes, zeolites and many others as materials. This method does not have the problem of heat management, which is not created due to the low temperature requirement for adsorptive bonds. The advantage of this method is clearly simplicity and low storage costs. Unfortunately, the main disadvantage, apart from the requirement of low temperature of the adsorption process, is the low volumetric and gravimetric density of hydrogen storage [13, 19, 20].

In the case of hydrogen energy, hydrogen storage is a very important aspect, especially when it comes to large-scale use of hydrogen. Due to the fact that hydrogen can exist in various states of aggregation, different methods of its storage are also needed, which must cooperate with each other. The methods of hydrogen storage discussed above can be used for both stationary and mobile storage.

## Conclusions

1. Hydrogen as an energy source can become an alternative to fossil sources, unfortunately it is difficult to determine when this may happen.
2. Currently used methods of hydrogen production, although there are relatively many of them, mainly as a raw material they use conventional sources, which are characterized by greater efficiency and economy in relation to raw materials from renewable sources.
3. The production of hydrogen from biomass and water seems to be an ideal solution, but in order for the entire production process to be as ecological as possible, it is necessary to use renewable energy sources not only as input for production, but also as a source of energy in production processes.
4. Hydrogen storage is one of the most important and critical elements of the hydrogen fuel logistics system on a global scale.
5. The use of hydrogen in transport is probably the right initiative, however, the analysis of the literature shows that today there is no specific legal framework related to the hydrogen economy.

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## PHASE TRANSITION AND PHYSICAL PROPERTIES OF DabcoKCl ORGANIC-INORGANIC HYBRID COMPOUND

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### **Abstract:**

The organic-inorganic hybrid of the following formula  $(C_6H_{14}N_2)K(ClO_4)_3$  (DabcoKCl) were synthesized using isothermal evaporation method, whereas its phase transition and physical properties were investigated. The differential scanning calorimetry (DSC) measurements have determined the thermodynamic parameters of phase transition. The dynamic impedance spectroscopy (DIS) revealed the presence of both relaxation and conduction mechanism processes which are attributed to ordering of organic elements of this compound. The experiments enable to study the role of organic Dabco in the structural phase transition. The switching of dielectric constant around the phase transition shows promising applications in the field of electrical and electronic devices, including phase shifters and rewritable optical data storage.

### **Keywords:**

*organic-inorganic hybrids, phase transition, differential scanning calorimetry, dielectric spectroscopy*

### **Introduction**

Materials exhibiting switchable properties with multiple alternative states can be successfully used as switches of electrical signals, in optoelectronic devices, sensors, actuators, capacitors or nonvolatile memories. In the last few years they received particular attention due to both the strictly fundamental features of hybrids materials and a promising basic elements in electrical and electronic industries. The organic-inorganic hybrid dielectrics pay attention due to attractive multiple structural diversities and prospective applications as functional materials. Generally, most interests concern research characterizing the physicochemical properties of functional materials from the hybrid organic-inorganic perovskites (HOIPs) which received exceptional attention due to the interesting electric, optical and magnetic properties [1-7]. Most common considered compounds are hybrid organic-inorganic compounds (HOICs) including AMX, where A is an organic cation, which held by H-bonds within the cage formed by the metal centers (M) and linkers (X) [1, 2]. The main feature of such crystals is the variety of A, M and X components, thereby providing materials with various chemical/physical properties in a rather simple crystal structure. Indeed, obtaining multifunctional hybrid compounds depends on the controlled synthesis as well as on comprehensive characterization

of the physical properties of dielectrics determined on the basis on measurements of electrical, thermal properties, non-linear dielectric behavior, magnetoelectric properties and optoelectronic characteristics. Recently, several hybrid compounds based on organic Dabco have been discovered and have shown that for this materials interesting physiochemical properties can be observed [8, 9]. Most of synthesized hybrid crystals undergo a reversible structural phase transitions. It was found that both the order–disorder transformations of polar organic cations and the weak displacements of inorganic frameworks make contributions for its dielectric properties. It has been shown the switching behavior between the high dielectric state (switch on) and low dielectric state (switch off) for some hybrid organics-inorganics materials [8,9]. It should be underline that switchable dielectric materials show promising applications in the field of electrical and electronic devices, including phase shifters, varactors, data communication and rewritable optical data storage.

An organic-inorganic hybrid compound  $ABX_3$  where  $A = 1,4\text{-diazabicyclo}[2.2.2]$  (Dabco);  $B = K^+$  and  $X = ClO_4$  has been previously synthesized by Sun et.al. [10]. It has been shown that DabcoKCl in the room temperature crystallize in the cubic system (space group  $Pa\bar{3}$ ). The results of differential scanning calorimetry revealed order-disorder first type phase transition of DabcoKCl compounds. Also the structural changes were detected by noticeable changes of dielectric permittivity at around 396 K [10].

This paper reports the differential scanning calorimetry (DSC) and dynamic impedance spectroscopy (DIS) studies on the structural changes of synthesized organic-inorganic hybrid DabcoKCl compounds. The main goal of the studies was to determine the role of organic cations to reveal the structural phase transition. Based on the complex electrical permittivity measurements both the dielectric relaxation process and conduction mechanisms in DabcoKCl has been discussed.

## Materials and Method

### Synthesis

1,4-Diazabicyclo[2.2.2]octane (Dabco), potassium perchlorate ( $KClO_4$ ) and perchloric acid ( $HClO_4$ ) were mixed in molar ratio of 1:1:2. Crystals of  $(C_6H_{14}N_2)K(ClO_4)_3$  (DabcoKCl) were obtained by slow evaporation at room temperature and were obtained in 75% yield.

### Thermal measurements

The differential scanning calorimetry (DSC) were performed in the temperature range of 150 - 420 K on a Mettler Toledo DSC instrument. Under the nitrogen atmosphere, the samples in hermetically sealed Al pans were heating and cooling with a rate of 10 K/min.

### Dielectric measurements

The complex electric permittivity ( $\epsilon^* = \epsilon' - i\epsilon''$ ) was measured using the Dynamic Impedance Spectroscopy (DIS) carried out on impedance analyzer (Novocontrol Technologies Alpha, Germany) in a frequency range between 10 Hz and 1 MHz with an applied voltage of 1V. The measurements were performed at 2 K/min from 500 K to room temperature (RT). The electric measurements were carried out in a controlled atmosphere ( $N_2$ ) with stability better than 0.1 K. For all electrical measurements on polycrystalline pressed sample ( $S = 20\text{ mm}^2$ ,  $d = 0.2\text{ mm}$ ) silver electrodes were painted.



## Results and Discussion

A differential scanning calorimetry was performed as a reliable way to investigate the phase transition induced by temperatures changes. As shown in Fig. 1, at around 400 K well defined thermal anomalies in a sample are observed during the heating and cooling cycles. This suggest that DabcoKCl compound exhibits reversible structural phase transition.

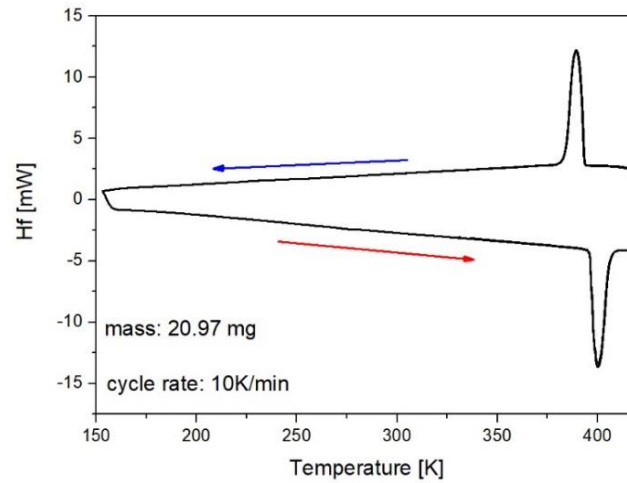


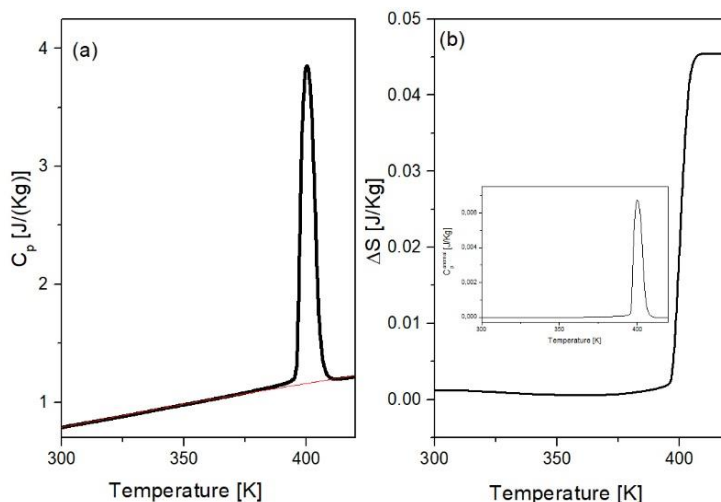
Fig. 1. DSC curves DabcoKCl measured from 150 to 420 K

The entropy changes ( $\Delta S$ ) accompanying observed phase transition were calculated on the basis of the Fig.1 using the following formula (1):

$$\Delta S(T) = \int_{T_0}^T \frac{c_p^{anomal}}{T} dT \quad (1)$$

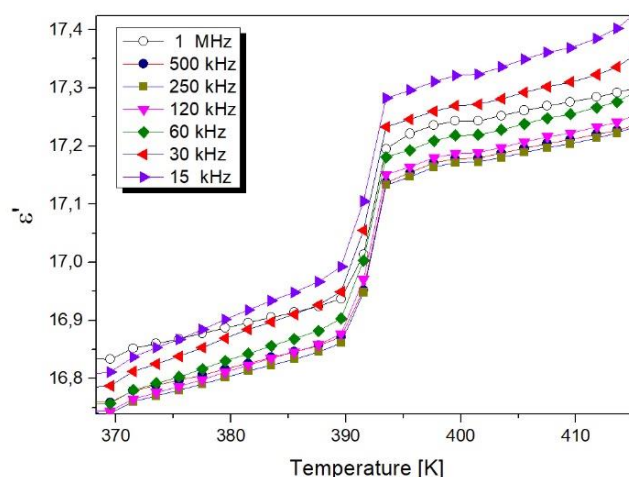
where:  $c_p^{anomal}$  denotes the anomaly part of the specific heat (see insert in Fig. 2b) determined by subtract the lattice heat  $C_{p,latt}$  from the total specific heat (Fig. 2a). Both, thermal hysteresis ( $\sim 12$  K) and visible at Fig. 2b jump-like character of entropy suggests first order character of reversible structural phase transition of DabcoKCl compound.





**Fig. 2. Temperature-dependent (a) specific heat (b) entropy of DabcoKCl measured during the heating mode. Insert shows the anomaly part of specific heat vs. temperature. Red line in Fig. 2a shows the fitting of lattice heat  $C_{p,latt}$**

The changes in the dynamic mobility of the organic components revealed by response of dielectric constant were investigated on the powder-pressed pellet of DabcoKCl. The dielectric constant ( $\epsilon'$ ) exhibits a sharp step-like anomaly around 400 K, which is in line with the results obtained from DSC measurements. The influence of observed thermally driven transition is attributed to dynamic changes of DabcoH<sub>2</sub><sup>2+</sup> cation, which is highly disordered in the high-temperature phase (above 400 K), while below 400K, in the low-temperature phase its mobility is frozen (ordered) [10].



**Fig. 3. Temperature-dependent dielectric permittivity of the pressed-powder sample of DabcoKCl in the cooling mode**

In order to discuss the relaxation process of DabcoKCl compounds analysis of the complex electrical modulus ( $M^* = M' - iM''$ ) were carried out. The temperature dependence of the imaginary part of electrical modulus ( $M''$ ) shows a characteristic behavior for relaxation processes (Fig. 4a). Thermally activated relaxation process is revealed by shifting of the electrical modulus ( $M''$ ) peaks

toward higher temperature. The temperature dependence of relaxation frequency ( $f_{max}$ ) can be expressed by Arrhenius equation (2):

$$f_{max} = f_{M0} \cdot e^{-\frac{E_M}{k_B T}} \quad (2)$$

where:  $f_{max}$  is the frequency at maximum in the  $M''(f)$  plot,  $f_{M0}$  – represents the characteristic frequency,  $E_M$  is the relaxation energy and  $k_B$  is the Boltzmann constant. After the least-square fitting and using Eq.2 the activation energies of dielectric processes resulting from the temperature changes of the sample have been obtained. An inflection around 400 K shown in Fig. 4b confirms the order–disorder phenomenon of the carbon and attached to them hydrogen atoms in  $\text{DabcoH}_2^{2+}$  [10]. This suggests that DabcoKCl compound can be a potential dielectric response switching material.

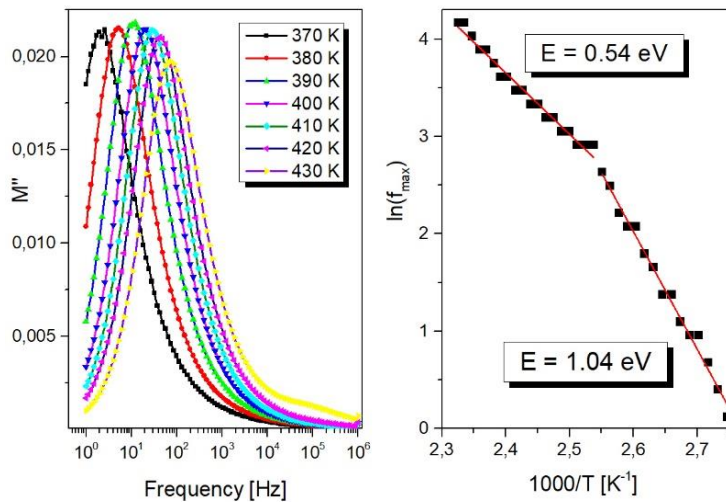


Fig. 4. (a) The frequency dependence of  $M''$  at the selected temperature (b) Arrhenius plot of DabcoKCl

The frequency dependence of the total electrical conductivity using double-logarithmic scale at selected temperature has been shown in Fig.5a. Fig.5b shows the plot of the DC conductivity ( $\sigma_{DC}$ ) versus temperature. As it can be seen this behavior fulfils an Arrhenius equation (3):

$$\sigma_{DC} = \sigma_0 \exp(E_{DC}/k_B T) \quad (3)$$

where:  $\sigma_0$  is the pre-exponent,  $E_{DC}$  is the activation energy for the DC conductivity and  $k_B$  is the Boltzmann constant. After the least-square fitting values of activation energies were determined from the slope of  $\log \sigma_{DC}$  vs. reciprocal temperature ( $1/T$ ) and they are shown in Fig. 5b. The similar value of activation energies of conduction and relaxation process suggests that the same structural compounds are responsible for both mechanisms.

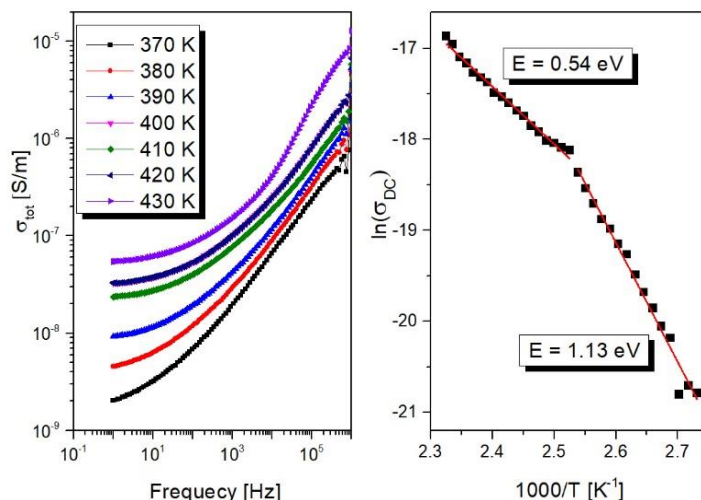


Fig. 5. (a) The frequency dependence of electrical conductivity ( $\sigma_{tot}$ ) at the selected temperatures (b) Dependence of  $\ln(\sigma_{DC}) = f(1000/T)$  for DabcoKCl

## Summary

In summary, the DabcoKCl hybrid organic-inorganic compound successfully has been designed. This compound underwent reversible structural first order phase transition at about 400 K. Variable thermal, dielectric analysis supplemented with structural information confirmed that the phase transition is attributed to the ordering of DabcoH<sub>2</sub><sup>2+</sup> cations. Changes of the activation energy of conduction and relaxation process refer to the energy of ordered Dabco cation above 400 K (order state) and disordered Dabco below phase transition temperature (disorder state), and describe the variation of molecular reorientation during the phase transition process. Thermal variation of dielectric disclosure between high- and low-dielectric states, obtained in DabcoKCl enrich the family of reversible structural phase transition hybrid compounds and may open a promising way to construct multifunctional materials for microelectronics.

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## X-RAY, SPECTROSCOPIC AND DFT STUDIES OF TETRABROMOZINCATE(II) GEMINI 3-HYDROXYPYRIDINIUM SALT

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### Abstract:

IR, Raman,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 1,3-bis(3-hydroxypyridinium)propane dibromide (1) and tetrabromozincate (2) have been compared. Both salts crystallize as monohydrates. The molecular structure of 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate have been characterized by X-ray diffraction and DFT calculations. The crystals of 2 are monoclinic,  $I2/a$  space group with one dication, one  $\text{ZnBr}_4^{2-}$  dianion and one water molecule in the asymmetric unit. In the crystal 1 and 2 hydroxyl groups are involved in  $\text{O-H}\cdots\text{Br}$  and  $\text{O-H}\cdots\text{O}$  hydrogen bonds formation. The FTIR spectra show an absorption attributed to the stretching vibrations of OH groups engaged in hydrogen bonds.

### Keywords:

3-Hydroxypyridine, Bis-pyridinium compounds, X-ray diffraction, DFT calculations, FTIR, Raman and NMR spectra

### Introduction

Gemini pyridinium compounds exhibit diverse biological properties depending on the type of the linker and substituent in the ring. They are active as acetylcholinesterase inhibitors and can be used in the cure of Alzheimer's disease, myasthenia gravis and glaucoma [1, 2]. Some of bis-pyridinium compounds show toxic effects on different microorganisms (e.g. bacteria, parasites, moulds [3-6]). They can also act as ligands in coordination complexes [7-9]. The salts consist of organic cation and tetrahalometalate anion of the general formula  $\text{A}_2\text{MX}_4$  (where A is an organic cation, M is a divalent transition metal ion and X is halide – Cl or Br) exhibit interesting magnetic, biological, optical, electrical, catalytic and structural properties [10-12]. Among them, zinc halide compounds show interesting electrical properties and potential different applications [13, 14]. The structure of the  $\text{MX}_4^{2-}$  anion shows a large flexibility in geometry between square planar and almost tetrahedral strongly dependent on the type of cation, which may be ammonium, phosphonium, pyridinium, imidazolium or pyrrolidinium ion. Several reports are devoted to studies of tetrahalometalates of pyridinium and bis-quaternary pyridinium salts [15-17].

Considerable interest of different studies is focused on the influence of intermolecular interactions on the structures of crystalline coordination compounds like weak and strong hydrogen

bonds, other weaker non-covalent interactions, such as C–H $\cdots$ X (X = Hal, O, N),  $\pi\cdots\pi$  stacking, and C–H $\cdots\pi$  or halogen bonding. X-ray studies of organic tetrahalometalate complexes show that the geometry of the MX<sub>4</sub><sup>2-</sup> anion depends on the stability of hydrogen bonds, electrostatic and steric interactions between the atoms of the cationic moiety of the complex and the halogen atoms [18-21]. It was also found that the decrease of the ability of organic cations to form hydrogen bonds with the inorganic anion leads to a reduction in the distortion of its tetrahedral geometry [22].

In this study it is reported on the crystal, molecular structure, FTIR, Raman and NMR spectra of 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate hydrate (2). Moreover, the comparison of spectroscopic properties of tetrabromozincate salt with the ligand 1,3-bis(3-hydroxypyridinium)propane dibromide hydrate (1) based on the experimental and quantum chemical calculations is presented.

## Experimental and calculations

### Synthesis

3-hydroxypyridine (32 mmol, 3.023 g) and 1,3-dibromopropane (16 mmol, 3.18 g, 1.6 cm<sup>3</sup>) were dissolved in 10 ml of anhydrous acetonitrile and refluxed for 1 h. After cooling the precipitate of 1,3-bis(3-hydroxypyridinium)propane dibromide (1) was filtered off and recrystallized from 12 cm<sup>3</sup> of ethanol-water mixture (10:1); yield 62%; m.p. 215-217°C. The salt crystallizes as monohydrate. Elemental analysis for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Br<sub>2</sub>·H<sub>2</sub>O calc.: %C 38.07; %H 4.42; %N 6.83; found: %C 38; %H 4.45; %N 6.73.

To 0.23 g (6 mmol) of 1,3-bis(3-hydroxypyridinium)propane dibromide dissolved in 2 cm<sup>3</sup> of ethanol-water mixture (1:1), 0.135 g (6 mmol) of ZnBr<sub>2</sub> in 2 cm<sup>3</sup> of the same solvent mixture (1:1) was added. The mixture was refluxed for one hour. The resulting precipitate of 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate (2) was filtered off. Yield 23%; m.p. 148-150°C. The salt crystallizes as a monohydrate. Elemental analysis for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>·ZnBr<sub>4</sub>·H<sub>2</sub>O calc.: %C 24.58; %H 2.86; %N, 4.41; found: %C 24.92; %H 2.76; %N 4.59.

### Measurements

The single-crystal X-ray diffraction data for 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate hydrate (2) were collected using Oxford Diffraction SuperNova diffractometer ( $\lambda = 1.54184$  Å). X-ray experiment was performed at 150 K using the CryoJet cooling system. Structure was solved and refined using ShelXT [23] and ShelXL [24], respectively. Positions of all hydrogen atoms were derived from a difference Fourier map and included in the refinement process.

FT-IR spectra were recorded on a NICOLET is5 instrument, with the resolution of 2 cm<sup>-1</sup>. Each spectrum was accumulated by acquisition of 32 scans. Compound samples were prepared as KBr pellets. The Raman spectra were measured on a Bruker FRA-106/S instrument with the resolution of 1 cm<sup>-1</sup>. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in D<sub>2</sub>O solution on a Bruker Advanced DRX spectrometer operating at 599.85 and 105.85 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively.

Elemental analysis was made using an Elemental Model Vario EL III instruments.



## Computational details

The calculations were performed with the density functional theory (DFT) using M06 functional. For hydrogen, carbon, oxygen and nitrogen atoms 6-311++G(d,p) and for zinc atom SDD bases sets were used, respectively. The calculations were made using Gaussian 09 program package [25].

## Results and discussion

### X-ray crystallography

1,3-Bis(3-hydroxypyridinium)propane tetrabromozincate (2) crystallizes as a monohydrate in the monoclinic  $I2/a$  space group with one organic dication, one  $\text{ZnBr}_4^{2-}$  dianion and one water molecule in the asymmetric unit (Fig. 1). In the crystal network, every dication interacts with counterions in two ways: directly through  $\text{O31-H31} \cdots \text{Br4}^{\text{ii}}$  hydrogen bond (Tab. 1), and *via* the water molecule as a "mediator" in the cooperative  $\text{O3-H3} \cdots \text{O1-H1B} \cdots \text{Br1}$  hydrogen bond (Fig. 1 and Tab. 1). Two  $\text{O-H} \cdots \text{Br}$  contacts with the participation of a solvent molecule as a proton donor for subsequent  $\text{ZnBr}_4^{2-}$  dianion molecules were observed. Halogen-halogen  $\text{Br} \cdots \text{Br}$  interactions between adjacent  $\text{ZnBr}_4^{2-}$  dianions were also noticed.

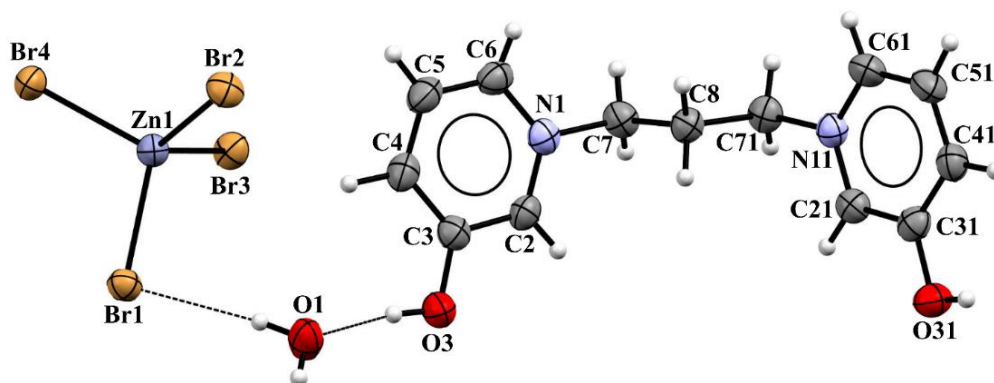


Fig. 1. Perspective ORTEP drawing of 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate hydrate (2)  
Source: Own source

### Optimized structure

The structure of 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate hydrate (2a) optimized by M06/6-311++G(d,p) is shown in Fig. 2. The geometrical parameters of hydrogen bonds are listed in Tab. 1. Similarly as in the crystal structure  $\text{ZnBr}_4^{2-}$  anion interacts with hydroxyl group and water molecule by  $\text{O-H} \cdots \text{Br}$  contacts.  $\text{O} \cdots \text{Br}^{\text{--}}$  distances are 3.155 and 3.326 Å. Additionally, the water molecule is involved in short hydrogen bond with the hydroxyl group of 2.620 Å. In the optimized structure 2a the  $\text{D} \cdots \text{A}$  (D – donor, A – acceptor) distances of hydrogen bonds are comparable with those in the crystal of 2, but the angles  $\text{D-H} \cdots \text{A}$  deviate from the linearity as compared to the crystal structure. The calculated energy is -12916.6345 a.u. and the dipole moment is 18.575 D.

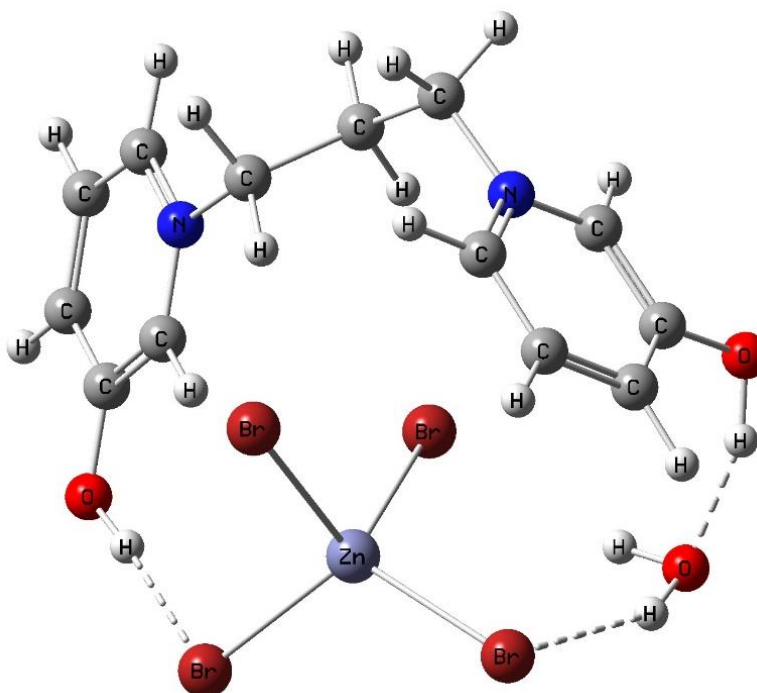


Fig. 2. 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate hydrate (2a) structure optimized with the M06/6-311++G(d,p) approach  
Source: Own source

Tab. 1. Geometry of the experimental and calculated hydrogen bonds (Å,°) for 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate hydrate 2 and 2a

|   | $D-H\cdots A$                      | $D-H$   | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|------------------------------------|---------|-------------|-------------|---------------|
| <b>2</b>  | O3-H3 $\cdots$ O1                  | 0.86(7) | 1.76(7)     | 2.606(5)    | 171(6)        |
|   | O1-H1A $\cdots$ Br2 <sup>i</sup>   | 0.71(6) | 2.61(7)     | 3.319(4)    | 171(7)        |
|   | O1-H1B $\cdots$ Br1                | 0.85(7) | 2.40(8)     | 3.251(4)    | 173(6)        |
|   | O31-H31 $\cdots$ Br4 <sup>ii</sup> | 0.74(8) | 2.53(8)     | 3.264(3)    | 167(8)        |
| <b>2a</b>   | O-H $\cdots$ O(w)                  | 0.999   | 1.662       | 2.620       | 159           |
|   | O(w)-H(w) $\cdots$ Br              | 0.975   | 2.148       | 3.326       | 154           |
|   | O-H $\cdots$ Br                    | 0.999   | 2.159       | 3.155       | 173           |
| Symmetry codes: (i) $x, y-1, z$ ; (ii) $x, -y+1/2, z+1/2$ . |                                    |         |             |             |               |

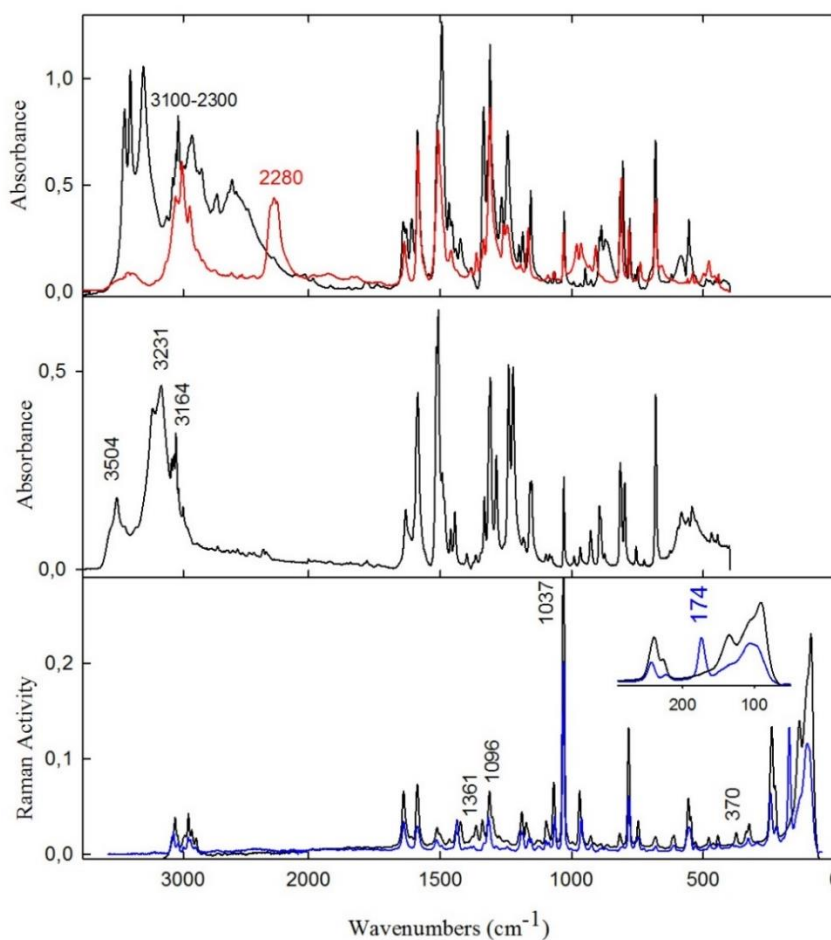
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### Raman and FTIR Spectra

The Raman and IR spectra of 1,3-bis(3-hydroxypyridinium)propane dibromide (1) and 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate (2) are presented in Fig. 3. In the FTIR spectrum of 1 the most intensive band in the range of 3200-2300  $\text{cm}^{-1}$  with center of gravity ( $\nu_H$ ) at 2797  $\text{cm}^{-1}$  is related to the stretching vibration of the OH groups engaged in the hydrogen bonds with bromide anions ( $\nu_O\text{-H}\cdots\text{Br}$ ). This absorption shifts after deuteration to lower frequencies and is observed as an intense band of  $\nu_{OD}$  at 2280  $\text{cm}^{-1}$  (Fig. 3a, red line). The isotopic ratio  $\nu_H/\nu_D$  equals to 1.22 and it suggests that the hydrogen bond is strong. In the Raman spectrum the intensity of the band connected with OH vibrations is very weak (Fig. 3c).

In the IR spectrum of (2) the greatest changes, in relations to IR spectrum of 1, are observed for the bands vibrations of the hydroxyl group. Compared to 1, the OH stretching vibration band in the range of 3200-2300  $\text{cm}^{-1}$  is shifted toward higher frequencies and appear at 3231 and 3164  $\text{cm}^{-1}$ . Bands related to the stretching vibrations of the OH groups of the water molecule at 3470, 3430 and 3321  $\text{cm}^{-1}$  in 1 after zinc complex formation disappear. The complex with zinc is also a hydrate and the OH-stretching vibrations band of the water molecule appear at 3504  $\text{cm}^{-1}$ .

The Raman spectrum of the 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate (2) is compared with this of 1,3-bis(3-hydroxypyridinium)propane dibromide (1) (Fig. 3c). These spectra slightly differ in intensity and in the position of some bands. In the spectrum of 2, bands at 1361, 1096, 370  $\text{cm}^{-1}$  disappear or shift. A new, intense band at 174  $\text{cm}^{-1}$  is attributed to the stretching vibrations of the bridging Br–Zn–Br. The dominant band at 1037  $\text{cm}^{-1}$  is characteristic of the "breathing" vibrations of the pyridinium ring and it is associated with the vibrations of 2,4,6 carbon atoms.



**Fig. 3. Infrared spectra of (a) 1,3-bis(3-hydroxypyridinium)propane dibromide (1) (black line) and its deuterated analogue (red line); (b) 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate (2); (c) Raman spectra of 1,3-bis(3-hydroxypyridinium)propane dibromide (1) (black line) and 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate (2) (blue line)**

Source: Own source

## NMR Spectra

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra measured in  $\text{D}_2\text{O}$  are presented in Fig. 5 and 6, and the chemical shifts are listed in Tab. 2. The atom numbering is shown in Fig. 4. For 1 the  $^1\text{H}$  NMR chemical shifts values of the ring protons are in the range 7.83 and 8.36 ppm. The protons of the linker give signals at 2.80 and 4.80 ppm with the coupling constant equal 7.51 Hz. All  $^1\text{H}$  NMR signals of protons in tetrabromozincate 2 are shielded in comparison to 1. The most meaningful changes are for signals of protons H(2), H(4) and H(6), which are shielded by 0.27, 0.21 and 0.26 ppm, respectively. The proton signal of H(8) is least shielded by only 0.02 ppm. In the  $^{13}\text{C}$  NMR spectrum seven resonance signals are present. Aromatic carbon atom chemical shifts for both compounds are in the range of 131.24 and 164.81 ppm. The signal of methylene carbon atom C(7) is strongly deshielded because of vicinity of quaternary nitrogen atom and it is found at about 61 ppm. The most significant change after zinc complex formation is observed for signal of carbon atom C(3), which is deshielded by 3.77 ppm. Additionally, the signal of C(2) is shielded by 1.53 ppm. For the remaining carbon atoms, the differences in the position of the signals for 1 and 2 are not greater than 1 ppm.

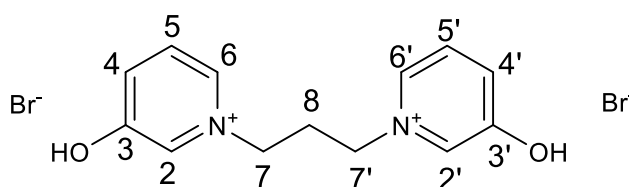


Fig. 4. The numbering of atoms of 1,3-bis(3-hydroxypyridinium)propane dibromide (1)  
Source: Own source

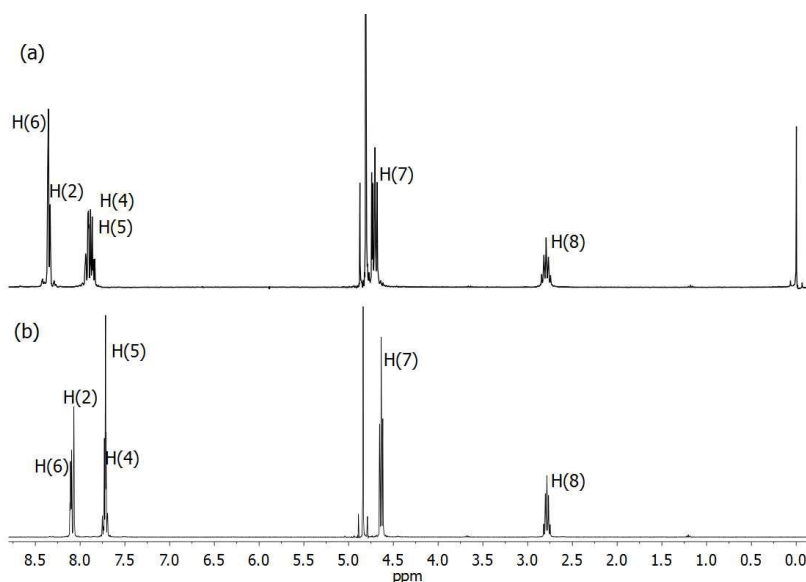


Fig. 5. The  $^1\text{H}$  NMR spectra in  $\text{D}_2\text{O}$  of (a) 1,3-bis(3-hydroxypyridinium)propane dibromide (1);  
(b) 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate (2)

Source: Own source

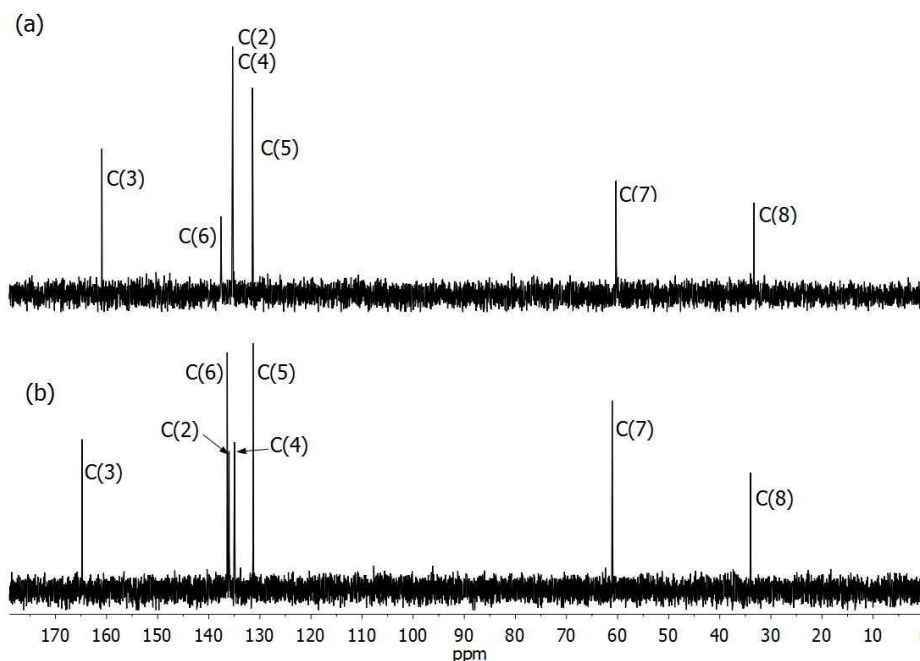


Fig. 6. The  $^{13}\text{C}$  NMR spectra in  $\text{D}_2\text{O}$  of (a) 1,3-bis(3-hydroxypyridinium)propane dibromide (1); (b) 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate (2)

Source: Own source

Tab. 2. Carbon-13 and proton chemical shifts (ppm) in  $\text{D}_2\text{O}$  for 1,3-bis(3-hydroxypyridinium)propane dibromide (1); and 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate (2)

| Atom      | 1      | 2      | $\Delta_{1-2}$ |
|-----------|--------|--------|----------------|
| Hydrogen  |        |        |                |
| H(2)      | 8.34   | 8.07   | 0.27           |
| H(4)      | 7.94   | 7.73   | 0.21           |
| H(5)      | 7.83   | 7.71   | 0.12           |
| H(6)      | 8.36   | 8.10   | 0.26           |
| H(7)      | 4.80   | 4.64   | 0.16           |
| H(8)      | 2.80   | 2.78   | 0.02           |
| $J_{7-8}$ | 7.51   | 7.27   | -              |
| Carbon    | 1      | 2      | $\Delta_{1-2}$ |
| C(2)      | 137.91 | 136.38 | 1.53           |
| C(3)      | 161.04 | 164.81 | -3.77          |
| C(4)      | 135.63 | 134.98 | 0.65           |
| C(5)      | 131.77 | 131.24 | 0.53           |
| C(6)      | 135.63 | 135.92 | -0.29          |
| C(7)      | 61.14  | 60.98  | 0.16           |
| C(8)      | 34.35  | 34.28  | 0.07           |

Source: Own source

## Conclusions

The crystal and molecular structure of 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate was determined by X-ray diffraction and DFT calculations. In the crystal hydroxypyridine dication and tetrabromozincate anion form supramolecular structure. 1,3-Bis(3-hydroxypyridinium)propane

tetrabromozincate crystallizes as a monohydrate and crystals are monoclinic,  $I2/a$  space group with one dication, one  $\text{ZnBr}_4^{2-}$  dianion and one water molecule in asymmetric unit. The structure is stabilized by  $\text{O-H}\cdots\text{Br}$  and  $\text{O-H}\cdots\text{O}$  hydrogen bonds involving  $\text{ZnBr}_4^{2-}$ , hydroxyl groups and water molecule. The solid state FTIR spectra of 1,3-bis(3-hydroxypyridinium)propane tetrabromozincate and 1,3-bis(3-hydroxypyridinium)propane dibromide were compared and the most visible changes are observed for frequencies of the stretching vibrations of hydroxyl groups. In the Raman spectrum an intense band at  $174\text{ cm}^{-1}$  attributed to the stretching vibrations of the bridging  $\text{Br-Zn-Br}$  is observed.

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## **TAKING UP ACTIVE TOURISM AMONG STUDENTS OF RZESZÓW UNIVERSITIES**

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### **Abstract:**

Active tourism is intended mainly for people who want to face new challenges, satisfy their ambitions or overcome weaknesses, but also for people who benefit from the pleasure of spending time outdoors. Such people are undoubtedly students who willingly undertake this type of tourism. The aim of the research was to learn about active tourism among students of the University of Rzeszów and the Rzeszów University of Technology. The results will show whether students are aware of the importance of active tourism in their free time. The method used was a diagnostic survey, while the technique used was a questionnaire. The study was conducted on 100 students of the University of Rzeszów (URz) and 100 students of the Rzeszów University of Technology (PRz). The results obtained after the survey show that in the group of student youth there is a huge demand and demand for active tourism. Students decide to engage in active tourism to spend time with friends and maintain physical and spiritual health.

### **Keywords:**

*tourism, active tourism, recreation*

### **Introduction**

The concept of tourism comes from the Latin word "tournus", it means circular, circular traffic, referring to the change of place of residence of people. In turn, in French the word "tour" means a roundabout journey, a journey, a race back to the place from which you set off. Over time, this word turned into the word "tourisme" [1].

Recently, tourism has become an essential part of the global economy. The development of the tourism industry was influenced by social, economic and political changes in the world and technical development. Due to the progressive changes, the possibility of tourism consumption concerned an ever wider group of people who were gradually fulfilling their needs on the tourism market. The criteria by which we can analyze tourist traffic include: the purpose of the trip, its nature and manner of organization, but also criteria describing the participants of tourist traffic, such as age, income or social status [2].

In addition to the positive impact of tourism on the human body and health, we also have equally important social functions: the possibility of learning and broadening horizons, social interactions, increasing self-confidence, developing independence, changing perspectives or escaping routine [3].

Tourist activity, influencing the quality, level and style of life, has become an important element in the management of the society's free time. The level of this activity depends on a large number of factors, including socio-demographic, cultural and economic factors. The most influencing of the level of tourist activity are socio-demographic factors, such as: gender, age, education level, place of residence and membership in a socio-professional group [4].

When referring to the forms of tourism related to physical activity and sport, we can distinguish many terms. Active tourism is the most frequently used concept, which has recently replaced more specialized and elite qualified tourism. It is a form of tourism, an important element of which is undertaking recreational or hobby activities. The basic forms of active tourism are: qualified tourism, adventure tourism and extreme tourism [5].

Active tourism is understood as a form of tourism in which the main or important element of a trip is undertaking a specific type of recreational or hobby activity [6].

Social motives are of particular importance in taking up activity, because thanks to them, young people become more involved in social life, which improves their ability to make contacts or better cope with activity stress [7].

Active tourism brings many benefits that positively affect the human body. The most popular ones are improving physical fitness and getting the look you want or improving your posture. As a result, a person feels good with their body, and the aging process of the body is slowed down. Active tourism contributes to the oxygenation of the body, which is important for the brain, heart and tissues. The blood circulation in the body also improves. Additionally, selected forms of active tourism stimulate and improve the functioning of the senses in the human body [8].

Active tourism is a popular form of spending free time among people of all ages, often requiring intense physical effort. Among students, it increases physical fitness, helps achieve better results in education, regenerates strength after all-year study and work at school, and also teaches cooperation in a group. The love of hiking and excursions among young people often results not only from the will to experience an adventure, but is an expression of the need to show independence or show initiative. A significant group of young people, apart from spending free time with their parents, wants to spend this time with friends or peers, wanting to decide for themselves about their behavior [9].

Although active tourism is considered a milder form in the literature on the subject and is addressed to a wider audience, it often emphasizes both physical and intellectual activity. However, active tourism participants do not have to be as well-qualified, intellectually and technically prepared as the participants of qualified tourism [10].

"The most popular types of active tourism on land or inland are:

- Lowland,
- hiking, mountaineering,
- climbing,
- speleological,
- tourism, cycling,
- skiing (downhill, cross-country, snowboarding and ski touring),

- horse riding,
- hunting.

The most popular types of active tourism in the aquatic environment are:

- sailing tourism (inland sailing, sea sailing, windsurfing, kitesurfing, ice yachts, ice kite),
- canoe tourism (canoeing, canoeing, ra'ing),
- underwater,
- tourism, motorboat tourism,
- fishing (inland, marine)" [5].

An increasingly frequent phenomenon in recent years is the emergence of types of tourist, recreational and sports activities, which are practiced as part of outdoor active tourism. Physical activity plays a significant role in caring for human health, which is pointed out by modern scientists from many countries [11].

## **Research assumption and purpose**

The aim of the research was to learn about active tourism among students of the University of Rzeszów and the Rzeszów University of Technology. Therefore, detailed research questions were developed.

1. How is the phenomenon of active tourism perceived?

2. What are the motives for practicing active tourism by students of selected universities in Rzeszów?

3. What is the frequency of tourism by students?

In this work, the diagnostic survey method was used. The technique was a questionnaire, and the research tool was a questionnaire created in the form of a web form. The research was conducted in December 2019 and January 2020. The questionnaire sheet consisted of three parts: a brief information on the purpose of the research, a set of questions, and a record. An important aspect of the research was to check whether the field of study has an impact on undertaking active tourism and the forms chosen during this activity. The study was conducted on 200 randomly met students of the largest universities in Rzeszów.

The first question is: Do you think there is such a form of tourism as active tourism? The results presented in Tab. 1 show that the state of knowledge on the existence of active tourism is very satisfactory and even very good. Both students of the University of Rzeszów and students of the Rzeszów University of Technology know about the existence of active tourism.

**Tab. 1. Knowledge of the respondents about the existence of active tourism (%)**

|  | Total<br>n = 200 | Students URz<br>n = 100 | Students PRz<br>n = 100 |
|--|------------------|-------------------------|-------------------------|
| Yes                                    | 88.00            | 100.0                   | 76.0                    |
| No                                     | 4.5              | 0.0                     | 9.0                     |
| I met / I have come across such a term | 7.5              | 0.0                     | 15.0                    |

**Source: Own study**

The next question concerned forms of tourism which are classified as active tourism according to students. Based on the results presented in Tab. 2, the students of the University of Rzeszów most often indicated hiking, water tourism, bicycle tourism or climbing tourism as forms of active tourism, while students of the Rzeszów University of Technology most often indicated hiking, water tourism and ski tourism as a form of tourism. The question was a multiple choice question.

**Tab. 2. Forms of active tourism defined by the respondents (%)**

|                       | Total<br>n = 200 | Students URz<br>n = 100 | Students PRz<br>n = 100 |
|-----------------------|------------------|-------------------------|-------------------------|
| Hiking                | 92.0             | 94.0                    | 90.0                    |
| Cycling               | 84.0             | 89.0                    | 78.0                    |
| Climbing tourism      | 67.0             | 80.0                    | 54.0                    |
| Speleological tourism | 10.0             | 17.0                    | 3.0                     |
| Ski tourism           | 71.5             | 79.0                    | 64.0                    |
| Equestrian tourism    | 9.5              | 11.0                    | 8.0                     |
| Hunting               | 2.5              | 3.0                     | 2.0                     |
| Tourism water         | 87.0             | 92.0                    | 82.0                    |

**Source: Own study**

In the next question, students were asked whether active tourism has an impact on human health. The results show that the vast majority of respondents, both students of the University of Rzeszów and the Rzeszów University of Technology believe that definitely yes, active tourism has an impact on human health. Rzeszów University of Technology students believe more often than students of the University of Rzeszów that active tourism has an impact on health. A small percentage of the respondents declare that active tourism has no effect on health or has no opinion.

**Tab. 3. Impact on human health through active tourism according to the respondents (%)**

|                   | Total<br>N = 200 | Students URz<br>N = 100 | Students PRz<br>N = 100 |
|-------------------|------------------|-------------------------|-------------------------|
| Definitely yes    | 74.5             | 87.0                    | 62.0                    |
| Rather yes        | 17.5             | 7.0                     | 28.0                    |
| Rather not        | 5.0              | 4.0                     | 6.0                     |
| Definitely not    | 1.0              | 0.0                     | 2.0                     |
| I have no opinion | 2.0              | 2.0                     | 2.0                     |

**Source: Own elaboration**

The fourth question concerned the motives of students when choosing active tourism. According to the responses for students of the University of Rzeszów as well as students of the Rzeszów University of Technology, the most important reason for choosing this type of tourism is activity. Students of the University of Rzeszów are also guided in this matter by health considerations and the theme of the community. On the other hand, students of the Rzeszów University of Technology, when choosing this type, are guided by ambition, which they can increase in this way. Several answers should be given to this question.

**Tab. 4. Motives behind the choice of active tourism by the respondents (%)**

|                            | Total<br>N = 200 | Students URz<br>N = 100 | Students PRz<br>N = 100 |
|----------------------------|------------------|-------------------------|-------------------------|
| Activity                   | 83.5             | 92.0                    | 75.0                    |
| Removing emotional tension | 29.0             | 25.0                    | 33.0                    |
| The health                 | 72.5             | 89.0                    | 56.0                    |
| emotionalism               | 42.5             | 44.0                    | 41.0                    |
| Community                  | 68.5             | 65.0                    | 72.0                    |
| Ambitność                  | 65.5             | 60.0                    | 71.0                    |
| Poznawczość                | 37.0             | 30.0                    | 44.0                    |

**Source: Own study**

The fifth question was aimed at obtaining information on the benefits of active tourism according to students. It turns out that the greatest advantage of active tourism for students of both universities in Rzeszów is the improvement of their condition. In this regard, students of the University of Rzeszów also point out that the advantages of practicing active tourism are its influence on the figure, spending free time with the family, and an important aspect for the respondents is the possibility of personal development. On the other hand, students of the Rzeszów University of Technology indicate spending free time and the opportunity to explore new areas as the main



advantages of practicing active tourism, apart from improving the condition. It was a multiple choice question.

**Tab. 5. Advantages of practicing active tourism according to the respondents (%)**

|  | Total<br>N = 200 | Students URz<br>N = 100 | Students PRz<br>N = 100 |
|--|------------------|-------------------------|-------------------------|
| Improvement of condition               | 82.0             | 92.0                    | 72.0                    |
| Better mood                            | 55.5             | 66.0                    | 45.0                    |
| Improving health                       | 64.0             | 74.0                    | 54.0                    |
| Spending time with family<br>/ friends | 76.5             | 88.0                    | 65.0                    |
| Exploring new areas                    | 54.0             | 46.0                    | 62.0                    |
| Impact on the figure                   | 76.5             | 96.0                    | 57.0                    |
| Personal development                   | 62.5             | 84.0                    | 41.0                    |
| Raising qualifications                 | 45.0             | 67.0                    | 23.0                    |

**Source: Own study**

In the next question, the respondents were asked how they spend their free time. A significant proportion of the respondents among students of the University of Rzeszów decide to spend their free time in an active or entertaining way, and least often choose sightseeing. Students of Rzeszów University of Technology declare in their choices that the most frequently chosen form of spending free time are meetings with family and passive rest, less often choosing active rest. It was a multi-answer question.

**Tab. 6. Spending free time by students (%)**

|                 | Total<br>N = 200 | Students URz<br>N = 100 | Students PRz<br>N = 100 |
|-----------------|------------------|-------------------------|-------------------------|
| Passive leisure | 56.5             | 47.0                    | 66.0                    |
| Active leisure  | 64.5             | 88.0                    | 41.0                    |
| Entertainment   | 61.5             | 72.0                    | 51.0                    |
| Sightseeing     | 40.0             | 33.0                    | 47.0                    |
| Family visits   | 64.0             | 56.0                    | 52.0                    |

**Source: Own study**

The next question in the questionnaire concerned the frequency of undertaking active tourism. The results show that university students much more often undertake this form of activity, most often every day or twice a week, less often once a week, the respondents also declare that they use this type of tourism least often during holidays and long weekends. On the other hand, students surveyed at

the Rzeszów University of Technology are more likely to engage in active tourism once a week or once a month, less often once a year or during holidays and long weekends.

**Tab. 7. The frequency of active tourism by the society (%)**

|                                   | Total<br>N = 200 | Students URz<br>N = 100 | Students PRz<br>N = 100 |
|-----------------------------------|------------------|-------------------------|-------------------------|
| Every day                         | 52.0             | 62.0                    | 42.0                    |
| Twice a week                      | 23.0             | 24.0                    | 22.0                    |
| Once a week                       | 11.5             | 6.0                     | 17.0                    |
| Once a month                      | 7.0              | 2.0                     | 12.0                    |
| Several times a year              | 4.0              | 4.0                     | 4.0                     |
| Once a year                       | 1.0              | 1.0                     | 1.0                     |
| During holidays and long weekends | 1.5              | 1.0                     | 2.0                     |

**Source: Own study**

The next question was as follows: In which group do you most often do active tourism? The responses showed that the majority of students of the University of Rzeszów decide to engage in active tourism together with their colleagues from studies or with friends, less often deciding to practice active tourism with family members or the sports section. On the other hand, students of Rzeszów University of Technology declare that they most often engage in active tourism individually or with their families, and very rarely decide to spend a tourist trip with members of the sports section.

**Tab. 8. Active tourism environment by society (%)**

|                                    | Total<br>N = 200 | Students URz<br>N = 100 | Students PRz<br>N = 100 |
|------------------------------------|------------------|-------------------------|-------------------------|
| Individual                         | 22.0             | 7.0                     | 37.0                    |
| With family                        | 14.0             | 5.0                     | 23.0                    |
| With friends                       | 24.0             | 31.0                    | 17.0                    |
| With colleagues from university    | 37.0             | 53.0                    | 21.0                    |
| With members of the sports section | 3.0              | 4.0                     | 2.0                     |

**Source: Own study**

The last question concerned the place where the respondents do tourism activity. Students of Rzeszów University of Technology declared in the questionnaire that they most often engage in active tourism in the mountains or at the seaside, less often choosing foreign or rural regions. On the other hand, students of the University of Rzeszów in a large group choose mountain areas and lakes as their

destination for active tourism, and less often they decide to choose foreign regions or cities for active tourism. The question was a multiple choice question.

**Tab. 9. Place of active tourism practiced by the society (%)**

|                    | Total<br>N = 200 | Students URz<br>N = 100 | Students PRz<br>N = 100 |
|--------------------|------------------|-------------------------|-------------------------|
| In the city        | 78.0             | 32.0                    | 46.0                    |
| In the countryside | 36.0             | 22.0                    | 14.0                    |
| W mountains        | 140.0            | 77.0                    | 63.0                    |
| At the seaside     | 96.0             | 41.0                    | 55.0                    |
| By the lake        | 106.0            | 65.0                    | 41.0                    |
| Abroad             | 39.0             | 15.0                    | 24.0                    |

Source: Own study

## Discussion

Work presents the main motives for active tourism undertaken by students of the University of Rzeszów and the Rzeszów University of Technology. Both of the above-mentioned universities are located in the Podkarpackie Province, where, thanks to the mountain and upland areas, this region can be considered one of the most suitable for active tourism. In the province Podkarpackie, there are very good conditions, mainly for hiking, water, cycling and canoeing.

Trips related to active tourism are gaining more and more popularity, mainly due to taking up physical activity while practicing them. Social media more and more often informs that physical activity has a positive effect on human health and well-being. Our own results can be compared with the results of the research by F. Mróz and R. Rettinger (2015), in which the analyzed students traveled at least three times, mainly on trips related to active tourism. On the basis of the presented research by F. Mróz and R. Rettunger, it can be concluded that each year student youth become more and more aware of the importance of their health and well-being in their lives, and the fact that they more often use healthy forms of spending free time, focusing on actively spent time [12].

It turns out that even a walk is one of the activities that are classified as active tourism, so each of us had some contact with it. The analysis of the results of the research conducted for the purposes of this study shows that the majority of students of the University of Rzeszów choose active leisure less often, choosing sightseeing or passive leisure, and students of the Rzeszów University of Technology more often choose passive leisure, visiting family, than active leisure. Comparing the research conducted by BD Alejziak (2015) to the research carried out by the authors of this study, it can be noticed that the preferred forms of active tourism differ slightly in the results. Alejziak shows the dependence that more engineers choose mass tourism (56.04%) than active tourism (34.07%), while students of tourism and recreation choose the opposite (19.78%; 71.43%) [13].

The comparison of these two research results can be additionally enriched by the results of the research conducted by R. Rosińska (2015). The analysis of the author's research shows what form of active tourism was preferred by the respondents. The results show that students preferred recreational

(47.6%) and sightseeing (31.1%) tourism, and a smaller group of students chose specialized tourism (21.3%) [14].

Active tourism is strongly associated with taking up physical activity. Research conducted by J. Herbert, P. Żegleń and P. Świder (2017) show what kind of activity students of the University of Rzeszów choose when undertaking physical exercise. Physical activity in the life of a young person is a very important and indispensable element of a healthy lifestyle. Making such an effort in young people very often introduces certain values, behaviors and habits that have a positive impact on their development and life in society. The authors presented the results of research conducted in 2017, which show that students most often choose walking as a form of physical activity, and less often cycling or a gym [15].

After analyzing the research carried out in this study, it can be concluded that students most often choose hiking or cycling. The results of this study show that in order to take up physical activity, mainly active tourism, we do not have to put on expensive and specialized equipment immediately, our willingness and commitment are more of a key issue.

## Conclusions

1. The respondents of both universities are largely interested in active tourism.

2. It is clear from the research that has been carried out that the main.

A factor contributing to being active is health.

3. In both surveyed universities, physical activity is undertaken relatively often.

There is a huge demand and demand for active tourism in the group of student youth.

Students very often decide to practice active tourism to spend time with friends, with a group of people with whom they feel good. A very large proportion of students decide to engage in all kinds of physical activity in order to maintain their physical and mental health.

The study also shows that students of both universities most often decide to engage in active tourism in our country and in nature, away from the hustle and bustle of cities. It certainly contributes to the improvement of their health and activity.

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## POSSIBILITY OF COMPLETE REMISSION IN INOPERABLE TUMOR - NEUROBLASTOMA CASE REPORT

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### **Abstract:**

The article presents a case report of a 5-year-old-girl diagnosed with neuroblastoma-frequent tumor of childhood. It localizes in the sympathetic ganglia. Nonspecific symptoms may occur. The diagnosis is based on imaging scans. The modality depends on the tumor location and stage. A 5-year-old girl was examined because of loose stools. By the use of abdominal USG and CT, a focal lesion was detected. It relocated the pancreas, liver, and IVC. The tumor enclosed the visceral trunk and upper mesenteric artery. The tests showed elevated NSE and DOPA. The diagnosis was: a differentiating neuroblastoma MYCN(-). The patient underwent the treatment for ten months. Due to the location, resection was excluded. Despite intensifying chemoradiotherapy, no regression was reached. Despite an extensive, inoperable residual abdominal mass, the girl stayed in complete remission. In follow-up imaging studies, the tumor's dimensions and nature indicated the stabilization. The observation lasted two years.

### **Keywords:**

*neuroblastoma, inoperable tumor, NMYC(-)negative*

### **Introduction**

Sympathetic embryonal neuroblastoma (NB) is one of the most common childhood cancers. It is also counted among the most common extracranial solid tumors occurring in children and adolescents. It accounts for up to 50% of all tumors detected in newborns. Nearly 90% of cases are diagnosed by the age of 5, although it can also be found in older children. Boys are more susceptible and get the disease slightly more often than girls (1.2:1) [1].

Despite many scientific studies, the etiology of the tumor is still unknown. Neuroblastoma is sporadic, with only 1-2% of familial cases described. They may be associated with a rare mutation of ALK, PHOX2b, and KIF1B [2]. Neuroblastoma occasionally occurs in the course of neurofibromatosis type 1 and Beckwith - Wiedeman syndrome [3]. Neuroblastoma may develop due to the presence of risk factors in the environment [4]. The effect of risk factors on fetal development during pregnancy and fertilization itself was studied. Factors studied included smoking, alcohol consumption, medications during pregnancy, birth factors, and parental exposure to chemicals or heavy metals. The results were inconclusive [5]. Further studies have looked at the association of



exposure to the infection in early childhood, prevalent atopy [6], hormone use, fertility drugs [7], and maternal hair dye use [8].

Genetic factors in the development of Neuroblastoma primarily involve amplification of the MYCN protooncogene. The degree of amplification shows a bimodal distribution: 3- to 10-fold or 100- to 300-fold. A correlation has been found between the presence of a given mutation, the disease stage, and the patient's prognosis[9]. In approximately 25-35% of embryonal neuroblastoma cases, genetic abnormalities are found in the form of a deletion within the short arm of chromosome 1(1p35-36)[10]. The presence of this deletion usually indicates a poor prognosis/prognosis. Duplication of segments of the LMO1 gene present in neuroblastoma tumor cells increases the risk of developing a very aggressive form of new growth [11].

Neuroblastoma originates from the sympathetic trunk crest cells from which the sympathetic ganglia and adrenal medulla develop under normal conditions. Its origin is associated with its primary location. The tumor is located in the course of sympathetic trunks, most often in the retroperitoneal space of the abdomen, less frequently in the posterior mediastinum, neck, and pelvis. Children with neuroblastoma development in both adrenal glands have been described. These were congenital cases [12].

Neuroblastoma is characterized by high tropism to blood and lymph vessels. It is not uncommon for the tumor to wrap large vessels around itself, to develop in their vicinity, but initially without invading their lumen, violating their structure, or destroying them. Nevertheless, it has a significant impact on their proper functioning. As the disease progresses, the tumor grows around the vessels, causing pressure on their walls. In the following stages of growth, it penetrates to the lumen of vessels impairing their proper functioning.

Neuroblastoma manifests itself with a variety of clinical symptoms. One of the most common symptoms is a palpable tumor detected on physical examination and a general picture of the child's condition indicating that he or she is ill. Unfortunately, the disease symptoms are very uncharacteristic and can imitate many other illnesses ranging from the common cold to other malignancies. Usually, general symptoms such as chronic fatigue, drowsiness, irritability, agitation, lack of appetite, weight loss, pale skin, anxiety, pain, fever, or muscle weakness appear in the later stages of the disease when the tumor has spread. In addition to the general symptoms, Neuroblastoma presents primarily with primary symptoms related to the tumor's location. If the neoplasm is located in the thoracic region, the following symptoms may occur dysphagia, untreatable cough, dyspnea, laryngeal wheezing, hoarseness, and Horner's syndrome. When the tumor is located in the pelvis, symptoms may include micturition disorders, constipation, low back pain, and diarrhea. Sometimes Neuroblastoma penetrates the spinal cord, causing compression and neurological disorders. When located in the abdominal cavity, the tumor can grow to a considerable size, causing displacement of internal organs and important arterial and venous vessels, manifested by abdominal dropsy, severe abdominal pain, vomiting, and lack of appetite. Patients with localized tumors may present with no symptoms at the beginning of the disease [13, 14].

Some paraneoplastic syndromes, a group of symptoms accompanying cancer unrelated to the core of the disease itself, are associated with Neuroblastoma. The cause of their occurrence is not fully understood. The symptoms probably result from a generalized immune response of the body. One of them is Horner's syndrome occurring with the cervical or pelvic location of the tumor.

Another example is cerebellar ataxia involving nystagmus, lack of balance coordination, and tremor with the tumor's intracranial growth. Neuroblastoma can secrete vasoactive intestinal peptide (VIP), resulting in diarrhea, abdominal pain, and intestinal atony. The presence of metastases in the bones causes bone pain. Orbital metastases are manifested by petechiae, bleeding eruptions, and ocular exophthalmos. Paraneoplastic syndromes usually resolve after stabilization of the neoplastic process, but not always. Nevertheless, they are infrequent, but children who present with them are considered to have a better prognosis [15, 16].

The diagnostic recommendations for Neuroblastoma primarily include imaging studies. Ultrasound is the simplest, publicly available examination that is able to provide a preliminary estimate of the nature and location of the lesion if it is located in the abdomen or pelvis. X-ray is the basis for the initial diagnosis in the development of Neuroblastoma in the chest. CT is used when a tumor is suspected in the retroperitoneal space. MRI is the primary examination for tumors of the pelvis, cervix, and spinal cord compression [17].

A bone marrow punch biopsy is performed to diagnose micrometastatic Neuroblastoma because of the frequent changes in the bone marrow [18].

A characteristic test in Neuroblastoma diagnosis is MIBG scintigraphy, which uses the active radioisotope Metaiodobenzylguanidine-131I (MIBG-131I). Neuroblastoma is not the only indication for MIBG scintigraphy. Additionally, it is used in scintigraphic localization of pheochromocytomas located in adrenal and extra-adrenal glands and their metastases, imaging paragangliomas, gastrointestinal carcinomas, medullary thyroid carcinomas, in diagnostics of myocardial ischemia and cardiomyopathy. MIBG scintigraphy allows imaging of disease spread throughout the body. Neuroblastoma tumor cells are characterized by increased uptake of isotopic tracer. As a result of the examination, an image of the primary focus and metastatic foci is obtained. Scintigraphy allows assessment of the stage of the disease at the time of diagnosis. The result of scintigraphy is also taken into account in the evaluation of response to therapy. After completion of treatment, scintigraphy allows to localize residual disease, detect relapse and local recurrence. MIBG is specific for Neuroblastoma, detecting more than 90% of tumors. The MIBG result can distinguish active tumor from therapy-induced changes. The combination of MRI and MIBG has the highest sensitivity for neuroblastoma diagnosis [19].

Laboratory findings include elevated levels of specific neuronal enolase (NSE) and urinary catecholamines. Elevated levels of dihydroxyphenylalanine (DOPA) and vanillylmandelic acid are typical of this tumor. Some suggest that serum ferritin levels should be studied as a prognostic marker for the disease. Elevated lactate dehydrogenase levels during treatment indicate a more aggressive form of neuroblastoma [20].

The goal of neuroblastoma treatment is to achieve complete remission. The treatment of Neuroblastoma is complex and involves multidrug chemotherapy, surgery, and radiation therapy. In the most advanced neuroblastoma forms with distant metastases, megachemotherapy with autologous peripheral blood stem cell (autologous-PBSC) transplantation is also used.

The prognosis of neuroblastoma depends on several significant factors. These include the child's age at diagnosis, MYCN gene amplification, and stage. MYCN gene amplification is present in approximately 20% of cases. It indicates a particularly aggressive form of Neuroblastoma. The presence of distant metastases indicates stage IV neuroblastoma. More than 60% of patients

diagnosed with Neuroblastoma have distant metastases at the time of detection. These usually involve the bone marrow or bone. Lung metastases are rare, even in cases of significant disease progression [21].

## **Case report**

This article presents the case of a 5-year-old girl admitted to the Gastrology Department of the University Children's Hospital in Lublin because of an episode of loose stools. In the initial diagnosis, abdominal ultrasound was performed, which revealed a focal lesion in the liver region. On physical examination, no abnormalities were found except mild epigastric muscle resistance. The patient was referred for abdominal CT, which revealed a well-demarcated lesion of heterogeneous echogenicity with numerous calcifications in the retroperitoneal space, measuring 29 x 23 x 19 mm. The lesion was undergoing contrast enhancement, anteriorly displacing the pancreas, right adrenal gland, and liver. The lesion surrounded the visceral trunk and superior mesenteric artery, displaced the inferior vena cava to the right side.

In view of these findings, the patient was transferred to the Oncology Department for further diagnostics. The laboratory parameters analysis showed the following abnormalities: slightly elevated NSE in serum and elevated DOPA in daily urine collection. To exclude metastatic foci, lung CT and bone marrow punch biopsy were performed. No additional metastatic lesions were found. Subsequently, MIBG scintigraphy was carried out, which showed increased isotopic uptake of the tumor in the retroperitoneal space. A tumor biopsy was performed - the histopathologic examination diagnosed differentiating Neuroblastoma N-MYC(-) negative. Based on the whole clinical picture's evaluation, the diagnosis of localized Neuroblastoma NMYC negative was made. The child was qualified for treatment according to the LINES Program - group 7 (intermediate risk). The therapy started in March 2018.

After two cycles of chemotherapy, follow-up examinations of the tumor were performed - ultrasound and MIBG scintigraphy. The tumor dimensions were comparable to the previous ones. A decision was made to intensify chemotherapy in subsequent cycles, but no apparent signs of regression of tumor dimensions were obtained. The results of follow-up MIBG scintigraphy were comparable to the previous ones. Urinary catecholamine levels normalized. The patient's case was consulted with the surgical team for possible tumor resection. Due to the location, the option of surgical intervention was ruled out. Radiotherapy (21 G) was given as local treatment. Chemotherapy was continued until the completion of treatment in December 2018.

Throughout and after treatment, the tumor showed no signs of growth. There were no clinical symptoms. The patient did not experience any side effects of the therapy. Laboratory parameters remained normal. Follow-up imaging examinations and the inoperable residual mass's nature indicated the achieved stabilization of the neoplastic process. Currently, the patient remains three years after the end of treatment. She undergoes periodic oncological follow-up.

## Discussion

Neuroblastoma is an uncommon neoplasm whose biology and nature are still entirely unknown. The disease can progress to spontaneous regression and the advanced disseminated process leading to a patient's death. The nature and development of the tumor depend on various prognostic factors. Nevertheless, 5-year survival is achieved in most patients [22].

One of the most important prognostic factors is the amplification of the NMYC oncogene in tumor cells. MYCN is defined as amplified when there is a multiplication of the copy number of the N-MYC protooncogene. Its number can vary from as few as a few hundred [23]. Patients with MYCN amplification are classified as high-risk patients [24].

Other important prognostic factors are the patient's age at onset and the presence of distant metastases. Any patient with metastatic disease 18 months of age or older is considered high risk, regardless of MYCN amplification [25].

The disease has a significantly milder course in younger patients, less than 12 to 18 months of age. Children younger than one year of age without NMYC gene amplification have substantially better treatment outcomes. The chances of a full recovery are about 90% of such patients. For Neuroblastoma with distant metastases present (stage IV) in a child over one year of age, the average median 5-year survival is less than 30%. Tumors with NMYC amplification present a higher local recurrence rate than those without an extra copy of the gene. They require more intensive treatment, both systemic and local. The treatment outcome within these patients depends more on the number of metastases than on the extent of resection. The dependence of treatment selection on the presence of NMYC amplification is described in a report by Mubarak M obtained from the treatment of 2 patients with stage IV neuroblastoma detected. In both patients, the tumor was identified in the first months of life. In the first child with negative NMYC amplification, the option of observation without any therapeutic intervention was chosen. The second patient with NMYC gene amplification was treated with multidrug chemotherapy with carboplatin and etoposide. Two-year event-free survival was achieved in both cases [26, 27].

Due to the equivocal nature of the disease and the complex biology of Neuroblastoma, deciding on the optimal therapy is challenging. Some cases of Neuroblastoma develop progressively, increasing in size at a very rapid rate and metastasizing to other organs and the bloodstream, despite intensive therapy. At the same time, it should be kept in mind that a high spontaneous regression rate characterizes Neuroblastoma. The term spontaneous regression is defined as spontaneous shrinkage of the tumor or its complete disappearance, leading to complete recovery and improvement of the patient's clinical condition without additional therapeutic interventions.

K. Yamamoto describes that spontaneous regression of immature embryonal Neuroblastoma is not uncommon. He describes 12 patients in whom the detected neuroblastoma tumor shrank without therapeutic intervention. However, none of the tumors had disappeared entirely by the last day of follow-up of 27 months [28].

Necessary to optimize neuroblastoma treatment is the precise staging and risk group of the tumor, based on the biological characteristics of the Neuroblastoma and its spread in the body.

Various similar classifications of Neuroblastoma have been developed to guide the selection of an appropriate therapeutic regimen. They are based on similar guidelines, taking into account the risk factors discussed earlier.

**Tab. 1. INRG Pre-Treatment Classification Schema**

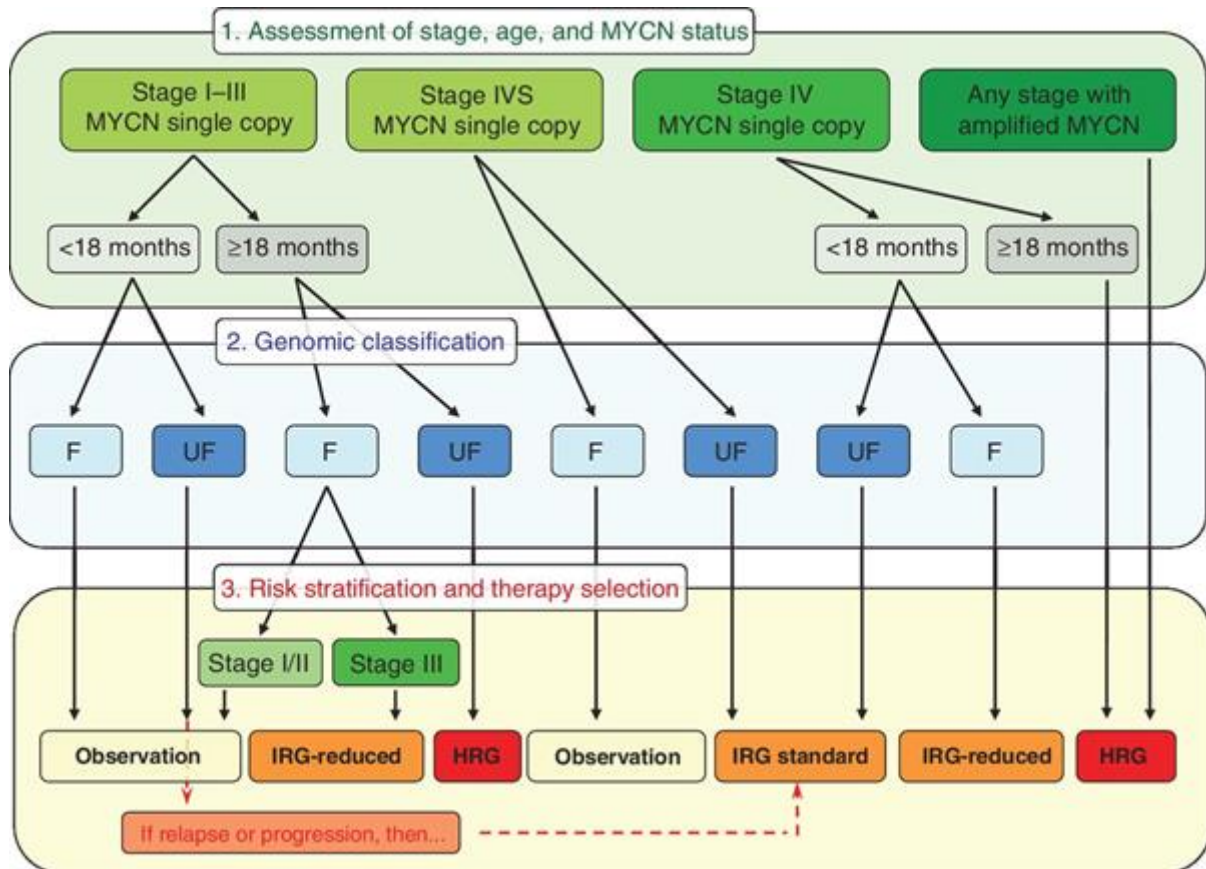
| INRG Pre-Treatment Classification Schema* |                |  |               |                |              |              |
|---|----------------|--|---------------|----------------|--------------|--------------|
| INRG Stage                                | Age            | Histology/Grade of Tumor Differentiation   | MYCN Status   | 11q aberration | Ploidy       | Risk Group   |
| L1/L2                                     |                | GN maturing; GNB intermixed  |               |                |              | Very Low     |
| L1  |                | Any except GN maturing or GNB intermixed   | Not Amplified |                |              | Very Low     |
|   |                |  | Amplified     |                |              | High         |
| L2  | <18 mo         | Any except GN maturing or GNB intermixed   | Not Amplified | No             |              | Low          |
|   |                |  |               | Yes            |              | Intermediate |
|   | =18 mo         | GNB nodular, differentiating NB, differentiating   | Not Amplified | No             |              | Low          |
|   |                |  |               | Yes            |              | Intermediate |
|   |                | GNB nodular, poorly differentiated or undifferentiated NB, poorly differentiated or undifferentiated | Not Amplified |                |              | Intermediate |
|   |                |  | Amplified     |                |              | High         |
| M   | <18 mo         |  | Not Amplified |                | Hyperdiploid | Low          |
|   | <12 mo         |  | Not Amplified |                | Diploid      | Intermediate |
|   | 12 mo - <18 mo |  | Not Amplified |                | Diploid      | Intermediate |
|   | <18 mo         |  | Amplified     |                |              | High         |
|   | =18 mo         |  |               |                |              | High         |
| MS  | <18 mo         |  | Not Amplified | No             |              | Very Low     |
|   |                |  |               | Yes            |              | High         |
|   |                |  | Amplified     |                |              | High         |

Abbreviations: GN = Ganglioneuroma, GNB = Ganglioneuroblastoma, NB = Neuroblastoma, L1 = Localized tumor confined to one body compartment with absence of image-defined risk factors (IDRFs), L2 = Locoregional tumor with presence of one or more IDRFs, M = Distant metastatic disease (except stage MS), MS = Metastatic disease confined to skin, liver, and/or bone marrow in children <18 months old, \*Table adapted from Cohn et al., 2009

Source: Cohn et al. 2009



**Tab. 2. Schematic overview of the proposed revised risk stratification system for therapy selection of patients with non-high-risk neuroblastoma in the upcoming NB2013-LR/IR trial**



**Abbreviation:** F, favorable genomic classification; UF, unfavorable genomic classification; IRG-reduced, intermediate risk with reduced treatment intensity; IRG-standard, intermediate risk group with standard treatment intensity (as in NB2004); HRG, high-risk group

**Source:** Clinical Cancer Research, <https://clincancerres.aacrjournals.org/content/21/8/1904.figures-only>

The analysis of the above-mentioned features of the tumor allows for choosing an appropriate treatment strategy and obtaining the desired results. The mainstay of treatment is various therapeutic modalities that have been used for years: chemotherapy, radiotherapy, and surgery. In the most advanced stages of the disease, even more intensive treatment has been introduced: megachemotherapy with autologous peripheral blood stem cell transplantation and immunotherapy with anti-GD2 antibody and isotretinoin.

Current treatment regimens in most cases are based on three main stages: induction, consolidation, and maintenance. The treatment regimen at each step depends on the tumor form, location, presentation, and grade. The following diagram illustrates the selection of treatment modalities depending on these prognostic factors.

The classic treatment regimen for Neuroblastoma begins with multidrug preoperative chemotherapy. During the initial chemotherapy blocks, some patients undergo peripheral blood stem cell separation for preservation and subsequent use in autologous peripheral blood stem cell (auto-PBSC) transplantation. This procedure is for high-risk patients. Preoperative chemotherapy is aimed at reducing the tumor mass and eliminating some of the metastases. In many cases, initial



chemotherapy allows inoperable masses to be converted to resectable ones over time. The continuation of this stage of treatment is local treatment - it concerns the primary tumor. If indicated, local therapy of metastatic lesions is also planned [29, 30].

The optimal way of local treatment of both primary tumor and metastatic lesions is radical non-incisional surgery. Tumors can be divided into complete resection (removal of more than 90% of the tumor mass), partial resection (50-90% of the tumor mass), and unresectable tumors (<50% of the tumor mass can be resected) [31].

The decision on the choice of treatment regimen or its intensification is based on the tumor stage analysis. In contrast, the decision on local treatment (surgical resection or radiotherapy) is selected individually. In the case of neuroblastoma, complete tumor resection has a significant impact on the course of treatment. This has been highlighted in numerous studies [32].

A study from the Department of Oncology in Bialystok evaluated the radicality of neuroblastoma resection and its impact on subsequent prognosis in 41 patients. In 10 children, primary tumor resection was performed, in the rest, elementary surgery was not possible, and surgical treatment was implemented after completion of induction chemotherapy. In 8 patients of the 41 operated on, the procedure proved to be non-radical. Of the 41 patients, 10 (24.4%) died (9 in stage IV and 1 in stage III disease). In 3 of them, the resection of the primary focus was incomplete. Among the 31 surviving patients, primary surgery proved to be non-radical in 5 children. After completion of postoperative chemotherapy, they were scheduled for repeat surgery. They currently remain in remission. This study allows us to conclude that the lack of radical surgery in patients with sympathetic ganglioneuroma does not rule out the possibility of a complete cure. After intensive multidrug chemotherapy, these patients are eligible for radical "second look" surgery [33].

Analysis of treatment outcomes at various Centers indicates that radical tumor resection is relatively common. In a 2004 study by The Children's Cancer Group, which collected 539 patients from multiple centers across the United States, complete resection was achieved in 17% of children without induction chemotherapy and 46% of children after chemotherapy [34]. Von Schweinitz et al., summarizing the results of the treatment of 2112 patients of the German Neuroblastoma Treatment Group between 1979 and 1999, described surgical completeness of 66.4% [35]. In British centers, 62% of children treated for sympathetic ganglioneuroma between 1995 and 2005 had radical resection of the primary focus [36]. Patients in whom radical surgery was not possible to require long-term follow-up and evaluation of the treatment efficacy. Matsumura et al. demonstrated from a study of a group of 214 patients that complete resection slightly improves the survival of patients in stage IV disease, but the differences are not statistically significant [37].

J.A. Kohler, in his article, describes the SIOPEX study, which analyzed the achieved treatment results and survival in children over one year of age with Neuroblastoma without MYCN gene amplification. The goal of the study was to achieve a 5-year patient survival rate of greater than 80%. For children with a localized disease without MYCN gene amplification, radical surgical treatment is considered the main requirement for a cure [38].

In contrast, a recent Localized Neuroblastoma European Group (LNEG) study that analyzed the outcomes of 160 patients with inoperable neuroblastoma tumors emphasizes the crucial role of the presence of NMYC. The study confirmed that all patients even above one year of age and thus with an unfavorable prognostic age factor had an excellent prognosis and achieved good treatment

outcomes despite inoperable tumors. Rubie H. presents similar conclusions in describing the results of the treatment of inoperable neuroblastoma tumor in the British Journal of Cancer 2003. He points out that in infants with detected localized neuroblastoma tumor, without amplification of the MYCN gene, not amenable to resection due to its difficult location, multidrug chemotherapy is sufficient. Patient follow-up was 55 months, event-free survival occurred in 100% of patients [38].

The analysis of the above-mentioned tumor characteristics allows us to choose the appropriate treatment strategy and obtain the desired results. Current treatment regimens are based on three main stages: induction, consolidation, and maintenance. The treatment regimen at each step depends on the tumor form, location, presentation, and background. The classic neuroblastoma treatment regimen begins with multidrug preoperative chemotherapy. During the initial chemotherapy blocks, stem cell separation is performed to preserve the stem cells for later use in autologous peripheral blood stem cell (auto-PBSC) transplantation. Preoperative chemotherapy is aimed at reducing the tumor mass and eliminating some of the metastases. In many cases, initial chemotherapy allows inoperable masses to be converted to resectable ones over time. Neuroblastoma tumors can be divided into those amenable to complete resection (removal of more than 90% of the tumor mass), partial resection (50-90% of the tumor mass), and unresectable (resectable <50% of the tumor mass) [39].

Also, in the analysis of Rubie H. Excellent Outcome With Reduced Treatment in Infants With Nonmetastatic and Unresectable Neuroblastoma Without MYCN Amplification: Results of the Prospective INES 99.1 in the Journal of Clinical Oncology 02.2011 described the achievement of 5-year survival in 62% of children under one year of age with inoperable Neuroblastoma only after low-dose chemotherapy without anthracyclines [39].

In contrast to this group, patients with unfavorable features (stage, MYCN gene) had a significantly worse prognosis, which further worsens with age, and in them, therapy should be intensified [40]. Ryan, Anne L. MBBS, in the paper The Role of Surgery in High-Risk Embryonal Neuroblastoma in the Journal of Pediatric Hematology, Oncology 01.2020, describes the treatment outcomes associated with surgical resection of Neuroblastoma. The study shows that patients with >90% resection but with metastases did not have improved survival. This result indicates that surgical resection is only one component of achieving a good neuroblastoma outcome [41].

In the present case, despite the intensification of preoperative treatment, there was no possibility of radical, safe resection. In this situation, radiotherapy was used as a local treatment. Radiotherapy is an essential element of the treatment of the primary focus in case of unresectable or challenging to access lesions. Radiation therapy is also used in locally advanced cancer cases (stage III) when the tumor has infiltrated regional lymph nodes, adjacent structures, and blood vessels while have failed to achieve favorable treatment outcomes with chemotherapy or surgery alone. Weltman Eduardo studied the efficacy of radiation therapy in cases of Neuroblastoma with brain metastases present. This study revealed that radiation therapy to the head region might prevent recurrence at that site. Unfortunately, reducing the cranial region's recurrence rate did not affect either the disease-free period or overall survival. It follows that head irradiation reduces the recurrence rate in this area but does not affect the overall prognosis [42].

The next stage of treatment after surgery is postoperative chemotherapy. It aims to prevent the early recurrence of the tumor and stop residual tumor growth. As mentioned above, in the group of children with the highest stage of the disease, megachemotherapy with autologous stem cell

transplantation (auto-PBSC) and immunotherapy with anti-GD2 antibody and isotretinoin may also be used.

In the case described, decisions were made to leave the inoperable mass. After completion of preoperative chemotherapy, radiotherapy was administered, and multidrug chemotherapy was continued. An important factor influencing the plan of further treatment was the fact that the patient was not found to have an extra copy of the N-MYC gene. This allowed the abandonment of radical tumor resection, which was associated with a significant risk of damage to adjacent organs and major blood vessels. Despite the unresectable lesion, the absence of N-MYC gene amplification was associated with a higher chance of survival. Currently, the patient remains under continuous oncologic follow-up. Since the end of anticancer treatment, more than three years have passed without adverse events. This allows us to assume that the girl has achieved complete remission.

She still requires frequent follow-up and evaluation of laboratory and imaging findings.

## Conclusions

- 1) In the case of tumors without increased amplification of NMYC(-) gene, in localized forms, lack of resectability does not rule out complete chances for a cure; with inoperable tumor long-term, event-free survival is possible.
- 2) The critical prognostic factor is the biology of the tumor cell, including the presence of NMYC amplification.
- 3) Because of its multiformity and differential response to treatment, Neuroblastoma requires further in-depth studies and analyses of response to different therapeutic modalities. A better understanding of these mechanisms may enable improved treatment outcomes.
- 4) Because of the tumor's malignant nature, early diagnosis with imaging studies allows for early treatment and more favorable outcomes.

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## **WILD-HIVE BEEKEEPING AS AN ELEMENT OF COGNITIVE TOURISM**

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### **Abstract:**

The rapid development of tourism from the mid-twentieth century made it an important sector of the economy. Due to the popularity of tourism, this department takes over or supports functions performed by other areas of human life, e.g. cognitive functions. Recreation as part of cognitive tourism is traveling combined with getting to know the world in a very wide range. The aim of the study was to analyze the role of wild-hive beekeeping as an element of cognitive tourism. Discouraging wild-hive beekeeping does many benefits to the functioning of the forest. Wild-hive beekeeping also performs non-production functions as a tourist attraction. Based on the analysis of the collected materials, it was shown that wild-hives beekeeping is part of cognitive tourism. It performs recreational, cultural, educational and economic functions, as well as shaping environmental awareness. Wild-hive beekeeping should be treated as one of the new elements of making cognitive tourism more attractive.

### **Keywords:**

*cognitive tourism, wild-hive beekeeping, forms of tourism, functions and motives of tourism*

### **Introduction**

In recent years, tourism has developed very dynamically. Currently, it is a permanent element of everyday life in society. There is an increase in the position of the domestic economy. As a leading branch of the economy, it influences the development of spatial development in regions and tourist destinations. The popularization of tourism in Poland is undoubtedly influenced by the increasingly attractive tourist and recreational base and the financial possibilities of holidaymakers. The increase in offers and the diversified level of services favor the development of tourism in Poland. Tourism allows you to get acquainted with local customs, including the Old Polish tradition (e.g. wild-hive beekeeping), culture, including national culture (e.g. painting, sculpture, literature, etc.) [1].

The functions of modern tourism deserve systematic evaluation. It should also be noted that the effects of the development of tourism may deserve a negative assessment when they are accompanied by certain pathological phenomena, such as the devastation of the natural and cultural environment, illegal trade, and inflation. In this case, we can talk about dysfunctions of tourism [2].

However, the main e-functions of tourism include, among others, functions recreational, health, cognitive, nature protection, educational [3].



One of the most important functions of tourism is the broadly understood cognitive function. Its importance is due to the fact that tourism is associated with a temporary change of place stay, which forces the tourist to undertake such activities as: identification tourist needs, choosing a vacation destination, getting information on place of stay. To make these decisions, a tourist needs broadly understood knowledge, which he acquires before and during a tourist trip.

Cognitive tourism broadens horizons, raises the level of knowledge, contributes to an increase in the level of education, expands knowledge of the world, develops attitudes and personality, and improves general culture. People undertake tourist trips to get to know the world, see interesting phenomena, use cultural goods, come into direct contact with the population of the visited place, learn about their lifestyle, behavior, patterns, traditions, customs, etc. [2]. The cognitive function of tourism includes, among others, recreational, educational, educational, ethnic and nature protection functions.

### **Functions and motives of cognitive tourism**

The rapid development of tourism from the mid-twentieth century made it an important branch of the economy, determining human behavior. This is due, inter alia, to the better economic status of customers who are more willing than ever to invest in travel. The rich tourist offers can be used in a group or individually. In summer, family trips prevail because parents go on vacation with their children. If tourists do not want to organize their trip on their own, they can always use the offer of travel agencies. There are many possibilities for traveling and meeting the needs of tourists. If needs are the starting point of human behavior, the motives determine consumer behavior and the immediate cause of human actions. Every human activity is driven by motives that guide him, define the types of activities and the goal. practicing tourism, including cognitive tourism. Cognitive tourism travels can be motivated by more than one reason, and the structure of tourism motivation is dynamic and changing [4]. There are some basic recurring themes in this topic. The main theme of cognitive tourism is of course:

- ✓ Cognitive theme. Tourism broadens horizons, raises the level of knowledge, contributes to an increase in the level of education, expands knowledge of the world, develops attitudes and personality, and improves general culture. People undertake tourist journeys to get to know the world, see interesting phenomena, use cultural goods, come into direct contact with the population of the visited country, learn about their lifestyle, behavior, patterns, traditions, customs, etc.

Additional motives for practicing cognitive tourism are also:

- ✓ Leisure and health theme. Tourism is about regaining strength, regeneration and healing. Traveling renews and restores the strength used in everyday life, work and study.
- ✓ Theme for change. Tourism is an escape from everyday life. It is a change of surroundings, a search for otherness, novelty, variety, return to nature, a search for silence, beauty, peace and sometimes loneliness [5].
- ✓ Due to the growing importance and popularity of tourism, this department takes over or supports the functions performed by other areas of human life. This also applies to the

cognitive function. So, cognitive tourism is another type of general term tourism is. This genus, as the name suggests, terms related to traveling mainly for broadly understood learning purposes. Cognitive tourism involves, for example, tourists and visitors getting to know the history of any chosen places and neighborhoods that interest us. In this case, cognitive tourism allows you to develop your own needs and, most often, to satisfy the curiosity caused by interest in a specific topic. Cognitive tourism also performs a number of other functions, especially for people who are interested in various issues.

- ✓ Recreational function - tourism in itself can bring pleasure and be a source of joy for life. Its development is also necessary from an economic point of view - for the renewal and maintenance of physical and mental strength spent at work and outside [6].
- ✓ Educational function - tourism means human entry into direct contact with the new social environment understood as a set of three components: natural, social and cultural. Tourism, in its educational assumption, can bring positive effects in the course of human life in its every phase.
- ✓ Educational function - the educational function of tourism is justified as an element of its educational function, so it can be fulfilled both in a cognitive and practical sense.
- ✓ The function of cultural education - it can stimulate the popularization of contemporary achievements and the cultivation of the heritage of the past. It can enrich the attitudes of patriotism understood as care for the national community.
- ✓ Economic function - domestic tourism is primarily an important socio-economic factor of tourist destination areas. Tourists are consumers of many services and goods, and thus carriers of the demand for tourist services.
- ✓ The function of shaping ecological awareness - the development of tourism depends on the attractiveness of the environment. The degradation of the landscape must sooner or later lead to the destruction of tourism. In light of these comments, the function of shaping awareness of the destruction of tourism. In the light of these remarks, the function of shaping the ecological awareness of contemporary tourism is gaining more and more importance [5].

Recreation as part of cognitive tourism aims to travel combined with getting to know the world, and in a very wide range. Cognitive tourism is based on expanding knowledge about the history of various places and objects. It allows to satisfy the curiosity of visitors to the extent and subject of interest to them. Tourists' perspective on many things is changing precisely thanks to the practice of cognitive tourism. It aims to enrich us with, for example, information on monuments and historical places, traditions and customs of our ancestors (e.g. wild-hive beekeeping) or the customs of the people living in the areas we visit. Expeditions also teach openness to other people. Tourism teaches tolerance, respect, understanding and accepting their differences. So, another advantage of traveling is the chance to meet new people and make friends and acquaintances. Cognitive tourism is becoming more and more popular [7].

Certainly, it greatly develops awareness and shapes the character and perception of the world. It simply allows tourists to know more about many topics. Therefore, within the framework of cognitive tourism, many different forms can be distinguished:

- ✓ Nature tourism - related to getting to know nature in general: animals, plants, landscapes,

- ✓ Sightseeing tourism - trips the main motive of which is the desire to visit a specific object, town or region; especially popular in schools where subject trips, green schools, camps, etc. are organized,
- ✓ Cultural tourism - visiting places with material and non-material values important for cultural, artistic and historical reasons; tourist traffic is concentrated mainly in cities where monuments, institutions and cultural events are located; there are also special hiking trails
- ✓ Ethnic tourism - getting to know social groups that differ in culture, customs and traditions,
- ✓ Film tourism - associated with places that were open air for film productions,
- ✓ Sentimental tourism - trips to places of birth and origin that people had to leave for political or economic reasons,
- ✓ Culinary tourism - something for gourmets from different regions of the country and all over the world. Connected with traveling to places where certain food products are made or where culinary festivals are organized,
- ✓ Festival tourism - trips wherever festivals are organized, in various forms: film, culinary, music, art, theater, parades,
- ✓ Polar tourism - its main goal is to learn about the areas and life in Antarctica and the Arctic, it is also associated with cruises in the Arctic Sea and around the polar regions, Iceberg - Antarctica
- ✓ Volunteer tourism - inextricably linked with social assistance, through which a volunteer gets to know the world and other people,
- ✓ Linguistic tourism - based on trips abroad during which we are to learn a foreign language,
- ✓ Black tourism - traveling to places associated with death, the extermination of humanity, e.g. the labor camp in Auschwitz-Birkenau,
- ✓ Birdwatching - watching birds in their natural habitats,
- ✓ Safari - a journey through the areas of wild Africa in order to observe and often also photograph local animals,
- ✓ Fan tourism - related to trips to sports events,
- ✓ Geotourism - learning about geological forms and mining areas,
- ✓ Ecotourism - aims to care for the natural preservation of nature forms and to reduce the negative impact of human activity on the environment [4, 8, 9].

The broadly understood cognitive function of tourism results from the growing role of knowledge in human life and the interdisciplinary of tourism. Therefore, the role of tourism is not it is limited only to allowing relaxation.

### **Wild-hive beekeeping yesterday and today**

Wild-hive beekeeping is an old form of forest beekeeping involving the breeding of bees in specially hollowed-out tree hollows, the so-called beehives [10]. The first records of Polish beekeeping were made by the traveler Ibrahim ibn Jakub in 965, while archaeological sources say that Polish beekeeping was already known about 2000 years ago. Primary bees were kept in blindness (natural hollows inhabited by bees), their use was based on the principle of collecting or hunting bees, i.e. obtaining honey. Then people started digging the hives by themselves.

The areas where wild-hive beekeeping was carried out are mostly forests belonging to the king, magnates or clergy. The right to practice wild-hive beekeeping was paid for with high tributes, including honey and wax. Royal wild beekeepers had certain privileges. Wild beekeepers formed associations of people of one craft. A candidate for this profession was forced to show an impeccable opinion and take an oath of obedience to the honey hunting court. In order to preserve the wild beehive complexes in some families, an inheritance law was written ensuring the transfer of rights from father to son. The wild beehives of their own boron were marked with one sign, the so-called a honey hunting mark [11].

Wild-hive beekeeping in the Kingdom of Poland developed most intensively in the governorates of Augustów, Płock and Lublin. It should be mentioned that in 1827 a record number of beehives was recorded in the Augustów Forest - 17,736 pieces. 1799 in the Kurpiowska Primeval Forest - 4,621 beehives. Beekeeping was also highly developed in the Świętokrzyska and Sandomierska Forests [12].

Historically, wild-hive keeping was one of the oldest forms of forest use and was an important branch of the economy. In its heyday, in the 16th century, it provided more income than trade in wood and hunting. The period of the most intensive development of wild-hive beekeeping in Poland falls in the 16th and 17th centuries, while the decline occurred in the 19th century not only due to the development of agriculture, industry and more effective methods of bee breeding, but also due to administrative prohibitions. Wild bees also died as a result of varroa - a parasitic disease that spreads among these insects in Europe [13].

The benefits of bees for agriculture have long been appreciated, but less is being said about their role in the natural, non-agricultural environment. Proper pollination of plants contributes to the maintenance of biodiversity which is very important for the proper functioning of ecosystems, including forest ecosystems. Wild-hive beekeeping is a form of sustainable use of forests, it contributes to the protection of nature and the old Polish tradition.

Originally, Poland was covered with forests. In our latitude, the forest was the natural habitat of the honeybee, which over thousands of years of evolution adapted to this environment. It was part of the natural fauna, and at the same time rendered invaluable services by pollinating the plants present in this community. Thus, the activity of the honey bee sustained the biodiversity in the forest environment, and thus the stability of this ecosystem. At first, man consciously used only bee products, mainly honey and wax, without realizing the real importance of the honey bee. Over time, human intervention began to change the primary habitat of the honey bee more and more. And man continued to benefit directly from the work of bees, not realizing their importance for the environment and agricultural crops. In the meantime, the honey bee was forced out of its natural environment, the forest [14].

Thus, wild-hive beekeeping makes it possible to recreate, at least locally, a group of insects-pollinators close to the natural in commercial forests and in forest national parks. Wild-hive beekeeping is a way to restore bees to forest ecosystems in a way that favors even distribution, which is not without significance for nature protection. Bees are an important link in the forest biocenosis and have an influence on increasing the amount of seeds produced by numerous tree species. Their presence promotes the natural renewal of the stand. The pollinated flowers of

numerous trees and forest shrubs increase the yield of their fruit, which in turn are food for many species of birds - the natural allies of the stand [15].

The tradition regained after 100 years will also help to preserve ancient honey trees, a refuge for many rare species of mushrooms, plants and animals. The oldest trees, in which swarms established nests in large numbers, have been cut down, and the structure of forests has often changed to monocultures. Moreover, the forest is located on soils that are not very useful for agriculture, and therefore are not very fertile, and thus are covered with a small number of species of food plants for bees.

Wild-hive beekeeping can also perform non-productive functions in forests and create the possibility of cultural revival of the region as an additional tourist attraction. An unquestionable attraction is wild honey, a unique product obtained using traditional methods. Bees inhabiting beehives and logs produce wild honey containing nectar and pollen of wild plants in forests. Common wild honey is considered a product of the highest purity class and excellent taste [16].

Therefore, recently there have been attempts to restore wild-hive beekeeping in Polish forests. The inhabited beehives and logs can be found in the Spała Forests, the Świętokrzyska Forest, as well as in two national parks, Biebrza and Wigierski. The largest undertaking in the country in this regard is undoubtedly the implementation of the project entitled "Traditional wild-hive beekeeping as the rescue of wild bees in the forests". Foresters want to restore wild honey hunting traditions in the forests of north-eastern Poland. The forest beekeeping reconstruction project financed by Norwegian funds as part of educational activities was implemented jointly by 4 forest districts located in north-eastern Poland: Augustow Forest District, Browsk Forest District, Maskulinskie Forest District and Suprasl Forest District. The project involves, among others building beehives, training potential honey hunters, creating educational paths and research. Cooperation with honey hunters from the Shulgan-Tash National Park in Bashkiria in the Urals (Russia) was of key importance, where honey hunting traditions continue to this day. Specialists from Bashkiria helped Polish foresters to restore traditional wild-hive beekeeping. The project assumed that in each of the four forest districts there will be at least three beehives and two logs. Beehives are carved in a standing, living tree; and the logs are cut pieces of wood (usually 1.5-2 m long), which are prepared for the needs of bees and then hung on trees.

As part of the scientific part of the project, research was carried out on the condition of bees inhabiting beehives and logs, their racial identity and the quality of wildhoney (Warsaw University of Life Sciences), and on the other - legal aspects of honey hunting, as there are currently no regulations regulating this activity ( University of Life Sciences in Białystok) [17].

One of the main goals of the project was to check to what extent bees still live in the forest and to what extent the activities carried out in the project improved their living conditions. Another very important task of the project was to raise awareness of the role of bees in the ecosystem, including forest ecosystems, increase social awareness of the need to actively and protect bees, and to stop the loss of biological balance and the degradation of ecosystem functions. Therefore, as part of the project, educational paths, gardens with honey plants, multimedia points were created, publications, albums, leaflets, guides on educational paths, educational games and a website devoted to the project were created. The basis of the educational message is to show the importance and dependence of traditional wild-hive beekeeping and to facilitate independent



action to improve the living conditions of bees. Due to the small, at this stage, the production of wild honey by bees inhabiting wild hives and logs [18,19].

Poland is the only country in the European Union that has attempted to restore wild-hive beekeeping on its territory as an opportunity to protect nature and the old Polish tradition. These activities indirectly contribute to creating the image of Poland as a country that not only cultivates its history, but also tries to bring its past elements back to life.

## Summary

The restoration of wild-hive beekeeping to Polish forests is the revival of a beautiful tradition, unique for Central and Eastern Europe, which in Poland was associated with rich, specific vocabulary and interesting customs. Due to the fact that this tradition is still strongly present in the minds of Poles, beehives have a chance to become a tourist attraction, and the wild honey harvested from them - an attractive, unique traditional product that can be an additional source of income for inhabitants of areas with high forest cover. Wild-hives beekeeping is not a time-consuming activity due to the fact that the hives are inspected only twice a year - in spring to clean the hive and in autumn to collect honey. Wild-hives beekeeping can be cultivated by people who have a small amount of time, strongly limited by already performed professional duties.

Wild-hives beekeeping restitution sites are mainly areas historically famous for beekeeping, which include, among others Puszcza Augustowska, Białowieska, Kurpiowska, Kozienicka, Świętokrzyska and Puszcza Pilicka. In the territory of the State Forests, wild hives are established mainly in promotional forest complexes, some reserves and landscape parks. They can constitute a valuable, cognitive and educational tourist offer, as well as serve to recreate the cultural values of Polish forestry (Zaręba 1986).

Demonstrations of beehives and logs, and honey harvesting shows are very popular among tourists.

Wild honey, as a unique traditional product, obtained in traditional ways from ecologically clean forest areas, is an amazing attraction for tourists. It is a product of the highest purity class and excellent taste. The price of one kilogram exceeds the price of wild honey from a traditional or large-scale apiary several times. Wild honey is more expensive than that of the hive. It is valued for its unique aroma, richness of micronutrients and healing properties. In Bashkiria, a liter of honey costs 150 euros. For now, however, we have too little beehives for mass production, but tourists can try this bee product during the tasting of honey.

In the future, tourists will be able to visit beehives, today they must be satisfied with an educational path illustrating the return of wild-hive beekeeping, arranged near the headquarters of the landscape park in Spała and Augustow Forest District. There are an active wild hive here, constantly inhabited by bees, as we hear - half of forest origin.

Wild-hives beekeeping as a tourist attraction also creates the possibility of cultural revival of the region. Organizing shows, festivals - honey picking in the wild, hayfields (e.g. the first Polish wild honey harvesting from beehives in over a hundred years. In the Spała Landscape Park on the Pilica river) or visiting prepared thematic - show wild hives, educational paths - attract tourists of all ages, but with a common theme - a cognitive theme.



Based on the analysis of the collected materials, it was found that wild-hive beekeeping is part of cognitive tourism. It performs recreational, cultural education, educational as well as economic and ecological awareness-building functions. The revival of wild hive beekeeping should be treated as one of the elements of making cognitive tourism more attractive.

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# **CONDITIONS FOR THE DEVELOPMENT OF ECO-TOURISM AND AGRO-TOURISM IN THE MACROREGION OF CENTRAL POLAND**

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## **Abstract:**

Agrotourism is an increasingly popular form of tourism in Poland. The aim of the study was to analyze the conditions for the development of agrotourism and ecotourism in the Macroregion of Central Poland. The analysis covers environmental conditions, demographic conditions, the activities of advisory institutions and legislative aspects. Considering available data about agro tourism development in the Macroregion of Central Poland we can affirm that in that domain region capability is not fully utilized. But we can also confirm, that last decade resulted in growth of agro tourism farms number in this region and the trend is rather national. Much more slowly grows ecological farms number, which scope of activity is adjusted by a number of legislations obstructing realization of this agricultural activity trend (ecotourism).

## **Keywords:**

*agrotourism, ecotourism, natural conditions, advisory institutions, legislations*

## **Introduction**

Agro tourism is one of the most popular form of rest. In the late decade it is observed very dynamic development of agro tourism. It is caused by some kind of people's boredom of rest in standard form in large holiday resorts, with every year rigid pool of attraction [1].

We can easily observe among society avidity to back to the roots. People during their rest want to contact something new, to learn something different and to be served in a special way. It can be also observed peoples desire to contact the nature, the atmosphere of countryside and contact with native inhabitants, and especially opportunity to benefit from silence and repose. That is why lately this form of rest amidst society is more and more popular and widespread [2].

Poland possesses big potential in that sphere of tourism in respect of unique natural value – flora and fauna, but also polish countryside specificity which is characterized of large number of small villages and farms creating entered into account of agro tourism base potential. People who are looking for rest in the countryside, on farms or in the forester's lodge are appealed by forests, rivers, beauty of agricultural landscape, contact with domestic and wild animals, contacts and good relations with people who are living there [2].

Agro tourism development is supported by legislation. Moreover it is more establishments, foundations and non-governmental organizations supporting this activity via financial support and legislation related to set up and run agro tourism farms. Example of that support is advisory and training activity of Agricultural Consultative Centers all around the country.

Difficult economic situation in small agricultural farms causes that agro tourism business is the way of generating additional income for those farms, and further life condition betterment in the countryside and its development [3].

### **Administrative division**

The Macroregion of Central Poland, due to its location, functions, unique development potential and functional and spatial connections, plays a special role in the country and Europe. In the face of the extraordinary dynamics of changes taking place in recent years, new needs and new market sectors, it constitutes a space stimulating development processes and becomes an area of concentration of Poland's competitive advantages on an international scale. The macroregion is made up of 2 voivodships: Mazowieckie and Lodzkie, covering 66 poviats, including 8 townships, and 491 communes, including 53 urban communes and 76 urban-rural communes. The spatial and socio-economic connections of both voivodeships allowed for the identification of a NUTS unit under the name of the Central Region (NUTS level 1) within the framework of official statistics [4].

### **Environmental and demographic conditions**

The population of the macroregion at the end of 2012 amounted to approx. 7.8 million people, which constituted 20.3% of the population of Poland and placed the macroregion in second place in the country. In terms of the total area (53,777 km<sup>2</sup>, which constitutes 17.2% of the country's area), the macroregion was ranked 4th in the country. The average population density in the Central Region was 146 people / km<sup>2</sup>, 1,511 people / km<sup>2</sup> for cities, and 56 people / km<sup>2</sup> for rural areas. In 2012, the share of the urban population was 63.4% (Poland 60.5%) [4].

Both the potential resulting from the resources and values of the natural environment and the features of the macroregion's location fundamentally determine the development opportunities and directly affect the quality of life. The Macroregion of Central Poland is located in the center of Poland, within the Central European Lowlands and the Polish Highlands. The surface relief of the macroregion is diversified and is characterized by the interpenetration of lowland features with those of upland areas. A significant part of the area is the landscape associated with the old glacial plateau (lakeless), there are less depressions, valleys, larger valleys and plains of water accumulation and uplands with carbonate rocks. The Macroregion of Central Poland climate is transitory and its most important feature is the great variability of meteorological elements over time and small spatial differentiation. West and south-west winds prevail throughout the year. Average annual air temperatures range from 7 to 8 °C. The greatest spatial differentiation is shown by the annual sum of atmospheric precipitation, ranging from 500 mm in the lowlands to 650 mm in the highlands. An unfavorable phenomenon is the rainfall deficit in the central-western part of the macroregion [4].

The Concepts of the Development Strategy of the Macroregion of Central Poland 2030 were developed jointly by the Mazowieckie and Lodzkie voivodeships. Concept The Development Strategy of The Macroregion of Central Poland 2030 responds to a number of challenges common to both voivodships. Its main assumption is to strengthen and better use the development potential of the macroregion and increase international competitiveness [5].

## **Nature and landscape protection**

The Macroregion of Central Poland are not the most attractive region of Poland in agro tourism. It stand down in that case to North-East macro region. Despite of that it owns natural values crucial for chance for this rest form development. Those values are varied diversified in every administrative district. To the important voivodships attraction we can numbered also national and landscape parks.

A significant part of the valuable natural and landscape areas in the Macroregion of Central Poland are under legal protection. Currently, all forms of legal protection are available in the macroregion.

These are:

- 1 national park (Kampinos National Park),
- 273 nature reserves,
- 15 landscape parks,
- 46 protected landscape areas,
- 12 documentation sites, ecological areas,
- 64 nature and landscape complexes and natural monuments.

In 2012, the area of legally protected areas in the macroregion (excluding Natura 2000 sites) was approx. Ha, which accounted for 26.3% of the total area (Mazowieckie Voivodeship 32.5%, Lodzkie Voivodeship 19.7%, Poland 32.5%). Since 2005, the area of legally protected areas in MPC has increased by 1.1 pp. In 2012, as part of the Natura 2000 network, in the macroregion there were 20 Special Protection Areas for Birds covering an area of approx. in the country [4].

The first-order watershed, which separates the basins of the Vistula and Odra rivers, passes through the macroregion. The western part of the macroregion (Lodzkie Voivodeship) is characterized by low surface water resources and relatively even density of the river network. Mazovian Voivodeship is crossed from south to north and north-west by Polish the biggest river – Vistula to which are fallen from the south side counting from the west side, big rivers like: Radomka, Pilica, Bzura and from the north Bug, Narew and Wkra. Tourist attraction may be also smaller rivers which are inflows of, for example,. Bzura river such as: Rawka and Skierniewka. And from the east side of Vistula attraction is determining by pure river Liwiec flowing into the Bug river and Narew inflows, Orz, Omulew, Rozoga, Pładowica i Szkwa [6].

The best naturalistic and demography conditions for agro tourism development are in Ostrołęka, Gostynin, Zyrardow, Plonsk, Losice, Szydłowiec, West Warsaw district. Important agricultural development is also seen in districts: Legionowo, Wolomin, Przasnysz, Wyszów and Siedlce.

West Warsaw district where the main tourist and agricultural attraction is Kampinos National Park and its protection zones especially on the river side. Warsaw in principle is touching the South-West part of Kampinos forest which is one of the largest National Parks in Poland 38544 ha and in that 27000 ha are forests. That area and its protection zone became in 2000 qualified by UNESCO as biosphere reserve MaB Kampinos Forest at area 76200 ha. On that area are 22 zones under the strict preservation (area of 4638 ha) like strict reserve where can't have a place any procedures but can be done only observations of free natural processes [6].

Areas under the partial preservation represent 26646 ha (80% of whole area). In that zones can be proceeded acts to maintain valuable plants and to reorganize artificial units. Landscape preservation area is 494 ha [6].

Gostynin district situated in the West side of Mazovian Voivodship is very attractive area. The most important value of natural environment of that zone are forests and valley of Skrwa and Osetnica river and also other natural and artificial water basin (e.g. holding tank). Administrative district area is included in the largest Landscape Park Gostyninsko-Wloclawski [7].

Gostyninsko-Wloclawski Park is located in Wisla old ravine and raised in 1979. Its area is about 16 750 ha in that 11 970 ha are forests and with its protection zone it reach out 53 145 ha. Having special naturalistic and landscape values it plays very important role in preserved areas net in Mazovia and Kujawy and also in national Preservation Net. Reach in animal shelters are variety of plant assembly, where predominate forests (over the 63% of park area). In the Park is over 40 lakes mainly located in postglacial tunnel-valley and surrounded by sand dune hills. The most valuable areas are under reserve preservation. In Poland is currently 12 nature reserves and another 4 are designed [6].

The main purpose of the Park preservation strategy is to establish management principles and area usufruct and ecological system substantiate. Ecological program comprises rich offer dedicated to adults as well as to children. It involves umpteen didactic pathways, ecological workshops, seminar, excursions, trainings, etc [6].

Gostynin district major attraction is water tourism, yachting, canoeing, horse riding, hiking, hunting and fishing. Large forest complexes, pure environment, variety of flora and fauna and development of both gastronomy and accommodation, are creating conditions for throng of tourists benefited from that kind of rest [7].

Next area noteworthy because of nature values Ciechanow district located on North part of Mazovia Voivodship [8]. This district territory belongs to Polish "green lungs". It dictate further direction of development throughout implementation eco-development rules like implementation environmental principles of natural resources and natural values management, economy elicitation via comprehensive and reasoned utilization natural resources and values [8]. Around 37% of district area (39,7 thousand ha) is under the preservation. Compact complex of this area is situated between Wkra river valley and Lydyna river valley in its down and upper stream. Wkra river valley is an ecological passage at national significance [6].

In West wooded part of Regimin community are 2 nature reserves: Lekowo with area 5.31 ha and Modla with area 9.36 ha. Total ecological territory area in district amount 16,9 ha concentrated in its South wooded part linked to Wkra river valley (Glinojek and Ojrzen community).

On the district territory are registered 44 Parks: 28 historical facilities still under the antique restorer supervision and country parks under the local government control. Under the protection are also live nature monuments (single tree, groups of trees, parkway) and inanimate nature monuments (boulder) [6].

The main rivers flowing over this region are: Wkra, Lydynia, East Sona and West Sona. Total length of watercourse with inflows is 229 km. Forests occupy 15.8% of district area of total 106 thousands ha. Rural population represents 46.04%. Ciechanowski district has a good road and railway communication. It also has 2 nature reserves. Total area of ecological terrain is about 16.9 ha [8].

District localization on the Polish "green lungs" territory is creating conditions to agro tourism and eko tourism development. That kind of landscape value harness contributes to extent service development, craft, handicraft, food processing industries. Those processes will require efficient and effective connection of own country residents funds, local governments funds, budget funds, UE funds and other sources of income. Ciechanow district as ecologically clean area possess prospective possibility of very fast agro tourism and eko tourism development [8].

### **Institutions supporting the development of agrotourism and ecotourism**

Advisory activity in agro tourism domain in Poland is fulfilled by agricultural consultative centers. In the Macroregion of Central Poland area exists 10 centers of that kind.

Mazovia Branch Agricultural Consultative Center

- Warsaw Department
- Plock Department
- Bielice Department
- Ostroleka Department
- Plonsk Department
- Radom Department
- Siedlce Department [9].

Lodz Branch Agricultural Consultative Center.

- Bartoszewice Department
- Kościerzyn Department
- Piotrków trybunalski Department [10].

In the Macroregion of Central Poland area altogether with consultative centers are cooperating only 360 agro tourist farms owners. People using this can count on different farms connected to agro tourism. Agricultural consultative centers are involved to farms promotion. Examples for that activity are making internet pages, catalogue printing, fair and entertainment organization, sending of inquiry materials, etc. Agriculture Consultative Centers co-found road signage, logo placed on farms and print maps with marked farms [11].

Consultative centers (ODR) classify brand name, logo to the farms cooperating with them.

- MODR Warsaw – department gave the logo to 150 agro tourism farms. It is economically active in 8 districts. One of the biggest agricultural consultative centers in Poland. Department leader in agro tourism farms number is West Warsaw district. Big attraction is archeotourism [12].



- MODR Plock – department cooperates with 42 agro tourism farms and with 3 of ecological production farms. Activity area is: Gostynin district, Plock district, Sierpc district. Leader in agro tourism is Gostynin district. Some of the farms have their own mini-zoos and riding schools. Big attraction is regional domestic meal [9].
- MODR Ostroleka – cooperates with 5 districts, the leader is Ostroleka district. Cooperate with 70 agritourism farms and with 2 certified ecological farms. In the last decade agro tourism farms dynamically developed from 5 in 1996 to 70 in 2006. They cooperate with 3 singing and dancing folk groups.
- MODR Bielice – gives service to 3 districts. Cooperates with 13 agro tourism farms. The leader is Zyrardow district. Farms have mini-zoos, horse riding courses. Most of farms is famous of old style cuisine [9].
- MODR Plonsk – activity area embraces 5 districts. There was created and published agro tourism atlas. It also organizes autumn and spring bazaars and organizes agro exhibitions and enterprise agricultural woman trainings. On MODRs initiative arose Mazovin Green Lungs Association, as a member of Polish Agro Tourism Federation.
- MODR Siedlce – cooperates with 6 districts. Constant cooperation leads with 90 agro tourism farms. Currently 1 ecological farm is registered. Next 3 are waiting for the certificate. Farms are baking bread, making potato sausage, crafting, organizing horse ride trainings, folk group performance.
- MODR Radom – The leader is Zwolen district. About 55 agro tourism farms and 3 ecological farms cooperate with that MODR. Form of support is trainings organization, trades, and individual consultancy. As a promotion: fairs, catalogues, trades, internet websites [9].
- LODR - covers 17 poviats with its activities. They cooperate with 10 agritourism farms. Several farms have a mini-zoo as well as horses. Attraction are regional home-made meals [10].

## Conclusions

Considering available data about agro tourism development in the Macroregion of Central Poland we can affirm that in that domain region capability is not fully utilized. But we can also confirm, that last decade resulted in growth of agro tourism farms number in this region and the trend is rather national. Much more slowly grows ecological farms number, which scope of activity is adjusted by a number of legislations (prohibitions and injunctions) obstructing realization of this agricultural activity trend.

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## FREQUENCY OF CONSUMPTION OF SELECTED FOOD PRODUCTS AMONG POLISH AND TURKISH STUDENTS BEFORE AND DURING THE COVID-19 PANDEMIC

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### Abstract:

The introduction of necessary restrictions connected to the spread of the pandemic influenced students' lifestyle and could result in changes in their diets. Both in case of students with normal and abnormal body weight, there were no statistically significant differences between the frequency of consumption of recommended in diet groups of food products both during and before the pandemic, but in both groups, the differences occur in the frequency of consumption of the majority of not recommended groups of food products. The main goal of the study was to compare the frequency of consumption of selected groups of food products by students of different body weights before and during the pandemic. The study was conducted in a group of 435 students, who were divided into two groups: those with normal (n=313) and abnormal (n=122) body weight. To examine the differences in the frequency of consumption of selected groups of products, the Wilcoxon test was conducted. The value of factor  $p < 0,05$  was considered statistically significant.

### Keywords:

COVID-19, eating habits, students, lifestyle

### Introduction

The COVID-19 pandemic is not only destructively affecting people's health, but also is responsible for numerous differences in their lifestyle in comparison to the time before its appearance. Lifestyle consists of many determinants such as eating habits, physical activity, amount of sleep during the day as well as drug use. The amount of physical activity and healthy diet are considered its paramount components. Insufficient level of physical exertion in cumulation with inadequate diet contributes to numerous chronic diseases of metabolic origin such as obesity, diabetes, arterial hypertension or arteriosclerosis [1-4]. A human's diet should be properly balanced and composed properly to ensure the provision of all nutrients required for the proper functioning and development of an organism while maintaining homeostasis. It is recommended to consume 4-5 meals daily, all of them properly composed with attention to nutrients delivered to the organism, eaten at regular times,

while maintaining specific intervals between them. It remains essential for those meals to include an appropriate amount of high-quality food products and for them to be eaten at appropriate frequencies. Plant foods, that are mandatory in a healthy diet, such as vegetables and fruits, grain products from a full-grain mill, pulses and nuts, due to their content of flavonoids, vitamins and fibre, demonstrate an anti-inflammatory effect, reducing the risk of metabolic diseases including diabetes, cardiovascular diseases and cancers [5-7]. However, consumption of candy, salty snacks, fast-food type products and energy drinks may influence the development of those diseases [8-10].

## **The objective**

The aim of this study is the comparison of the frequency of consumption of selected groups of food products among students of varying body weight before and during the COVID-19 pandemic.

## **Material and methods**

The study was conducted during the winter season at the turn of 2020 and 2021. The participants were 435 students of Polish and Turkish nationality including 340 women and 95 men. All the data required to conduct the study was gathered by the use of the original survey questionnaire, which was shared by electronic media. The questionnaire included questions connected with the frequency of consumption of selected groups of food products before and during the COVID-19 pandemic. Students were also asked about their body weight and height, which then allowed to calculate the body mass index (BMI), by which the surveyed students were split up into two groups: those with normal body weight (N=310) and others, whose body weight was abnormal (N=122). The results were then established with use of programs: Microsoft Office 2010 and Statistica 13. To study the differences occurring between the frequency of consumption of selected groups of food products before and during the pandemic, the Wilcoxon test was conducted. The value of factor  $p < 0.05$  was considered statistically significant.

## **Results**

Tables 1-2 present the frequency of consumption of selected groups of food products and differences in the frequency of consumption among subjects with normal body weight before and during the pandemic.

**Tab. 1. The frequency of consumption of pro-health groups of products among the subjects with normal body weight**

| Frequency of consumption    |                       | Before the pandemic |      | During a pandemic |      | p-value    |
|-----------------------------|-----------------------|---------------------|------|-------------------|------|------------|
|                             |                       | N=313               | %    | N=313             | %    |            |
| Vegetables                  | Several times a day   | 115                 | 36.7 | 121               | 38.7 | 0.23<br>NS |
|                             | Once a day            | 74                  | 23.6 | 68                | 21.7 |            |
|                             | Several times a week  | 103                 | 32.9 | 105               | 33.6 |            |
|                             | Several times a month | 8                   | 2.6  | 11                | 3.51 |            |
|                             | Occasionally          | 11                  | 3.5  | 5                 | 1.6  |            |
|                             | Not consume           | 2                   | 0.6  | 3                 | 1    |            |
| Fruits                      | Several times a day   | 100                 | 32   | 101               | 32.3 | 0.18<br>NS |
|                             | Once a day            | 74                  | 23.6 | 76                | 24.3 |            |
|                             | Several times a week  | 97                  | 31   | 103               | 32.9 |            |
|                             | Several times a month | 23                  | 7.4  | 22                | 7.0  |            |
|                             | Occasionally          | 18                  | 5.6  | 10                | 3.2  |            |
|                             | Not consume           | 1                   | 0.3  | 1                 | 0.3  |            |
| Legumes                     | Several times a day   | 9                   | 2.9  | 10                | 3.2  | 0.63<br>NS |
|                             | Once a day            | 10                  | 3.2  | 13                | 4.2  |            |
|                             | Several times a week  | 126                 | 40.3 | 123               | 39.3 |            |
|                             | Several times a month | 90                  | 28.8 | 89                | 28.4 |            |
|                             | Occasionally          | 60                  | 19.2 | 59                | 18.9 |            |
|                             | Not consume           | 18                  | 5.6  | 19                | 6.1  |            |
| Whole grain cereal products | Several times a day   | 142                 | 45.4 | 140               | 44.7 | 0.74<br>NS |
|                             | Once a day            | 70                  | 22.4 | 65                | 20.8 |            |
|                             | Several times a week  | 70                  | 22.4 | 75                | 24   |            |
|                             | Several times a month | 17                  | 5.4  | 24                | 7.7  |            |
|                             | Occasionally          | 11                  | 3.5  | 7                 | 2.2  |            |
|                             | Not consume           | 3                   | 1    | 2                 | 0.6  |            |
| Nuts                        | Several times a day   | 18                  | 5.8  | 13                | 4.2  | 0.87<br>NS |
|                             | Once a day            | 32                  | 10.2 | 32                | 10.2 |            |
|                             | Several times a week  | 87                  | 27.8 | 92                | 29.4 |            |
|                             | Several times a month | 103                 | 32.9 | 110               | 35.1 |            |
|                             | Occasionally          | 58                  | 18.5 | 50                | 16   |            |
|                             | Not consume           | 15                  | 4.8  | 16                | 5.1  |            |

**Source: Own calculations**

Both before the pandemic and during its time, the most numerous group of students was eating vegetables several times a day (respectively 36.7% and 38.7% of the subjects), and consuming fruits several times a day and several times a week (respectively 32%; 32.3% and 31%; 32.9% of people). Both before the pandemic as well as during its time, the majority of students were eating legumes several times a week (40.3% and 39.3%) and whole grain cereal products several times a day (45.4% and 44.7%) as well as nuts a couple times a month (32.9% and 35.1%). There was no appearance of statistically significant differences between the frequency of consumption of pro-health products by students with normal body weight before and during the pandemic (Tab. 1).

**Tab. 2. The frequency of consumption of anti-health groups of food products among the subjects with normal body weight**

| Frequency of consumption |                       | Before the pandemic |      | During a pandemic |      | p-value        |
|--------------------------|-----------------------|---------------------|------|-------------------|------|----------------|
|                          |                       | N=313               | %    | N=313             | %    |                |
| Sweets                   | Several times a day   | 41                  | 13.1 | 33                | 10.5 | 0.06<br>NS     |
|                          | Once a day            | 51                  | 16.3 | 48                | 15.3 |                |
|                          | Several times a week  | 135                 | 43.1 | 139               | 44.4 |                |
|                          | Several times a month | 44                  | 14.1 | 44                | 14.1 |                |
|                          | Occasionally          | 36                  | 11.5 | 39                | 12.5 |                |
|                          | Not consume           | 6                   | 1.9  | 10                | 3.2  |                |
| Salty snacks             | Several times a day   | 22                  | 7.0  | 12                | 3.8  | 0.01<br>P<0.05 |
|                          | Once a day            | 14                  | 4.5  | 19                | 6.1  |                |
|                          | Several times a week  | 115                 | 36.7 | 104               | 33.2 |                |
|                          | Several times a month | 90                  | 28.8 | 90                | 28.8 |                |
|                          | Occasionally          | 63                  | 20.1 | 75                | 24   |                |
|                          | Not consume           | 9                   | 2.9  | 13                | 4.2  |                |
| Fast-food                | Several times a day   | 5                   | 1.6  | 2                 | 0.6  | 0.00<br>P<0.05 |
|                          | Once a day            | 4                   | 1.3  | 8                 | 2.6  |                |
|                          | Several times a week  | 71                  | 22.7 | 52                | 16.6 |                |
|                          | Several times a month | 109                 | 34.8 | 92                | 29.4 |                |
|                          | Occasionally          | 112                 | 35.8 | 123               | 39.3 |                |
|                          | Not consume           | 12                  | 3.8  | 36                | 11.5 |                |



|               |                       |     |      |     |      |                |
|---------------|-----------------------|-----|------|-----|------|----------------|
| Energy drinks | Several times a day   | 4   | 1.3  | 3   | 1    | 0.00<br>P<0.05 |
|               | Once a day            | 13  | 4.2  | 11  | 3.5  |                |
|               | Several times a week  | 24  | 7.7  | 14  | 4.5  |                |
|               | Several times a month | 29  | 9.3  | 29  | 9.3  |                |
|               | Occasionally          | 59  | 18.9 | 48  | 15.3 |                |
|               | Not consume           | 184 | 58.8 | 208 | 66.5 |                |

**Source: Own calculations**

Both before the pandemic and during its time, the highest rate of students with appropriate body weight was consuming sweets and salty snacks usually several times a week (respectively 43.1%; 44.4% and 36.7%; 33.2%). The majority in both periods was consuming fast-food type products occasionally (35.8% and 39.3%) and was not drinking energy drinks (58.8% and 66.5%). The statistically significant differences in the frequency of consumption of salty snacks, fast-food type products and energy drinks in researched periods are known to be present. ( $p<0.05$ ) (Tab. 2).

Tab. 3-4 present the frequency of consumption of selected groups of food products and differences between the frequency of their consumption among the subjects with abnormal body weight before and during the pandemic.

**Tab. 3. The frequency of consumption of pro-health groups of food products among the subjects with abnormal body weight**

| Frequency of consumption |                       | Before the pandemic |      | During a pandemic |      | p-value    |
|--------------------------|-----------------------|---------------------|------|-------------------|------|------------|
|                          |                       | N=122               | %    | N=122             | %    |            |
| Vegetables               | Several times a day   | 40                  | 32.8 | 40                | 32.8 | 0.19<br>NS |
|                          | Once a day            | 39                  | 32   | 30                | 24.6 |            |
|                          | Several times a week  | 29                  | 23.8 | 36                | 29.5 |            |
|                          | Several times a month | 9                   | 7.4  | 11                | 9.0  |            |
|                          | Occasionally          | 5                   | 4.1  | 4                 | 3.3  |            |
|                          | Not consume           | 40                  | 32.8 | 1                 | 0.8  |            |
| Fruits                   | Several times a day   | 30                  | 24.6 | 28                | 23   | 0.61<br>NS |
|                          | Once a day            | 28                  | 23   | 31                | 25.4 |            |
|                          | Several times a week  | 39                  | 32   | 36                | 29.5 |            |
|                          | Several times a month | 18                  | 14.8 | 19                | 15.6 |            |
|                          | Occasionally          | 7                   | 5.7  | 8                 | 6.6  |            |

|                             |                       |    |      |    |      |            |
|-----------------------------|-----------------------|----|------|----|------|------------|
|                             | Not consume           | 30 | 24.6 | 0  | 0    |            |
| Legumes                     | Several times a day   | 2  | 2.5  | 3  | 1.6  | 0.41<br>NS |
|                             | Once a day            | 11 | 9.0  | 7  | 5.7  |            |
|                             | Several times a week  | 37 | 30.3 | 39 | 32   |            |
|                             | Several times a month | 45 | 36.9 | 40 | 32.8 |            |
|                             | Occasionally          | 19 | 15.6 | 25 | 20.5 |            |
|                             | Not consume           | 8  | 6.6  | 8  | 6.6  |            |
| Whole grain cereal products | Several times a day   | 54 | 44.3 | 54 | 44.3 | 0.65<br>NS |
|                             | Once a day            | 30 | 24.6 | 25 | 20.5 |            |
|                             | Several times a week  | 30 | 24.6 | 35 | 28.7 |            |
|                             | Several times a month | 5  | 4.1  | 5  | 4.1  |            |
|                             | Occasionally          | 2  | 1.6  | 3  | 2.5  |            |
|                             | Not consume           | 1  | 0.8  | 0  | 0    |            |
| Nuts                        | Several times a day   | 4  | 3.3  | 2  | 1.6  | 0.07<br>NS |
|                             | Once a day            | 15 | 12.3 | 10 | 8.2  |            |
|                             | Several times a week  | 36 | 29.5 | 38 | 31.6 |            |
|                             | Several times a month | 34 | 27.9 | 34 | 27.9 |            |
|                             | Occasionally          | 23 | 18.9 | 23 | 18.9 |            |
|                             | Not consume           | 10 | 8.2  | 15 | 12.3 |            |

**Source: Own calculations**

Both before the pandemic and during its time, the most numerous group of students was consuming vegetables several times a day (32.8% of subjects in both periods) and eating fruits several times a week (32% and 29.5%). The highest rate of subjects both before as well as during the pandemic was consuming legumes several times a month (36.9% and 32.8%) and eating whole grain cereal products several times a day (44.3% in both periods). Nuts were consumed by the largest group of students both before, as well as during the pandemic several times a week (29.5% and 31.6%). There was no appearance of statistically significant differences between the frequency of consumption of pro-health food products by students with abnormal body weight before and during the pandemic (Tab. 3).

**Tab. 4. The frequency of consumption of anti-health groups of products among the subjects with abnormal body weight**

| Frequency of consumption |                       | Before the pandemic |      | During a pandemic |      | p-value        |
|--------------------------|-----------------------|---------------------|------|-------------------|------|----------------|
|                          |                       | N=122               | %    | N=122             | %    |                |
| Sweets                   | Several times a day   | 16                  | 13.1 | 21                | 17.2 | 0.03<br>p<0.05 |
|                          | Once a day            | 29                  | 23.8 | 13                | 10.7 |                |
|                          | Several times a week  | 40                  | 32.8 | 43                | 35.3 |                |
|                          | Several times a month | 22                  | 18.0 | 24                | 19.7 |                |
|                          | Occasionally          | 11                  | 9.0  | 13                | 10.7 |                |
|                          | Not consume           | 4                   | 3.3  | 8                 | 6.6  |                |
| Salty snacks             | Several times a day   | 6                   | 4.9  | 5                 | 4.1  | 0.12<br>NS     |
|                          | Once a day            | 9                   | 7.4  | 7                 | 5.7  |                |
|                          | Several times a week  | 46                  | 37.7 | 46                | 37.7 |                |
|                          | Several times a month | 35                  | 28.7 | 35                | 28.7 |                |
|                          | Occasionally          | 17                  | 13.9 | 15                | 12.3 |                |
|                          | Not consume           | 9                   | 7.4  | 14                | 11.5 |                |
| Fast-food                | Several times a day   | 0                   | 0.0  | 1                 | 0.8  | 0.03<br>p<0.05 |
|                          | Once a day            | 4                   | 3.3  | 5                 | 4.1  |                |
|                          | Several times a week  | 35                  | 28.7 | 24                | 19.7 |                |
|                          | Several times a month | 40                  | 32.8 | 40                | 32.8 |                |
|                          | Occasionally          | 36                  | 29.5 | 34                | 27.9 |                |
|                          | Not consume           | 7                   | 5.7  | 18                | 14.8 |                |
| Energy drinks            | Several times a day   | 0                   | 0    | 2                 | 1.6  | 0.01<br>p<0.05 |
|                          | Once a day            | 7                   | 5.7  | 4                 | 3.3  |                |
|                          | Several times a week  | 19                  | 15.6 | 12                | 9.8  |                |
|                          | Several times a month | 14                  | 11.5 | 12                | 9.8  |                |
|                          | Occasionally          | 21                  | 17.2 | 23                | 18.9 |                |
|                          | Not consume           | 61                  | 50.0 | 69                | 56.6 |                |

**Source: Own calculations**

Both before as well as during the time of the pandemic, sweets and salty snacks were eaten by the most numerous group of subjects several times a week (respectively 32.8%; 35.3% and 37.7%; 37.7%). Fast-food type products were consumed by the highest rate of students several times a month in both researched periods (32.8% and 32.8%). Both before, as well as during the pandemic, energy drinks were not drunk by the largest group of subjects (50% and 56.6%). The statistically significant differences in the frequency of consumption of sweets, fast-food type products and energy drinks by the subjects with abnormal body weight before and during the pandemic are known to be present ( $p < 0.05$ ) (Tab. 4).

Tab. 5 presents the change in students’ body weight in comparison to time before the pandemic.

**Tab. 5. The change in students’ body weight during the pandemic**

| Body weight | Normal |    | Abnormal |    |
|-------------|--------|----|----------|----|
|             | N=313  | %  | N=122    | %  |
| Not changes | 108    | 34 | 35       | 29 |
| Increased   | 118    | 38 | 50       | 41 |
| Decreased   | 87     | 28 | 37       | 30 |

**Source: Own calculations**

The obtained results indicate, that both in case of the subjects with normal body weight, as well as those with abnormal body weight, the highest rate of students declared that they have increased body weight during the pandemic.

## Discussion

Regardless of body weight, students who took part in the study have shown insufficient consumption of groups of food products that are widely known as healthy and recommended in everyday diet (vegetables, fruits, grain products, dairy products and nuts). Vegetables and fruits are the sources of mineral salts, vitamins and fibre. They also show antioxidant activity and have health-promoting properties and that’s the reason why they shall appear as a part of every human’s everyday diet [11]. In the study, among students with normal body weight, 38.7 % of them declared, that at that time period they were consuming vegetables a few times a day. Although before the pandemic, such response was given by 36.7 % of them. Amongst the students with abnormal body weight, 32.8 % of them declared that they were eating vegetables a few times a day both before and during the pandemic. In the study conducted by Ndagire et al., the consumption of vegetables was determined on the basis of the amount of consumed portions. The number of consumed portions of vegetables at recommended level-5 or more-was declared by 11.8 % of subjects, whereas 20.5 % of subjects declared consumption of below 1 portion of vegetables per day [12]. In the study conducted by Nawrocka et al., amongst the students aged 20-25, 60 % of them declared that they almost never eat vegetables, or eat them rarely [13]. In the personal study, 32 % of subjects with appropriate body weight declared that they were eating fruits a few times a day during the pandemic. The response to

the same question, but referring to the time before the pandemic was identical for 32.3 % of subjects. There was no significant difference in case of the subjects with inappropriate body weight – 24.6 % of respondents were eating fruits a few times a day before the pandemic, whereas during the pandemic the consumption rate was equal to 23 %. In the study conducted by Grabowska-Sander et al. to analyze nutritional preferences of students of the first year of nursing, 66.6 % of the participants stated that they were often eating fruits and vegetables and 16.7 % answered that they almost always eat them [14].

Wholegrain foods are a source of B group vitamins and dietary fibre. It is commonly believed, that consumption of dietary fibre reduces the risk of cardiovascular diseases, gastrointestinal disorders and even cancers [15]. In the personal study, students with appropriate body weight were consuming wholegrain food products a few times a day both before and during the pandemic (respectively 45.4 % and 44.7 % of responses). Amongst the students with inappropriate body weight, 44.3 % of them declared that they were eating wholegrain foods a couple times a day both during and before the pandemic. The study conducted by Subramanian et al. has shown, that 23.3 % of people were eating wholegrain food products more than 3 times a week. The most frequent consumption of wholegrain foods was reported by Chinese students – 42.9 %, whereas the least frequent consumption was reported by Malayan students – 60.8 % [16].

Amongst the people with normal body weight, 43.1 % of them were eating candy a few times a week before the pandemic. 44.4 % of subjects gave the same answer when asked about the time during the pandemic. In case of subjects with abnormal body weight, those ratios were equal to respectively 32.8 % and 35.3 %. For comparison in a study conducted by Niba et al. to assess the differences between the eating habits of 906 students, proved that 31.5 % of surveyed men and 21.4 % of examined women were consuming cookies at least two times a week, whereas the percentages of surveyed men and women who declared that they were consuming candy and chocolate more than twice a week, were respectively equal to 53.2 % and 38.2 % [17]. In the study conducted by Misarz et al., the goal was to assess the consumption of selected food products among 1945 students of UAS in Nysa. Amongst the medical students, 2.76 % of them declared, that they were not eating candy at all. 2 % of surveyed non-medical students also claimed that they were not eating candy [18].

The personal study has shown that there is a difference in the frequency of consumption of fast-food type products between the subjects with normal and abnormal body weight. In the examined group, 35.8 % of people with appropriate body weight declared that before the pandemic they used to occasionally consume fast-food type products. Whereas during the pandemic, this ratio increased to 39.3 %. Amongst the subjects with inappropriate body weight, 29.5 % of them declared that they used to consume fast-food type products occasionally before the pandemic. The percentage of people decreased to 27.9 % during the pandemic. In the study conducted by Scully et al., which assessed the frequency of consumption of fast-food type products among students of high schools, 38 % of the subjects declared the consumption of such products once a week [19]. However, the study conducted by Zhao et al., which aimed at examination of risk factors of high consumption of fast-food type products and their connection with health, stated that amongst the students of primary and secondary school, 35.3 % of them were eating fast-food type products once or twice a week. In case of high school students of this rate was equal to 44.4 % [20].

Energy drinks contain high doses of caffeine and simple carbohydrates. After drinking them, adverse effects such as insomnia, nervousness and headaches might occur [21]. In the personal study, amongst the students with abnormal body weight, 50 % of them declared that they were not drinking energy drinks before the pandemic and 56.6 % of the students were not drinking such drinks during the pandemic. Amongst the people with normal body weight, this ratio was equal to respectively 58.8 and 66.5 %. However, in the study conducted by Majori et al., which aimed at assessing the frequency of consumption of energy drinks and ginseng among Italian students, 38.6 % of the subjects declared regular consumption of energy drinks [22]. A similar result in the aspect of the consumption of energy drinks was declared by 27.7 % of subjects of the study conducted by Scuri et al. The majority of the consumers were men and especially people who practised physical activity [23].

## Conclusions

1. Both among students with normal and abnormal body weight, there were no statistically significant differences occurring between the frequency of consumption of recommended in diet groups of food products before and during the COVID-19 pandemic.
2. Both among students with normal and abnormal body weight, there are statistically significant differences in the frequency of consumption of most of the non-recommended groups of food products before and during the COVID-19 pandemic.

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# MODELLING UNIVARIATE TIME SERIES WITH ONE-DIMENSIONAL CONVOLUTIONAL NEURAL NETWORKS

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## **Abstract:**

The goal of this article is to present theoretical concepts and applications of one-dimensional convolutional neural networks in univariate time series data modeling and prediction. While highly popular, CNNs are mostly used for working with two-dimensional image data. This work shows that they can also be successfully applied for modeling time series data. The methodology used in this research is computer simulation. A model based on one-dimensional convolutional network is programmed to train on two different time series data sets - daily temperature data and Tesla stock prices. Root-mean-square error (RMSE) and Mean absolute percentage error (MAPE) measures were used to evaluate model performance. In both cases, the model performs quite well, although the results obtained on the stock prices data are slightly better. The work also indicates the possibilities of improving and streamlining the models based on the described methods.

## **Keywords:**

*deep learning, forecasting, convolutional networks, time series*

## **Introduction**

Artificial intelligence and machine learning popularity has been on the rise during the recent years. One of the most popular fields in this area is deep learning, which is currently widely used in many aspects of technology and science, including everything from self-driving cars to complex medical examinations. One of the deep learning methods are convolutional neural networks (CNNs), which are very popular in computer vision and image recognition tasks.

Input data used in these tasks is usually two-dimensional (images, video feeds), but they can also be successfully applied to one-dimensional modeling of sequential data, like the time series.

This article explains the basic methods used in designing and implementing convolutional networks, how to prepare data for one-dimensional convolution modelling and how to use the model for time series prediction. In the first example a simpler daily temperature dataset was used for training and testing the model, and the results were a bit better than those from the second example, where more complex stock prices data were used.

Convolutional networks in general are very good at detecting informative features and when working with data that contains a lot of noise. The benefits of using one-dimensional CNNs instead

of recurrent networks or other types networks that are used for sequential data modelling is that they require significantly less computing power.

## **Theoretical aspects of convolutional networks**

Convolutional neural networks are a type of deep learning networks - hierarchical multilayer networks, where each layer represents successive levels of abstraction. Basic features are extracted by the lower layers, and the information is then transferred to the higher layers where additional computations and transformations take place. The idea of convolutional networks is based on neurobiological research on the visual cortex.

Typical convolutional networks consist of three types of layers: convolutional layer, pooling layer and flattening layer. Convolution is a linear mathematical operation that is used in place of matrix multiplication function in other types of networks (Goodfellow, Bengio and Courville, 2016). The main task of convolution operation is deriving a features map. Doing this helps to reduce the amount of information, maintaining only the most important features, which also helps to increase the network performance and reduce the memory resource requirements and computing power. The basic convolutional operation is denoted as follows:

$$s(t) = \int x(a)w(t - a)da \quad (1)$$

or more commonly:

$$s(t) = (w * x)(t) \quad (2)$$

Function of  $x$  is an input signal,  $w$  is the kernel filter and the output is a feature map. When dealing with a discrete time  $t$ , the function looks as follows:

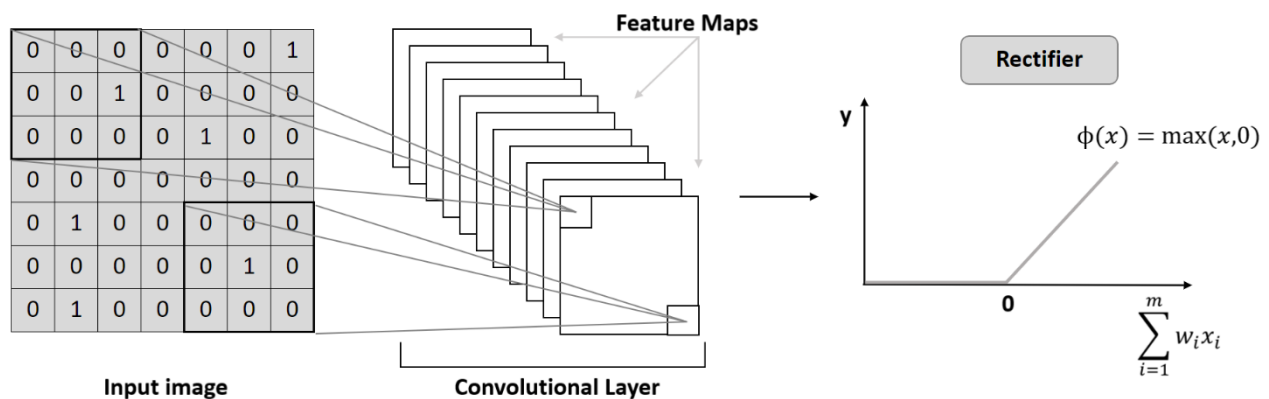
$$s(t) = (x * w)(t) = \sum_{a=-\infty}^{\infty} x(a)w(t - a) \quad (3)$$

When we have two or more dimensions, for example if the input is an image, we can denote it as follows:

$$S(i, j) = (K * I)(i, j) = \sum_m \sum_n I(i - m, j - n)K(m, n) \quad (4)$$

where  $I$  is a two-dimensional image input and  $K$  is a two-dimensional kernel.

During convolution operations it is common to use a specific activation function called Rectified Linear Unit (ReLU). The basic task of this function is to increase the non-linearity of features. This essentially means that ReLU will break up any linearity that may have been imposed during the convolutions operation.

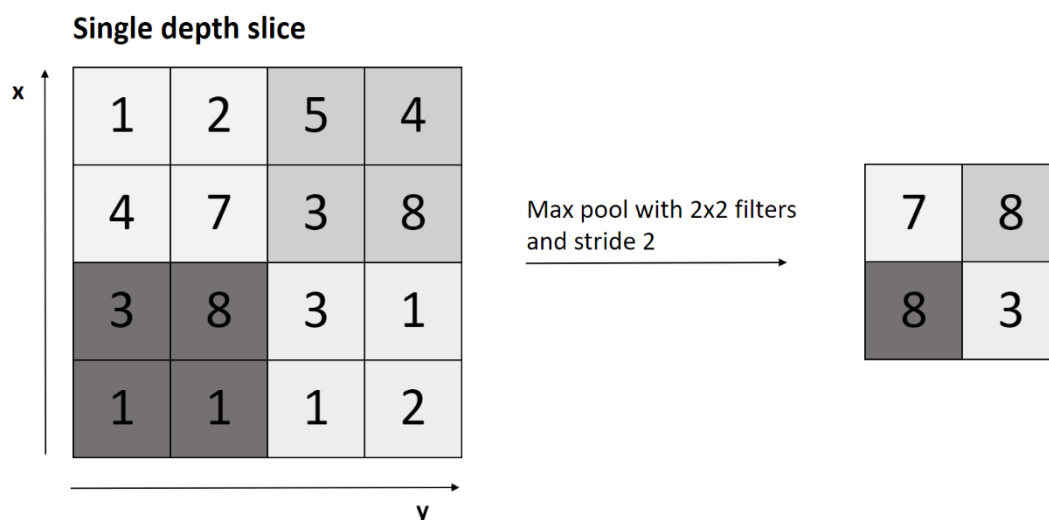


**Fig. 1. Applying the Rectified Linear Unit during the convolution operation**

Source: Own study, modified from superdatascience.com

Next layer in a CNN structure is the pooling layer. This layer further reduces the amount of information by sampling the input image, and at the output it creates a pooled features map, which stores only the most important information for the network, discarding all unused details. This process further improves the network performance and reduces the computing power requirements, and makes the network more resistant to overfitting by reducing the number of parameters. It also helps to make the network more resistant to small changes in the input data, like rotating or changing the width of the image.

Pooling operation uses a summary of nearby area statistics to replace the network output at a specific area. There are three hyperparameters that need to be defined here: size of the receptive field, the stride (step) size and the size of  $z$  zero-padding (filling the input with zeros around the edges). There are several types of pooling. Max pooling, which retrieves the maximum values from a given field of adjacent inputs, is the most popular one. Other examples of pooling types include average pooling, sum pooling or L2-norm pooling.



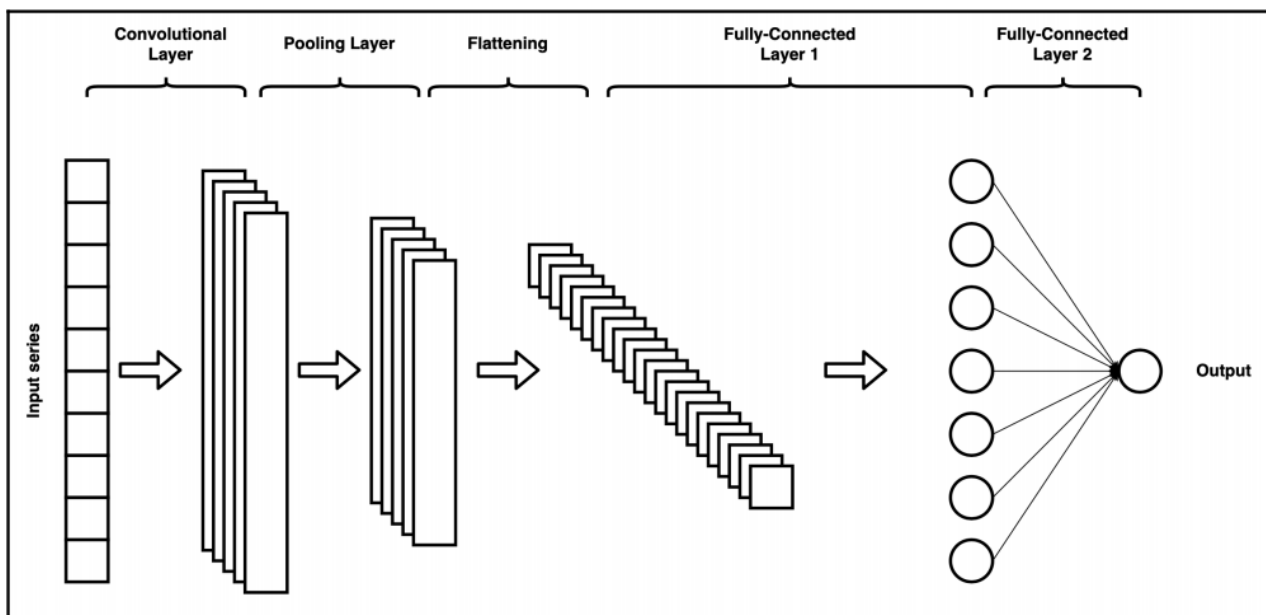
**Fig. 2. Max pooling**

Source: Own study, modified from wikipedia.com

Another layer commonly used in the convolutional networks is the flattening layer in which the data is transformed into a column vector form, so that it is easier to pass them on to the final neural network, which makes the final classification. The final network is usually a regular neural network that includes fully connected layers, where neurons are connected to all activations in the previous layer. The purpose of this network is to combine the features into attributes that help with classification (Géron, 2017).

## Methodology and examples

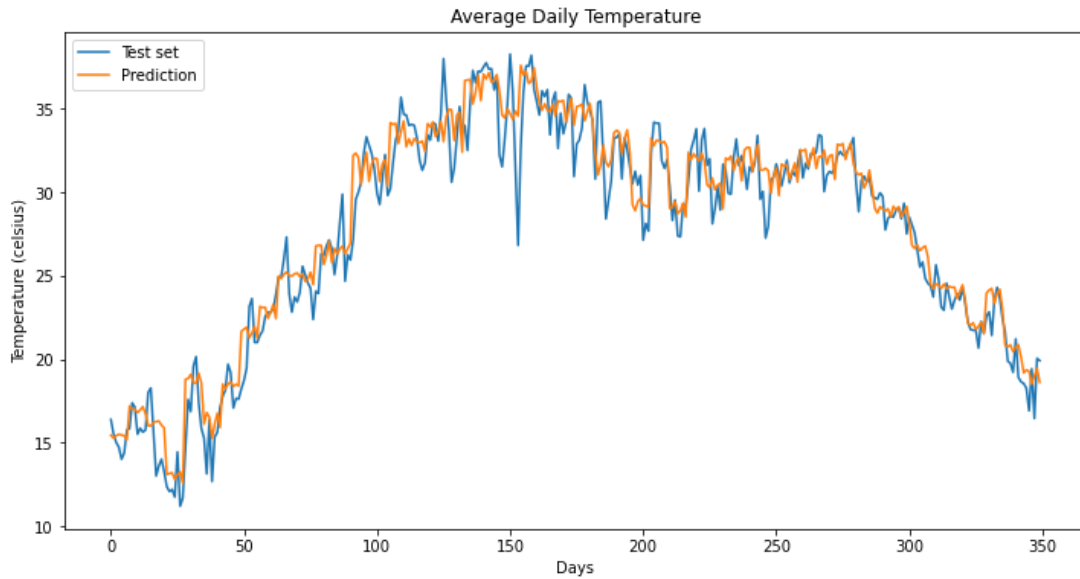
To use convolutional networks for time series it needs to use one-dimensional convolutional layers. The main difference here is the dimensionality of the input data, and how the kernel is moving across the data (Brownlee, 2020). In this case the data has a sequential structure with a different length, so the kernel is moving in only one direction, as opposed to when working with images where it moves to the right or left.



**Fig. 3. One-dimensional convolutional network**  
Source: Lewinson (2020)

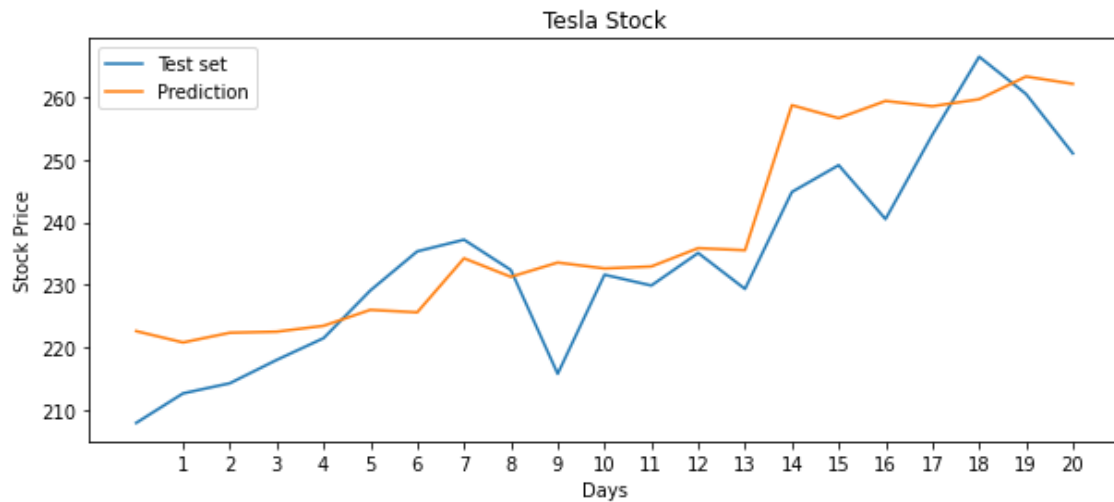
As an example of one dimensional data modelling, a convolutional network was used to model simple time series data. In the first example, dataset was built using daily average temperature, as observed in New Delhi, India, over the period from 1st January 2013 to 24rd April 2017, with the total of 1456 observations<sup>1</sup>. The data was divided into training and testing sets, where the test set consisted of the last year of the data. The 1D CNN model is used for predicting the temperature for 365 days ahead and the results compared with the test data set. The overall RMSE (root-mean-square error) score for this example was 2.466, while the MAPE score was 7.8%.

<sup>1</sup> As provided on <https://www.kaggle.com/sumanthvrao/daily-climate-time-series-data>



**Fig. 4. Time series modelling - average daily temperature**  
**Source: Own study**

For the second example, the dataset was built using Tesla stock prices data from the period starting in July 2010 to March 2017 (total 1687 observations)<sup>2</sup>. The data was split into test and train sets where the test set is one year long (252 days). We then use the model to predict the prices for 4 weeks (20 days) ahead and compare the results with the four weeks of data from the test set. The overall RMSE for this example was 13.2070, and the MAPE score was 4.67%. We can observe that it was able to detect the overall trend direction.



**Fig.5. Tesla stock prices**  
**Source: Own study**

<sup>2</sup> As provided on <https://www.kaggle.com/rpaguirre/tesla-stock-price>



**Tab. 1. Overall 1D CNN model scores**

|      | Daily temperature<br>example | Tesla stock prices<br>example |
|------|------------------------------|-------------------------------|
| MSE  | 6.0855                       | 174.4273                      |
| RMSE | 2.466                        | 13.2070                       |
| MAE  | 1.931                        | 10.3623                       |
| MAPE | 7.800                        | 4.6794                        |

**Source: Own study**

## Conclusion

Based on the research presented above, it can be concluded that CNN networks can be successfully used for one dimensional time series data modelling. The model did well in both examples. Since the examples use different measurement units and scales, it's best to compare MAPE measure, which gives the possibility to compare the model performance between the two datasets. Based on this measure, the model did slightly better in predicting the stock prices dataset.

The research can be further improved by applying the models based on convolutional networks to other types of time series data such as stock returns, and for more complex tasks such as volatility forecasting. Performance could also be tested using multivariate time series data. Models would also benefit from connecting CNNs with other types of networks such as LSTM (Long-Short Term Memory) networks and GARCH models for volatility and Value-at-Risk forecasting. Convolution operation and CNNs can also be used as tools for smoothing the average of the time series data, similar to the more commonly used moving average (MA) method.

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## METHODS OF PRODUCTION SECOND GENERATION BIOFUELS

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### **Abstract:**

The article presents methods of production of second generation biofuels. For the production of 2nd generation biofuels, products containing cellulose and lignin, waste vegetable oils, animal fat and sewage sludge are used. In this study authors focused on classification of biomass, biofuels generations and technological aspects of production. Furthermore, it shows challenges for each method of production of biofuels and technological process problems.

### **Keywords:**

*biofuels, second generation, biomass*

### **Introduction**

It is believed that [3] the use of biofuels can reduce carbon dioxide and greenhouse gas emissions. However, on the other hand [5], the large-scale use of biofuels poses a potential threat to the environment.

The production of second-generation biofuels should not compete with crops intended for food, and should not have the least possible impact on environmental biodiversity [3]. Each subsequent generation of biofuels is a modification of the previous one. The current regulations oblige the use of biofuels, especially those that do not compete with the food market. According to the National Index Target, the use of biofuels in transport by 2020 should amount to 8.5 %. This means the necessity to use biofuels as an additive to conventional fuels or as a standalone fuel.

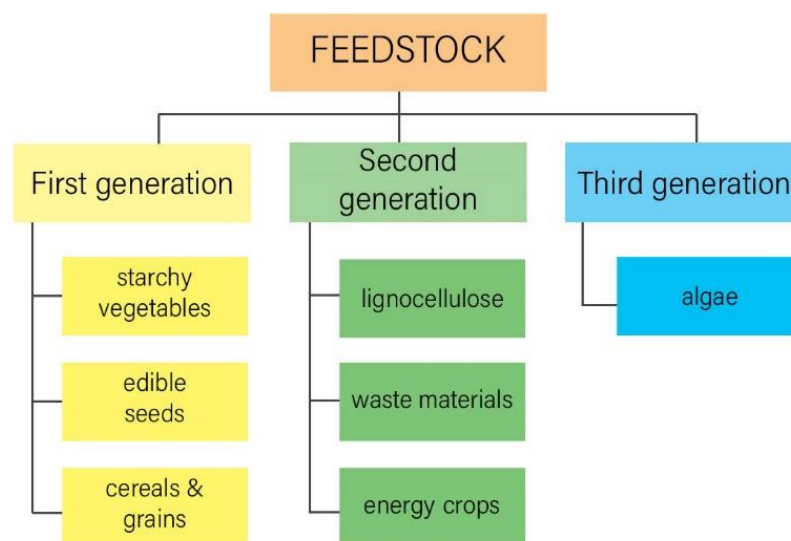
### **Biomass and classification of biofuels**

There are many definitions [1, 3, 8] of biofuels, which appear both in legal documents and scientific studies - they are called alternative, substitute or unconventional fuels. In this study, biofuels are understood as unconventional fuels produced from biomass, which contain energy elements - carbon and hydrogen [7].

Currently, there are four generations of biofuels. The third and last generation of biofuels is at the research stage [4]. It is planned to use genetically modified raw materials for the production of fourth-generation biofuels, which can be produced on land unsuitable for cultivation. The fourth generation

of biofuels, like the third generation, can be produced from biomass obtained from marine algae [3, 4]. Biomass, used for the production of biofuels or as an energy source, can be divided into:

- I. Products containing sugar and starch - the main ingredient of plants grown for consumption;
- II. Products containing lignin, cellulose and hemicellulose;
- III. Vegetable fats;
- IV. Other biomass processing waste from the three groups above, as well as substances of organic origin.



**Fig. 1. Classification of biofuels by raw material [5]**

**Source: Own study**

Taking into account the above classification of biomass, the following generations of biofuels are distinguished (Fig.1):

- I generation – produced from biomass used in the food industry, e.g. bioethanol, bioethers (ETBE, TAE), fatty acid alkyl esters;
- II generation – for that generation biomass can not competition with food production. Second generation biofuels are produced from used vegetable oils, animal fats, waste substances and products containing cellulose and lignin. These include biogas, catalytic fat hydrogenation (HVO) fuels;
- III generation – the methods of obtaining biofuels are similar to the methods used in the production of previous generation biofuels. The main difference is the raw material used - algae and sea algae - which is genetically modified already at the stage of cultivation.

## Second generation biofuels – production methods

For the production of 2nd generation biofuels, products containing cellulose and lignin, as well as waste vegetable oils and animal fat as well as sewage sludge are used. The properties of biofuels vary depending on the raw material used and the production method [6].

According to [2], used vegetable oil is a promising raw material used for the production of biofuels, as it is a final product in the food industry and is treated as waste. It is worth noting that the use of a mixture of diesel oil and biofuel in the right proportions does not require the modification of a compression-ignition engine. However, on the other hand, the use of pure vegetable oil as an independent fuel for diesel engines may adversely affect the engine operation [6].

The conversion of biomass into biofuels can be divided into two categories depending on the method used:

- Thermochemical: gas production - gasification - conversion of lignocellulosic raw materials into synthesis gas that can be used for the production of DME (dimethyl ether) – production of DME using the BTL method - biomass to liquid; liquid - pyrolysis; HTL - hydrothermal liquefaction.
- Biochemical: fermentation - biogas and liquid production.

There are three main pathways of thermochemical biofuel production: gasification (F-T method) and HTL hydrothermal liquefaction / liquefaction and pyrolysis (Fig. 2).

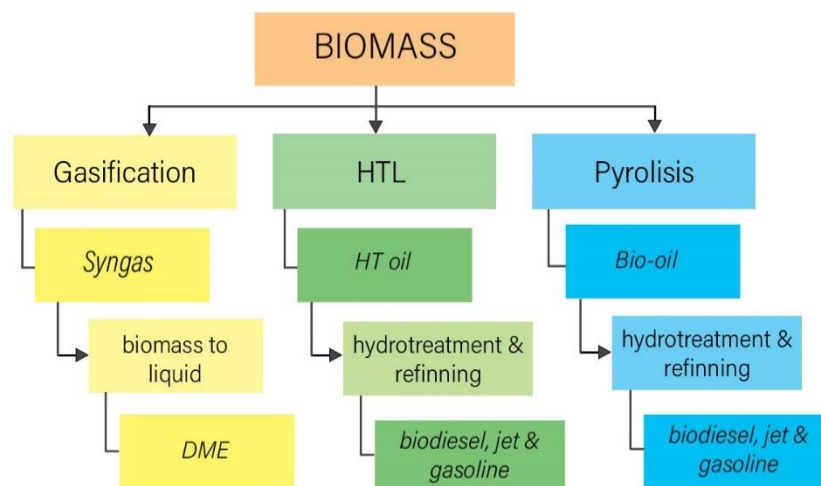
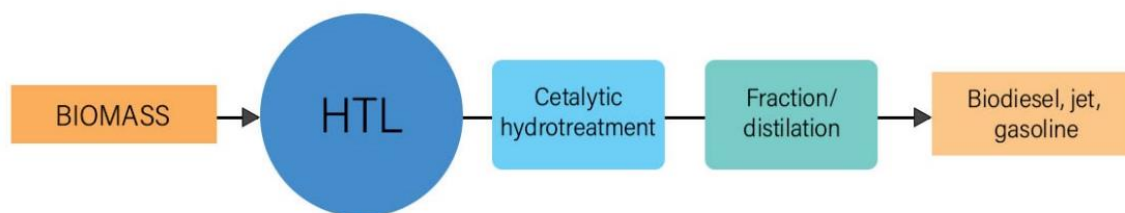


Fig. 2. There are three main pathways 2nd biofuel production [5]

Source: Own study

HTL method is the processing of wet biomass. Biomass in the water environment is subjected to the thermal depolymerization process at a temperature in the range of 250-550°C and a pressure from 5 to 25 MPa. The water in these conditions can behave in two ways: as the reactants and catalyst. In this way, the so-called "Bio-oil" that can be used in diesel engines. Fig. 3 shows a simple schematic of the HTL method.



**Fig. 3. HTL method**  
Source: [5]

The advantage of this method is the possibility of using raw materials containing up to 80 % by volume of water, but it requires continuous operation at high temperature and pressure. This method has relatively high production costs and complex downstream processes and struggles with the following problems:

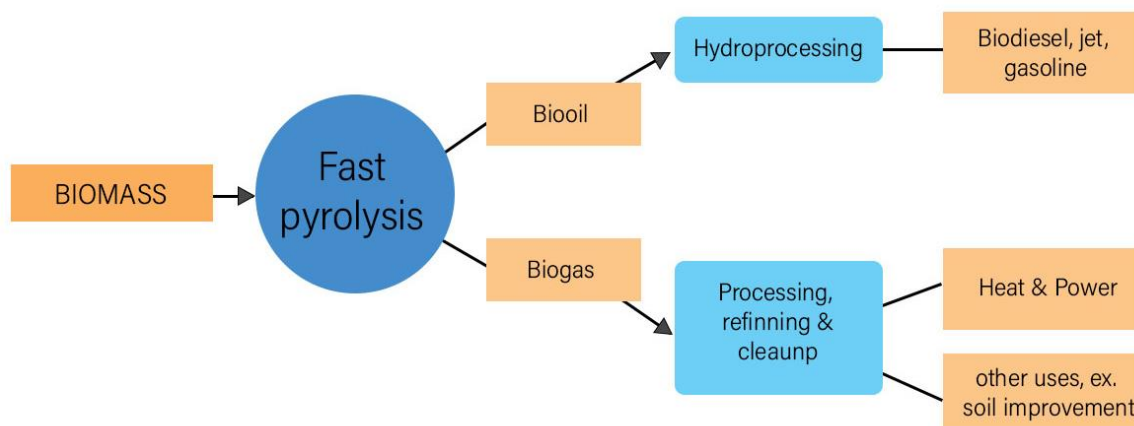
1. Limited knowledge of the processes related to the extraction of biomass during continuous operation at high temperature.
2. Need to use low solids fraction.
3. High costs of separation of bio-oil and water components.
4. Reduced calorific value of bio-oil resulting from carbon loss during depolymerization processes.
5. High costs of treatment of wastewater subjected to the HTL process.
6. The necessity to use corrosion-resistant equipment.
7. Complicated final biomass treatment processes due to the high concentration of oxygen and nitrogen, which affect the physicochemical properties of bio-oil.

Pyrolysis is a process that uses biomass products with a moisture content of less than 10%. The process temperature range is 450-550°C, and the heating rate is 20-200°C/s. fast pyrolysis (Fig. 4) – the main product of which is bio-oil and biogas. The raw materials used for this method are cellulose products, lignocellulosic products - however the most desirable are raw materials with high volatility and low moisture content [5].

The pyrolysis products are characterized by high viscosity, acidity and water content. They are unstable chemical, which has a significant impact on storage and utility processes. Bio-oil is a complex mixture of organic compounds with carbon numbers from C6 to C27. The pyrolysis reactions of fatty waste are very complex, which means that the chemical structure of the obtained products is very complex [1].

There are following challenges to this method:

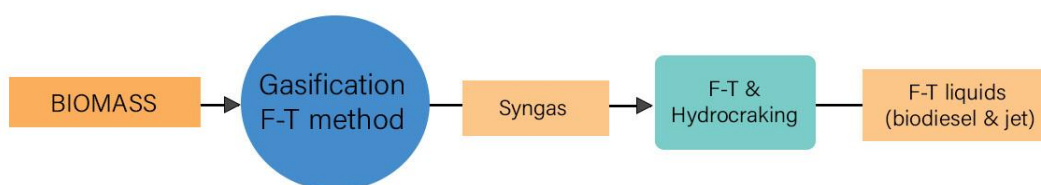
1. Method of storage and thermal and chemical stability for bio-oil, which is characterized by a tendency to polymerization, high viscosity, high acidity and hygroscopicity.
2. Elimination of alkali metals and other nitrogen compounds that affect the bio-oil yield.
3. Presence of water and oxidized compounds in bio-oil.
4. Low conversion of bio-oil.



**Fig. 4. Methods of obtaining biofuels by the method of fast pyrolysis**  
Source: [5]

Gasification is partial thermal oxidation. The reaction takes place in the presence of a suitable oxidant - usually air, oxygen and steam. The synthesis gas obtained must undergo thorough cleaning and conditioning. The gas can be subjected to standard refinery methods (e.g. hydrocracking, distillation) to obtain liquid biofuels.

Gasification in combination with Fisher-Tropsch synthesis is a well-known technique using coal as a feedstock. However, the biomass as a raw material used for this method is still at the stage of early commercialization. Before starting the gasification process, it is necessary to pre-treat the biomass, which can consume 10-15 % of the energy of the raw material. The products obtained by the F-T method require additional processing, which increases the cost of biofuel production [5].



**Fig. 5. Methods of obtaining biofuels by gasification method**  
Source: [5]

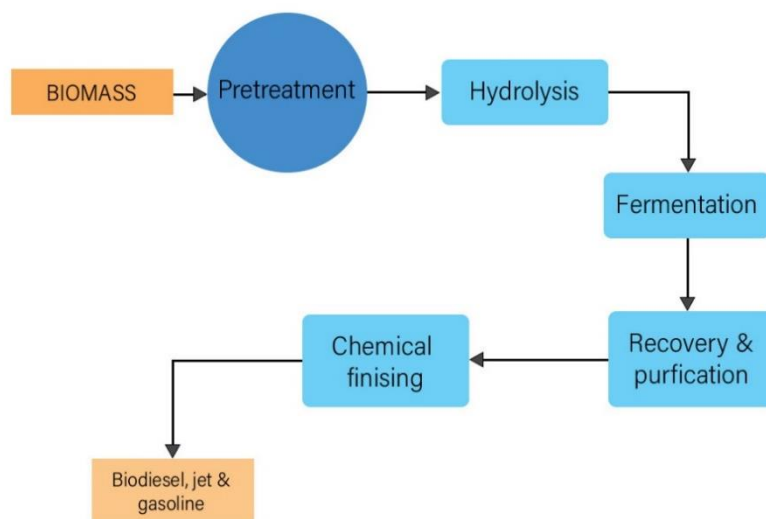
Gasification by the Fisher-Tropsch method with the use of raw materials for the production of second-generation biofuels encountered the following problems:

1. The need to apply pre-treatment of biomass in order to homogenize the raw material before the drying process.
2. Complicated processes of purification and conditioning of synthesis gas.
3. Removal of impurities, such as tar during syngas production.
4. F-T products require further processing in the form of fractionation and distillation.

Biochemical methods include fermentation, which can be divided into aerobic or anaerobic fermentation. Currently, three pathways have been developed for this process [5]:



1. Genetically modified yeast feeds on sugars and then excrete liquid alkenes, e.g. isobutene, which is recovered from the fermenter, purified and treated with water.
2. Sugars can be converted into lipids by yeast or algae. They are recovered using solvents that break the cell. Lipids are purified and converted to liquid fuel using conventional Hydrotreated Vegetable Oil (HVO) technology.
3. Genetically modified bacteria feed on sugars and excrete short-chain alkenes, which are subjected to oligomerization and hydrotreatment.



**Fig. 6. Diagram of biofuel production by biochemical method**

Source: [5]

The fuel - HVO - resulting from biochemical changes is a mixture of paraffinic hydrocarbons with a high cetane number. The chemical structure is similar to conventional diesel, meaning both fuels can be mixed, can use the same fuel supply infrastructure, and can use the same driveline or vehicle engines [8].

The aerobic fermentation process is used to process sugars that are part of the first generation biomass. The inclusion of raw materials for the production of second-generation biofuels in this process is still under development. The main challenge is to obtain the right quality of raw materials.

## Conclusions

1. Currently, there are four generations of biofuels - the last two are still at the research stage.
2. For the production of second-generation biofuels, raw materials are used that do not compete with the food market.
3. There are thermochemical and biochemical methods of biofuel production.
4. The production of second-generation biofuels often involves high costs and complex biomass processing.

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## **ASSESSMENT AND COMPARISON OF DIFFERENT ASPECTS OF DOG NUTRITION IN POLAND**

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### **Abstract:**

Feeding dog correctly has a huge impact on its health and quality of life. The main consequence of nutritional mistakes is obesity of dogs. Knowing the most common dietary mistakes made by owners can be helpful for a veterinarian to diagnose and treat a patient. The aim of the research was to check the diet of dogs in Poland in relation to generally accepted norms of proper nutrition of this species. One of the diagnostic survey methods was used for the study - a questionnaire, which was made available via social media. The survey was aimed at owners of dogs over 8 weeks of age. 3,268 people of all ages participated in the study. The answers of most of the respondents correspond to the current knowledge in the field of basic veterinary dietetics. However, there is a group of owners who pay little attention to the diet of their charges.

### **Keywords:**

*nutrition, dogs, veterinary*

### **Introduction**

The dog (*Canis familiaris*) was domesticated by man about 12,000 – 17,000 years ago [1] and is assumed to have been the first domesticated species in history. Man found a partner in the dog to help with tasks such as hunting or protecting the house [2]. The origin of the dog is not entirely known. Assumingly it comes from a wolf, a jackal or both [3]. In the wild, dogs hunted in groups. This behaviour increased the chances of successfully obtaining food and led to social behaviour and a stud hierarchy. Thanks to its physiology and metabolism, the dog also used protein of plant origin [1]. Among other things, thanks to its hunting abilities, the dog has become such a valuable companion of man. Currently, dogs are still used in hunting as faithful companions of hunters, but nowadays the vast majority of dogs primarily act as companions and friends of their owners. The modern approach to dog breeding dates back to the 19th century. More than 400 dog breeds are registered at this time [3].

The feeding of domesticated animals has a huge impact on their health and quality of life. The search for optimal dietary solutions for companion animals goes back a long way, but it was not until the twentieth century that the development of science made it possible to make a breakthrough in veterinary dietetics. Awareness of the importance of adequate nutrition on health is a motivating factor in numerous studies aimed at developing this area. Until the 1970s, the main focus was on adapting the supply of energy and macronutrients to the physiological needs of dogs, and it was only

in the 1990s that characteristics such as size and race began to be taken into account. Understanding the role of nutrition in the prevention of many disorders has led to the transformation of the concept of "being" nutrition into the concept of "optimal" nutrition.

Dogs as human-close companion animals are exposed by their caregivers "on the humanization of their diet". It is necessary to remember the numerous differences in their physiology and dietary requirements in relation to the human diet. Many components of the human diet are poisonous for dogs. In veterinary offices, patients with symptoms of poisoning appear more and more often after eating chocolate, raisins, grapes or some ornamental plants. The education of owners by veterinarians on these risks is a prophylactic factor.

Dogs are relatively carnivorous animals and require the supply of nutrients and energy suitable for their needs, without being confined to meat as their source. Feeding dogs only with meat can be harmful [5].

The main consequence of dietary errors is obesity of dogs. Research indicates that about 22% - 40% dogs are obese [6]. A significant increase in weight contributes to the development of diseases such as insulin resistance, diabetes, hypertension, arthritis, hypothyroidism, hyperadrenocorticism and many others [6]. The growing importance of the problem confirms the value of research into dog nutrition and mistakes made.

Improper nutrition can lead to poisoning or development of the aforementioned disease units. Knowing the most common dietary mistakes made by owners can be helpful for the veterinarian to diagnose and treat.

## **Purpose and method**

The aim of the study was to analyse the diet of dogs by their owners and to identify the most common dietary errors in relation to current knowledge of veterinary dietetics. An additional objective was to determine the impact of certain socio-demographic characteristics on the way dogs are feeded. One of the methods of the diagnostic survey was used for the study – a questionnaire of the survey, which was made available via social media. The survey was addressed to owners of dogs over 8 weeks of age. The survey involved 3,268 people surveyed. The survey was completely anonymous and allowed some questions to be omitted.

**Tab. 1. Socio-demographic characteristics of respondents**

| Age of respondents            |                   |
|-------------------------------|-------------------|
| People aged 18-35 years.      | 64.7% 2115 people |
| People aged 36-45 years old   | 18.7% 610 people  |
| People aged 46-55             | 11.2% 367 people  |
| People over 55 years old      | 5.4% 176 people   |
| Agglomeration of residence    |                   |
| Up to 10,000 inhabitants      | 30.3%             |
| 10,000 to 100,000 inhabitants | 31.4%             |
| More than 100,000 inhabitants | 38.3%             |

**Source: Own study**

**Tab. 2. Characteristics of dogs**

| Sex of the animal             |       |
|-------------------------------|-------|
| Feet                          | 50.7% |
| Girl                          | 49.3% |
| Whether the dog is purebred   |       |
| Purebred dog                  | 52.4% |
| Non-purebred dog              | 47.9% |
| Age of the animal             |       |
| 8 weeks - 12 months           | 15.5% |
| 1 year - 7 years              | 57%   |
| over 7 years old              | 27.4% |
| Sterilization/Castration      |       |
| Spayed / neutered             | 52.1% |
| Non sterilized / Non-neutered | 47.9% |

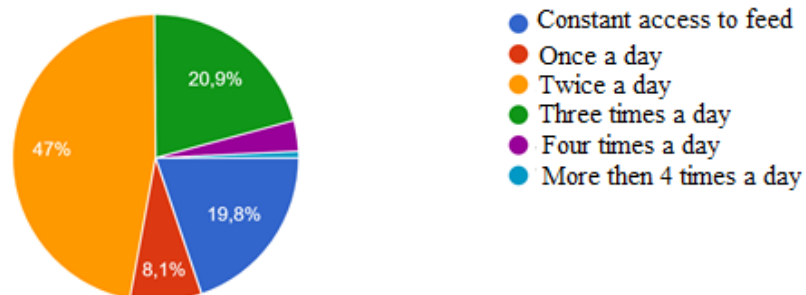
**Source: Own study**

The results were developed using Microsoft Excel and presented as graphs.

## Results and their discussion

56.1 % of people declare that they feed their dog once or twice a day, which is in line with the natural behaviour of dogs (Fig. 1). Wild canine animals acquire food as a result of hunting, and are therefore adapted to eat large quantities less often [7]. 19.8 % of dog owners prefer nutrition with constant access to food. With such a feeding regimen, there is a high risk of obesity due to the consumption of increased amounts of food [7]. Results of the study states the opposite. On average, 4.4 % of all respondents said their dog was obese. For people who feed with permanent access to food, this result was only 3.85 %.

### How often the dog is fed ?

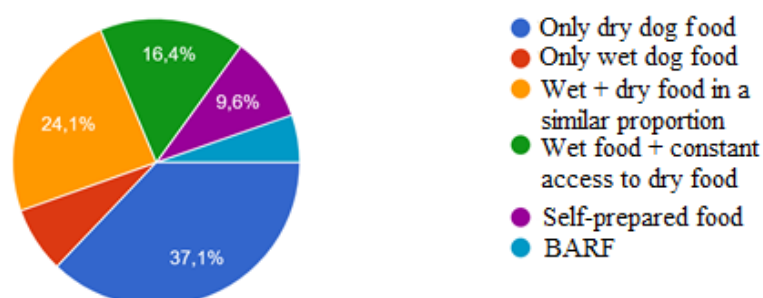


**Fig. 1. How often dog is fed?**  
Source: Own study

Feeding dogs only with dry food is declared by as many as 37.1 % of respondents (Fig. 2). Dry food contains on average about 11 % water [8]. For this reason, feeding them exclusively with it is considered to be conducive to the development of obesity. The results, on the other hand, show that only 3.7 % of people who feed only dry food answered the question of their pet's obesity in the affirmative.

5.4 % of respondents use the BARF diet for their dogs. Only 1 % of BARF feeding people said their dog was obese. The results show that the BARF diet did not reduce the susceptibility to food allergies, as 24 % of those using it said their dogs suffer from food allergies. This coincides with the answers of the other respondents.

### What is the dog fed with?

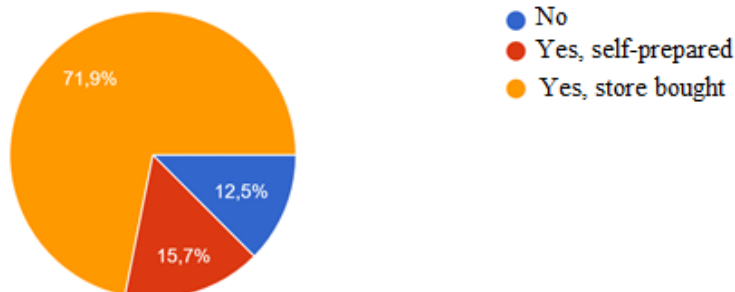


**Fig. 2. What is the dog fed with?**  
Source: Own study

Commercially available delicacies are served by as many as 72 % of owners (Fig. 3). 12.5 % of respondents declare their own preparation. It should be borne in mind that additional energy doses between fixed meals may be a factor in the development of obesity in companion animals.



Does the dog get "treats"  
between meals?

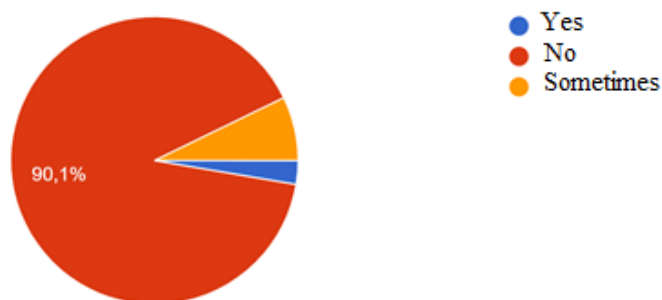


**Fig. 3. Does the dog get "treats"?**  
Source: Own study

As many as 10 % of owners declare that the dog happens to eat chocolate (Fig. 4). For cities with less than 10,000 inhabitants, the figure was 12.3 %.

Chocolate contains large amounts of theobromin, which is highly toxic to dogs. Its toxicity is due to a long half-life (17.5 hours). Even a single administration of chocolate to a dog can have fatal consequences. LD50 for theobromin is 250-500 mg/kg.bw. However, fatalities are known at only 90 mg/kg .c. Clinical signs are further exacerbated by caffeine contained in chocolate [5].

Does the dog eat chocolate?

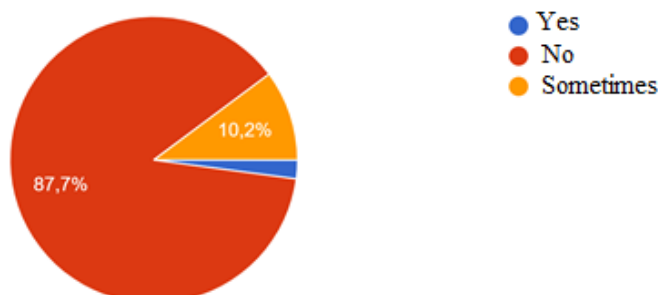


**Fig. 4. Does the dog eat chocolate?**  
Source: Own study

Studies show that 12 % of all respondents give the dog milk (Fig. 5). Among only people over 55 years of age, the result rises to 15 %. The amount of people aged 18-35 who introduced milk into their dog's diet was 11 %. For people living in cities with less than 10,000 inhabitants, this result increases to as much as 17 %.

Milk is not needed in the diet of adult companion animals, and can prove downright harmful. This is due to the decreasing with age amount of lactase, an enzyme that breaks down lactase. For this reason, milk administration can lead to diarrhoea and disorders of the digestive system. In individuals who tolerate dairy products well, it can be used as a variation of the diet [9].

### Whether the dog is given milk

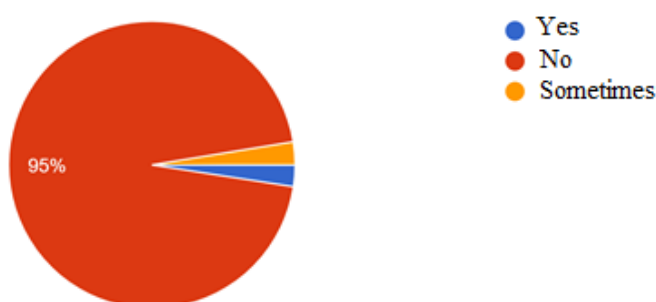


**Fig. 5. Whether the dog is given milk?**  
Source: Own study

As many as 5 % of respondents said that their dogs happen to eat grapes or raisins (Fig. 6) that are toxic to dogs.

The first cases of grape poisoning were described in 1998, when ingestion led to acute renal failure. The mechanism of toxicity is not fully understood. Consideration shall be given, inter alia, to the effects of taanin, contamination of fruit with heavy metals, pesticides or mycotoxins, a large amount of vit. D or idiosyncrasy [10]. A dose of up to 10 grapes can prove dangerous for the life and health of the dog. Clinical manifestations are vomiting, diarrhea and severe abdominal pain, then acute renal failure develops. Treatment is based on provoking vomiting, gastric lavage and fluid therapy [5].

### Does your dog eat grapes or raisins?



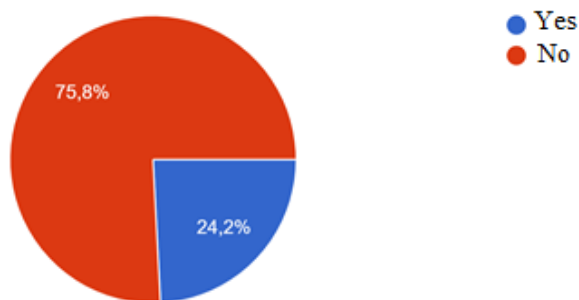
**Fig. 6. Does your dog eat grapes or raisins?**  
Source: Own study

Among respondents, 24.2 % responded positively that their dogs suffer from food allergies (Fig. 7).

Common causes of food allergy are pork, beef, rabbit or chicken meat and dairy products. Fish can also be allergenic. The main symptom of food allergy is itching occurring up to 24 hours

after ingestion of a given substrate. Erythema, pustules, purulent clumps and Quincke's edema are common.

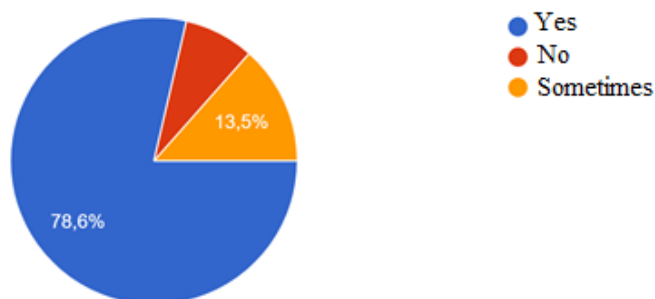
### Does the dog suffer from food allergies?



**Fig. 7. Does the dog suffer from food allergies?**  
Source: Own study

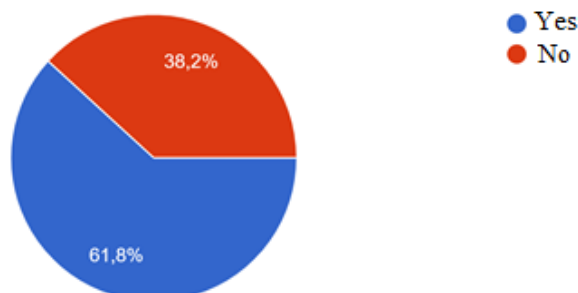
Most people declare that they pay attention to both the caloric content of meals and the content of nutrients (Fig. 8, Fig. 9). The results also indicate that people whose dogs suffer from obesity or food allergies are more likely to pay attention to these characteristics of a meal.

### Do you pay attention to the nutrient content of your dog's meals?



**Fig. 8. Do you pay attention to the nutrient content of your dog's meals?**  
Source: Own study

### Do you pay attention to the calorific value of the dog's meals?



**Fig. 9. Do you pay attention to the calorific value of the dog's meals?**  
Source: Own study

## Summary

Nutrition is a very important element in the welfare and health of animals. When composing a diet for a dog, you should take into account that they are relatively carnivores. When selecting the optimal diet, many factors should be taken into account, such as age, race, health and many others. Obesity in animals is a growing problem, the repercussions of which are visible in reducing the quality of life and the development of disease entities accompanying overweight. Knowing the most common dietary mistakes made by owners can help veterinarian diagnose and treat a patient.

The results of the study indicate that a large number of owners are highly aware of the proper nutrition of dogs. The answers of most of the respondents correspond to the current knowledge in the field of basic veterinary dietetics. However, there is a group of owners who pay little attention to the diet of their charges. Some of their practices are even dangerous to animal health. The high percentage of responses about including the dogs' nutrition with milk or chocolate indicates the ongoing phenomenon of humanizing the animal diet.

The obtained results indicate a further need to educate dog owners in the field of dog nutrition, and in particular to avoid introducing poisonous substances into the diet and factors that may lead to the development of obesity, which may lead to diseases of the cardiovascular and respiratory systems, diabetes or bone diseases.

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## THE USE OF CLAYS AND HYDROGELS IN DRUG RELEASE

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### Abstract:

Controlled release drug delivery systems allow an active substance to be slowly unblocked and released to the body. Various matrices are used to create them. Hydrogels belong to the group of materials with great potential in science, especially in biomedicine. Clay nanocomposite hydrogels have been developed in response to the growing demand for multifunctional materials with mechanical and biological products. Clays are materials commonly used in pharmacy. Their hydrophilic, naturally occurring inorganic mineral salts are used as excipients or active substances. It has been observed that they may interact with drugs reducing their absorption. Such interactions can be exploited to obtain technological and biopharmaceutical benefits in the control of drug release.

### Keywords:

*clays, hydrogels, drug release*

### Introduction

Over the years nanocomposite hydrogels have been gaining more and more popularity, and their possibilities of use are increasingly frequently studied by scientists. Nanocomposite hydrogels belong to the group of materials with great potential in science, especially in biomedicine. They can be used as superabsorbents, drug carriers, tissue scaffolds, dressings, and biosensors [1-3]. Due to their structure, the synergistic molecular combination of a polymer matrix with a nanometric inorganic chemical compound, the matrix acquires features such as high sensitivity to physical stimulations (light, heat, magnetic field), chemical factors, and pH change. They are characterised by high mechanical strength, high ability to be saturated with a drug, mucous and bioadhesive properties. They also have a high ability of self-regeneration [2, 4, 5].

Clay nanocomposite hydrogels and polymers are well known for having high mechanical and biological properties [3]. Clays are a common ingredient in pharmaceutical products used as excipient substances and active substances. Already in antiquity, the interest in clays was high. They were used,



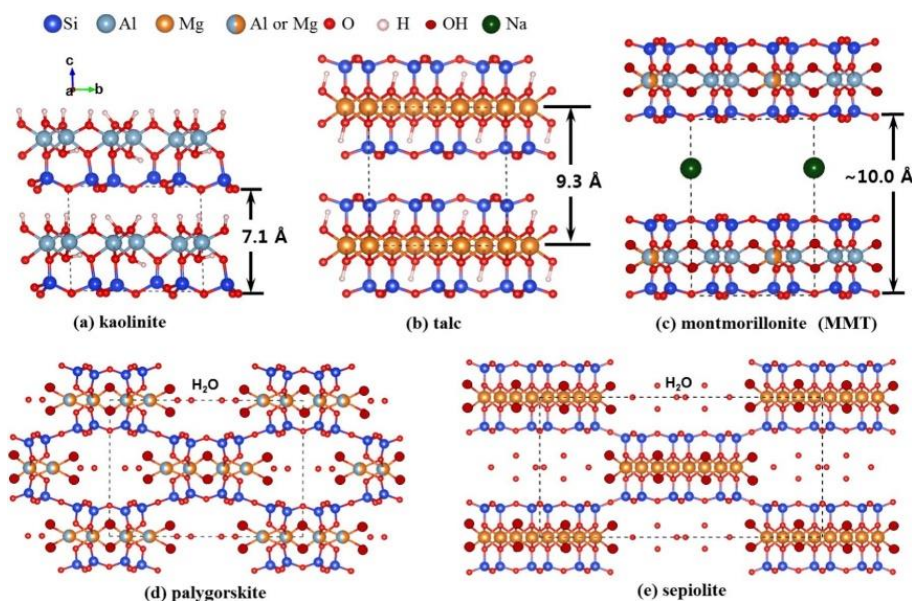
for example, to improve wound healing or for cosmetic purposes [6]. In the 1960s, it was observed that absorption of the drug administered orally was reduced by co-administering a drug and a clay-based adsorbent. One of the examples of such an effect was promazine, which is antidepressant drug. Drug was administered together with antidiarrheal mixtures containing palygorskite (attapulgit) [7-9]. Many other studies also reported a decrease in the bioavailability of the drug after the use of formulations containing clays [10-12]. After this discovery, it was realized that the simultaneous use of clay minerals with the drug may have a positive application in modified drug delivery systems [7].

## Clays

Clay is hydrophilic, naturally occurring mineral, which can form very fine-grained sediments (so-called mud or clay, too). Clays are represented by different kind of minerals, where their structure is often layered. The thickness of a single crystal is approximately 1-1.6 nm and is approximately 100-400 nm long. They are hydrated aluminum silicates, where the cation position can be occupied by e.g. different metals, oxygen, and hydroxyl groups. They contain a high percentage of bound water. There are 2:1 (trioctahedral) layered silicates, e.g. the structure of layered phyllosilicate clay, which consists of a centrally located octahedral aluminum plate ( $Al(OH)_6^{3-}$ ) and surrounding by two tetrahedral silicon sheets ( $SiO_4^{4-}$ ) or 1:1 (dioctahedral), if it consists of two layers - tetrahedral and octahedral and their thickness is about 1 nm. Due to the imperfection of the crystal lattice of isomorphic substitution, the clay surface has a constant negative charge, which allows cation exchange and adsorption [2,6,13]. Clay minerals surface polarization can be reduced by ion exchange (replacement of inorganic cations with ammonium or phosphonium salts) or by the formation of covalent bonds (sol-gel reaction) [14-16]. The most common clay minerals are kaolinite, talk, vermiculite, sepiolite, illite, montmorillonite, and chlorite group minerals as well as synthetic clays [6].

Clays are commonly used as ingredients in the pharmaceutical industry, they are used as ingredients of oral antacids, gastrointestinal protection and anti-diarrheal drugs. They are widely used in dermatology as protective and anti-inflammatory agents [17-19]. They are also used as auxiliary substances: thickeners, anti-caking agents, emulsifiers, flavour correctors. Clays are widely used due to their physicochemical properties, such as the ability to adsorb, large specific surface area, exchangeability, colloidal and thixotropic, high swelling potential, low toxicity [17].

The crystal structure of clays used in pharmacy was shown on Fig. 1.



**Fig. 1. Crystalline structure of pharmaceutically used clays: (a) kaolinite, (b) talc, (c) montmorillonite, (d) palygorskite and (e) sepiolite; dashed lines indicate a unit cell**

Source: [17]

## Hydrogels

Information on the use of hydrogels dates back to 1960 when Wichterle and Lim were the first to propose the use of poly (2-hydroxyethylmethacrylate) (PHEMA) hydrophilic networks in contact lenses [20, 21]. Since then, hydrogels have become more and more popular in the scientific community, and they have been used for biomedical or pharmaceutical purposes [21].

Hydrogels can be called polymer networks that absorb large amounts of water. Hydrophilic groups or domains are present in the polymer network, which are hydrated in an aqueous medium, thus forming a hydrogel structure. To maintain the structure of the hydrogel, the presence of cross-links is necessary, in their absence, the polymer dissolves in water. The presence of cross-links between different polymer chains causes the hydrogel to obtain viscoelastic properties and in some cases even purely elastic [1, 16, 24]. Hydrogels are polymers that are biocompatible with human tissues. They are nontoxic and therefore can be used in medicine [24, 25].

Due to their ability to absorb water, hydrogels have been used as materials for the production of contact lenses, diapers, matrices for cell encapsulation and systems for the controlled release of drugs [26]. The concept of a drug release system is usually based on the physicochemical and pharmacokinetic properties of the drug [21, 22]. Conventional dosage forms provide immediate drug release with virtually no release control. In order to achieve and maintain therapeutically effective drug plasma levels, careful control of drug dosage is needed to avoid significant fluctuations in plasma drug concentration. These fluctuations may cause the plasma drug concentration to fall below the minimum effective concentration (MEC) or exceed the minimum toxic concentration (MTC), which may result in the appearance of negative adverse side effects or even a lack of therapeutic effect [22, 27].

## Controlled drug release systems

Drug Delivery System (DDS) allows a drug to be gradually released in the body. In order to achieve the desired therapeutic effect in the body for a given drug it must be administered in a dose not lower than that which ensures the minimum effective concentration and is not greater than the maximum. These are systems that ensure some real, therapeutic, time-defined and/or spatial control of drug release [7, 28-31]. These systems also have their drawbacks, there is potential for toxicity in the case of premature and over-release and the need for using invasive procedures as with implants. The lack of correlation between *in vivo* and *in vitro* tests is also very often observed [22].

Based on the applied technological approach, four main systems were distinguished: systems with a programmed rate - controlling the molecular diffusion of drug molecules through the polymer barrier, systems with activation modulation - drug release is activated and modulated by physical, chemical or biochemical factors, systems with a regulated feedback concentration - release when the drug is activated by feedback mechanisms occurring in the human body and by targeted drug delivery systems [7, 32].

## Hydrogel-clay nanocomposites

Conventional chemical cross-linking hydrogels are often weak and/or brittle, limiting their wider use. The hydrogel-clay nanocomposites have shown that this disadvantage can be overcome. Highly functional clay can form physical, reversible crosslinks to dissipate energy efficiently and stabilize the hydrogel network, leading to hydrogels with increased mechanical strength. These properties play an important role in directing unchanged drug delivery to a specific location in the body. Clay nanoparticles enclosed in a hydrogel network affect its morphology, and thus the drug diffusion process in the body, which is reflected in the process of delayed drug release [2, 13, 16, 33].

A series of poly (N-isopropylacrylamide) and synthetic hectorite nanocomposite hydrogels have been developed. Unlike conventional nanocomposite hydrogels, these hydrogels can reach a tensile strength of 109 kPa [33-35].

The mineral-polymer clay nanocomposites can be synthesized by various methods. We distinguish among others: melt mixing, in-situ polymerization and exfoliation with adsorption [14]. In one of the syntheses, nanocomposites were synthesized by emulsion polarization, in which latex polymethylmethacrylate particles were covered with mineral plates of silted clay. Modified montmorillonite was encapsulated inside polymethacrylate methacrylate by surfactant-free polymerization [14, 36].

Many raw materials are used in the production of nanocomposite hydrogels. The most frequently used synthetic polymers over the years are poly (n-isopropylacrylamide), poly (acrylamide), poly (acrylic acid), poly (vinyl alcohol), while of natural origin are chitosan, alginate, chitin, and its derivatives [6, 37, 38].

Hydrogel-aluminum nanocomposites are a promising material for drug-controlled release systems. These systems are made of an organic part, i.e. a hydrogel network and an inorganic one - clay. They are able to encapsulate the drug, adsorb it or add it directly. Fig. 2 illustrates an exemplary aluminum hydrogel system saturated with a drug [37-39].

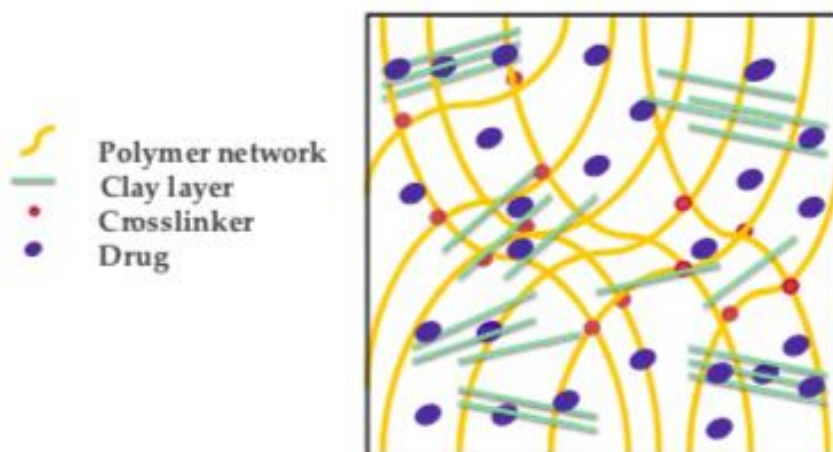


Fig. 2. An exemplary system based on an aluminum hydrogel network containing a drug

Source: [6]

Examples of nanocomposite aluminum hydrogel systems for controlled drug release are shown in Tab. 1.

Tab. 1. Nanocomposite aluminum hydrogel systems for controlled drug release

| Polymer                           | Clay mineral    | Drug                      | Application  |
|-----------------------------------|-----------------|---------------------------|--|
| Poly (2-hydroxyethylmethacrylate) | Montmorillonite | Paracetamol               | palliative care, postoperative pain  |
| Cellulose                         | Halloysite      | Curcumin                  | potential anticancer, anti-inflammatory and wound dressing properties                    |
| Poly Lactic-glycolic acid         | Montmorillonite | Propranolol hydrochloride | medicine for high blood pressure   |
| Chitosan                          | Sepiolite       | Tetracycline              | potential treatment of bacterial infections/gastritis and peptic ulcers                  |
| Chitosan                          | Laponite        | Ofloxacin                 | model drug, treatment of bacterial infections  |
| Chitosan                          | Montmorillonite | Platinol                  | metastatic testicular cancer, metastatic tumour of the ovary and advanced bladder cancer |

Source: [6, 39]

The controlled release system must meet the following conditions: control the amount of the drug released, the speed of its administration and ensure reaching the target site of drug action in the body [6, 19, 38].

The main advantages of nanocomposite aluminum hydrogel systems are targeted drug release, alleviation of drug-induced side effects, lower drug toxicity, the possibility of reducing the frequency of drug administration, and faster recovery time for the patient administered the drug in this form. The disadvantages of this type of system are high production costs, long-term process of creating a balanced system, unpredictable *in-vivo* and *in-vitro* correlations [6, 37-39].

## Summary

Nanocomposite aluminum hydrogel systems for controlled drug release, which apart from controlled drug release, have a wide range of different applications, are gaining more and more popularity in the scientific community. Due to the new, broader approach to the treatment of many diseases, in the future, they may become one of the important factors influencing both the improvement of the patient's quality of life, as well as better therapeutic effects. They prove that mineral compounds, of great historical importance in medicine, can also be an important element of the medicine of the future, not only because of their natural origin, but also due to their high efficiency of use. Extensive and multi-directional research is required that can accelerate the implementation of the proposed solutions in practice.

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# **ILLEGAL TRADE OF ANCIENT MESOPOTAMIAN ARTEFACTS FROM SYRIA AND IRAQ BY THE ISLAMIC STATE**

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## **Abstract:**

The paper focuses on the illegal trade of Ancient Mesopotamian relicts from the area occupied by the Islamic State on the territory of Syria and Iraq. The dissertation touch upon not only the problem of illicit trafficking but also its routes. Prohibition of illegal looting and trade is adjudicated by the international law. The paper focuses on some of the most crucial legislatives and analyses them, such as Resolution 2199, Resolution 69/281 titled 'Saving the cultural heritage of Iraq' and the main pillar of international law protecting cultural heritage form theft and illegal trade - Convention on the Means of Prohibiting and Preventing the Illicit Import, Export and Transfer of Ownership of Cultural Property from 1970. The income form the years of illicit exchange of ancient goods is hard to estimate. Although, the dissertation put focus also on the numbers and examples of traded Mesopotamian artefacts.

## **Keywords:**

*Islamic State, ancient Mesopotamia, artefacts, illegal trade*

## **Introduction**

Through centuries, noble men, kings and even ordinary privates brought back home spoils of war as a proof of their military success. From ancient times it was a sign of victory and often an affirmation of economic power. During more modern times, wealthy representatives, especially of western society, perceived the desire of artefacts collecting to display their love and care towards antiques and culture. Additionally, through the prism of their antiques, collectors could show their high status and richness. According to professor Evangelos Kyriakidis of Kent University, such behaviours weren't any different from modern looting and illegal artefacts trade. Thousands of illegitimately deported cultural properties are now displayed inter alia in British Museum in London and Paris Louvre. Such institutions have kept on holding national treasures of other countries for decades [1]. Nevertheless, maybe because of that, numerous artefacts remained untouched and protected while abundant amount of those remaining especially in the middle eastern countries have vanished forever.

Problem of historical sites looting, trade of stolen artefacts and illegal transfer of ownership appeared during numerous modern days conflicts. In the times of the Islamic State occurrence international community issued several resolutions to stop the illicit actions undertaken on antiques.

Deeper and broader understanding of common goods represented by the world heritage was a motive to undertake actions on the matter of black-market transactions on heirloom.

Convention on the Means of Prohibiting and Preventing the Illicit Import, Export and Transfer of Ownership of Cultural Property from 1970 is considered to be the principal document on illegal trade of antiquities. Until 2020, 140 state parties have signed the document along with Iraq and Syria [2]. In its preamble it is highlighted that the interchange of cultural objects, knowledge of traditions and customs leads to the mutual respect and enriches people of all nations in the broadening of awareness on diverse societies, lifestyles and heritage. Besides the obvious message contained in the title of the document, resolution underlines the importance of fair collections, museums and archives, libraries. As a bedrock of its principles, the convention features respect towards state's own heritage, as well as all signatory parties and all cultures of the world. Cooperation on the interstate level ensure fruitful works on the cease of the illegal trafficking and trade of artefacts [3].

Among its essentials, the 1970 Convention introduced 5 main pillars of organized and sufficient fight with illicit trade and transfer of ownership of antiques. First of all, it imposed a regular state inventories of nations' cultural properties. Secondly, each of the relocated objects has to acquire a valid export certificate. Thirdly, all traders must be credible and are subjects to controls imposed by the purchasing state and international agreements. Additionally, there are severe and high penalties for any fraud behaviours. Lastly, educational and informative campaigns are conducted on the state, interstate and UNESCO level [4].

As additional legal documents concerning illicit trade and transfer of ownership of antiques, in 2015 United Nations issued four substantial resolutions fuelled by concerning issues of trafficked cultural objects from Syria and Iraq. Resolution 2199 highlighted that collective work on the trade prohibition on looted and transferred from Iraqi and Syria artefacts will decrease financial income of the Islamic State. It also shed light on the matter of deliberate destruction of heritage and religious sites, as a tool of advanced terror [5]. Later, on 28<sup>th</sup> of May, the UN General Assembly adopted Resolution 69/281 titled 'Saving the cultural heritage of Iraq'. This legal act recalled Resolution 2199, Hague convention and numerous legal documents on cultural heritage. The main emphasis was put on the matter of destructed cultural and religious sites. Again, international community was summoned to take appropriate measures on the issues of illegal trade of Iraqi artefacts on state and interstate level. Nevertheless, it is noticeable that UN and UNESCO members can mostly use soft power and act preventively on the matter of illicit transfer of cultural property. However, countries can ban IS followers from entering United Nations member states territory or freeze monetary assets of the terrorist group members. The lack of direct solution especially on the matter of deliberate destruction of Iraqis' heritage is visible in constant requests addressed to the Islamic State. This alleged caliphate wasn't recognized as a state and thus it never joined any lawful international organization. This is why most legal threats from states alone or collectively under the UN agenda did not affect the Islamic State actions [6].

On the eve of year 2015, during the UN General Assembly on 9<sup>th</sup> of December, a legal document on 'Return or restitution of cultural property to the countries of origin' was adopted. This legislative act underlined that stolen cultural property is a huge loss not only for the country that it originated from but again for the entire international community. In its core the document appealed for the constant improvement and extension of global and regional artefacts databases. Information flow

followed by extensive and accessible data collection enables smooth and fast detection of illicitly transferred and traded cultural property for the international organization and all states [7]. Additionally, Resolution 70/76 recalled the 2030 Sustainable Development Agenda which emphasized the importance of natural and cultural diversity, its protection and significant influence of diversity on common progress creation [8].

In the late 2015 another UN legislative act on the matter of Islamic State was issued. Although Resolution 2253 of Security Council focused mainly on IS assets freeze, travel ban for the organization members and supporters and arms embargo, in its preamble it involved a strong condemnation of cultural heritage destruction. Additionally, it appoints all contracting parties to undertake appropriate steps in the matter preventing cross-border illegal trade of artefacts and cultural property. Documents oblige also to the safe return of the recaptured items to Iraq and Syria [9].

Continuous appeal was again exercised in the Resolution 2347 of UN Security Council. This 2017 document prompted international community to the constant fight against trade and cross-border transit of artefacts stolen and illegally excavated on the territory occupied by the Islamic State. It encourages the cooperation of member states, cultural organizations and international special units such as INTERPOL [10]. The text of Resolution 2347 involves a reminder and admonishment that since the unprecedented case of prosecution on the matter of intentional destruction of heritage during armed conflict such actions are perceived as war crimes. After the decision of International Criminal Court Trial Chamber in 2016 felonies committed on art and culture are also to undergo litigation [11].

## **Motives behind illegal trade of archaic goods**

On the international area, the Islamic State is perceived as a terroristic organisation, not as a recognised state. As a consequence, most of its actions undertaken to increase its financial gains are illegal. One of the significant ways of fast income are illicit transfer of antiques commonly described as *artnapping*. Classified as external incomes of the IS, it is hard to estimate the total value of smuggled items due to the changing artistic uniqueness and cultural meaning of each and every piece. Financial worth of numerous objects derived from Syria and Iraq were described as immeasurable. Through the conflict over 4500 archaeological excavation sites were controlled by the Islamic State. Additionally, the IS troops were controlling museums, galleries and confiscated private collections on its area of influence [12].

The practice of extensive looting and smuggling of artistic goods from Syria and Iraq for financial benefits was not invented by the IS. This common practice was used by numerous illegal groupings through times. Furthermore, the northern part of the Middle East was extensively looted earlier in history, for instance during the 2003 Iraq invasion of US-led coalition. Even though the Islamic State was not an original inventor of the cultural property plundering for financial gains, it is believed that during its occupation time on the territory such actions had enormously intensified in the region. It is believed that artefacts trade and smuggling represented the second largest way of the IS financial income [13].

As mentioned before, the Islamic State is commonly known for its usage of cultural heritage for its propaganda scheme. Nevertheless, the organisation managed to find another profitable usage of cultural property. According to available data there are three main forms of financial benefits when

speaking of antiques trafficking. Firstly, the IS fighters supply individual fences, smugglers and also collectors who are willing to pay for looted goods. Secondly, the Islamic State facilitate illegal transfer of cultural property. They protect already existing smuggling routes and create new ones. Furthermore, the organisation shelters and supports fences. Lastly, mandatory fees are charged from independent smugglers operating on the territory of the Islamic State. When speaking of such transactions due to the fact of possibility of fast income, value of the items is often underestimated. However, financial benefits are still very high [14]. Over the years of military operations, the Islamic State put a great importance on their income from illegal transactions of cultural property, often described as *bloody antiques*, especially at times when organisation was losing the territory of oil-producing fields [15].

Apart from selling artefacts on the black market to finance its military activity and functioning of the state it has additional, but then not that lucrative money inflows. In its February 2015 report FATF (The Financial Action Task Force) stated that financing of IS can be decided into 5 major channels: "(1) illicit proceeds from occupation of territory, such as bank looting, extortion, control of oil fields and refineries, and robbery of economic assets and illicit taxation of goods and cash that transit territory where ISIL operates; (2) kidnapping for ransom; (3) donations including by or through non-profit organisations; (4) material support such as support associated with FTFs and (5) fundraising through modern communication networks" [16]. To govern these actions better, the state established a *Diwan al-Rikaz* responsible for valuable natural resources (such as oil) and antiques: its acquisition and illegal trade [14].

### **Estimated income**

International community has been trying for years to estimate the financial income gained by the Islamic State from ancient artefacts black-market trade. Unfortunately, due to the incomplete data, scholars were unable to evaluate possible earnings obtained through the years of looting and smuggling cultural property out of Syria and Iraq. When speaking on approximated IS profit from this practice, there are 3 main challenges. Firstly, there are no trustworthy quantitative data on the artefacts legally traded from this area, so it is even harder to get hold of any reliable information on illegal transactions. Secondly, it is impossible to evaluate the worth of what was dug out from the ground [17]. Additionally, when speaking of museums, there is no data on what exactly was sold on black market, which objects were hidden and whatever was destroyed on purpose [18]. Lastly, because of the uniqueness of the objects there is no universal methodology to evaluate the possible worth of such goods. As a result of so many misconceptions, the estimated income stretched from 4 million US dollars to 7 billion US dollars [17]. Recent reckonings of the United States officials indicated that since mid-2014 100 million US dollars of annual income benefited to the Islamic state from the illicit trade of cultural property. The same estimations were issued by Mohammed Ali al-Hakim the UN Ambassador from Iraq. According to Russian Federation sources, numbers might have been even higher [19]. Specialists indicate that some artefacts can reach up to 1 million US dollar price per piece when some are sold for only little percentage of their value or are immediately traded for guns [20]. As reported by 2014 data, estimated profit from only several archaeological sites in Qalamun mountains in western Syria could have enriched the IS with 36 million US dollars [14].

## **Examples of pieces traded by ISIL**

Region controlled by the Islamic State is perceived as one of the most valuable areas considering archaeological remains and diverse cultural property that have accumulated there over the centuries. Due to the fact of fast and easy money income, the IS mostly traded small pieces such as ancient coins, jewellery, small monuments and sculptures that were smoothly transported [19]. Considering the high demand on ancient Mesopotamian artefacts and the fact that the second largest bid ever made on antique art auction was put on an old Assyrian relief which costed 31 million USD, illegal smuggling was a lucrative business [21].

As the easiest way to obtain valuable artefacts for further illegal transaction the Islamic State fighters aimed for museums and art galleries where a great deal of cultural objects was accumulated. According to the international reports after looting Raqqa Museum in Syria, over 1500 objects were displayed on the black market. Nevertheless, because of the common knowledge on the IS' destructive and illicit behaviours towards cultural property, 29 out of 34 ancient art museums were emptied in 2014. Most artefacts transported by the antiquities officials to Damascus were hidden in unobvious for terroristic organisation places. The whereabouts of storages were known only to couple ancient art experts [19].

When speaking of looting the ancient sites most commonly IS fighters were searching for small valuable objects, again such as coins, jewellery and small sculptures. After the search in historical areas including Hatra, Nimrud and Khorsabad were bulldozed for propaganda reasons [19]. Through the years antiquities black market was full of Middle Eastern items. Surprisingly, it didn't lower the high demand on such goods, but even intensified the interest. The requests from collectors were not discouraged by the fact of common lack of paper proving the authenticity of the items. According to current data, over 80% of illegal sold goods had no legal documents attached to them. Additionally, due to the frequently occurring lack of anti-smuggling laws in countries challenged by terrorism, the duty of tackling and preventing illegal trafficking of artistic features was put on other nations, regional bureaus and international organisations [15].

The Islamic State very often put on a show of heritage destruction to disguise its true intentions towards cultural property. According to the investigation of numerous international scholars and archaeologists that watched the videos showing demolition of ancient collections, a great deal of artefacts was already missing, or the destruction was performed on worthless copies. Additionally, Zeid al-Obeidi who formerly worked in Mosul Museum believes that the lack of scattered remains indicates that most of the movable objects were designated to supply the IS' black market revenue. He furtherly concluded that only heavy and impossible to move objects such as Lamassu sculptures were used to propaganda purposes. According to most recent data it is estimated that between 60-70% of all Iraqi ancient artefacts are still missing and 50% of the remaining number are severely damaged. Obeidi draws attention to the fact that sometimes collectors and antiquarians seek specially desired parts of monuments or sculptures. That is why after liberation of several historical places a lot of sculptures were beheaded very delicately to not disturb fragile ordered parts. When it came to financial profits the Islamic State troops handled artefacts extremely carefully. Walls and glass-cases of museums and archaeological areas are full of empty spaces where previously



mosaics and artefacts were displayed. Items were removed with such precision that hardly ever even small pieces of clay or tile were left behind [21].

Over the years of conflict, the IS specialised in more sufficient usage of antiques in means of financial profit. At first, looting was conducted by smugglers loosely tied to the organisation or by regular fighters of the Islamic State who often kept some items to themselves. Along with the increased market demand on stolen ancient goods that heightened up to 30% between year 2011 and 2015, the IS government appointed its own antiquities director. People who through the years overtook this position were responsible for contacting dealers with great expanded relations especially with Western buyers, acquiring archaeologists to evaluate looted artefacts and designating labour force for illegal excavations [20].

### **Channels of illegal trade**

The strategy of the Islamic State illegal trade of artefacts is no different from other loosely tightened organisations engaged in this activity. The strategy is split in two ways, one is based on traditional commerce between private black-market buyers, antique shops or auction houses and sellers whereas the other one is based on online selling on internet platforms such as eBay or Facebook [22]. Transnational trade of illegally excavated cultural property occurs in four stages. Firstly, the object is excavated and/or stolen from historic area most commonly by a local looter or smuggler. Secondly, the object is transported by the early stage middleman because most of the local thieves lack the financial possibilities of international undercover trip. Traffickers most commonly smuggle great deal of goods at one time. Through extensive connections across borders, customs services bribes and deep understanding of security of particular states items are unnoticeably transported out of the country of origin. The success of the third step depends on reliable laundering of the item into the legal market. Cultural goods often have no earlier designated buyers in the grey sphere, so the only way of gaining profit is to issue it on legitimate retail space. The group of the late stage middleman is the smallest and most crucial for the undertaking. People appointed to the conduction of the phase must not only have extensive knowledge of history, antiques and value of items but also maintain extensive contacts with private collectors, galleries and museums. On the last, fourth level there are buyers who are seeking for products. Sometimes purchasers are unaware of illegality of acquired item, but there is also a great number of customers that have no stings of remorse to invest in *bloody antiques* [23].

The Islamic State was believed to cautiously manage the circulation of cultural property in addition to keep the market prices high. The taxes put on smugglers reached even 20% of the income. Looters often insisted on searching the particular area then the percentage contribution to IS was indicated by the importance of the region. Along with the growing demand on ancient goods, authorities of the Islamic State encountered alternative way of fast income. Specially designated artists were manufacturing fake artefacts that were later sold as original ones. According to the statement of Syria's antiquities director, over 70% of recaptured Syrian and Iraqi relicts in Turkey and Lebanon in year 2016 were fake. At first, quality and embodiment of forged items were inaccurate. As the time passed, the IS hired qualified forgers and significantly increased incomes [19].



In most cases artefacts were first transported to states neighbouring with Iraq and Syria such as Turkey, Iran Lebanon and Bulgaria. Some of the commodities were used to bribe border controllers. Moved across land borders in trucks antique items were later on passed further to other transition countries to disguise its place of origin. Middlemen in passage lands were further forwarding antiques to dealers in Israel, UAE and European states. As soon as an artefact entered into the territory of Europe it was passed between different conservators and dealers. Frequent change of owners and locations allowed to create an artificial trail of legal documents to hide the original place of provenance. When the trace was long enough, items previously smuggled from Iraq and Syria were sold on legitimate auctions in New York or London [20]. Sometimes smugglers shipped artefacts as far as to the overseas harbours in Thailand and Singapore [15]. Some private collectors from Western European countries such as France, Germany, Switzerland, United Kingdom and North America aware of the unrighteous source of the artefacts are still willing to buy unique pieces representing heritage of the Middle Eastern region. Considerable number of looted objects can be found in antique shops that doesn't require specific documentation, but hence the prices of displayed objects are correspondingly lower [20].

As an alternative way of quick monetising the stolen artefacts, IS individuals used web pages and applications. Multiple repeatedly renewed Facebook groups gathered people who ordered specific artefacts or were just in search for new items to their illegal collections. Additionally, members of the chats exchanged ideas and tips on where and how to loot in the most sufficient way. Although most of such conversation concerning buying and selling particular objects are documented in the online chat, the substantial purchases happened out of the limelight [24]. Along with progressing technological development it was also easier for smugglers, traffickers, dealers and buyers to communicate. Online meetings via Skype, Kik or WhatsApp allow better communication between clients and sellers and enable online check-ups of the purchased items [25]. According to some archaeologists, such transactions are made in cases of artefacts that are not worth enough to engage in a cost of professional middleman [19].

When liberating Iraq and Syria from the Islamic State's hegemony, a high number of antiquities was found in private houses and hideouts of IS officials and high-ranked fighters.

Cultural property could have been stashed in such places for various reasons. Apart from not overflowing the market, some believe that some dignitaries were collecting antiques as a war treasure [19].

### **Tools to fight illicit trade and transit of artefacts**

The indisputable key element needed for prevention and fight with the illegal trade and transit of cultural property is the international cooperation. Closely tightened relations of multinational organizations, state officials and services, followed with mutually respecting laws are necessary for the reduction and further elimination of these illicit practices. It is crucial to understand that to achieve a successful transaction of illegitimate sale several people of different skills are needed. It is a long road for an antique to reach its final destination in the safe-haven of an unlawful buyer. Often the routes, looters, smugglers and middlemen remain the same over years or are being passed from one generation to another. It is a concern of international community to trace and prevent further illicit transits of cultural property [13]. As stated by former head of UNESCO, Irina Bokova, through the

years of the Islamic State occupation of Iraqi and Syrian territory historical sites were looted on the 'industrial scale' [26].

Apart from international legal acts such as 1970's 'Convention on the Means of Prohibiting and Preventing the Illicit Import, Export and Transfer of Ownership of Cultural Property' there are several multinational, regional and state managed law enforcement authorities on the matter of illegal trade of artefacts. INTERPOL is one of the biggest and most effective organizations on this matter. The International Criminal Police Organization gathers 194 countries and helps to maintain sufficient and effective investigational work between member states. Additionally, INTERPOL permit access to their databases if needed and ensure a wide range of operational and technical support [27]. Organization provides experts in the field of organized trafficking as well as information, databases and educates how to prevent and minimize illegal trafficking of artistic goods. 'Works of Art Database' constructed by the International Criminal Police Organization enables national law enforcers to verify legality of artefacts and their status. Additionally, twice a year in June and December INTERPOL issue a list of 'most wanted works of art' [28].

Additional help in fighting illegal transit of artefacts is provided by the World Custom Organization. A communication tool called *ARCHEO* is both a communication platform and database on stolen and missing objects. Containing manuals, guidelines, online workshops seeks to educate on the matter of illegal trade, custom laws, identification guidelines and background information [29].

When speaking of illicit trafficking of artistic property, it is important to mention International Council on Museums and its 'Red Lists'. The catalogue was invented to support inhibition of illegal trade and transit of artefacts. First published in 2000 presents objects that are most vulnerable to be illegally depleted. ICOM issues regional lists among which are those dedicated to Iraqi and Syrian cultural objects. National and international experts on specific areas catalogues artistic property and in the cooperation with museums, galleries and lawful private collections display items that are likely to be found on black market [30]. International Council on Museums constructed supplementary online database of those most vulnerable to theft and illicit trafficking [31]. Furthermore, ICOM appointed 'International Observatory on Illicit Traffic in Cultural Goods'. The platform was designed to share information and encourage multinational cooperation on the subject of fight against illegal trade of artefacts. This innovative tool not only works as a database but also operates as international cooperative platform. It assembles multinational partners, inter alia law enforcement agencies, global organisations, independent experts and research institutions. Since the project launch in early 2013 observatory issued numerous publications on prevention and combat of illicit transit of artefacts [32].

Continuously for the last 55 years international cooperation of researchers, historians, archaeologists, anthropologists, art historians, geographers and other scholars associates under the non-governmental organisation called ICOMOS (International Council on Monuments and Sites). The main statutory works of the council circulate around conservation and preservation of historical sites. Organisations' main strength is the fact of associating together experts from various fields which enables the multidimensional cooperation on heritage protection. As one of the main goals of ICOMOS are extended practices to improve technical aspects and standards of cultural property such as: buildings, archaeological sites, cultural landscapes and historical cities. The council assembles over 10 500 professional experts from over 150 countries, 107 National Committees including the Turkish branch and 27 Multinational Scientific Commissions [33]. Additionally, ICOMOS is

responsible for the publication of 'Heritage at Risk Report. Addressed to the general public and international community, it seeks to raise social awareness in the matter of destruction of cultural heritage. These thematic reports are issued to spread information on threats lurking for historical sites. Furthermore, publications are aimed to provide help and promote necessary measurements to reduce and, in the future, bring to stop both decays caused by atmospheric conditions and damage to cultural areas caused by human activity. Latest issue was released in 2016 and illustrated alarming events and cases that happened in 2014 and 2015. The whole part of the report dedicated to the Near East was focused on Syria and Iraq [34].

## Conclusions

Undoubtedly, one of the biggest milestones in fighting illicitly trafficked artefacts from the Middle Eastern region was the adoption of UN Security Council *Resolution 2199*. This historical turn point was commented by Irina Bokova, a Director-General of UNESCO at that time, "This resolution acknowledges that cultural heritage stands on the frontline of conflicts today, and it should be placed at the frontline of security and political response to the crisis" [35]. Nevertheless, no legal documents will be respected globally without international cooperation of states, multinational organisations, law enforcement agencies and worldwide community. Illegal looting and trade of ancient artefacts for years has been an alarming issue that UN, UNESCO and several non-governmental institutions aim to prevent and bring to an end.

In case of the Iraqi and Syria occupation by the Islamic State ancient artefacts were used by the terroristic organisation for several purposes. Firstly, as a part of its propaganda machine cultural property was ruined and damaged because of the ideological reasons. Secondly, thousand years old archaic goods were a fast and significantly safe way to gain a substantial income for terroristic activities. Cultural property was used to finance illegal operations in the Middle East as well as the attacks in Europe and Asia. Additionally, Mesopotamian heritage was traded for guns, used as a bribery or sometimes collected by the Islamic State officials as their spoils of war. Due to the fact of easy transport of small but very valuable objects apart from oil smuggling, trade of artefacts was second biggest income of the IS. Transported mostly by land to the neighbouring states like Turkey and Lebanon items were later spread around the globe, but the significant majority went to North America and European countries.

According international data hundred thousand of objects were looted and transported out from Syria and Iraq. Out of 15 000 objects located in Palmyra Museum almost 6 000 vanished and are considered sold or missing [36]. Turkish authorities alone are in possession of over 6 800 ancient artefacts that were supposed to be smuggled via Turkey and sent to further destinations between year 2011 and 2016 [19].

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## **PHYSICAL ACTIVITY OF ADOLESCENTS AGED 12-14 ON THE EXAMPLE OF STUDENTS FROM THE SCHOOL AND KINDERGARTEN COMPLEX NO. 9 IN RZESZÓW**

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### **Abstract:**

Physical activity is an essential factor for maintaining health and proper development, therefore it should be undertaken from an early age. The main aim of the study is to analyze the physical activity of young people aged 12-14 attending the School and Kindergarten Complex No. 9 in Rzeszów. The research used the International Physical Activity Questionnaire (IPAQ) and the "pedometer-free step and calorie counter" smartphone application. The study uses the recommendation to perform 10,000 steps a day. As shown, only 14% of the surveyed adolescents achieve the recommended number of steps per day (10,000 steps). On the other hand, referring to the IPAQ questionnaire, it was found that the physical activity of students in terms of gender and intensity did not show any significant difference.

### **Keywords:**

*physical activity, health, youth, IPAQ, the "pedometer" application*

### **Introduction**

Physical activity is an important element in the life of every human being, the decrease or lack of it may contribute to the development of civilization diseases, while if taken regularly it helps to maintain good health and physical condition throughout life. Particular attention should be paid to the physical activity of children and adolescents of school age. In addition, nowadays, there is an increasing development of digital technologies, which may result in its radical reduction. However, some devices, thanks to their functions, can exert a positive influence on it if they are used well. Examples of such devices are smartphones or smartwatches that allow you to monitor activity during the day.

The broadly understood concept of physical activity is defined as various tasks performed during the day related to the movement of skeletal muscles, which require energy expenditure beyond resting. Such activities include: activities related to movement: cycling, walking, performing specific work such as sweeping, carrying or digging, as well as activities related to recreation, such as roller skating,

gardening [1]. Physical activity is also considered in two categories: pedagogical and biological. The first perspective points to the educational process, the main goal of which, in terms of physical culture, is to obtain the habit of movement. On the other hand, from the biological point of view, it is the work of skeletal muscles that is repeated and planned many times, causing energy expenditure beyond the rest or leading to fatigue [2].

According to the recommendations of the World Health Organization (WHO), children and adolescents from 5 to 17 years of age should spend at least 60 minutes a day on moderate to intensive physical activity (MVPA) based on a variety of exercises and adapted to the development of the young human body [3]. On the other hand, the Presidential Active Lifestyle Award (PALA +) states that the physical activity of children and adolescents aged 6 to 17 years should be 300 minutes per week [4]. According to the recommendations contained in "2008 Physical Activity Guidelines for Americans", children and adolescents should spend most of their daily physical activity on moderate or vigorous aerobic exertion, and intense exercise should be performed at least 3 days a week. It is also recommended that during the daily physical activity, 3 days a week, time should be allocated to activity strengthening the muscles and bones [5]. Average norms of daily steps for young people aged 5 to 19 range from 12,000-16,000 steps for boys, and for girls from 10,000-13,000 steps [6].

The school is a place to promote activity through physical education lessons, which, as compulsory activities, constitute an important part of the physical activity of children and young people during the day. These classes have a special task, because not only the level of physical fitness or sports achievements is checked, but also knowledge and skills that are helpful in maintaining good health as long as possible [7]. The leading goal of physical education is to shape the habit of taking care of the body in young people. It also creates the opportunity to deepen knowledge in the field of physical culture [8], develop motor skills, acquire and improve motor activities [9]. It also teaches how to effectively solve various tasks that may appear in human life [10].

## **Research methodology**

The aim of the research is to analyze and determine the level of physical activity in the sixth, seventh and eighth grades of the School and Kindergarten Complex No. 9 in Rzeszów. The basic research questions relate to the daily physical activity undertaken and they are as follows:

- Do students meet the recommendations for youth physical activity during the day?
- Does physical activity for boys and girls differ between school and non-school days?
- Is there a difference between physical activity for boys and girls, with regard to its intensity, frequency, type and duration?

Based on the research problems presented above, the following hypotheses were formulated:

- Adolescents take the minimum recommended number of 10,000 steps a day.
- Compared to boys, girls spend more time on moderate-intensity physical activity

### **Characteristics of the studied group**

The study involved adolescents aged 12 to 14 who attended the sixth, seventh and eighth grades of the School and Kindergarten Complex No. 9 in Rzeszów in the 2018/2019 school year. The invitation to participate in the research was given to 80 parents whose children attended the above-mentioned school. All participants and parents were informed in writing and orally about the nature and conduct of the study. Ultimately, the study group consisted of 51 students (26 girls, 25 boys) aged 12-14 (the average age was 13.53).

### **Characteristics of the research place**

The research was conducted in the Municipality of the City of Rzeszów in the School and Kindergarten Complex No. 9. It consists of the Primary School No. 19 named after Fr. Piotr Skarga and Public Kindergarten No. 39. It is a public institution supervised by the Podkarpackie Board of Education.

### **Methods and forms**

In order to answer the research questions, the objective method was used, in which the telephone application "pedometer-free step and calorie counter" (version 1.0.37) was taken into account. The adolescents participating in the study used the above-mentioned step counter for 7 consecutive days. This application is based on automatic counting of steps, lost calories, time spent on physical activity and distance covered. It is age rated "pegi 3" which means it is allowed for any age group and does not contain any content that could scare children. The research also used a subjective method in which a shorter version of the IPAQ questionnaire was used. It consists of 7 questions about physical activity performed during the day related to work, everyday life and leisure. The information contained therein relates to the time spent sitting, walking and practicing physical activity (intense and moderate). In the short version of the questionnaire, as well as in the long version, only activities that last continuously for at least 10 minutes are taken into account [11]. This questionnaire was given to the youth to be completed after the seven-day period of using the aforementioned pedometer. It was completed with the help of the person conducting the study and attached to it was a personally prepared table for recording the data contained in the pedometer (steps, calories, time, distance) and a record of data on gender, age, date of birth, height and weight.

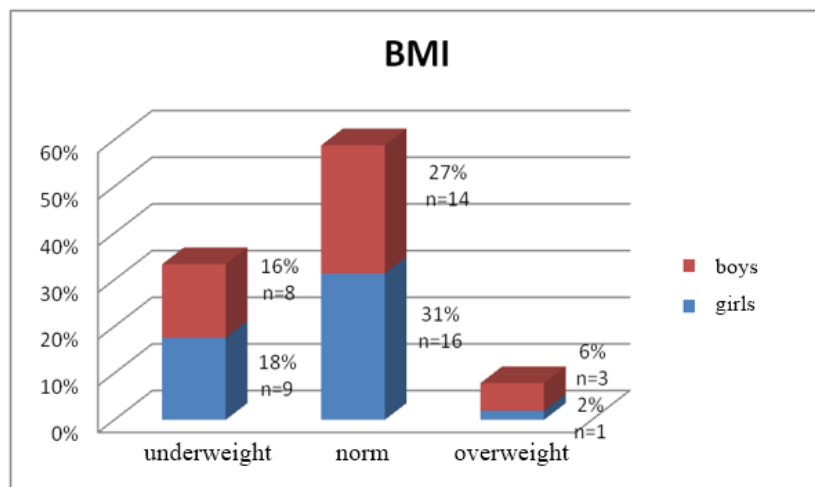
### **Findings**

51 students participated in the study, among whom girls constituted (51%), while the percentage of boys was 49%. In the group of respondents, the vast majority are students aged 14 (68%), while the smallest percentage is 12-year-old youth (8%). The percentage of 13-year-old students is 29%.

The average age of all surveyed students is 13.55 years. Among girls, it reaches 13.46 years, and in boys it reaches 13.64 years.

According to the data obtained as a result of the research, it is possible to conclude an average body height of 1.65 cm and an average body weight of 54.95 kg of the study group. The average body height of girls 1.65 cm and boys 1.60 cm were also distinguished. Meanwhile, the average values of body weight oscillate around 54.09 kg for girls and 53.7 kg for boys.

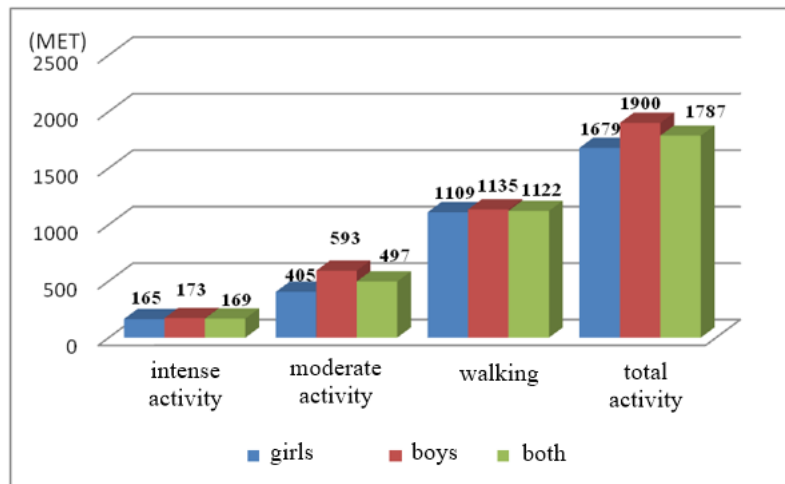
Based on the data on body weight and height, the Body Mass Indx (BMI) of the subjects was calculated. The performed calculation and the ranges proposed by the WHO [7] allowed to determine the percentage division of students who are underweight (<18.5), overweight (25.0-29.9) and normal weight (18.5-24.9 ). The most numerous group were students of normal weight (30 people - 58%). Taking into account the division of BMI by gender, it was found that 14 boys (27%) and 16 girls (31%) had normal body weight. Fig. 1 shows that the second largest group is underweight (33%), among whom there are 9 girls (18%) and 8 boys (16%). On the other hand, overweight was found only in one student (3%) and three students (6%) (Fig. 1.).



**Fig. 1. Percentage breakdown of students by BMI and gender**  
Source: Own research

#### Physical activity measured by the IPAQ questionnaire

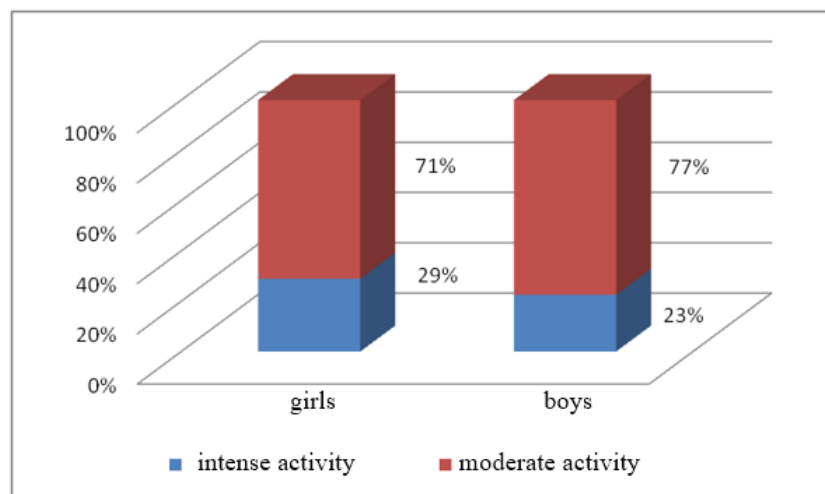
The average total energy expenditure of the studied students is 1787 MET-min / week, while the average energy expenditure for vigorous activity is 169 MET-min / week, for moderate activity 497 MET-min / week, and for walking 1122 MET-min / week. Boys have a slightly higher total energy expenditure than girls, which on average is 1,900 MET-min / week, versus 1,679-MET min / week (Fig. 2).



**Fig. 2. The level of physical activity by gender**

Source: Own research

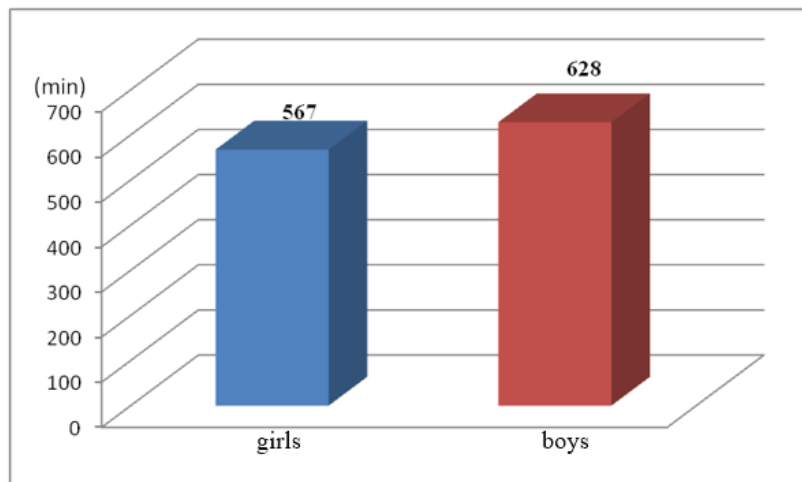
When paying attention to the area of students' activity and gender, there is no significant differentiation. Boys, just like girls, more often undertake moderate-intensity activity than vigorous activity (girls 71% - boys 77%), and intensive activity (girls 29% - boys 23%) (Fig. 3).



**Fig. 3. Percentage breakdown of students by physical activity and gender**

Source: Own research

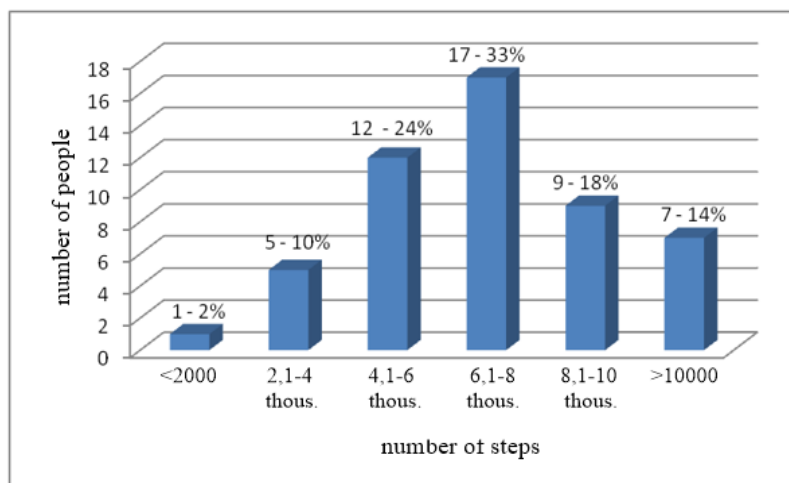
The average amount of sedentary time for boys is much greater than for girls, at 628 minutes (about 10 hours), and for girls it is 567 minutes (about 9 hours) (Fig. 4).



**Fig. 4. Average amount of time spent sitting, broken down by gender**  
Source: Own research

#### Analysis of physical activity measured with a pedometer

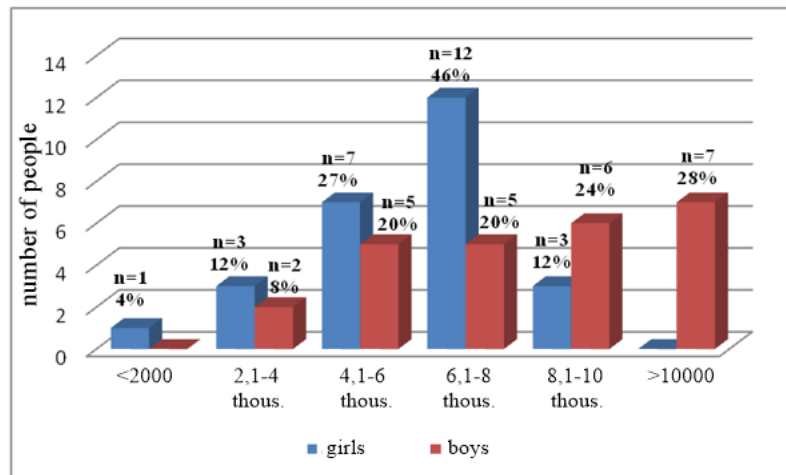
Recommendations for health promotion in terms of the number of steps performed indicate the number of 10,000 steps a day as a positive factor for health [12]. Fig. 5 informs that only 14% of the study group (7 people) achieved the recommended number of steps. The largest part of the group are people (17 people - 33%) with an average activity range of 6,100 to 8,000 steps a day. By contrast, only one person (2%) did not exceed an average of 2,000 steps per day.



**Fig. 5. Average number of steps per week**  
Source: Own research

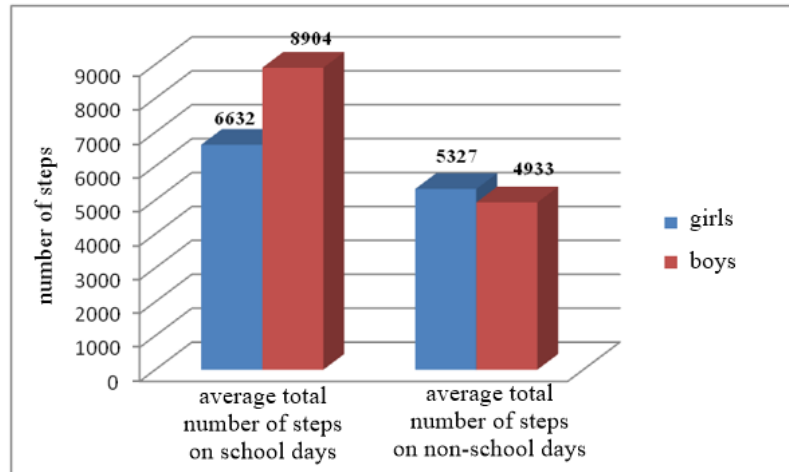
Analyzing the results in terms of recommendations and gender of the respondents, it was shown that the recommended result of 10,000 steps a day was achieved by 28% of the boys ( $n = 7$ ) and not a single girl. The most characteristic is the range from 6,100 to 8,000, where girls predominate (12 girls, 5 boys) (Fig. 6).





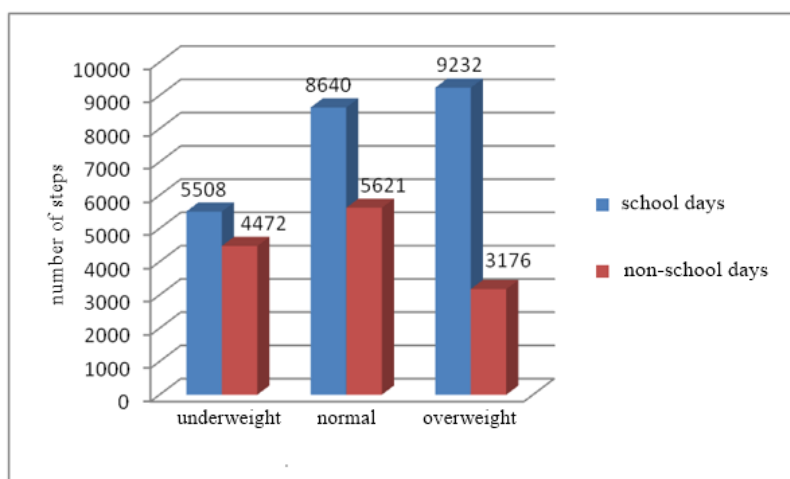
**Fig. 6. Average number of steps performed, broken down by gender**  
**n - number of people (girls n = 26, boys n = 25)**  
**Source: Own research**

By characterizing the number of steps by gender, non-school days and school days, it can be clearly stated that boys are more active during school days. On the other hand, girls take more steps during days off from school (Fig. 7.).



**Fig. 7. Average number of steps broken down by gender, school days and non-school days**  
**Source: Own research**

When analyzing the results in terms of BMI, non-school days and school days, it can be seen that overweight students take more steps on school days than people with normal or underweight. On the other hand, on weekends, people with normal weight can boast the greatest activity measured by steps. The results presented in the graph clearly show that students, regardless of BMI, are more active on non-school days than on school days (Fig. 8).



**Fig. 8. The average number of steps on non-school days and school days and the BMI index of the respondents**  
Source: Own research

## Summary and Conclusions

The aim of the research was to analyze and determine the level of physical activity in the sixth, seventh and eighth grades of the School and Kindergarten Complex No. 9 in Rzeszów. The following conclusions were made:

1. A small proportion of the surveyed students (14%) meet the recommended recommendations for physical activity measured in steps.
2. Taking into account the gender of the respondents and the days of the week, it was found that there is a difference between the physical activity of boys and girls.
3. There was no greater difference (6%) between the intense and moderate activity of boys and girls.
4. The recommended number of 10,000 steps a day was achieved by 14% of respondents, and they were only boys.
5. Paying attention to the BMI index, overweight people meet the condition of undertaking physical activity two days a week, and people with a normal weight at least once a week. In terms of gender, only boys meet this condition (once a week).
6. The hypothesis that girls were more moderately active was not confirmed in the research.

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## THE INFLUENCE OF ENVIRONMENTAL FACTORS ON EXOPOLYSACCHARIDE SYNTHESIS IN *RHIZOBIUM* *LEGUMINOSARUM* BV. *TRIFOLII*

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### **Abstract:**

Nitrogen-fixing bacteria, including *Rhizobium leguminosarum* bv. *trifolii* are Gram-negative microorganisms, which are able to adapt to changing soil conditions. In a symbiotic form with legumes, they are involved in the process of biological nitrogen fixation. One of the secondary signals involved in process of establishing symbiosis is the exopolysaccharide (EPS), which is responsible for a number of different functions. During symbiotic interactions, it is responsible for the adhesion of bacteria to the plant root, it is a structural component of the infection thread and suppresses the plant's defense response. The production of EPS is regulated not only by genetic factors derived from bacteria, but also by environmental factors like deficiency of phosphorus and nitrogen source, type of carbon source, plant root secretions, temperature, pH, salinity, light and *Quorum-Sensing*.

### **Keywords:**

*nitrogen-fixing bacteria, symbiosis, exopolysaccharide, synthesis, Rhizobium leguminosarum* bv. *trifolii*

### **Introduction**

The bacteria from the *Rhizobium* genera are responsible for the process of biological nitrogen fixation (BNF), a mechanism that provides about 200 billion tons of this element annually [1]. These microorganisms are mobile sticks, characterized by high metabolic plasticity, which allows them to adapt to environmental conditions in both: free-living or symbiotic forms with legume plants. Thanks to this phenomenon, the use of artificial fertilizers, which can cause an eutrophication of water reservoirs, may be limited [1]. The establishment of symbiosis is a complex process and requires the exchange of many molecular signals. These signals are of plant origin (flavonoids), as well as, those coming from bacteria (Nod factors and exopolysaccharide (EPS)), which are responsible for various functions [2, 44, 47] (Fig.1).

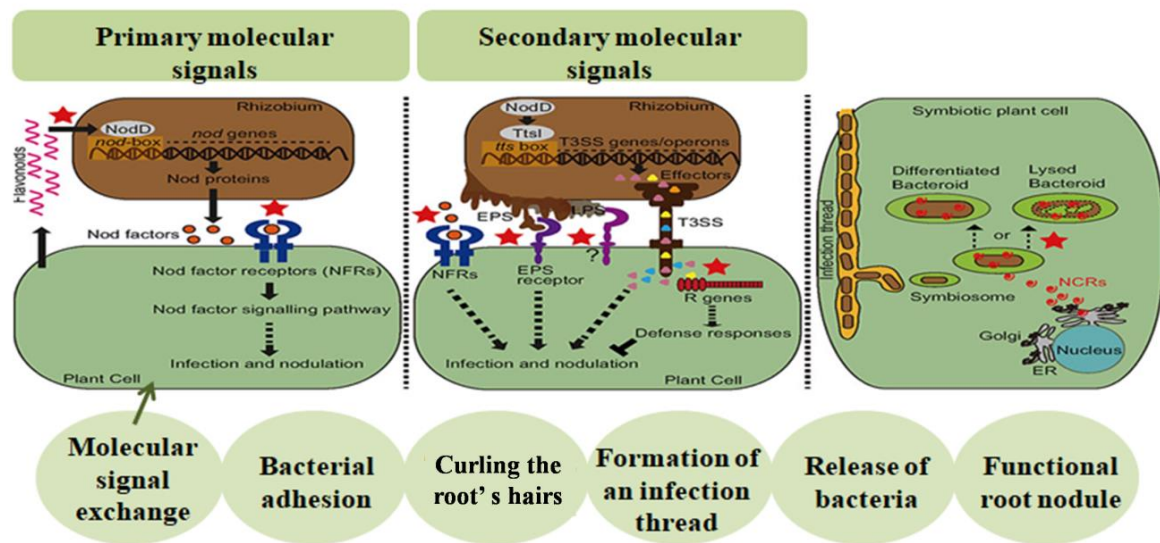


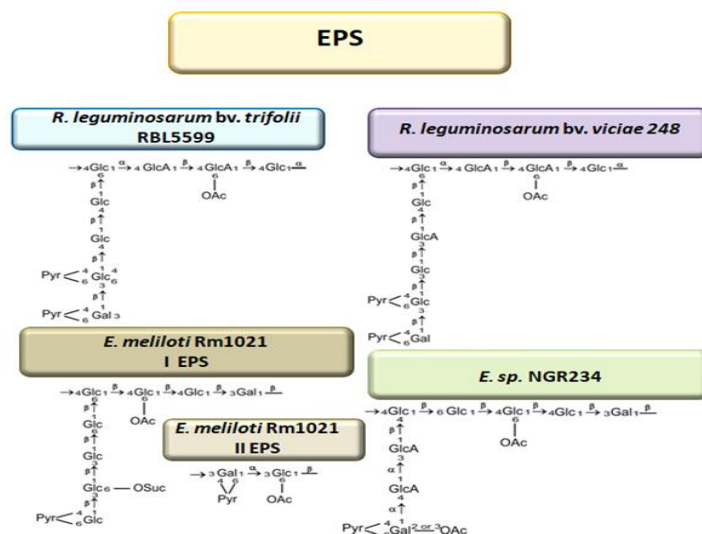
Fig. 1 The process of root hair infection and nodule development in Rhizobium- legume symbiosis  
Source: [2] with own modification

The genome of bacteria from the genus *Rhizobium* is characterized by a circular chromosome, which is a core, and plasmids, which carry information that allows bacterial cells to adapt to environmental conditions. Plasmids occupy 30% to 50% of the entire genome [3-5]. In the case of some rhizobia, there are also present chromides, called extrachromosomal replicons, having features of both chromosomes and plasmids [6, 14].

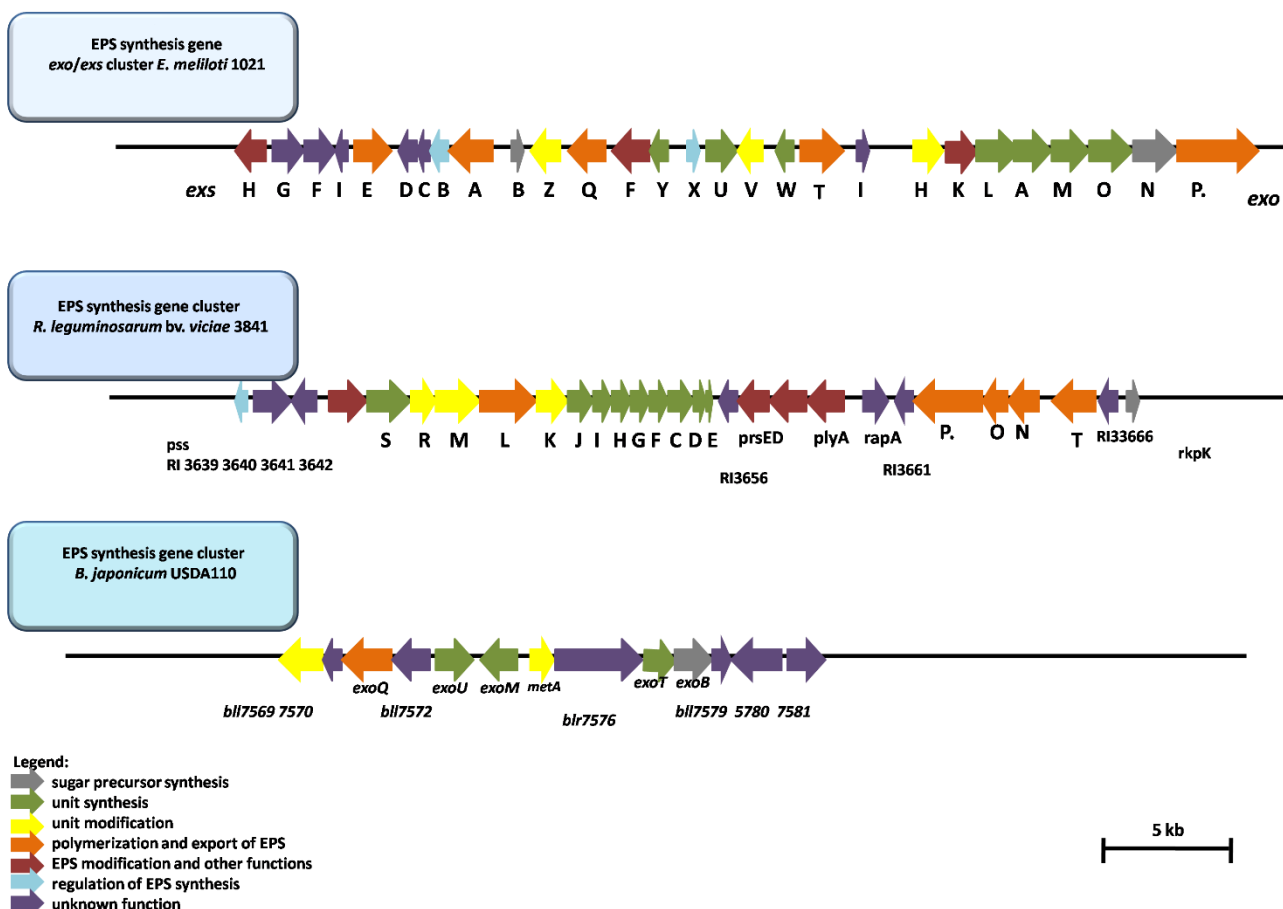
## Characteristics of Rhizobial Exopolysaccharides

Exopolysaccharide (EPS) is a sugar extracellular polymer that is the most external surface layer of the bacterial cell, and is secreted in a large amount into the environment. The chemical composition of this heteropolymer is unique not only in terms of a given bacterial species, but also in terms growth conditions in which this strain is exist [48]. The basis is octasaccharide repeating units composed of D-glucose, D-glucuronic acid and a D-galactose residues in a molar ratio 5: 2: 1. These subunits are decorated with non-sugar substituents: acetyl, pyruvate, succinate or methyl groups, and their arrangement depends on a type of the strain and the medium, in which they are grown [7- 9, 42, 43, 46] (Fig. 2).

The synthesis and regulation of EPS production was most studied in *Ensifer meliloti*. In this bacterium, genes responsible for the synthesis of succinoglycan are located on the pSymB, mega plasmid in a large cluster which contains 28 *exo* / *exs* genes. This region carries information about enzymes synthesizing nucleotide sugar precursors (*exoN*, *exoB*), unitassembly (e.g. *exoY*, *exoF*, *exoA*), and modification (*exoH*, *exoV*, *exoZ*), EPS polymerization and transport (*exoP*, *exoQ*, *exo* , *exoA*) (Fig. 3) [10-12, 37].



**Fig. 2. Chemical structures of subunits of EPS produced by various rhizobial species**  
(Abbreviations: Glc - glucose, Gal- galactose, GlcA - glucuronic acid, Man- mannose, Rha - rhamnose, Succ- succinate, Ac - acetyl, Pyr – pyruvate)  
Source: [10] with own modification



**Fig. 3. Genetic organizations of clusters involved in exopolysaccharide synthesis in various rhizobial species**  
Source: [10, 13-15] with own modification



Many enzymes and proteins are responsible for the process of EPS synthesis, its polymerization, and transport outside the bacterial cell. In the case of *R. leguminosarum*, *pss* genes encoding these proteins are located in a large chromosomal region called Pss-I [51]. The *pssA* gene, which is an individual transcription unit, is located at a long distance from this region [33, 40, 41, 49, 50]. The protein encoded by this gene (PssA) is responsible for the first step of EPS subunit synthesis. It transfers D-glucose from UDP-glucose to C<sub>55</sub>-isoprenylphosphate, which is a lipid carrier located in the inner membrane of bacterial cell [16]. In the next step of EPS synthesis, the PssDE protein, encoded by the *pssDE* genes located in the Pss-I region is engaged. It transfers D-glucuronic acid to D-glucose to form a  $\beta 1 \rightarrow 4$  bond (Tab.1). The next residue of this acid is attached by PssC protein of glucuronosyl- ( $\beta 1 \rightarrow 4$ )-transferase activity. The fourth sugar residue (D-glucose) is added by PssS enzyme, which is involved in the formation of the  $\alpha 1 \rightarrow 4$  bond. The PssF, PssG / PssI glucosyltransferases, as well as PssH / PssI are responsible for the subsequent steps of subunit synthesis. The PssJ enzyme is required for addition of the last sugar residue to the EPS subunit [16]. Among non-sugar modifications of EPS, we can distinguish the addition of the pyruvate group to D-glucose residue (the penultimate sugar residue) with the action of the PssM protein, and to D-galactose (the last sugar residue) by the PssK enzyme. When the second sugar residue is modified, PssR acetyltransferase is engaged (Tab.1) [15, 16, 35, 36].

**Tab. 1. Genes involved in EPS synthesis in *R. leguminosarum* and functions of encoded proteins with their length (aa) and molecular mass in kilodaltons [kDa]**

| Gene        | Name                    | aa length | Weigh [kDa] | Gene         | Name   | aa length | Weigh [kDa] |
|-------------|-------------------------|-----------|-------------|--------------|--|-----------|-------------|
| <i>pssA</i> | Glucosyltransferase     | 263       | 29.31       | <i>pssF</i>  | Glycosylotransferase                           | 294       | 32.05       |
| <i>pssB</i> | Monoinositolphosphatase | 283       | 13.28       | <i>pssD</i>  | Glycosylotransferase                           | 152       | 16.43       |
| <i>pssV</i> | EPS synthesis protein   | 262       | 29.14       | <i>pssE</i>  | Glucuronosylotransferase                       | 179       | 19.53       |
| <i>pssW</i> | Endo-1,4-xylanase       | 357       | 39.98       | <i>prsE</i>  | Hemolysin                                      | 435       | 47.51       |
| <i>pssS</i> | Glycosylotransferase    | 383       | 42.05       | <i>prsD</i>  | ABC transporter                                | 600       | 64.14       |
| <i>pssR</i> | Acetyltransferase       | 160       | 17.81       | <i>plyA</i>  | Exopolysaccharide hydrolase                    | 381       | 39.83       |
| <i>pssM</i> | EPS synthesis protein   | 360       | 41.05       | <i>rapA1</i> | Autoaggregation protein                        | 232       | 24.38       |
| <i>pssL</i> | EPS synthesis protein   | 508       | 55.47       | <i>pssP</i>  | Exopolysaccharide transport protein            | 710       | 78.32       |
| <i>pssK</i> | EPS synthesis protein   | 334       | 37.97       | <i>pssO</i>  | Sugar transporter                              | 240       | 23.16       |
| <i>pssJ</i> | Glycosylotransferase    | 273       | 30.96       | <i>pssN</i>  | Exopolysaccharide export protein               | 403       | 43.04       |
| <i>pssI</i> | Glycosylotransferase    | 314       | 35.56       | <i>pssT</i>  | Exopolysaccharide synthesis and export protein | 487       | 53.91       |

Source: [17]

Next, the polymerization of octasaccharide subunits and the transport of EPS outside the bacterial cell are conducted. Contrary to most types of transport, this process is performed by a system called Wzx / Wzy, which requires the activity of Wzx flipase and Wzy type polymerase [18, 40]. The Wzx flipase is responsible for the transport to the periplasmic side of the bacterial cell membrane, while Wzy is responsible for polymerization [18]. Protein of a Wzc-type, having copolymerase functions, is responsible for the regulation of the length of the growing exopolysaccharide chain. At a later stage, thanks to the oligomers of the Wza protein, a channel is formed in the outer membrane, through which EPS is transported outside the cell. In *R. leguminosarum*, the flipase protein is encoded by the *pssL* gene, the polymerase is encoded by the *pssT* gene, and the helper polymerase by the *pssP* gene. The channel produced in the outer membrane is created thanks to the

PssO and PssN proteins, which are homologous to the Wza proteins. In addition the PssP2 protein is involved in determination of the EPS chain length [19].

Inhibition of EPS synthesis is caused by mutations affecting the *pssA*, *pssD* and *pssS* genes. Moreover, a mutation in the promoter region of the *pssC* gene resulted in 2-fold reduction of EPS production [16].

## The biological role of rhizobial exopolysaccharides

The biological role of EPS largely depends on the life style of rhizobial cells. When released in large amounts, EPS helps bacteria to adapt to the environmental conditions [50]. In the case of free-living bacteria in the soil, it is engaged in accumulation of nutrients, a component of the biofilm matrix, as well as plays a role in mechanical protection against environmental stresses and plant antibacterial compounds. In the case of the symbiotic interaction with a legume plant, EPS is important in the adhesion of bacterial cells to the macrosymbiont's root, it is a structural component of the infection thread, suppresses the plant's defensive reaction and is a signal molecule, which is necessary to establish an effective symbiosis with plants. A mutation in the some *pss* genes of *Rhizobium leguminosarum* bv. *trifolii* causes inhibition of EPS production in this bacterium, and thus these mutants are unable to properly infect the plant, induce root nodules and fix atmospheric nitrogen (Fig. 4) [12].

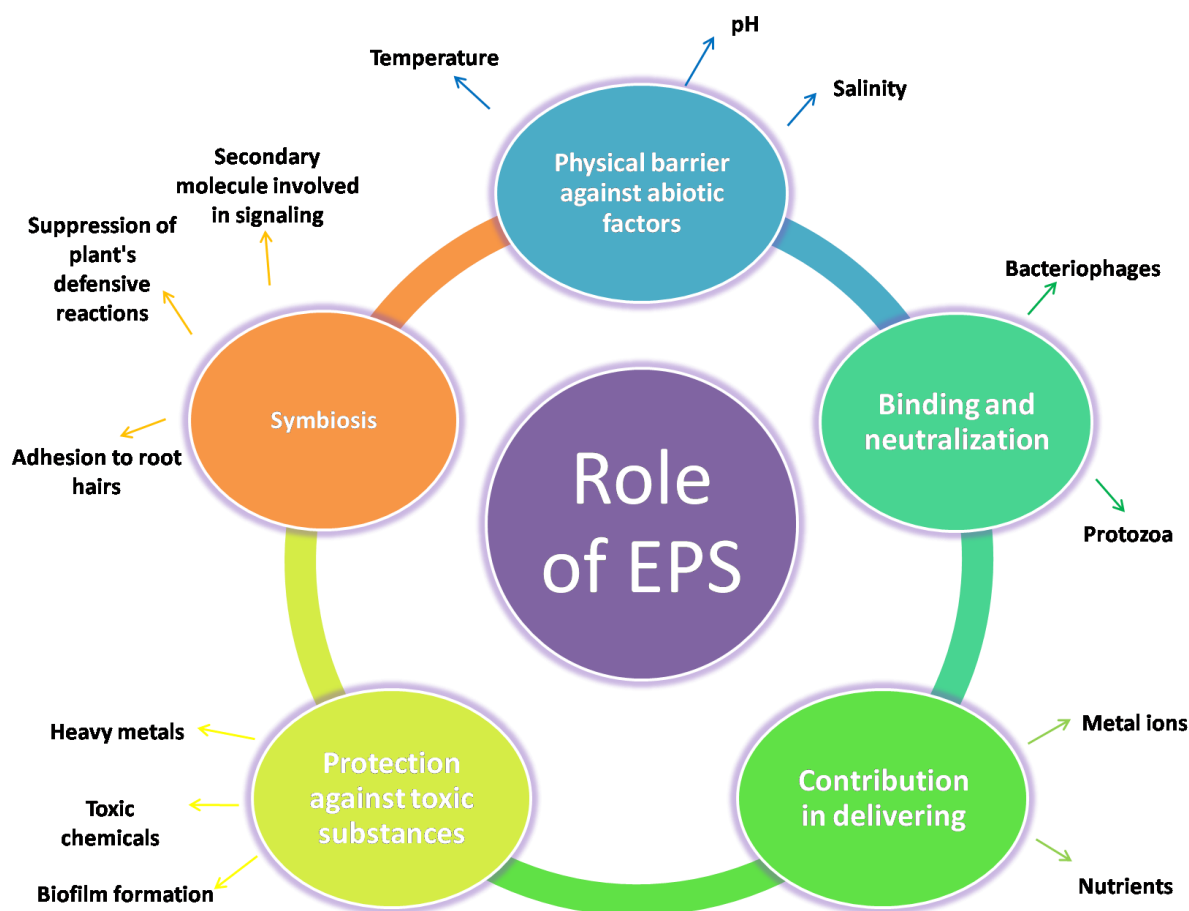


Fig. 4. The role of exopolysaccharide in functioning of rhizobia bacteria

Source: [16], own graphical figure

## The influence of various factors on exopolysaccharide production

In the case of the bacterium *R. leguminosarum*, the PsiA, PsrA, ExoR and RosR proteins are involved in regulation of EPS synthesis. Moreover, environmental factors (e.g. nitrogen and phosphorus deficiency, carbon source, macrosymbiont root exudate, temperature, soil pH, and salinity) influence the level of EPS production [10, 16]. The *psiA* and *psrA* genes were first discovered in *R. leguminosarum* bv. *phaseoli* on the symbiotic plasmid pSym. Their participation in the synthesis of EPS is negative, as additional copies of the *psiA* gene inhibit polymer synthesis. This phenomenon can be reversed by the introduction of copies of other regulatory genes, e.g. *psrA* or *pssA*, which may confirm that *R. leguminosarum* needs a balanced copy numbers of these genes. In the case of *exoR*, the strains carrying a mutation in this gene are characterized by an increased amount of EPS produced compared to the wild strain, which depends on the amount of nitrogen in the culture medium [37]. The protein RosR, which regulates the transcription of the *pssA*, *pssC*, *pssI* and other *pss* genes, has a positive effect on the production of EPS. It contains the zinc finger motif of Cys2His2, which is responsible for the recognition and binding of the regulator to the RosR-box nucleotide sequences located in the promoter regions of the regulated genes [20, 45]. In addition, proteins belonging to RosR/MucR family are engaged in regulation of the EPS in many related species of the *Rhizobiaceae* family, eg *Ensifer meliloti*, *Rhizobium etli*, *Agrobacterium tumefaciens* [21].

The *Quorum-Sensing* (QS) phenomenon is also important in the synthesis of EPS. It is a bacterial cell communication system that signals the bacterial population. Along with the increase in the microbial population density, QS regulates gene expression. This phenomenon is extremely important for bacteria in order to gain new ecological niches, and it also determines the conditions to which bacteria are to adapt [22, 23]. QS is necessary for the replication of bacterial genetic material, plasmid conjugational transfer, the synthesis of various compounds (e.g. enzymes, toxins, polysaccharides, antibiotics), as well as cell mobility [24]. This communication involves small particles called autoinductors. When an appropriate number of bacterial cells is reached, the so-called "quorum", there is a change in gene expression, which is mandatory for the bacterial population to function properly. In Gram-negative bacteria, the autoinductors are N-acyl-L-homoserine lactones (AHL) [22]. Apart from the autoinducers synthesized by the LuxI protein, this process involves LuxR proteins which regulate its own gene transcription, as well as target genes [25, 26]. QS, participating in the regulation of biofilm production, may help microorganisms survive and also in the adhesion and colonization of macrosymbiont's roots [27]. In *Rhizobium leguminosarum* bv. *viciae*, four QS systems (*cin*, *rhi*, *rai* and *tra*) were characterized [27]. Cin, in which CinR, CinI and CinS proteins are engaged, plays the most important role, because this system is able to activate other genes involved in the Quorum-Sensing process. CinI is responsible for the synthesis of autoinductors, CinR in response to this signal initiates the transcription of *cinI*. CinS, belonging to a group of small proteins, has an anti-repressant effect by activating the transcription of the *raiR* and *rhiR* genes. With the increasing copy number of the *cinS* gene, bacterial colonies lose their mucilage due to a small amount of EPS, which is a phenomenon, for example, during colony aging [28].

One of the basic signals controlling the development, growth and behavior of many different living organisms is light [29]. Higher plants, algae, fungi and bacteria have protein domains (LOV) (light-oxygen-voltage), which are blue light receptors, thanks to which they perceive the length and

intensity of light and use it as a signal for many cellular pathways [16]. Genome sequence studies have shown that not only photosynthetic bacteria possess photoreceptor proteins, but also heterotrophic bacteria, such as *Brucella*, and also *Rhizobium*. The *lov* gene located in *R. leguminosarum* bv. *viciae* 3841 on the mega plasmid pRL11, encodes a histidine kinase (LOV-HK) [30]. The protein encoded by this gene contains a domain at the N-terminus followed by an HK domain followed by a histidine residue which is the target of an autophosphorylation. Thanks to this photoreceptor, *R. leguminosarum* bacteria react to light through the EPS production process, biofilm production, flagella count, as well as competitiveness and nodulation [30]. Wild-type strains are characterized by a reduction in the efficiency of EPS production and biofilm formation, which proves that light negatively affects the synthesis of exopolysaccharide [16]. This is also confirmed by mutants that did not have the *lov* receptor, so there were no visible differences in the amount of EPS and biofilm produced under the influence of light and dark [16]. Light is also important in conquering ecological niches, as competition as well as nodules production are dependent on the *lov* receptor [30].

Some species of the genus *Rhizobium*, which produce large amounts of exopolysaccharide, are more resistant to acid pH and soil salinity. In the case of high salt concentration, cells surround themselves with EPS reducing the contact surface, making them more resistant to osmotic stress [13].

In tropical climates, where the soil temperature is as high as 40°C, there is little calcium and a high content of heavy metals, it is noted that plants cope less with these stresses, while bacteria are able to infect the host and fix nitrogen from the atmosphere. *Ensifer meliloti* strains, which are subjected to acidic pH and also have reduced access to calcium ions, significantly reduce the production of EPS [31].

This polymer additionally strongly binds metal cations because it has anionic properties. Strains of the genus *Bradyrhizobium*, subjected to the presence of iron, aluminum and thorium cations, formed a gelatinous precipitate by binding them with EPS. The increase in EPS production with high concentrations of cadmium and lead by *Ensifer meliloti* may suggest that this polymer can be used in bioremediation [31].

The research conducted so far and the constantly deepened knowledge of the biosynthesis and function of exopolysaccharides allow for searching for strains in the natural environment that contain a high content of this polymer. The ability of EPS to bind heavy metals, fight plant pathogens, and play an important role in symbiosis as a secondary signal molecule, could contribute to the development of new vaccines for use in agriculture [16].

## Conclusion

Nitrogen-fixing bacteria, including *Rhizobium leguminosarum* bv. *trifolii* are Gram-negative microorganisms are able to produce large amounts of EPS. This polymer is responsible for many different biological functions. This polysaccharide ensures the rhizobial cells to adapt to changing soil conditions. Moreover, EPS is one of the secondary signals involved in the establishment of symbiosis with legumes. During symbiotic interactions, EPS is required for adhesion of bacteria to host plant roots, it is also a component of infection threads matrix and a suppressor of the plant's

defense reaction. The production of EPS is regulated by several bacterial proteins. But also various environmental factors influence the level of EPS synthesis.

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## QUALITY OF LIFE AND PHYSICAL ACTIVITY OF PEOPLE OVER 60 YEARS OF AGE IN THE ERA OF COVID-19

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### **Abstract:**

Quality of life is sometimes defined as the state of health, both mentally and physically. Psychophysical well-being depends on many factors, including factors such as physical well-being, sleep quality, pain, and access to health care. It is also worth realizing the importance of non-obvious factors - social relations, support for relatives or the possibility of pursuing personal interests. In own research, an attempt was made to analyze the issue of the quality of life of people over 60 years of age with the help of the WHOQoL questionnaire of the World Health Organization at a specific time, which is the Covid-19 epidemic. The subject of interest in particular was to assess the differences between respondents over 60 years of age in the exercise and non-exercise groups in terms of subjectively assessed quality of life, health, and the extent to which pain interferes with daily functioning and psychophysical state.

### **Keywords:**

*quality of life, physical activity, the elderly, Covid-19, lockdown*

### **Introduction**

According to Eurostat forecasts, in 2050 the share of old people in the demographic population will exceed 30% in six EU countries such as Portugal, Greece, Spain, Germany, Slovakia and Bulgaria [1]. In Poland, in turn, it will approach 30%. Increase in the average life expectancy and decrease in the number of deaths in the oldest age groups means an increase in the number of people in these groups and a share of the oldest age groups in the age pyramid [2].

The World Health Declaration [3] and the recommendations of the World Health Organization [4] emphasize that the concept of health is integrally related to quality of life. It is supposed to mean functioning well into old age enabling greater productivity at work and better earnings and life satisfaction. It is therefore the quality of life that has become a key component of projects designed for the elderly due to the phenomenon of aging societies [5]. Among the areas of particular emphasis are activities aimed at improving the standards of medical care and the emergence of highly specialized medical procedures for the elderly, the development by culture and mass media of a new, positive image of old age emphasizing the vitality of the elderly and the development of various systems of quality of life assessment for seniors and related procedures of institutional support [6]. It has been observed that an increasing number of researchers focus on issues related to summary

measures of population health, and it is worth emphasizing that nowadays they go beyond negative indicators of mortality and life expectancy.

They include other dimensions of health status and health-related quality of life, such as: Disability Free Life Expectancy - DFLE, Healthy Life Years - HLY, Active Life Expectancy - ALE, or Quality-adjusted Life Expectancy - QALE [7]. Especially the last two measures seem to be interesting in the context of demographic changes described above. Brown et al. [8] in their analysis of research tools useful for assessing the need and effectiveness of measures of quality of life of older people indicate that health indicators provide opportunities for more targeted and accurate improvement of public health. A step further is the HRQoL measure - Health Related Quality of Life and Well-Being [9]. It is a multidimensional concept encompassing domains related to physical, mental, emotional, and social functioning. Quality of life is defined here as more than activities of daily living, health status, type of condition or functional ability. It assesses the ability of people to actively participate in the world around them and to participate in activities that are common to most people in society. Although the questionnaire most frequently used and recognized in terms of reliability and credibility in the world is the questionnaire World Health Organization Quality of Life – *WHOQoL* [10].

Since December 2019, the coronavirus disease (COVID-19) has spread around the world and in April 2020 more than 950 000 cases and more than 48 000 deaths were confirmed [11]. The World Health Organization declared the situation as public health emergency and on March 2020 classified Covid-19 as a pandemic [12]. Many countries have declared unlimited quarantines to reduce infection rates, avoid overloading health systems in the sense that they it is the best way to protect the health of an older section of the population. A sedentary lifestyle combined with the compulsion of lockdown seems to have a significant and detrimental effect not only on the functioning of the cardiovascular system, but also on mental health in the group of elderly.

In this paper, the author attempts to find connections between the ALE and QALE scales by analyzing not only the quality of life in terms of social participation and physical and mental health, but also the intensity and type of physical activity undertaken in the era of Covid-19 pandemic.

## **Aim of the study**

The purpose of this study was to assess the differences between respondents over 60 years of age in the exercise and non-exercise groups in terms of subjectively assessed quality of life, health, and the extent to which pain interferes with daily functioning and psychophysical state.

## **Material and methods**

In the following studies, the research material was constituted by a group of people over 60 years of age, Caucasian, living independently. 65 participants were analyzed, of which 83% (54 people) were women. The most numerous group (38.5%) were people aged 65-69. The first step was to divide the group into groups known as the exercising (E) and the non-exercising (NE).

Due to the epidemiological threat, the questionnaire method chosen for the quality of life research was sent by e-mail. The questionnaire contains 33 questions based on the 2004 World Health Organization Quality of life - *WHOQoL* survey, extended to include questions about physical activity (PA) during Covid-19. The survey was sent to the respondents in December 2020 - 10 months after the lockdown, which was introduced in the country due to the threat of the virus. This paper uses some of the responses from the survey above.

The respondents who pledged to take up physical activity – E group participants (Fig. 1) joined previously (before the time of pandemic) organized physical activities conducted by an Author of the study and continued this participation from September 2020 through an online platform. These participants have been trained thoroughly how to use this internet tool by an IT specialist.



**Fig. 1. Sample workout with the participants of group E**  
**Source: own materials**

These classes were carried out twice a week, including 60 minutes of exercise program with a time devoted to social relations. Empowering activities were conducted once a week; the second was focused on improving the performance parameters. Each time they proceeded with a different scenario to induce adaptation mechanisms to motor stimuli. The classes used accessories that are often found at home, such as pillows, scarves, poles or towels, which can be used to make the exercises more attractive. To reduce stress, Schultz autogenic training and breathing techniques were used.

The survey results were statistically analyzed using the program Statistica (data analysis software system), version 13. <http://statistica.io>. TIBCO Software Inc. (2017). To assess the differences between groups on the study variables, the u-Mann test was used, and  $p < 0.05$  significance level was assumed.

## **Results and discussion**

Among the group of respondents in the group E the most willingly chosen physical activity that improves cardiovascular and respiratory parameters from among several possible simultaneously in the survey was: walk - 44 people, gymnastics -25 people and a bicycle 22 people. Over 30% of the



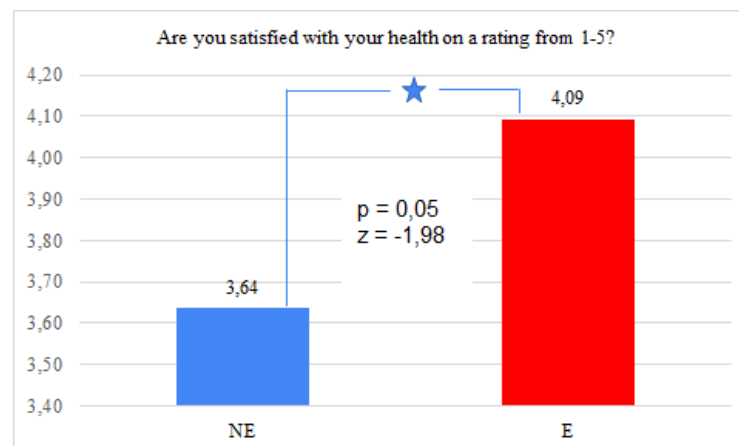
respondents also practiced Nordic walking. The most frequently chosen - over 43% of respondents - form of AF improving muscle strength was strengthening gymnastics with weight bearing.

According to new research on PA [13] the frequency of exercise should range 5-7 days per week with the amount of aerobic exercise from 150-300 to 200-400 min/wk. Authors recommend more strength training, balance and coordination routines. They emphasized the importance of controlling the intensity, which should be moderate to avoid detrimental effects.

Early research shows that before the pandemic, 1 in 4 adults worldwide did not meet the minimum recommendations, and the current lockdown makes that even more difficult [14].

The research group (E) in this study undertook similarly varied workouts, however, the duration of the exercises in light of the above research seems to be still insufficient. It is confirmed that maintaining physical activity levels is key to addressing sedentary behavior as well as to mitigating the psychological impact of quarantine [15]. It is provided the same general recommendations both by American College of Sports Medicine [16] and American Heart Association [17] and which is to remain active at home, take short active breaks, and avoid excessive sedentary periods. However, it needs further research to clarify whether any type of exercise (volume, intensity) increases susceptibility to infection [18].

In the study it was found apparent differences in reported life satisfaction between the E group and the NE group when calculating the grade point average (Fig. 2).

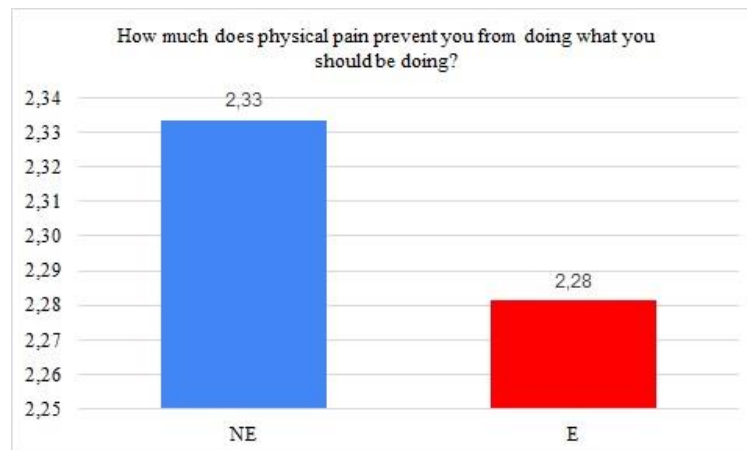


**Fig. 2. Mean differences between group E and NE in the level of satisfaction on subjective rated health in the scale 1-5**

Participants who exercise report subjectively higher levels of satisfaction with their lives as well as with their health ( $p=0.05$ ,  $z=-1.98$ ). Answer for this question was rated 1-5, where 5 was the highest possible score with the total life satisfaction.

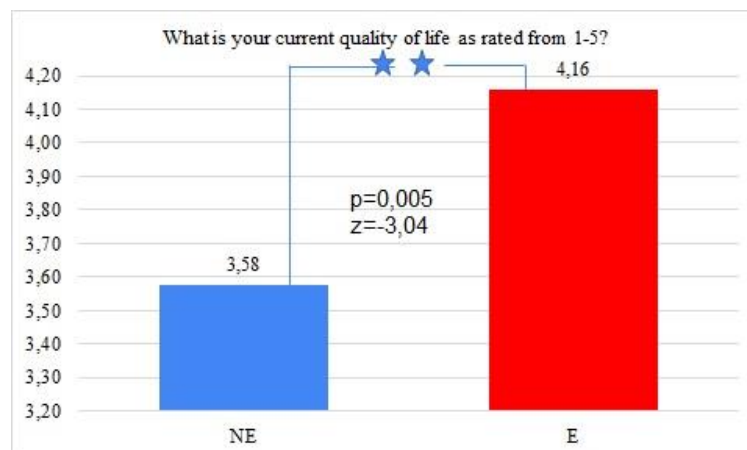
Admittedly not statistically significant, but the differences were also observed in the question about the degree to which physical pain interferes with participants' daily functioning, where participants in the group E declared lower levels of problems in this area of life (Fig. 3).





**Fig. 3. Mean differences between group E and NE in the level of subjective pain that disturbs in daily living rated in the scale 1-5**

Chronic pain is known as one of the most common reasons that link to restrictions in mobility and daily activities, anxiety, depression and poor perceived health or reduced quality of life [19]. Therefore, it seems important to ask about its existence and level among the elderly, who may experience pain in intensity due to poorer access to health care during a pandemic.



**Fig. 4. Mean differences between group E and NE in the level of declared quality of life rated in the scale 1-5**

The quality of life of the elderly population, mentioned in the introduction, is another element that represents an important issue for the analysis of health care institutions, and it was found as statistically significant:  $p=0.005$ ,  $z= -3.04$  (Fig. 4).

The psychological impact of quarantine has been recently reviewed. There have been reported negative psychological effects, including post-traumatic stress symptoms, confusion, and anger [20]. It is also suggested that prolonged quarantine and fear of infection, frustration or boredom may further become stressors [13].

For all these arguments, physical activity becomes especially important for the elderly during quarantine because maintaining physiological function and reserve of most organ systems can provide protection against the mental and physical consequences and severity of Covid-19.

## Summary

There are still doubts on the most suitable characteristics of the exercise to be taken, such as type, frequency, duration, volume, and intensity. Especially it concerns those who are aged over 65 years, and those with diabetes, serious heart conditions, chronic lung disease or obesity. This indicates the need for further analysis despite the difficult time that is the Covid 19 pandemic era.

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**PROMOVENDI**

**Oferujemy:**

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