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UNDERNUTRITION, CACHEXIA OR ANOREXIA OF AGEING – ETHIOPATHOGENESIS, CLINICAL IMPLICATIONS, NUTRITIONAL THERAPY AND PREVENTION, IN ELDERLY

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Abstract:

Decline of body weight may escalate along with advancing age. As the PolSenior project reports, poor nutritional status refer to 44.2 % of subjects. This review article aims at presenting aspects of undernutrition, cachexia and anorexia of agening among elderly. Weight loss in elderly can arise from mentioned or mixture of them. Anorexia of ageing has physiological underground – diminished/lack of apetite, of hunger, reduced caloric intake. Late diagnosis can lead to multisystem organ failure. Changes connected to melanocortin system may have potential link with anorexia and cachexia in old groups. They contribute to overlong hospitalization, greater treatment costs, increased morbidity and mortality. Optimization of nutritional status of seniors is one of the most significant target in geriatrics. Nominal notions are often regarded as synonymous. Reasons, effects, dietary proceeding and prevention of them will be showed.

Keywords:

undernutrition, cachexia, anorexia of ageing, elderly

Introduction

Nutrients intake of elderly people generally diverges from their needs at all. PNS (Poor Nutritional Status) is not rare [1]. This group is marked by multiple morbidities and many psychological changes which increase a risk of undernutrition or related. Nutritional status becomes crucial prognosis factor among them [2]. In case of hospitalization, treatment is overlong what generates additional costs and mortality rate in older people. Independence and quality of life of such people and their caregivers are also diminished [1].

According to Central Statistical Office in Poland, beginning of senility falls on greater age than 65 or equal to it. It has background in biological division on groups of people. The average length of age is elongated [3]. Participation of older groups in polish society is still growing, but not only there. Such tendency has worldwide character and present–day demographic predictions are not optimistic in this aspect [1]. In 2035 number of elderly people will be account approximately 25 %

for citizens and it will be 2.5 times more 90–year–old seniors. It is essential to implement mechanisms which improve health status and standard of living of these people [3].

Further epidemiological statistics are not optimistic. As Mizray M et all runs, malnutrition in hospitalized old patients oscillates at level of 30–65 %, while in nursing homes at level of 25–60 %. Frequency like 2–32 %, is percent of undernourished living at own homes. However, the most crushing data seems to be 70 % of malnourished in whom nutritional status is compounding during hospitalization [4].

Malnutrition seems to be multifactorial and it is hard to point leading–edge cause. Against geriatrics and fields related to it appears quite a challenge. The most important is prevention, but also diagnostics and treatment of it [3].

The aim of this paper was to discuss the problem of poor nutritional status, its kinds, ethiopathogenesis, clinical implications, nutritional therapy and prevention.

Terms

Undernutrition

Malnutrition is equivalent term for poor nutrition, whether is talked about overnutrition (excess consumption of nutrients) or undernutrition (inadequate consumption or absorption of one or more nutrients). Undernutrition is inadequate nutrition over long periods of time (including poor maternal nutrition and poor infant and young child feeding practices) and/or repeated infections. Periodic acute undernutrition is rapid deterioration in nutritional status over a short period of time [5]. Malnutrition may be described as: „a state resulting from lack of intake or uptake of nutrition that leads to altered body composition decreased fat free mass) and body cell mass leading to diminished physical and mental function and impaired clinical outcome from disease" [6].

Cachexia (chronic Disease–Related Malnutrition (DRM) with inflammation)

First of all, cachexia is not a last stage of malnutrition, it should not be used in that context. Cachexia should be consociated as: „a complex metabolic syndrome associated with underlying illness and characterized by loss of muscle with or without loss of fat mass. The prominent feature of cachexia is weight loss in adults" [6].

Anorexia of agening

This term can be explained as: „unintentional decline in food intake caused by factors such as altered hormonal and neuro–transmitter balance affecting hunger and satiety which may contribute to age–related weight loss" [6].

Ethiopathogenesis of poor nutritional status amid seniors

According to Polsenior Study, which was conducted in 2007–2011, PNS of polish seniors is highly interlinked with depression and its manifestations. Group of seniors who should be monitored for malnutrition is group which is characterized by neurodegenerative changes – dementia, polypragmasy, anemia and entire anodontia [1].

Risk factors of malnutrition can be divided into 3 main groups: social factors, physiological factors and psychological factors. This division shows Table1 [7]

Table 1. Factors contribute to PNS

Social factors
Incompetence of cooking, unawareness of food and nutrition
Desolation, living alone, social isolation
Small earnings, low social status
No possibility to buy/prep food
No possibility to make food
Physiological factors
Dysfunction of gastrointestinal tract, for example diminished absorption
Decreased appetite and low quality of diet
Oral difficulties, for example edentuilsm, swallowing disorders
The weakening of the senses – taste, smell
Respiratory system disorders
Hormonal disfunctions, for example type 2 diabetes mellitus
Neurological diseases, for example Parkinson's disease
Infections, for example Clostridium difficile infection
Inability to eat independently
Drug interactions with food and unacquaintance of tchem
Biliousness and vomitus
Increased energy requirements
Cancer and other with enhanced catabolism
Psychological factors
Cognitive disorders, for example dementia
Depression
Disorientation
Anxiousness

Source: own elaboration

Depression – cause or consequence?

It is difficult question and nowadays researches still did not answer on it. I. Brabcová et al. postulates, that depression occurs in 7–15 % of seniors who are 65 year old or older. Elderly in hospitals or in nursing homes, are significant percent – 20–30 % have depression. In lost of close person, relative, reason can be looked for. Senior's appetite diminishes and weight is loosing, like in malnutrition. This factor may be considered as key, is of great value. Practically, almost every third has depression. After all, there is no confidence, that this is a reason or a cause of malnutrition [8, 9]. Specific group is group of old people with cancer. They need not only nutritional treatment, but also support due to cognitive impairment and right depression [10].

Nutrition physiology of agening

Gastrointestinal tract during agening becomes modified, not only in anatomical aspects, but also its functions changes. Due to this situation bioavailability of nutrients varies.

Macronutrients. Excreting of pepsin and pancreatic enzymes is insufficient in seniors, proteolytic activity also. According to that, small intestine digestion of proteins does not proceeds properly. There is no clinical researches which would evidence functioning of brush–border peptidases and many transporters, such as peptide or aminoacide in old people. There is probably no changes in absorption of amino acids. It it assumption that peripheral amino acids have lowest bioavailability. Amylase and lipase are subsequent enzymes whom secretion is decreased. In other words, digestion of starch and lipids could be a little disturbed.

Vitamins and minerals. There is reduced secretion of pepsin and acid and decline of intrinsic factor, so availability of vitamin B_{12} is lessened. Absorption of calcium is bated in intestines. Women have more disrupted response to 1.25 $(OH)_2D_3$ than men what yields in loss of bone.

Water. Currently, there is no evidence for disfunctional availability of water due to possible changes in aquaporins, tight junction proteins and membrane transporters [7].

Conditions linked with old age and favourable for PNS:

1) adjustment of taste and smell;
2) inaccurate chewing (edentulism);
3) slower emptying of the stomach;
4) unprompted gastroesophageal reflux;
5) smaller quantities of gastric and pancreatic juices;
6) diminished level of testosteron in men (boosted leptin's concentration);
7) bad eating patterns (eating food poor in nutrients) [12].

Undernutrition

Elementary diagnostic criteria was created by an ESPEN (European Society for Parenteral and Enteral Nutrition) Consensus Statement and are alike to ASPEN (American Society for Parenteral and Enteral Nutrition) and to the Academy (Academy of Nutrition and Dietetics). Those criteria are used regardless of ethiopathogenesis and are used when malnutrition is suspecting.

There are some cases in which malnutrition may be taken into account (ESPEN):

1) Decreased BMI (Body Mass Index) <18.5 kg/m^2, in pursuance of WHO (World Health Organization), which determined when underweight is.
2) Decreased BMI and weight loss (age–related).
3) Decreased FFMI (Fat Free Mass Index) (gender–related).

Two of mentioned sets is needed for diagnosis.

ASPEN and the Academy suggested, that there are six criteria needed for diagnosis of malnutrition and two of them are needed:

1) insufficient energy intake;
2) decline of weight;
3) decline of muscle mass;
4) decline of fat mass (subcutaneous);
5) retention of fluid;
6) low grip strength in hand.

There is no worldwide criteria for diagnosis malnutrition and there is any organization which would collected one [6].

Cachexia

There is such type of patient who can be described as cachectic. He has:

1) decline of weight;
2) decreased BMI;
3) decline of muscle mass and its functionality.

Those outcomes proceed with an inflammatory condition which has a reflection of blood biomarkers. Cachexia reveals during organ failures, meaningfully when there is last phase of conditio, such as chronic kidney disease, cancer or congestive heart failure. In these cases catabolism is increased and inflammation which is reflected into CRP (C–reactive proteins) concentration at level of > 5–40 mg/L.

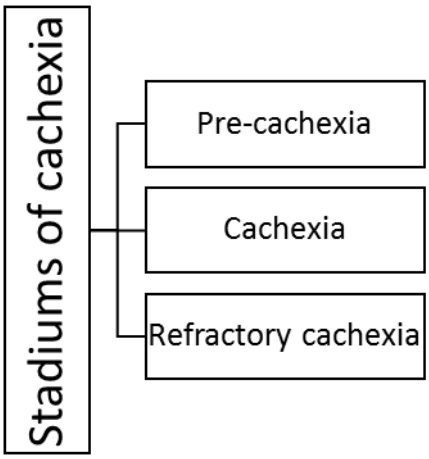

Figure 1. Types of stadiums of cachexia
Source: own elaboration realting to refferences [6]

There are some types of cachexia – Figure 1.

Cancer cachexia is a characteristic type of chronic DRM with inflammation. It is recognized, if decline of body mass is over 5 %, or if decline of body mass over 2 % and BMI is under 20 kg/m^2 or FFM (Fat Free Mass) is diminished. Morover, there is some index for skeletal muscle – appendicular skeletal muscle index and for men is <7.2 kg/m^2 and for women is < 5.5 kg/m^2 means this type of cachexia.

Cardiac cachexia occurs in chronic heart failure. People with this cachexia loose weight >7.5 what is unintentional and without oedemas. There are four kinds of factors which have influence:

1) disfunction of neuro–endocrine system;
2) disfunction of immune system;
3) course of ilness and its intensification.

Pre–cachexia is related to chronic diseases and an iflammatory disorder which appears during them.

Diagnosis for cachexia is similar to diagnosis of undernutrition with occuring disorder which is at the heart of this nutritional status and blood markers or inflammation [6].

Anorexia of agening

In brain, therein hypothalamus, there are some changes over time – reduced activity due to signals from fat cells, nutrients and hormones.

Anorexia is an element of the cachexia syndrome and plays a role in sarcopenia. In addition, loss of weight and concomitatnt sarcopenia, can induced physical frailty syndrome. Morover, there is such a paradox, called „obesity paradox", when obesity plays positive role, protecting senior who

is ill. When growth of inflammatory cytokines or growth of tumours which produces lactate, is set down, is greater risk of anorexia with serious course and decline of weight and higher risk of developing anorexia of ageing.

Many causes may drive anorexia of agening. Some of them have minor function, some have major. This section will present major.

Changes are connected to stomach's fundus – nitric oxide is in insufficient quantity and antral stretch is diminished. Cause of it, postprandial anorexia develops and emptying of stomach is impaired and slower (in case of big portions of food).

CCK (Cholecystokinin) in older people is satiety agent which work more successfully, grelin also. Smaller concentration of CCK contribute to poor caloric intake. These are hunger homones. Concentartion of GLP–1 (glucagon–like peptide 1) is rised by fat meal and acetylated–to–destylated grehlin ratio is higher. Hunger is smaller and unintentional decline of body mass occurs.

Food intake would be scaled–down in impaired energy homeostasis way. In, for example, hypothalamus (areas in central brain) insulin sensitivity is boosted by GLP–1 and grelin.

Other hormone, leptin, has an influence on boosting fat mass and on anorexia of agening, but higher concentration of triglicerydes lead to stop leptin towards penetrating the blood–brain barrier. On the other hand, there is a rise in leptin's concentration during hypogonadism.

Patients with anorexia of agening may get anorexia with hard course, when there is high concentration of cytokines, underlying anorexia–cachexia syndrome. Pro–opiomelanocortins are stimulated by cytokines and neuropeptide Y neurons are stunted, so signals of satiety or hunger are weaker. Anorexia and/or cachexia occurs.

In addition, elderly with chronic disease, often polypramgasy, are at risk of depression, during which would be an growth of anorectic neurotransmitters, serotonin and corticotropin–releasing factor [11, 12].

Health implications of organ systems

Neurological causes

Decline cognitive functions and neurodegenerative diseases, such as Parkinson's disease and Alzheimer's disease could aid undernutrition. Earlied mentioned depression may be a cause or a result of malnutrition, diminishing food intake [7].

Muscoskeletal causes

According to undernutrition, nutrients defficiencies occurs, such as defficiency of protein, antioxidant vitamins, minerals and fatty acids. The downturnn food intake due to anorexia causes taper of exercise capacity and loss of muscle mass and those strength. All of them contribute to the frailty syndrome [7].

Cardiovascular causes

PNS boosted sickness rate and number of deaths connected to cardiovascular diseases in relevant way. Deficiences of vitamins A, C, E, vitamins from B group, D, selenium, zinc and copper procure to heart failure. Cardiac injury and then diminished heart capacity, may contribute to intestinal edema – „unintentional severe weight loss caused by heart disease". People with heart

failure have malabsorption in intestines due to gut edema, raised loss of urinary, thanks to drugs and boosted oxidative stress [7].

Immunological causes

Generally, elderly people with malnutrition have decreased immune response to patogens and to vaccines. Proper nutritional status provides pertinent T cell responses. Deficiency of vitamins: A, D, E, B_6, folate, B_{12}, C lead to insufficient reaction to infections and threatening virulence of pathogens [7].

Skin causes

Properly nutrition is relevant in wounds healing. When there are deficiency of nutrients or undernutrition exists, inflammatory stage is elongated, proliferation of fibroblast is diminished and synthesis of collagen is impaired. There are more cases of pressure sores, infections and lower wound tensile strength [7].

Dietary intervention against undernutrition and prophylaxis of PNS in elderly

Methodical assessment of nutritional status in elderly and its control are essential solution for prevention of imminent clinical outcomes. Every senior poses an individual and is different, so there is no possible to create one recommendation for all. Economical status, taste preferences, eating habits vary this group of people. It is also important to realize rules of proper nutrition [4].

Raised numbers of meals during a day do not brighten level of energy intake in older people. Better solution is enriching a diet, as possible way to enhance energy and protein intake. On the other hand, seniors at risk of PNS, eating meals enriched in small portions of energy and protein, can be treated cheaply [13].

To prevent malnutrition, elderly people should also: eat daily products of all groups, increase intake of unsaturated fatty acids, starch and fiber, diminish intake of fat, cholesterol, sugar and salt, reduce consumption of alcohol.

There some prescriptions suggested that elderly at risk of malnutrition should get a diet of an increased energy value – 25–30 kcal/kg/day for women and for men – 30–35 kcal/kg/day.

Nutritional treatment should set about giving high in calories munchies, between meals and vitamins, minerals or products, which boosted appetite.

Meals should be served in pleasant, peaceful, full of safety and comates atmosphere. Food is not only energy fuel, but also occasion to spending time. Seniors, especially with dementia, need this.

In some cases, medical drinks may be used, they are concentrated source of nutrients and energy.

If oral nutrition will be not possible or sumbersome, gastrostomy or jejunostomy may be used (gastrostomy – short–term nutrition, jejunostomy – long–term nutrition). Parenteral nutrition can be used in cases of inability of usage of mentioned [4].

Summary

PNS among elderly is nowadays unnoticed problem which gain strength. There are several types of it. This article is related to undernutrition, cachexia and anorexia of agening. There are many factors which contribute to these conditions. Main kinds are social, physiological and psychological. Every third old person have depression which may be a reason or cause of malnutrition. There are many clinical outcomes due to PNS – it affect neurological, muscoskeletal, cardiovascular, immune and skin systems. The most important is early diagnosis and regular nutritional assessment. Proper nutritional treatment may in effective way diminishes negative causes of PNS.

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SIGNIFICANCE OF FOOD CONSISTENCY IN SWALLOWING DISORDERS – THE NEWEST GUIDELINES

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Abstract:

Dysphagia is a condition in which food passage to stomach, through mouth, throat and oesophagus, is straitened. Dysphagia hurts approximately 8 % people in the World. This review article aims at presenting the newest guidelines of The International Dysphagia Diet Standardisation Initiative. Consistency modification became one of the most popular forms of interventions in dysphagia, as solution providing safety and effectiveness of swallowing. For defining character of fluid and it's measurement, „syringe" test should be applied. „Spoon" test enables determining if material can maintain it's shape. „Fork" test is used to investigation of concentrated fluids' flow and pureed consistency. 8 consistency levels can be pointed. Swallowing difficulties become more common and gain position of public health problems. Using appropriate consistencies in these conditions, we may influence on better nutritional status of patients, those quality of life, diminish painfulness and risk of gasp.

Keywords:

swallowing disorders, food consistency, terminology

Introduction

Dysphagia is connected to approximately 590 millions of people in the World what represents thereabouts 8 % of habitancy of the World. This disorder burgeons, more and more people have swallowing difficulties due to different reasons. Simultaneously, there were no worldwide guidelines by now, including aspects of texture modification of foods and thickened drinks which may prevent, people which such disorders, from chocking and aspiration. Risk of mentioned is real and can cause fatal outcomes [1].

There were many misunderstandings connected to nonhomogeneous terminology of consistencies used in dysphagia's proceeding. Patient's safety is the most important and necessity of create worldwide guidelines have been existed long since. In 2015, IDDSI (International Dysphagia Diet Standardisation Initiative) came out with framework which refers to people of all ages, cultures and health requirements [2].

The purpose of this review paper was to delineate brieflya problem of dysphagia, IDDSI and its guidelines.

Dysphagia

Definitions

Word „dysphagia" comes from Greek and mean „eat with difficulty". It is a condition in which food passage to stomach, through mouth, throat and oesophagus, is straitened. It can be a result of anomaly of every stage of swallowing.

Dysphagia should not be mix up with odynophagia, knob pharyngeal or aphagia. Odynophagia is soreness sensation during swallowing. Knob pharyngeal is a sense of existence of the obstacle at a height of throat, non–interfering swallowing. Aphagia is in turn complete inability of swallowing – food of solid and liquid consystency, on the way of mechanical, functional disorders or neurogenic–based [3].

Clinical outcomes is related to difficulties with beginning of swallowing process, frequent aspirations of gastric contents or returning meals throught nose. All of them may lead to malnutrition and different disorders of respiratory system. There is some kind of relationsship between speech disorders and swallowing disorders – several months before dysphagia took place speech disorders. It could brighten prognosis of patient, if they will be pick up in time [4].

Types of dysphagia

Mechanical dysphagia is linked with inappropriate proportions of size of food bolus and width of the lumen of the oesophagus. Functional dysphagia in turn, with peristalsis disorders [3].

Swallownig disorders cant turn out during every of three stages of swallownig: in mouth, throat or oesophagus [4].

IDDSI

What is IDDSI?

As organization described: „A global initiative to improve the lives of over 590 million people worldwide living with dysphagia". This is a group of volunteers from different fields – dietetics, medicine, speech pathology, occupational therapy, nursing or engineering, from all the world [5].

What are IDDSI goals?

The goal is development of terminology and definitions which is worldwide and standarised, and pertain to texture–modified foods and thickened liquids [5].

Guidelines described by IDDSI – what do they consist of?

The guidelines consist of framework with detailed definitions and testing methods – for drinks and foods [6].

IDDSI Framework

There are 8 levels (0–7) of dysphagia diet framework – 0–4 for drinks and 3–7 for meals. These are showed on Figure 1.

8 consistency levels can be pointed: regular, soft, minced&moist, purred/extremely thick, liquidised/moderately thick, mildly thick, slightly thick, thin [7].

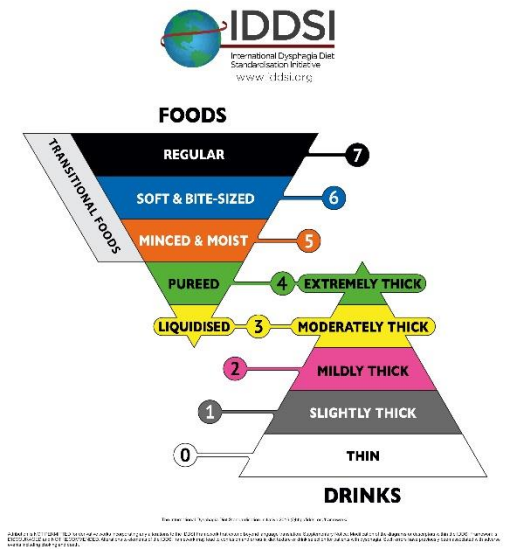

Figure 1. IDDSI framework
Source: The International Dysphagia Diet Standardisation Initiative 2016 @http://iddsi.org/framework/.

Testing methods

Drink Testing Methods

For drinks and other liquids – the Flow Test. It is condusted with syringe and consists of several steps:

1) Removing plunger from syringe.
2) Covering nozzle with finger and fill 10 ml.
3) Releasing nozle and starting timer.
4) Stopping at 10 seconds.

For defining character of fluid and it's measurement, „syringe" test should be applied.10 ml syringe is used, after filling it's by fluid, content will be gradually dropped for 10 s, then syringe wiil be blockaded and remaining amount of liquid will be gauged. Test is sensitive, despite own's simplicity – it shows changes in consistency, depending on serving temperaturę [7].

Food Testing Methods

„Spoon" test enables determining if material can maintain it's shape or cannot. „Fork" test is used to investigation of concentrated fluids' flow and pureed consistency There is also „fork pressure test" and „spoon pressure test". Thumb with which we press shuld be white [7].

Summary

Problem of dysphagia touches more and more patients and is key to use normalized guidelines which can refer to people around the world. This topis is relevant not only for dietetics and doctors, but primarily for patients and them caregivers, for quality of life of all of them.

IDDSI for years has been created framework which now may practical use in treatment and assessment of those patients.

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INFLUENCE OF CUSTOMIZATION ON THE OPTIMIZATION OF PRODUCTION PROCESSES

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Abstract:

The purpose of this article is to indicate the essence of customization and personalization of products often associated with the Fast Moving Consumer Goods industry. These concepts are one of the modern forms of customer and producer agreement. Mass customization means personalizing the company's offer on a large scale through rapid technological development blending with production, as well as detailed tracking and thus understanding the needs and preferences of consumers. In this publication, in order to achieve the established goal of the article, an analysis of the case study from the Ikea enterprise was made. An internet–based survey was carried out for this purpose. Analyzing the presented research results in the empirical part, it can be concluded that customization and personalization are important elements of shaping products in the process of designing production processes. In addition, three hypotheses have been put forward for the purpose of the work, aimed at investigating whether BESTÅ and PAX systems appearing in Ikea are based on the same ideology and introduction of optimization in production processes.

Keywords:

mass customization, personalization, production, consumer, IKEA

Introduction

Nowadays, we experience various forms of marketing communication, between the producer/ seller and consumers/ clients, one of them is mass customization. Through the use of mixed marketing elements, consumption is constantly modernized – tailored to individual needs of even the most demanding customers. Through the rapid development of the global market, enterprises must monitor the expectations of customers, which are constantly changing. This phenomenon occurs because consumers want to participate in their individualized output – they expect "tailor–made" products. The biggest barrier for enterprises to stay on the market is currently the high competition.

The forerunner of the phenomenon of mass customization was Stanley Davis with his book "Future Perfect". "He described the phenomenon of "tailoring" shirts in mass production without significant cost increase [1]. In addition, Davis first used the term "Mass Customization" in 1987.

"The first scientific research was conducted by B. Joseph Pine II from the Massachusetts Institute of Technology in the USA and published in 1993 in the book "Mass Customization: The

New Frontier in Business Competition". He is considered the father of massive customization." [2]. Pine is considered to be the founder of its theoretical basis. By comparing the mass customization with mass production, the creator saw some discrepancies regarding the client's and the entrepreneur's point of view.

"The term Mass Customization is an artificial creation and consists of two opposing terms– «Mass Production» (mass production) and «Customization» (production for an individual customer). The word "mass" refers to large–scale production, and in turn "customization" refers to individualized and specific production for a specific client. [...] Under the concept of Mass Customization, we will therefore determine the production of goods and services for the needs of (relatively) large market, taking into account the individual needs of the customer and based on prices approximate to the mass product's."[3]. Therefore, customisation is understood as the production of individualized products using appropriate marketing tools, which will improve the financial situation of the company. Customers expect products tailored to their needs at attractive prices comparable to standard products of high quality.

Table. 1. The Four Faces of Mass Customisation

Variants	Description
Collaborative Customisation	Consumer and producer engage in a dialogue to determine customer requirements Computers, clothing and footwear, furniture, some services, companies like Asian Paints.
Adaptive Customisation	Product is designed so that users can alter it themselves to fit unique requirements on different occasions High–end office chairs, certain electronic devices
Cosmetic Customization	Product is unique in appearance only Customer's chosen text or image on T–shirts, mouse mats, baseball caps, mugs etc. Also called 'Personalization'
Transparent Customization	Producer provides customized product without consumer being necessarily being aware that it has been customized Can be used when consumer's needs are predictable or can be easily deduced, and when customers do not want their requirements repeated. Example– repeat orders for customized clothing, chemicals.

Source: https://slideplayer.com/slide/10730543/, 2.08.2018r

Companies around the world have begun using mass customization to meet the diverse needs of customers. During production planning processes, managers are faced with the task of choosing the right type of customization to meet customer expectations as precisely as possible. Easily accessible information technology and flexible production processes allow them to customize goods and services to individual customers in mass quantities at low costs (Table1).

Mass customization in the FMCG industry

The phenomenon of massive customization is most often associated with the most marketable products, which constitute the major part of products on the world market. Companies that offer products that are regularly bought and at the same time meet the everyday needs of consumers are

referred to as the FMCG industry – Fast Moving Consumer Goods. In this industry competition is high and demanding, the consequence of which are difficulties with running business activities.

Consumers doing daily shopping are constantly encouraged by various brands to buy their products. Market entry barriers are high, however, companies that have been successfully implemented must constantly look for solutions that will allow them to stay in a high position.

In order for personalization to be effective, it is necessary to carefully collect information about both customers and their behaviours by carrying out, among other things, numerous research through the media or research on the opinion of a particular narrow group of recipients. "In business operations, predictive models and analyses are used to process current and historical data in order to predict consumer behaviour and identify potential threats and opportunities for the company" [4]. Through predictive segmentation, it is possible to choose the right marketing activities that can put the company a step before the Client – allowing for prediction of his actions.

The Ferrero Group is a classic example of implementing massive customization, which began in 2015 with the Nutella personalization venture. The "Your Nutella" promotional action consisted of designing two labels by the customer with any name or phrase. The client was able to order and design personalized labels on the website [5]. Another example of a popular brand that has implemented massive customization is Nike. Buyers can personalize sports shoes by choosing the material and colour. Thanks to this, the consumer receives a unique product that is fully compliant with individual preferences. Customers can create their footwear using the NIKEiD app [6].

Another example are the customized chocolate gifts offered by Chocolissimo. The company offers its clients several variants: chocolates in packages with a photo or engraving on a wooden casket, as well as individually composed, edible chocolate prints. Chocolissimo products are personalized in a variety of ways, depending on the amount of demand and customer preference. These types of products are a great idea for a special occasion for a relative or a friend [7].

The above–mentioned examples demonstrate the use of e–customisation tools, that is in the Internet environment. The first publication on the use of these tools could be seen in 2003, where it was shown that the essence of using these tools is appropriate communication between the customer and the producer, which helps the decision–making process and creates a lasting bond between the participants. The authors in the article also refer to statistical matters related to the use of online customization tools [8].

E–Customization tools provide a certain level of communication between the producer and the consumer, using online tools. The customer can indicate all his individual preferences for a given product, without the need for a direct conversation [9]. The companies that have been described above are similar in the degree of intensity of activities targeted at individualizing the offers they propose. From the perspective of enterprises, massive customization dwells in personalizing the products offered on a large scale. Selected examples of companies that have implemented mass customization are just a "drop in the sea" of offers currently present on the market.

Mass customization on the example of Ikea – case study

Ikea was founded in 1943 in the south of Sweden, its founder was Ingvar Kamprad. "He named his company IKEA from the first letters of his first and last name, and the names of his family farm

Elmtaryd and the village of Agunnaryd. The company initially dealt in feathers, frames, wallets, tablecloths, watches, jewellery, stockings and small furniture. In order to transport his goods, Kamprad borrowed a truck from a local milkman. As far back as 1947 he came up with the idea to focus exclusively on the production of furniture, and in 1958 he opened his first furniture store. There, Kamprad he exhibited the interiors of individual rooms that resembled those of today's IKEA stores [10].

Cooperation with Poland began in the 1960s, Ikea [11] signed a contract with a factory in Radomsko. "The vision of IKEA is to create better conditions for everyday life for many people. Our business idea is to offer a wide range of functional and well–designed home furnishings, at prices so low that as many people as possible can afford them" [12].

Poland is the second largest furniture sub–contractor for the Swedish brand in terms of size. About 20 % of all Ikea furniture sold in the world is produced there [13].

By optimizing the value chain, continuous relationship with suppliers, as well as investment in the modernization of production processes, they are offering the customer high quality products at affordable prices.

Ikea and most of today's companies face the challenge of meeting the increased customer requirements for personalizing the product, taking into account relatively low costs. Therefore, the essence of customization is to offer the customer a product that offers more than the standard one.

Ikea systems include a variant that provides information about the client's depth of influence in the value chain as well as the supply chain. The variants consist of customized, "tailor–made", standardized and purely standardized.

During the production process, Ikea is guided by the idea of standardized customization – it is based on the fact that the customer takes an active part in personalizing the product during the assembly or distribution phase. From the list of standard options like the catalogue, the customer selects a specific product and configures it according to his own needs. An example is choosing the colour of the front from the available range of colours available in the catalogue [14].

When buying furniture, the customer can choose individual elements. In BESTÅ and PAX systems, there is a large availability of various types of parts such as fronts, frames, shelves and accessories. Frames and fronts are available in a wide range of colours as well as different sizes, so the customer can choose and adapt them to his needs.

For the purpose of the process, three hypotheses were introduced in order to verify in detail not only the functioning of the systems used in Ikea, but also to examine their similarity. Ikea is an example of compliance with customization, and the verification of the hypotheses allows to indicate the behaviour of producers, what are they directed by when planning mass production processes while optimizing the production costs of the products that the customer can personalize.

The frame production of both BESTÅ and PAX systems is limited to only three colours in both systems, moreover, it is a common feature of these systems. They are distinguished only by one additional colour, which occurs only in the PAX system. Personalization of the casing colour is very limited – the manufacturer imposes a range of only 4 colours. We can observe that personalization occurs, because the customer can choose the colour that suits him, while the producer, thanks to a limited range of colours, is able to apply mass production of custom products.

The colour database for BESTÅ and PAX systems has a very wide range of choices – 49 items. White, black–brown and white–stained oak appear in both systems. In addition, they occur most often in individual models

Table 2. Characteristics and presentation of assumed hypotheses.

<table>
<tr><td>BESTÅ and PAX systems use similar colors for both the frames and the fronts.</td><td><table>
<tr><th>Colour names</th><th>BESTÅ</th><th>PAX</th></tr>
<tr><td>WHITE BEISHED OAK</td><td>X</td><td>X</td></tr>
<tr><td>WHITE</td><td>X</td><td>X</td></tr>
<tr><td>BLACK–BROWN</td><td>X</td><td>X</td></tr>
<tr><td>EF OAK BEISHED WHITE</td><td></td><td>X</td></tr>
</table></td></tr>
<tr><td>Among the characterized BESTÅ and PAX systems, the convergence of dimensions of individual elements is considered.</td><td>PAX and BESTÅ systems are completely different in size, there are no similarities between frames and fronts. However, the dimensions in each system are limited to a certain amount, as shown in the description of each system. The customer has a limited choice of catalogue options.
Mass production of elements of furniture components – fronts and casings of each System, allows to optimize the cost of the production process – mass production reduces costs.</td></tr>
<tr><td>The same materials are used for the production of each BESTÅ and PAX system components.</td><td>Consideration of BESTÅ and PAX systems in terms of materials used.
The materials used to make the fronts and frames of the cabinets were also analysed. Fronts and enclosures are made of the same materials: chipboard, fibreboard, foil and ABS plastic. The only additional material is glass used on the Besta system for the production of glass doors. The use of the same materials for the production of personalized goods allows you to optimize costs.</td></tr>
</table>

Source: Own study on permanent research.

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PAX and BESTÅ systems are completely different in size, there are no similarities between frames and fronts. However, the dimensions in each system are limited to a certain amount, as shown in the description of each system. The customer has a limited choice of catalogue options.

Mass production of elements of furniture components – fronts and casings of each system, allows to optimize the cost of the production process – mass production reduces costs.

The aim of research and analysis of results was meant to check whether BESTÅ and PAX systems are based on the same ideology. The article presents three hypotheses:

Hypothesis no. 1 regarding the colour of PAX and BESTÅ systems has been proved. The enclosures are produced in the same colours, only one exception in PAX (additional one colour).

The hypothesis no. 2 concerning the size of both the fronts and the housing was not confirmed – the dimensions are very divergent.

Hypothesis no. 3 regarding materials proved to be true, because the main materials used in both systems are: chipboard, ABS plastic, foil, fibreboard, plastic.

Currently, customers accustomed to the large selection and privileged position in which they find themselves expect more than just the best quality product at the lowest price. More and more often they expect products that will reflect their tastes, needs, adapt to their lifestyle, fit in the desired space, be unique, and available at the price of a mass production product [15].

The research results

For the purpose of this article, a questionnaire was carried out, the goal of which was to determine the role of customization in relation to marketing communication activities on the example of the Swedish company Ikea. The questionnaire consisted of 8 questions. The number of respondents in the conducted questionnaire was 100 people. The largest number of respondents, as many as 63 % were in the 18–23 age range. The study used the convenience sampling method, by using an online tool – a questionnaire. Links to the questionnaire were distributed on various forums and social networks. At the beginning of the questionnaire, the respondents were asked to provide information about their shopping preferences regarding the places where they buy their furniture. Respondents answered the question: "In which furniture stores do you buy furniture?". The vast majority, 78 % of the total responded that they buy furniture in Ikea (Table 3).

Table 3. The distribution of answers to the question from the questionnaire.

In which furniture stores do you buy furniture ?	
Store	Percentage of answers
Ikea	78 %
Black Red White	11%
Bodzio	7 %
Abra	3 %
Castorama	2 %
Jysk	2 %
Custom furniture	2 %
Leroy Merlin	1 %
Empir	1 %
I make my own	1 %

Source: Own study on permanent research.

Nowadays, all campaigns reach the recipients with a personalized message, engaging their emotions at the same time. Thanks to personalized products, the customer can feel special. That's why the question was asked: "Does personalizing the product (taking into account individual customer needs) influence the choice of the store's brand in which you make the furniture purchase?" which aimed to verify the level of customer awareness, as well as to examine the knowledge about personalization. Referring to the result of the study of said question (Figure 1), it turns out that as many as 58 % of respondents claim that personalization "rather" affects their shopping choice, 26 % of respondents said "definitely yes". However, only 2 % of respondents claim that it does not affect their preferences at all.

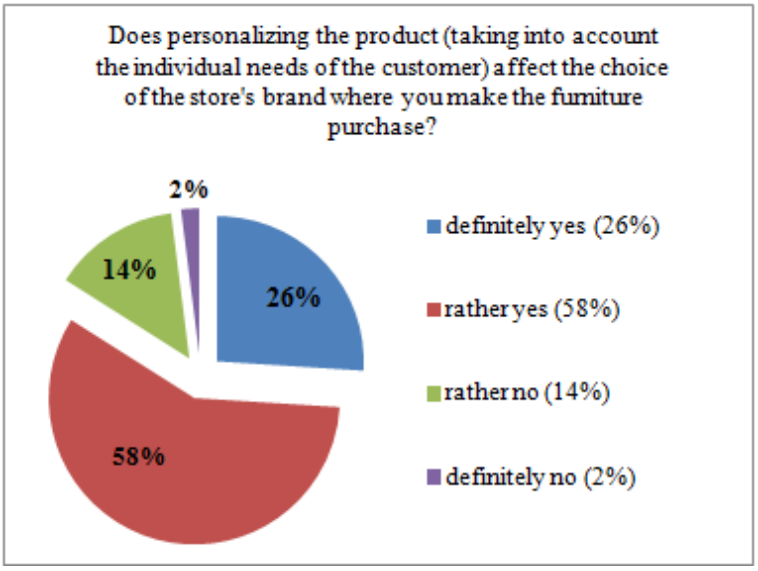

Figure 1. Structure of the answer to the question: "Does personalizing the product (taking into account the individual needs of the customer) affect the choice of the store's brand where you make the furniture purchase?"
Source: Own study on permanent research.

In the next step, the respondents were asked to answer the question: "What do you mean by customizing/ personalizing the product?" In order to examine the knowledge of the very concept of personalization. The vast majority of respondents know the concept and believe that it means: "Taking into account individual customer needs". To know the needs of customers, it is important to understand their preferences and listen to them.

An analysis of the received answers to the question: "How many times did you buy furniture in Ikea?" Showed that only 7 % of respondents claim that they do not buy furniture in Ikea, while 48 % of respondents answered that they shopped there "several times" (Figure 2.). A minimum of one purchase in this store was made by as many as 93 respondents. We can see just how popular the Ikea chain of stores is, even among just such a small number of consumers taking part in the survey.

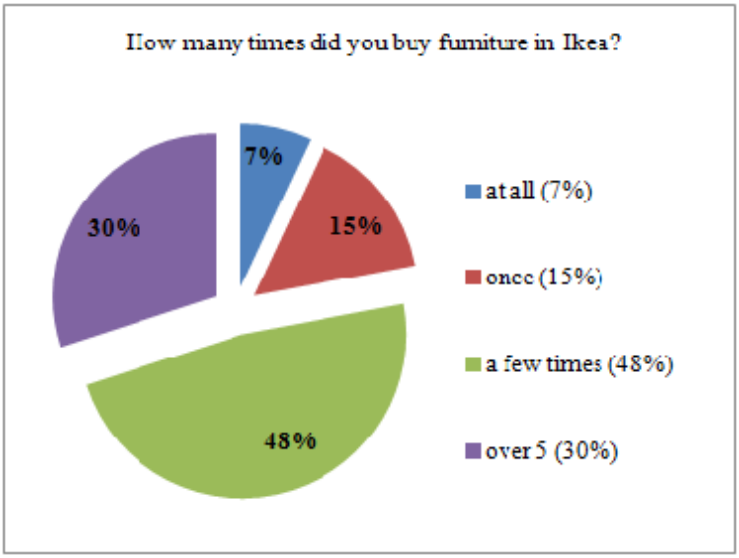

Figure 2. Structure of the answer to the question: "How many times did you buy furniture in Ikea?"
Source: Own study on permanent research.

People who took part in the survey mostly make purchases in Ikea. Consecutively, respondents were asked what prompted them to buy furniture in the store. Therefore, a question was asked to verify the significance of the factors: "What factors prompted you to purchase furniture from Ikea?". Undoubtedly, it turned out that the fact of choosing furniture is associated with the price (33 % of respondents hold this view) and the quality of products (18 % of respondents). However, the least–leading factor influenced by the decision to buy furniture in Ikea for respondents was the "approach to the customer" meaning the perceived quality of service (Figure 3).

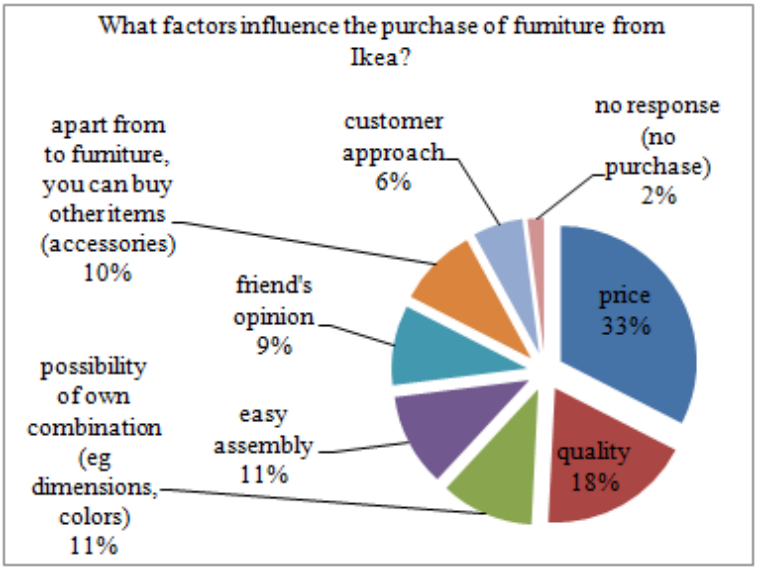

Figure 3. Structure of the answer to the question: "What factors influence the purchase of furniture from Ikea?"
Source: Own study on permanent research.

Further analysis of the tests consists of two parts. The first includes information about the systems they know in Ikea. In order to examine the knowledge of the respondents, the question was

asked: "Do you associate Ikea furniture with any furniture systems?". 35 % know of them and 65 % think that they do not associate Ikea with any systems (Figure 4).

The second part thoroughly verifies the question asked earlier (Figure 4). This means that if the respondent indicated the answer "yes", that is, he associates Ikea with some systems, he was then required to give answers as to what these systems are exactly (their names should have been mentioned). In connection with the above, respondents were asked to answer the question: "Which furniture systems do you associate with Ikea – give an example of a name?". Of 35 % of respondents who answered yes to the question (Figure 4). The most frequent answers were systems.

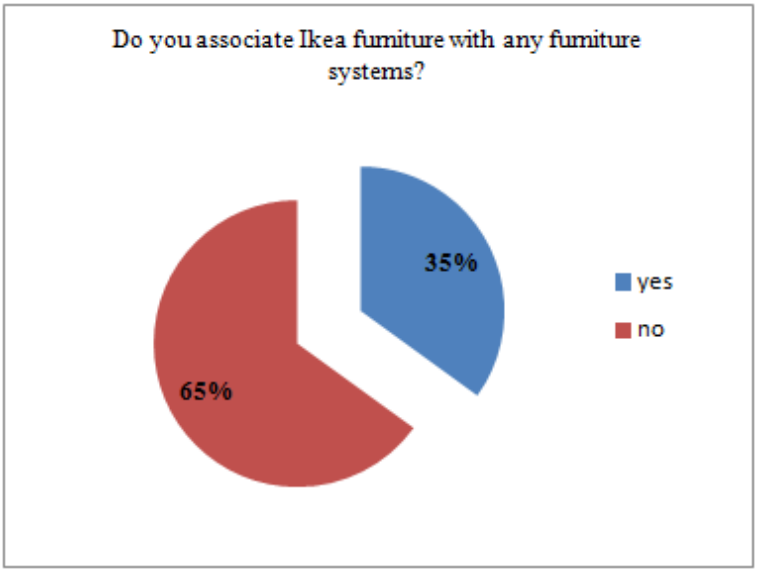

Figure 4. Structure of the answer to the question: "Do you associate Ikea furniture with any furniture systems?"
Source: Own study on permanent research.

Summary and conclusions

Mass personalization means offering products or services that meet the requirements of each individual customer. They are manufactured and delivered with mass production efficiency at prices comparable to standard products. The classification of four different approaches to personalization was created to help processes when designing or re–designing the product. Managers, thanks to available information, analyze each approach to best match production processes with their customers. There are also cases in which managers will have to apply a combination of some or all of the four approaches to meet the requirements of a specific customer group. The use of appropriate approaches will mean that mass customization will meet the expectations of both customers and entrepreneurs. Continuous pursuit to achieve a high level of satisfaction of buyers will make them come again for the goods.

On the example of two systems – BESTÅ and PAX, the process of personalization and dependencies that occur in the optimization of production costs were discussed.

Three hypotheses have been considered to verify the functioning of the systems and the similarities occurring in them. Consideration of them made it possible to indicate which values are the driving forces for the producers when planning production processes on a mass scale.

From among the hypotheses put forward, the first and third were confirmed. The colors used to make the casing in these systems are almost the same. Three colors are mainly used, namely white, white stained oak and black. The only exception is that in some products in the PAX system the color EF EF BJ BEJC BIA is used. The third hypothesis, which has also been confirmed, concerns whether these systems are manufactured from the same materials. Thanks to its confirmation, it can be noticed that the use of the same materials for the production of personalized goods, allows you to optimize costs.

Referring to research in the empirical part, consumers were asked to answer a few questions, which were mainly aimed at verifying their knowledge of customization, but also to examine their preferences and factors that guide their purchases (Figure 3). The general knowledge of the respondents concerning, among others, the systems used in Ikea and customization was varied, but quite correct, which is confirmed by the analysis of the survey results. However, the research sample was not a representative value. For this reason, it can only indicate certain dependencies and show trends and values associated with personalized products in production processes, the identification and verification of which should be confirmed by more in–depth research.

Research on the process of personalization and dependencies that occur in mass production have been addressed in many publications. Synthesis and analysis of four case studies was carried out, in the production of forklifts, electromechanical equipment, telecommunications systems and paper products. Based on the research, the product customization has been identified in three aspects: typology, concepts and organizational matters [15].

According to the next publication, manufacturers adjust only one of the two attributes of the product. A competitive market of products tailored to individual needs was analyzed. The study concetrated at two different sleeping bag manufacturers, which were characterized by two attributes: length and temperature comfort assessment. If companies adjust various attributes, many consumers stay indifferent to both companies, therefore with partial personalization, competing companies do not differentiate product attributes when using mass production [16].

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AUDIT AS A METHOD OF IMPROVING PROCESSES IN AN ORGANISATION

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Abstract:

The issue of improving processes in an organization is an important aspect of management. The article discusses the use of an audit by organizations. The purpose of the article is to verify whether the implemented auditing process has a positive impact on the processes and helps to improve the company. The auditing process was presented on the example of an organization from the service industry, where employees were also interviewed with regard to the impact of conducted audits on the functioning of the company.

Keywords:

Internal audit, improving organisation, PDCA, 5S method

Introduction

Effective functioning of an organization is a complicated process. As many organizations use methods that help effectively and successfully manage processes in the organization, it is important that not only employees, but also the top management should understand the nature and purpose of implementing these tools. The question should be asked: which method works best and will allow the organization to achieve the set goals in the fastest way?

One of the methods used by organizations is an audit. The purpose of this article is to answer the question whether this method allows the organization to improve its processes. An example of an organization from the service industry will be presented.

Basic concepts related to an audit

The word audit is derived from Latin (*audito*) and means *hearing* [1]. The meaning of this word is related to its interpretation and definition. There are many explanations of the term audit in the professional literature and most often they refer to a financial audit. However, the focus of this work is a system audit. According to the definition from the Polish Language Dictionary, an audit is "the control of the company in financial and organizational terms, evaluation of its assets and analysis of its development prospects, carried out by experts" [2]. The Institute of Internal Auditors IIA Polska defines an internal audit as "an independent and objective activity whose aim is to add value and improve the operating activities of the organization. It is based on a systematic and

ordered evaluation of the processes: risk management, control and organizational order, and contributes to improving their performance. It helps the organization to achieve its goals by providing assurance that these processes are effective, as well as by consulting" [3].

An audit is also understood as a systematic and independent evaluation process, whose main task is to search for and collect evidence that will allow to check to what extent the organization meets the set criteria [4]. With reference to the definition above, the term included in PN–EN ISO 19011: 2012 should be mentioned as well, where an audit means "systematic, independent and documented process of obtaining evidence from audit and its objective evaluation in order to determine if the audit criteria have been met" [5]. Records, all information, as well as documents that are recorded and can be verified are the evidence from the audit; the audit criteria are procedures, requirements, specifications, to which the evidence obtained from the audit is compared [5].

An audit is often equated with control, but these are two different concepts. Control is understood as checking, comparing the actual state with the one that is required [6]. The differences between control and audit are shown in Table 1.

Table 1. Control and audit

Control	**Audit**
carried out after completion of all activities related to the project or after carrying out part of the activities;	carried out systematically, without specific time intervals;
obligatory in order to achieve the set goals;	recommended in order to achieve the set goals
refers to the detection of errors;	focuses on searching for compliance with specific requirements;
is irregular;	carried out regularly on the basis of the audit plan;
the area of control is unknown;	the scope of the audit is determined in advance and presented to the interested parties;
the noticed non–conformances constitute a record after the control;	in addition to non–conformances, potential areas where the organization can improve are also recorded;
the noticed non–conformances are immediately removed.	the time limit for the implementation of corrective actions or corrections is determined between the auditor and the auditee.

Source: Ejdys J., Kobylińska U., Lulewicz–Sas A., Zintegrowane systemy zarządzania jakością, środowiskiem i bezpieczeństwem pracy, Białystok, Oficyna Wydawnicza Politechniki Białostockiej, 2012.

The comparison of the differences between the concepts of control and audit shows that audit is a more extensive process. Good understanding of the term "audit" is very important not only for the organization itself, but also for people who carry out audits or are audited. It is important that the organization should not equate audit with control, and should realise that audit is a tool allowing verification of activities and perfecting implemented tools or systems. By systematically conducting audits, the organization is able to undertake activities that will improve the quality and effectiveness of its processes.

An audit may be carried out in various areas of the organisation, and may concern its various aspects. When analysing criteria, it is possible to differentiate several types of audits. Among the most often distinguished classification criteria we can mention [7]:

- organizational affiliation of the team carrying out the audit – e.g. the audit of the first, second and third party,
- the subject of the audit – e.g. the audit of the system, process, product or documentation,
- accuracy of the audit carried out – a compliance audit or improvement audit,
- audit planning – planned and unplanned audit.

The organization decides itself which audit is suitable for it. Sometimes the client determines which audit the organization is to carry out. The organisation can also use other goals and functions of conducting audits in its operations apart from the desire to improve by means of audits.

Aims and functions of an audit

The aim of conducting an audit by an organization is to improve and optimize its processes. An important element in the process of audit management is the company's understanding of the audit's function and aim. An audit is an added value not only for the company, but also for other interested parties.

An audit can be classified according to various criteria. This classification will also determine the functions performed by the audit. The following functions of an audit can be distinguished [8], [9]:

- the verifying function – this function refers to verifying whether the system/processes are established, implemented and maintained by the organization and whether they are operating efficiently,
- the evaluating function – conducting an audit makes it possible to check to what degree the system fulfils the set goals,
- the informative function – an audit tells the organization how the system works, which makes it possible to improve processes and identify potential areas for improvement,
- the corrective function – an audit allows us to verify the compliance of the process with the requirements, and, after detecting non–conformances, it also makes it possible to determine corrective actions, who are to eliminate the cause of the error,
- the preventive function – the auditor and the auditee are able to notice the potential areas for the appearance of non–conformances, which may cause the auditee to consider it right to introduce preventive actions that will prevent non–conformances in the future,
- the instructional function – an audit for the auditor or the auditee may be a place for exchanging good practices, the owner of the process or the auditor may give important and relevant information about the process,
- the improving function – the audit itself is not an improving activity, but allows to improve the functioning of the process using the obtained audit results.

An audit also allows the company to determine processes that are important for the organization, to check the effectiveness and successfulness of the implemented solutions. It is also a method that allows it to monitor the status of the organization's goals. Thanks to an audit, the company can create and implement solutions that help to remove the resulting non–conformances. It should be noted, however, that the main task of an audit is to obtain evidence that confirms the system's compliance with the requirements of the organization.

Audit on the example of an organisation from the service industry

The service company, on the example of which the process of internal audit management will be presented, has implemented a quality management system and it carries out systematic audits in accordance with the requirements of ISO 9001: 2015. An additional element is the implemented 5S system, in which internal audits are carried out once a quarter. Internal audits are conducted in accordance with the binding procedure as well as the PDCA (Plan – Do – Check – Act) cycle, shown in Figure 1.

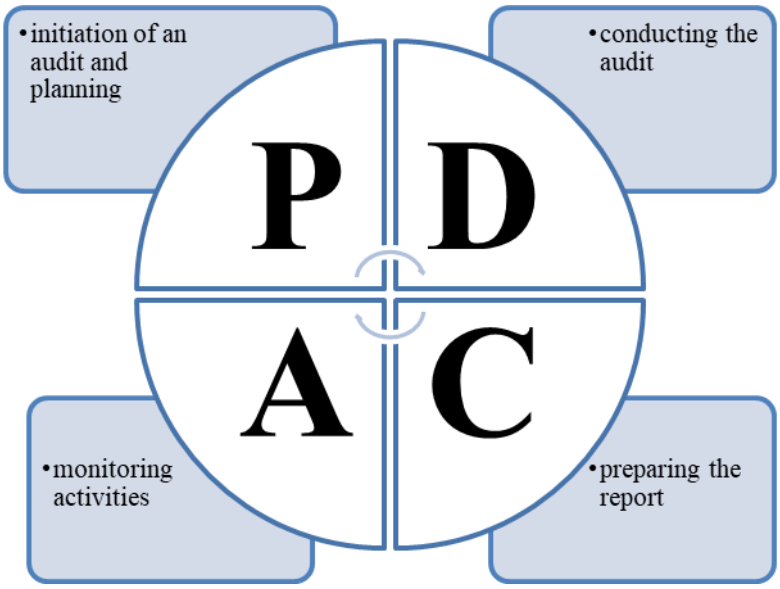

Figure 1. PDCA cycle regarding the audit process
Source: own elaboration on the basis of the materials made available by the organisation

The first stage is planning the internal audit, which proceeds in a different way comparing to the system audit and the 5S audit. System audits are planned at the beginning of the calendar year, and their frequency depends on the complexity of the process, as well as on the number of non–conformances detected in the previous audit. The planned date is not an exact day, only the time interval during which the audit must be carried out. After establishing the plan of audits, the management system coordinator sends information about the planned dates to the owners of the processes for approval. One week before the planned audit, the coordinator presents the owners with the exact scope and date of the audit. In the case of an audit related to the implemented 5S system, its dates are set one week before the end of the quarter after consulting it with the auditor and the auditee.

System audits are carried out in accordance with the binding internal auditing procedure. During the audit the requirements of PN–EN ISO 9001: 2015 and internal requirements of the organization, procedures, are in force. Two internal auditors are appointed in the organization and they, according to the audit definition, carry out audits of processes to which they are not directly related.

In the case of a 5S audit, the auditors carry it out in accordance with the schedule. The 5S audit

is carried out in designated zones, i.e. areas separated in the office part of the organization. Each zone owner performs an audit. It might happen that the person responsible for a given zone carries out a so–called self–audit, i.e. he/she audits her/himself.

The employees of the organization are aware that audits do not control their processes or work zones, but they allow for improvement and that thanks to them it is possible to confirm compliance with regulatory requirements. After the system audit, the auditor completes the report, while in the case of the 5S audit, the so–called checklist 5S is completed during the audit, which makes it possible to verify the compliance of work standards with all stages of the 5S method, which are [10]:

- sorting,
- setting in order,
- shining,
- standardizing,
- sustaining.

When non–conformances are detected during the audit, they are recorded by the auditor. Non–conformances after the system audit are recorded on the report, and in the case of the 5S audit are entered into the checklist. The auditor can also identify potential areas for improvement; such observations are also recorded on the above–mentioned forms. After the documents are completed, they are sent to the auditee. An important element of recording non–conformances is explaining on what basis the decision was made about the non–conformance between the actual situation and the regulatory requirements.

It is the duty of each employee to enter the detected non–conformances in a suitably prepared file, the so–called *PDCA file*, in which the detected non–conformance is recorded, along with the correction and corrective action undertaken. The implementation of the developed activities follows the PDCA file, which is compatible with the Deming cycle (Plan, Do, Check, Act). In addition to the non–conformances, activities concerning potential areas for improvement are also entered. Such a system for monitoring non–conformances helps employees of the organization to update the actions undertaken, as well as supervise which activities have already been implemented and at what stage the current work is carried out.

Planned meetings, taking place once a quarter, are an important element of the system's functioning and of conducting audits. During such reviews, performed activities are analysed, which serves to eliminate the effects as well as the causes of the non–conformances detected. During such meetings, employees also share their doubts concerning the implementation of corrective actions.

Trainings are an important element in the process as they allow employees to understand the nature of conducting internal audits and auditors to improve their competences regarding the auditing process. In this way, such trainings allow employees to develop and improve.

The implemented system and conscious conducting of audits make it possible to monitor and improve the employees' processes and skills. In order to verify whether the implemented auditing system positively affects the functioning of processes as well as the quality of employees' work, a study was conducted using a questionnaire.

The scope of the study and its results

The aim of the study was to check if the audit is a method improving the processes in the organization. The survey was conducted among the employees who carry out audits and/or are audited. The research method used was the personal interview and its purpose was to recognize the benefits as well as problems related to audits. The interview questionnaire consisted of 5 open–ended questions regarding the usefulness of audits and their results. 12 people took part in the study.

In the first question, the respondents were asked what concept they associated with an audit. The employees could choose more than one answer. 12 respondents indicated that an audit equated with verification, 7 people – monitoring, 4 – comparing the actual status with the required one and 4 respondents that an audit was an overview of the documentation.

The second question concerned issues related to detected non–conformances. Over half of the respondents stated that the detected non–conformances referred to the regulatory procedures, which were not always up to date, missing documents, errors occurring in messages addressed to customers, or in situations related to the organization's employees missing deadlines. With regard to 5S audits, employees have indicated that errors detected are related to ordering documents or electronic cables. Non–conformances in about 90 % occur at the stage related to cleaning, but rarely in the visual sphere.

In the next question, the respondents were asked to answer a question about the impact of conducted audits on the improvement of functioning of the process or zone for which the audited person was responsible. Over 50 % of the respondents said that an audit allowed them to verify errors in processes, as well as to thoroughly get to know the processes. Audits help to detect errors before they cause adverse effects for the process. Four of the respondents focused on 5S audits and indicated that audits helped maintain cleanliness and order in 5S zones. One of the respondents stated that the first audit had caused anxiety, but subsequent ones made it possible to observe deficiencies or possibilities to improve the process and, as a result, eliminate potential non–conformances.

In the next part of the interview, the respondents were asked about problems that occur during audits. One of the respondents does not conduct audits, therefore he did not answer this question. People who only carry out 5S audits (9 people) stated that they experienced difficulties while using the checklist and did not always know if the question asked was correct. The respondents also pointed out that if they had problems related to granting an appropriate mark to the auditee, they used the help of the 5S System Coordinator. Two people find it difficult to audit the organization's management. The employees stated that they felt uncomfortable when they carried out an audit related to the processes managed by the President of the company.

The fourth question concerned the record of non–conformances and potential areas for improvement in *the PDCA file*. The employees were asked if they believed it was right to run a system to monitor the detected non–conformances and why. All the respondents stated that *the PDCA file* they completed allowed them to monitor the status of activities. They also observed that during subsequent audits fewer and fewer non–conformances were detected, while new, possible areas for improvement appeared. The employees also stated that the created *the PDCA file* helped to collect all detected errors in one place and the employees were aware that no non–conformance

would be omitted.

In the last question, the respondents were asked to provide an answer to the question whether they believed it was right to implement systematic audits in the organization. All the respondents stated that audit was the right tool and in addition to the benefits they had already mentioned, it also helped improve communication between departments and employees. Systematic audits also help employees improve the existing system as well as 5S zone for which they are responsible. The respondents also drew attention to the issue related to the optimization of processes in the organization. One person stated that thanks to the fact that the zones were audited by other independent people, potential areas for improvement were shown which might not necessarily be noticed by the owner of a given process.

The interview made it possible to notice that the employees are aware of the purpose of conducting audits, and that the conducted audits allow the organisation to improve processes and areas. Audits improve not only the functioning of the quality management system and the implemented 5S method in the organization, but also have a positive impact on internal communication between employees.

Summary

Organisations make use of audits more and more frequently in order to improve the functioning of a company. The aim of an audit is to confirm that the system is consistent with requirements. By effectively running audits the company knows where the non–conformances appear and is able to react earlier to the non–conformances. Training of employees is one of the important elements of managing audits. An informed and competent employee is a person who knows why audits are conducted and what benefits they bring to the organisation, as well as to himself/herself.

On the example of the analysed organization, one can observe how the process of audits, not only qualitative, but also regarding the 5S system, can be managed. No organization is perfect, but conducting audits is an effective way to strive for perfection. Detected non–conformances help to prevent critical errors. Identifying potential areas for improvement makes it possible to improve processes and areas within the organization.

Summing up the discussed issue, it can be concluded that properly and deliberately conducted audits are one of the methods used to improve an organization. This statement is confirmed by both literature studies and questionnaire conducted among the employees who make us of this method.

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SPECTRAL CHARACTERISTICS OF FLAVANONE AND ITS THIOCARBOHYDRAZIDE DERIVATIVE

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Abstract:

Flavanones are one of the main flavonoids' groups. These secondary plant metabolites are widespread in nature. The large diversity of their biological activity depends on the modification of the structure. On the other hand, thiocarbohydrazides are widely used in heterocyclic synthesis as contain the functional group RNHCSNHR. Substituted thiocarbohydrazides (RNHCONHNHCSNHR) are key to the synthesis of many organic heterocyclic ring systems. This work is devoted to the synthesis and characterization of a new thiocarbohydrazide Schiff base N'–((E)–2–phenylchroman–4–ylidene)–2–((Z)–2–phenylchroman–4–ylidene)hydrazine–1–carbothiohydrazide derived from flavanone . It was characterized by elemental, UV–visible, IR and ^{1}H NMR spectra. The preliminary results support the formation of novel flavanone derivative.

Keywords:

flavanone, thiocarbohydrazide, Schiff base, spectroscopic methods

Introduction

Flavonoids are the largest group of polyphenols. They occur in many plants and have different properties, such as antioxidant or anti–inflammatory. Flavanones are an interesting class of flavonoids widely present in food products of plant origin. The basic moiety of these molecules is flavanone (Figure 1) [1–3].

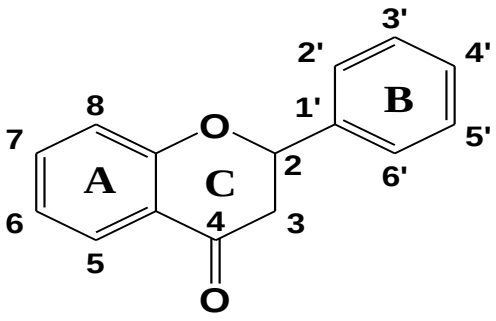


Figure 1. Chemical structure of flavanone

The flavanones include compounds with modifications in rings: A, B or C. Their chemical nature affects their bioavailability and bioactivity. They have great potential in the treatment of cancer and cardiovascular diseases [4–7].

Thiocarbohydrazides (Figure 2) are an important class of chemical compounds that have applications in organic chemistry, biology and medicine due to their valuable reactions and a variety of antibacterial, antiviral and antifungal activities.

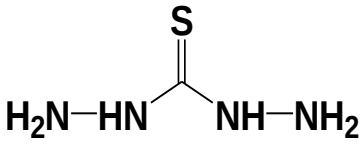


Figure 2. Chemical structure of thiocarbohydrazide

Medicinal chemistry has recently concerned on a creation of new bioactive molecules that could be successfully used as potential drugs. Thiocarbohydrazide Schiff bases are chemical compounds of great importance in medicinal and pharmaceutical fields. The bioactive properties of Schiff bases of thiocarbohydrazide have motivated us to synthesize new flavanone thiocarbohydrazone derivative N'–((E)–2–phenylchroman–4–ylidene)–2–((Z)–2–phenylchroman–4–ylidene)hydrazine–1–carbothiohydrazide and explore its physical and chemical properties. It was characterized by elemental, UV–visible, IR and NMR spectra [8–11].

Experimental

Materials

The flavanone, thiocarbohydrazide and thiocarbohydrazone derivative of flavanone in this work are presented in abbreviation forms, respectively F, TCH, FTCH. All other compounds were purchased from Sigma–Aldrich Co. All reagents were of analytical quality and were used without further purification. The stock of F, FTCH solutions were prepared by dissolving in the exact amount of DMSO.

Synthesis of N'–((E)–2–phenylchroman–4–ylidene)–2–((Z)–2–phenylchroman–4–ylidene)hydrazine–1–carbothiohydrazide (FTCH)

1 mmol Flavanone (F) was quantitatively transferred to a round bottom flask and dissolved in 15 ml of dry ethanol at 80 °C. The contents of the flask were stirred for 10 minutes until the flavanone was completely dissolved. 0.5 mmol of thiocarbohydrazide (TCH) was added to the solution obtained, then three drops of concentrated sulfuric acid (VI) were added to reach pH 4 as a catalyst and the reaction was carried out at 80 ° C for 24 hours. Then, the reaction mixture was cooled and transferred to a refrigerator (4 ° C). After two days of storage at a low temperature, a pale brown precipitate of thiocarbohydrazone derivative of flavanone was formed (Figure 3). The precipitate was suction filtered, washed with anhydrous ethanol and allowed to dry in the desiccators [12,13].

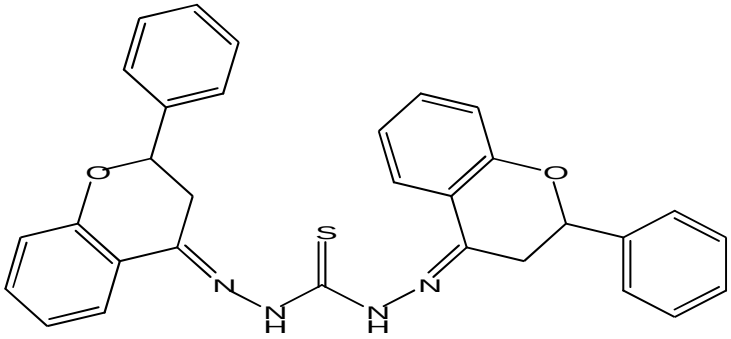


Figure 3. Chemical structure of thiocarbohydrazone derivative of flavanone (N'–((E)–2–phenylchroman–4–ylidene)–2–((Z)–2–phenylchroman–4–ylidene)hydrazine–1–carbothiohydrazide).

Physicochemical measurements

Elemental analysis (C, H, N) of FTCH was carried on a EuroVector 3018 analyzer (see SI). Anal. Calc. for C 71.17 %, H 5.11 %, N 10.71 %, O 6.88 %, S 6.13 %. Found: C 71.18 %; H 5.29 %; N 10.50 %.

The infrared IR spectra were recorded employing a Nicolet 6700 (Thermo–Scientific) FT–IR spectrometer in the 4500–500 cm^{-1} region. IR νmax(cm–1): ν(N–H): 3274, ν(C═S): 1683, ν(C═N): 1603, ν(C–O–C): 1224, ν(N–N): 1063.

^{1}H NMR spectra were recorded on a Bruker AV200 200MH spectrometer in DMSO with TMS (tetramethylsilane) as internal standard. The ^{1}H NMR spectra of the flavanone (F), thiocarbohydrazide (TCH) and the derivative (FTCH) are assigned as follows: F (DMSO–d_6 , 200 MHz), 2.83 (1H, dd, J = 3.0, 2.8 Hz, 3(a)–H), 3.25 (1H, dd, J = 14.8, 3.8 Hz, 3(e)–H), 5.68 (1H, dd, J = 2.6, 2.8 Hz, 2–H), 7.10 (2H, dd, J = 5.0, 6.0 Hz, 6, 8–H), 7.38–7.49 (3H, m, 3', 4', 5'–H), 7.53–7.65 (3H, m, 2', 6', 7–H), 7.80 (1H, dd, J = 1.4, 1.8 Hz, 5–H); TCH (DMSO–d_6 , 200 MHz), 4.48 (2H, s, NH_2), 8.69 (1H, bs, NH); FTCH (DMSO–d_6 , 200 MHz) 2.73 (1H, s, 3(a)–H), 2.89 (1H, s, 3(e)–H), 5.29 (1H, d, J = 7.6 Hz, 2–H), 7.02 (2H, dd, J = 7.6, 5.8 Hz, 6, 8–H), 7.25–7.57 (7H, m, 2', 3', 4', 5', 6', 7, 5–H), 10.58 (1H, bs, 2',NH).

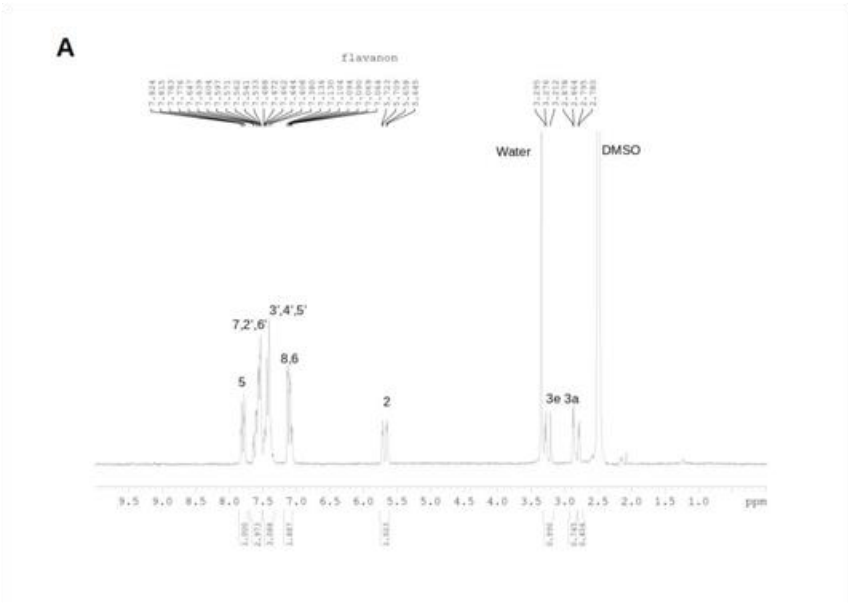
UV–Vis spectrophotometric measurements were carried in the range of 200–800 nm with solutions containing F, TCH, FTCH at the concentrations: 2.5×10^{-5} M or 5×10^{-5} M. Spectra were recorded at DMSO, DMF and binary solutions consisted of DMSO(DMF)/water in the 1:1 volumetric ratio, using quartz cell with a path length of 1 cm.

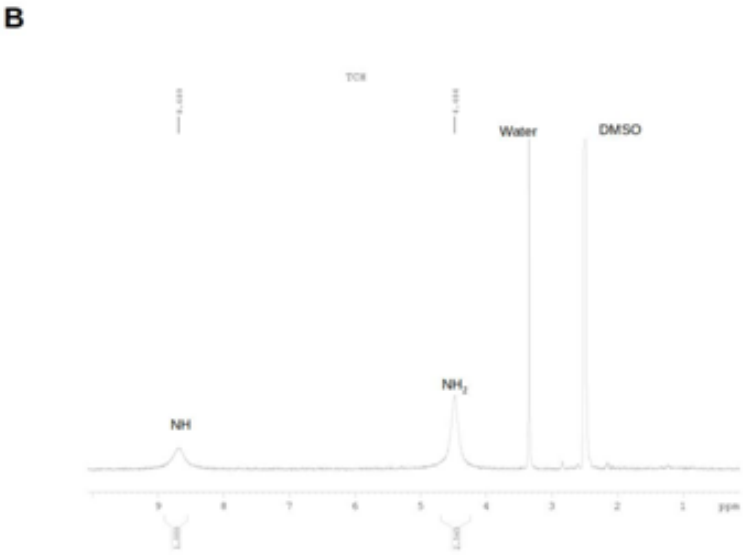
Results and discussion

^{1}H NMR and IR spectroscopy

Spectroscopic methods are useful tools to support structure of new compounds. ^{1}H NMR, IR, and UV–Vis spectroscopies have been used in this work to characterize a novel flavanone derivative FTCH without destroying the sample.

^{1}H NMR spectroscopy is a very useful method for the characterisation of molecule in solution. DMSO–d_6 was used as a solvent for F, TCH, FTCH. The spectra are presented in Figure 4.


A
flavanon
Water
DMSO
3',4',5'
7,2',6'
8,6
5
2
3e 3a
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm


B
TCH
Water
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NH
NH2
9 8 7 6 5 4 3 2 1
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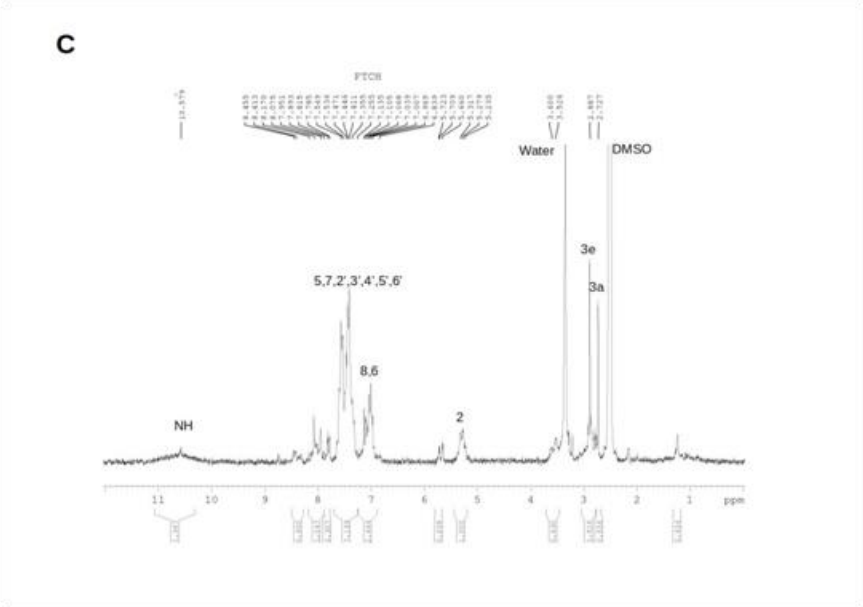
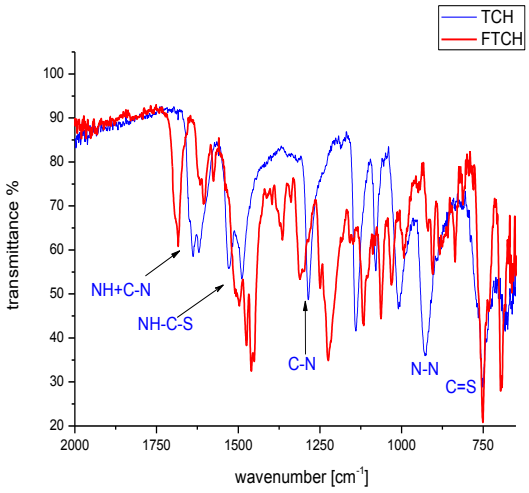


Figure 4. ^{1}H NMR spectra: **A** flavanone, **B** thiocarbohydrazide, **C** FTCH
Source: Own elaboration

Formation of the new derivative is supported by the spectrum of FTCH. The positions of chemical shifts of FTCH protons are changed with respect to F or TCH and a characteristic peak 10.58 (bs, 1H, NH) is clearly seen. Moreover, the characteristic position of $–NH_2$ was not observed in Figure 4C. The further evidence of FTCH formation comes from IR spectrum (Figure 5). Peaks of TCH at 1639, 1528–1486 and 753 cm^{-1} assigned to NH+C–N, NH–C–S, and C=S cm^{-1}, respectively, are shifted in the FTCH spectrum to lower values of wave numbers which can confirm the newly synthesized product.



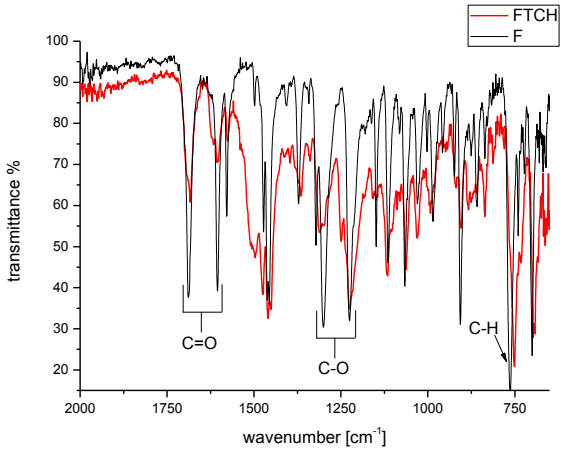


Figure 5. IR Spectra of FTCH and F or TCH for comparison

UV–Vis spectrometry

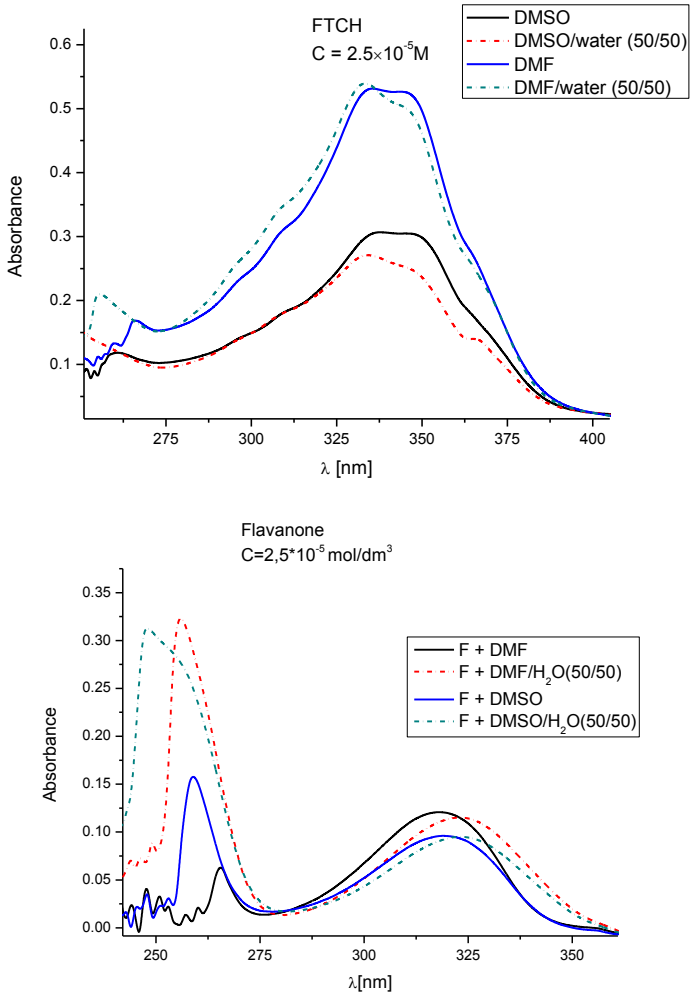


Figure 6. Electronic absorption spectra of F and FTCH DMSO, DMF and DMSO(DMF)/water mixtures

For the determination of flavanones' contents, UV–Vis spectrometric method, which is fast and simple, is still used. Substitutions on the A–C– or B–systems may produce hypsochromic or bathochromic shifts depending on conjugating effect of substituent; it can be used for structural elucidation [14].The spectra of the compounds studied in this work are presented in Figure 6. Analysis of these spectra provides the information that modification of flavanone molecule by incorporation thiocarbohydrazide as bridging moiety between two F molecules has clear impact on electronic absorption characteristics. The spectra of F and FTCH differ between each other in shapes, the position and intensity of maximum absorption bands. The λ_{max} at around 318 nm in flavanone is shifted to 340 nm in FTCH. The results can indicate a formation of new flavanone derivative.

The UV–Vis electronic absorption characteristics of F and FTCH were investigated in neat DMSO or DMF and binary solvent mixtures consisting of DMSO or DMF and water in ratio of 1/1 (v/v). Figure 6 shows the characteristic electronic absorption spectra of F and FTCH recorded in these solvents. The water addition in binary solvents exerts the clear influence on the electronic absorption of both F and FTCH, changing spectral maxima positions but slightly their shapes. The spectra of F exhibit two absorbance maxima (band I and band II). Band I can be found in 318 to 323 nm range and band II in 265 to 247 nm depending on the solvent used. They can be attributed to the B–ring and to the A–C benzoyl system, respectively [15]. However, attention should be paid to the fact that band II may overlap with DMSO (265 nm) or DMF (240–280 nm) bands. The difference in the maximum absorption wavelength (λ_{max}) of the band I of F is only 1 nm in neat solvents but in water mixture is shifted towards longer wavelengths. The shift of band I with respect to FTCH is visible in the shorter wavelength range.

These results indicate that very likely intermolecular hydrogen bonds between solvent–solvent and solute–solvent are more responsible for variation of the absorbance red (F) or blue (FTCH) shifts in polar protic water mixtures as comparing with neat polar aprotic solvents such as DMSO or DMF. The specific and non–specific interactions in protic solvents may stabilize the excited state of F more than the ground state, resulting in bathochromic shift [16].

On the other hand addition of water into neat DMSO or DMF has slight impact on FTCH UV–Vis profile. One can suppose that electron redistribution in FTCH molecule occurs in a very low extent upon addition of polar protic water as a fraction of binary solvents.

Conclusions

The formation of a novel flavanone derivative (N'–((E)–2–phenylchroman–4–ylidene)–2–((Z)–2–phenylchroman–4–ylidene)hydrazine–1–carbothiohydrazide) has been investigated by different spectroscopic methods: ^{1}H NMR, IR and UV–Vis. Our data showed that the application of spectroscopic methods can confirm appearance and structure of new compound. The NMR and IR or UV–Vis spectra reveal significant differences between F and FTCH. The UV–Vis studies show that addition of water into neat DMSO or DMF exerts a clear contribution into absorption maxima positions of flavanone and its novel derivative. The bathochromic or hypsochromic effect observed in binary solvents for F and FTCH spectra, respectively, is very likely affected by the hydrogen bond donor abilities and the dipolarity/polarizability of the solvent. Concluding, a new Schiff base

derived from thiocarbohydrazide and flavanone was obtained, and it can be used for further research.

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SEPARATION OF BIOGAS COMPONENTS BY ADSORPTION ON ACTIVATED CARBON

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Abstract:

Today the huge challenge is to increase the production of fuels and chemical products by using innovative 'green' technologies. Although, biogas is environment friendly renewable energy source, needs to purification by minimizing CO_2 and maximizing CH_4 content before using. Biomethane from biogas can be treated as local source for production electric and heat energy or fuels. This work presents adsorptive technologies for biogas upgrading and gives a special focus to PSA technology. Additionally, removing CO_2 from biogas by pressure swing adsorption was verified in experimental unit. Preliminary results shown that using activated carbon, it was possible to enrich 50% CO_2/50 % CH_4 mixture up to at over 90% of methane.

Keywords:

Biogas, pressure swing adsorption, activated carbon, methane, carbon dioxide

Introduction

Biogas is a gas mixture produced from the degradation of organic compounds in the anaerobic fermentation process. The composition of the biogas is variable and depends on the type of raw matters and the process conditions [1]. The main sources of biogas are landfill wastes, industrial wastewater, agricultural residues, animal manure etc.[2]. Generally, it contains two main components: methane (50–75 %) and carbon dioxide (25–45 %) as well as, some trace components like: hydrogen sulfide, hydrogen, nitrogen, ammonia, oxygen, carbon monoxide, dust particles, siloxanes, volatile organic carbons (VOC), aromatic and halogenated compounds. Furthermore, typical biogas is also saturated with water [3].

Upgrading biogas to high energy biomethane allows for a wider variety of uses, either for heat and/or electricity, for injecting into natural gas grid (substitute natural gas – SNG) or for vehicle fuels (compressed natural gas – CNG). For use as a SNG and fuel, purification to remove carbon dioxide and hydrogen sulfide is required. For other applications purification to remove hydrogen sulfide and moisture is enough [4].

Nowadays exist a number of different commercial biogas purification technologies have proven to be technically and economically useful to produce biomethane stream of sufficient quality to be injected into the natural gas grid or to act as a vehicle fuel. Applying these technologies also

provide reductions in greenhouse gases (GHG) emissions as well as several other environmental benefits. Nevertheless, intensive research is still in progress to search for innovative and highly effective technologies to the field of biogas upgrading [5].

Application of adsorption for separation of biogas is of a very interest. Thus, the main objective of this work was analysis of the adsorptive separation methods for biogas components separation. The separation of CH_4/CO_2 mixture by pressure swing adsorption (PSA) on activated carbon was studied. Experimental verification of new concept of PSA process presented previously in [6] was done.

Adsorptive H_2S removal

Hydrogen sulfide is in a biogas in a concentration range from 10–30 to 1000–2000 ppm [7]. The presence of hydrogen sulfide can cause corrosion in equipment, turbines, pipelines or other transmission units, thus its preremoval is required [5]. Different processes are used to remove H_2S, for example by adsorption on metal oxides or hydroxides, on zeolites or activated carbon. Most commonly iron oxide is used, also zinc and copper. During the adsorption metal sulfide is formed. In next step material can be regenerated. A number of regeneration is limited, because during this process active surface is blocked by elemental sulfur. This technology can be used to produce of biomethane because very low H_2S levels can be reached (<1 ppm (v/v)). In case of activated carbon, adsorbent is typically impregnated with potassium iodide or sulfuric acid. Additionally, in order to oxidize H_2S to elemental sulfur the oxygen is dosed to the biogas [7–9]. This technology is often combined with PSA biogas upgrading, because adsorption on activated carbon is the most attractive desulfurization method among the available methods [10].

CO_2 removal

Biogas consists mainly of methane and carbon dioxide. The presence of CO_2 in high concentration decreases the calorific value of the gas etc. Thus the removal of CO_2 to obtain biomethane is imperative. Common methods to separate CO_2 from raw biogas includes: physical and chemical absorption like as high pressure water scrubbing, organic solvent scrubbing, amine scrubbing, pressure swing adsorption (PSA), membrane separation, cryogenic separation and so on [1]. The typical gas after the upgrading process has an increased CH_4 content of 95–99 % (v/v) [5].

Pressure swing adsorption

Pressure swing adsorption is a typical industrial operation for separation and purification of multicomponent gaseous mixtures. This technology is developed and commercialized by several companies: Acrona, Carbotech, Cirmac, Gasrec, Xebec Inc, Guild Associates etc. [11]. PSA is applied in industry for air drying, production of oxygen or nitrogen from air, purification of hydrogen, separation linear paraffins from branched ones, methane enrichment of biogas and coal mine gases [3]. PSA is a dynamic process operated in a cyclic manner and performed by changing the total pressure of the system. PSA process is based on physical adsorption. The interaction forces between the solid and the sorbate are relatively weak, involving only van der Waals forces [12]. PSA cycle are typically used to produce a high–purity light (weakly adsorbed) product from a feed

during the adsorption step at the high pressure and to recover a heavy (strongly adsorbed) product during the desorption step at the low pressure [13]. PSA processes have four basic steps schematically shown in Figure1: pressurization (with either feed gas or light product gas), adsorption, depressurization (desorption), purge. Pressurization and depressurization are the pressure–changing steps, while adsorption and purge are flow steps [3].

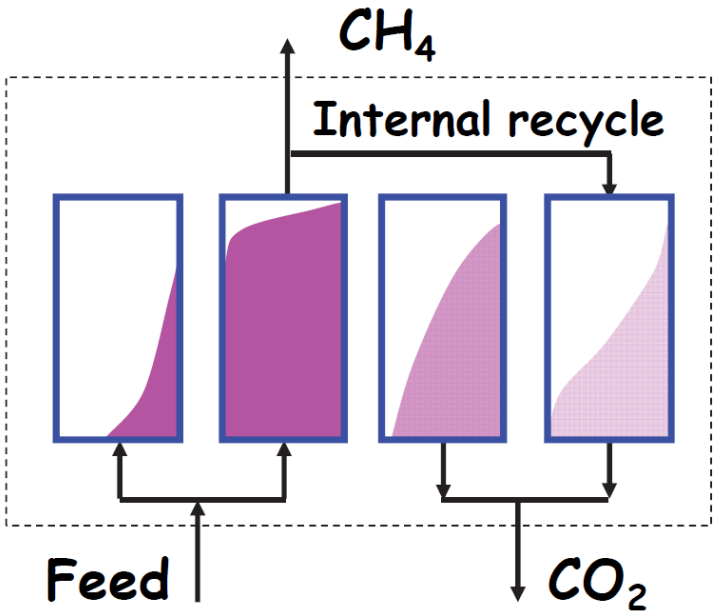

Figure 1. Schematic representation of the basic steps of one column in a single PSA cycle.
Source: [11]

One of the most important factors for separation of CO_2/CH_4 mixtures by microporous materials is pore size. When both molecules can readily diffuse into the pores, because the pore size is large enough, one can separate the two gases by an equilibrium separation, which is achieved by the difference in their equilibrium adsorption. When only the smaller molecule (CO_2) can diffuse into the pores (the larger molecule of methane is totally excluded) or if the pore size is slightly larger than the kinetic diameter of the larger molecule, the process is 'kinetic driven' in the sense that the selectivity by differences in the diffusion rates [2, 13]. Carbon molecular sieves, activated carbons, zeolites, silica gels and titanosilicates typical adsorbent materials [11]. The PSA technology advantages are [3]:

- low energy requirement,
- using in small or intermediate–scale for high purity methane production from biogas, coal mine gas or natural gas,
- short cycle time.

Experimental

The key of the separation of biogas components CH_4/CO_2 by means of PSA is properly selected adsorbent. Coconut shell based activated carbon was chosen. The textural parameters of activated carbon were calculated from the adsorption/desorption isotherm of nitrogen gas at 77 K (Figure 2) measured with the automatic volumetric sorption analyser (Autosorb–1–C,

Quantachrome). The isotherm behave as type I according to IUPAC classification, characteristic for microporous materials with narrow micropores.

Values of selected characteristics of porous texture of activated carbon under study are listed in Table 1.

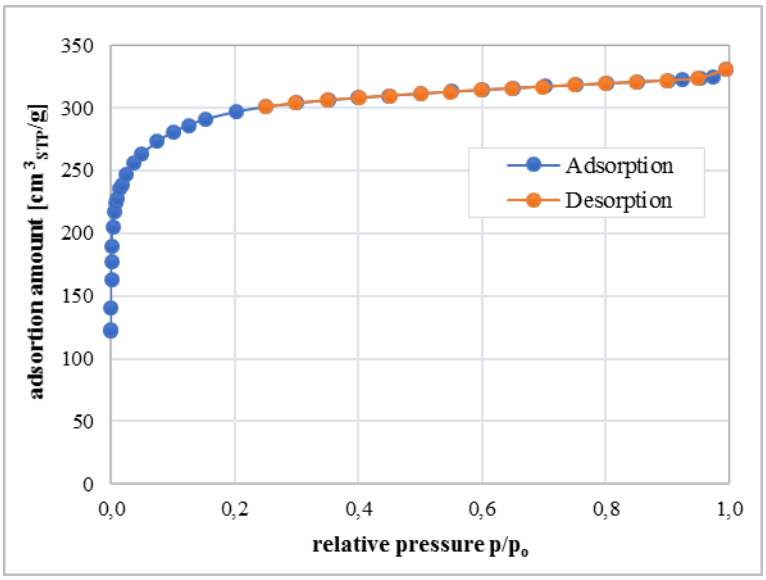

Figure 2. Adsorption isotherm of nitrogen on activated carbon
Source: own work

Table 1. Textural characteristics of activated carbon

Parameter	Value	Unit
BET surface area	1120	m^2/g
Micropore volume	0.416	cm^3/g
Mesopore volume	0.061	cm^3/g
Total pore volume	0.501	cm^3/g
Average width of micropores	1.15	nm
Average diameter of mesopores	2.18	nm

Source: own work

The new concept of PSA process was verified in our small scale experimental unit schematically shown on Figure 3.

The gas mixture (50 % CO_2/50 % CH_4) is fed into the column packed with the adsorbent. The specifications of adsorption column are: 18 mm in internal diameter and 1500 mm in length. Biogas components concentration was measured with gas analyser.

When the separation between CH_4 and CO_2 is realized, the CH_4 rich stream on the top of the column is collected as the product. Column is regenerated by reduce the pressure to vacuum. Desorbed gas is recovered on the bottom of the column. The PSA cycle applied in this work consists of three consecutive steps:

- Column pressurization with feed gas up to 2 bar,
- Co–current feed adsorption,
- Counter–current depressurization up to 0.05 bar.

The CH_4 average content in product was at over 90 %.

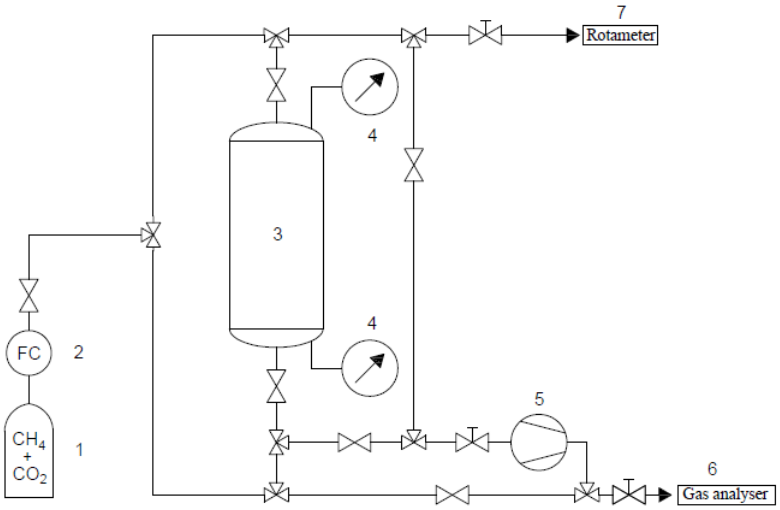

Figure 3. Scheme of adsorption separation unit. 1 – gas bottle, 2 – mass flow controller, 3 – adsorption column, 4 – pressure sensor, 5 – vacuum pump, 6 – gas analyser, 7 – rotameter. Source: own work

Conclusion

The PSA process using activated carbon was applied to the effective removal of CO_2 from CH_4/CO_2 mixture. The experimental results indicated that selected activated carbon can be successfully applied in CO_2/CH_4 separation for biogas upgrading. Further experiments will be continued to improve in the performance of the unit, optimize of process variables, as well as search new types of carbonaceous adsorbents.

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ABRASION OF ENAMEL CAUSED BY FORCES OF DENTAL RESTORATIONS ACTING ON NATURAL TEETH

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Abstract:

The aim of this paper was to analyze the method of testing retentive forces of clasps and friction between the enamel and dental materials. The focus was also on the quality of the enamel volume wear tests when using materials from which the removable partial denture clasps are made. Abrasion of enamel caused by dental restoration is related to the mechanical properties of the materials used. Dental ceramics or metal alloys, acting by forces, cause the formation of enamel defects, which can significantly weaken natural teeth. There are a few studies on the volume wear tests of the enamel caused by dental clasps. They do not relate to changes in retention forces that decrease as a result of the length of use. By using FEM in near future it will be possible to know the data associated with enamel damage caused by long–term use of removable partial dentures.

Keywords:

Dental clasps, removable partial dentures, wear tests, enamel, dental materials

Introduction

Dental restorations help restore natural and normal functions of the oral cavity and improve the aesthetics. Distinguishes full denture, removable partial denture, dental bridges and dental crown [1]. Each of them differs not only in the area of rehabilitation but also in the materials there are made of. Through the action of several harmful factors in the oral cavity, durable, biocompatible and corrosion resistant materials are used [2–4]. However, they differ in the mechanical properties, such as Young modulus or hardness. This affects the length of use of the dental restoration [5] as well as the impact on the remaining natural teeth [6].

The enamel to which the greatest forces are transmitted is the most exposed to damage. Although it is the hardest tissue in the body [7], it often degrades. Teeth wear is a physiological phenomenon, which is the result of the friction of opposing teeth. However, it occurs very slowly, and the convexity of the cusps are removed mainly from occlusal surfaces where the largest thickness of the enamel is present [6]. The appearance of materials with larger hardness may cause a pathological wear, so this topic is widely research by scientists.

The aim of this paper was to recognize the test method and results of enamel wear test caused by differs dental materials, especially occurring in the removable partial dentures. There are a few

literature reports dealing with the abrasion of natural enamel by dental clasps, and the available articles do not provide reliable information on the amount of volume of the wear material.

The retentive force of clasps

Dental clasps that are used in dental prosthetics are made by means of forming a metal wire or casting technique using the lost wax method. They play the role of so–called hooks holding the dental restoration in the oral cavity. There are many types of the dental clasps and their shape is selected for the situation in the oral cavity and selected restoration [8]. Dental wrought wires are made for the acrylic partial denture and they cover only one tooth surface. For metal partial dentures is possible to make wider variants of shapes of the dental clasps [9].

One–arm wrought wire clasps are built of the retentive arm, rest and minor connector. Two–Armed clasps additionally consist of stabilizing or leading arm [10]. Retentive arm through to the action of friction forces between an abutment tooth and its surface maintains the entire dental restoration in the oral cavity [9]. Materials used to create the dental clasps must have a good corrosion resistant because in the oral cavity occur aggressive environment. Mainly, stainless steel, nickel–chromium alloys, cobalt–chromium alloys or aesthetic acetal clasps are used [11, 12].

Dental removable partial denture, when is putting on or taking off in the oral cavity, is associated with the transition of the retention arm of the clasp from the tooth's undercuts through its largest convexity. Flexible properties of the material used to create dental elements allow to do not change the shapes of the clasps. However, the use of a dental prosthesis for several years may cause deformation or fatigue of the material due to acting stresses [11]. Largely it depends on the thickness of clasps and size of tooth undercuts.

In a comparative study of retentive forces after simulation 36–month using cobalt–chromium and acetal clasps, lower values of forces acetal material were demonstrated, where for metal clasps are 297.4 g and for acetal, clasps are 110.7 g [11]. Retentive forces of metal clasps decreased for each simulated time of use from 694.1 g in the initial state to 297.4 g after 36 months. Acetal clasps do not show a significant decrease of retentive forces (for thickness 1.2 mm– from 111.6 g to 110.7 g; for thickness 2.0 mm from 178.4 g to 177.5 g).

Results of research [13–16] confirm the dependence of the length of use of clasps on the deterioration of retention forces. The increase of this value was noticed in Rodrigues et. al. research, however, the explanation of this phenomenon is the fact that the clasps have been subjected to extended cold work [17].

Change of shapes dental clasps, which are used in restoration, for changes of retentive forces were checked in [18] research, where E–clasps and back–action clasps were compared. The result of tests confirms the change in properties depending on the type of clasps used, where larder retentive forces were obtained by an E–clasp. A significant reduction in forces was also noted when the samples were loaded with cyclic loads (from 13.0 N to 3.4 N for the E–clasp).

Test of removable partial denture components with fatigue tests is also possible by numerical analysis programs. Oyar et. al. used FEM to investigate stresses in gingivally approaching clasps during removing the restoration [19]. The largest value is noticeable on the retentive arm regardless

of the material used in the test. However, in models, where cobalt–chromium alloy was used, higher stress values were observed than in case of titanium and gold.

Wear of dental materials

A widely occurring phenomenon in the mouth is friction, which results in removing material from surfaces of dental restoration or natural teeth by attrition [20]. The most common types of friction are adhesive wear, where two surfaces of solids are in sliding contact under the action of forces, what result in removing small particles from the material surface. In prosthetics, many types of materials are used, which significantly differ in properties, which changes their frictional properties [21].

Prosthetic restorations in the form of removable partial dentures consist mainly of metal and acrylic teeth. There are also ceramic or composite dental crowns, which is why many researchers investigate the abrasiveness of these materials in contact with the enamel of natural teeth. The largest amount of abrasive material in the research [21] was noted for dental ceramics, which is due to the high hardness of this material. Cobalt–chromium alloy caused the largest enamel defects. The reason for this phenomenon was the increase of contact stresses beyond the elasticity limit of the enamel, initiating cracks and fatigue wear. The smallest weight losses were observed for PMMA and high–strength resin. They also showed the lowest hardness.

Increasing the amount of wear material from the surface of the sample with the lowest hardness was achieved in the research [22]. Higher hardness resulted in the formation of smaller amounts of abrasion products from the sample, increasing the amount of grated material from the opposite element at the same time. In this test, a pressure force of 41 N was used, much higher compared to the research [21] where 1N was used, which may lead to different results. The environments in which the test was performer are also different. Using artificial salvia in research [22] can cause the removal of the abraded particles from the contact point and abrasive wear of hard materials occurred to a lesser extent. The reduction in the coefficient of friction between surfaces in the environment of liquids has been confirmed in the research [23].

Ceramic restorations are widely used in prosthetics due to their biocompatibility and aesthetic appearance [24–29]. Due to the higher hardness of ceramic materials than natural enamel, the interaction of these materials is also tested. In research [30] a zirconium oxide and glass–ceramics abrasion test in artificial saliva was made. Both materials achieved a similar value of the coefficient of friction, and hard particles chipping from the surface caused wear of abrasive enamel much larger compared to Ni–Cr and Au–Pd alloys.

Enamel wear caused by clasps

For the larger edentulous areas in the oral cavity, prosthetic restorations in the form of partial dentures are made [31]. They mainly consist of denture plate, artificial teeth and metal clasps, which are the most important element that keeps the prosthesis in the oral cavity. As it has been described above, they work to a greater or lesser extent on retentive force on abutment teeth. In addition, when placing or removing the prosthesis, the brackets glide over the tooth surface. This

mechanism can cause wear of enamel, weakening the teeth and increasing the possibility of caries and reducing the retention forces that hold the prosthesis in the oral cavity [32].

The problem of abrasion of the enamel with metal clamps was known already in 1956, where Phillips and Leonard performed tests on natural teeth [33]. Two–armed clamps build of various materials were made, which were mounted to the machine making a cyclical motion. After 25,000 cycles, tooth surface images were compared with images made before the test. Only in the case of two teeth was find a loss of enamel, regardless of the used material. Slightly more recent studies (1984 year) [34] regarding the abrasion of enamel by metal clasps describe the test results after 4500 cycles. In this case, slight (less than 20 μm) tooth enamel defects were observed on the tooth surface. The SEM microscope was used for the tests. The tooth surface was marked with points that were used to compare the surface before and after the tests.

Willems et. al. in 1992 used a surface 3D laser scanner for the analysis of samples surfaces before and after the enamel wear test [35]. The use of a large number of cycles (100,000) with a small displacement amplitude (100 μm) allowed to observe a greater abrasion of materials, which facilitated the researcher's comparative analysis with other dental materials. The volume wear of both enamel (0.000632 mm^3) and stainless steel (0.000562 mm^3) was observed. The volume wear of the enamel during the friction test was also confirmed in the research [36], where a cobalt–chromium alloy. In this test, 250,000 friction cycles were performed and the surface of the sample after the test was subjected to scanning with a surface profilometer and software. The results of enamel volume wear of 0.008 mm^3 were obtained.

The change in the roughness of the natural enamel after the test of placing on and taking off clasps was confirmed in the study [37]. After performed 3,000 cycles the tooth surface was compared to that before the test. The results show a significant increase in surface roughness from approx. 0.638 μm to approx. 8.173 μm with the use of cobalt–chrome alloy clasps. The acetal clasps do not cause such a deterioration of the enamel roughness, where the values before and after the test are almost the same. The change in the value of the results in the case of Co–Cr alloy clasps confirms the occurrence of enamel wear.

Discussion

Natural teeth are loaded with many harmful factors such as chewing forces, harmful effects of microorganisms that cause caries or periodontal disease or enamel abrasion by friction mechanisms [38–43]. Prosthetic restorations can cause additional damage to the teeth. Analysis of results from literature reports confirms the effects on natural teeth of forces associated with the use of prostheses.

The clasps, which are components of the partial denture, exert pressure on the abutment teeth associated with the material properties and shape. It has been shown that the aesthetic acetal clasps generate lower loads compared to those made of metal alloys. However, these are insufficient values to properly maintain the restoration in the oral cavity [11]. In this case should be made a greater number of hooks, which can not always be fulfilled by a limited number of abutment teeth. Elements made of metal alloys are more elastic and maintain the prosthesis in a proper way, through to obtaining large values of retention forces. However, long use of the prosthesis degrades the clasps properties, which has been confirmed by numerous researchers. At the beginning of the use of restoration, the retention values of dental clasps made of cobalt–chromium alloy varied

between 6–8 N, after the test they were 2–4 N. For acetal clasps, these values were approximately 1–2 N throughout the study. It was also confirmed that different clasps shapes affect differently on abutment teeth [18]. In the case of the E–clasp the value of the retention force before the test was 13 N, and for the back–action clasp, it was 11 N. These are much higher values compared to the results presented above. This is due to the fact that in the case of previous tests, metal teeth models were used for the test. Natural teeth after extraction were used until the last test. Thus, it can be concluded that in the case of the natural environment of the oral cavity the values of retention forces are higher.

During the putting on or removal of the restoration with clasps, the metal elements glide over the surface of the abutment teeth through the largest convexity of the teeth, acting on them with retention forces. The presence of this mechanism may cause abrasion or fatigue crushing of hard enamel. Materials with higher strength properties cause abrasion wear of natural teeth. Long use of prosthetic restorations may have negative effects on the health of other teeth.

Several researchers became interested in the impact of metal clasps on the tooth surface, checking the volume wear of materials. The largest number of articles on this subject comes from the twentieth century, where the devices used for research did not allow to know the exact results. In none of the presented research, where the value of used material was announced, the reduction of retention forces of clasps was not taken into account, which may affect the test results. In the era of modern science, we have a lot of possibilities, through which it is possible to get to know the effects of the long–lasting impact of metal clasps on natural enamel. The use of FEM will allow analyzing the behavior of teeth on which different force values affect. This method is increasingly used to study biomaterials and their behavior in various parts of the human body, which is why it may be suitable for enamel abrasion tests.

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DESIGN THINKING – AS A TOOL USED IN THE DESIGN PROCESS

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Abstract:

The article is devoted to the presentation of empathy as a tool used in the process of designing products or services. In the article, empathy has been presented as an inseparable element of the whole Design Thinking process, which is based on getting to know your target audience. Another element that has been touched is the tools used, such as interviews, observations that are an inseparable element for effective understanding of the recipients'needs and their daily problems.

Keywords:
Design thinking, empathy, the design process, research methods

What is empathy?

Empathy, according to the dictionary definition, means:
1. The ability to empathize with another person's inner state;
2. Bringing somebody one's own feelings to a given situation.

In turn, K. Lampert defines empathy in the following way:
„Empathy is what happens to us when we leave our own bodies... and find ourselves either momentarily or for a longer period of time in the mind of the other. We observe reality through her eyes, feel her emotions, share in her pain" [1].
Empathy, contrary to appearances, is a very valuable tool that can be used in the process of designing products or services. Its application allows to enter the user's skin and get to know his everyday life in a significant degree. Empathy is understanding what the other person feels at the moment, thanks to that, we can find the actual solution to the observed problem or find a solution to a specific need [2].

How can empathy be used and what for?

Nowadays, the user requires from the designers not only a nice look, but also products and services that will in a appropiate way provide him with the fact that thanks to him is important or it will facilitate his functioning. For this empathy need to be, hence it should be included in the design. It is justifiable to describe a design that uses empathy here. One of the methodologies that uses

empathy to create products and services is Design Thinking. In the entire systematized process, empathy is the first stage. It's about entering our target audience's shoes, which is why we do not look at a given problem from our perspective but from the perspective of that user, i.e our client. It causes that we are able to forget about our habits and hence the design will actually be directed to the needs / problems of the user [3].

The products that were identified as innovative, began at the level of empathy. At this stage it is necessary to understand the hidden and intuitive motivations that affect product selection. In this case, it is very important that the design is aimed at the target recipient. Design is a social activity, so it must be directed to recipients. The second such important aspect is that people often choose these products which evoke positive emotions. When creating a product, it is not always possible to create something that will be one and unique and therefore it must be distinguished from a very wide range of products [4].

How the first stage of design thinking works?

The stage of empathy in Design Thinking allows to get to know our recipients despite all this, what is not so obvious and simple.For this purpose, we need to use tools that will allow us to get to know everyday life, habits that are very valuable information for us as designers. Empathy is differently called *for whom*? Why exactly?, because we get all the important information about our recipients at this stage. During this stage, we must remember about some slogans, rules:

- user is important, not me
- we enter the shoes of another person
- we should answer the question: what is important to him?
- we should understand the user's conscious and unconscious needs.

However, to do all this, some research methods should be applied. They allow to get huge amounts of information that will be the basis for success [5].

Research methods used in the first stage of design thinking

Interviews – design based on the DT methodology fastens our attention primarily on the user. According to this rule, interviews are the first method. The first type of interviews are ones with users thanks to that we achieve getting to know the needs, behaviors and everyday life of each target group. At this point it is important to define the target group – it is necessary for the conversations we lead to direct in the right direction. Contrary to appearances, this is necessary because each personalized group of people is different and a bad description of such a group can cause very big problems. This type can be used at the moment when we are at the right stage of the design process. This is a significant facilitation to focus our work direction.

The second type are interviews with specialists. In this case it is very important to know the environment in which the design process is carried out. Understanding the main principles, content and substantive base becomes key to appointing and getting to know experts from a given field. Very important is getting to know the whole environment focusing on given problems because

many significant issues could already be solved in earlier ones. Such an interview allows us to look at specific solutions from the professionals and appropriate criticism or good advice can help the project team work on the solution. Experts already have their observations and they could work on the given solution in their carrier so it is necessary to get to know their experience. This type of interviews is helpful to quickly understand the given problem we are working on [5].

Observations – this method allows to get the difference between what people say on interviews and what they do. In spite of everything, people say one thing and they do something else. It is caused by a lack of trust because the person with whom we conduct interviews not always want to tell us about all things. It is very important to observe the actual behaviour of people in everyday life, where they behave naturally. During this method, it is very significant to pay attention to their behaviour, gesticulation and ways of doing activities related to our subject. This method allows us to make sure that the information, which has been earlier presented, is authentic and allows s to better get to know the target group [6].

Cognitive experiences – are a method called participative observation. Such observation is the actual entering the user's shoes. It is based on the fact that people working on the solution should feel the real problems of target groups, as it is for example with disabled people. It's hard to imagine certain behaviours and problems with which target groups must daily deal and to which they are addicted, hence as designers we need to understand the most important problems or needs.

The analogies – when using this tool, it is necessary to look from many perspectives and places for the environment in which we work. It is important not to focus only on one place of observation, but to see how a person behaves in a public place, while working and to get to know many other factors that affect his behavior or choices. The using of this method complets missing elements for earlier methods [4].

The methods described above are the most frequently used, however, to get to know our target recipient, we can use several methods that will allow us to get even more information about our future client. Used secondary methods are:

Photo diaries and essays – these are the methods in which the people – our recipients– have to evereyday write on a piece of paper events that made them curious or take a picture. This procedure allows to check what is important for that person, what he is paying attention to or what is guided.

Travel map – during the whole day the user creates a map on which he marks the places he was in and creates a notes, where he describes his impressions. It is worth to find here information about his feelings and how they were received or many others insights that we consider appropriate at the moment [5].

Cards and pictures – this method is based on the fact that we create cards with illustrations or information that the recipient must arrange in order from the most to the least important. The second issue is that how a person reacts to given photos, thanks to which we are able to specify more precisely, e.g. what color is perceived better, what is worse and many other information that can decide about the product's success [5].

In summary, empathy is an intrinsic element of design based on the Design Thinking methodology. Acting in accordance with it, we base all the solutions on the experience associated with getting to know our target group. Thanks to that the risk, that the product will not go to a predetermined group, it is relatively small. Empathy allows us to get acquainted with recipients

and create a solution desired by them.

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ELEMENTARINESS OF CONTEMPORARY SACRED ARCHITECTURE

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Abstract:

The article presents a research topic the author is preparing a research paper on. The following study addresses the issues resulting from the subject area of the scientific conference, i.e. subject matter, method and motivations behind the choice of the subject matter.
Elementariness is a design idea, i.e. a way of organizing space, a thought leading to simplicity and the basics.
The method of conducting research manifests itself in two aspects. The first one concerns the analysis of existing structures, while the second encompasses experiences from the author's own design practice.
The primary reason for the undertaken scientific activities is to demonstrate the importance of elementariness in contemporary sacred architecture. The collation, comparison and systematization of the most valuable realizations and design projects will serve to find and present the positive features of this kind of architecture. We strive for beauty and perfection through simplicity.

Keywords:

elementariness, contemporary sacred architecture

Subject matter

Sacred buildings constructed today are characterized by the lack of a concrete and shared idea. We observe spatial and aesthetic chaos. Some of the design projects and realizations imitate old styles, while others try to slightly modify them. However, the contemporary lifestyle is completely different. Public spaces have acquired a new dimension, the characteristics of transport and the scale of structures have changed. The development of technology has made it possible to use solutions hitherto unreal. As a response to these changes, we see a clearly emerging tendency in shaping contemporary sacred architecture, which in its general expression can be described as elementariness. The feature in question primarily determines the simplicity of the expression of forms, but also positively affects the spatial coherence of different types of structures. It is not only large buildings, such as churches and monasteries, but also chapels and tombs that share a unified idea expressing a contemporary approach to shaping space. The realisation of the statement that "…the evolution of culture marches with the elimination of ornament from useful objects" is clearly set out here [1]. The elementariness of the forms and meanings of contemporary sacred architecture

corresponds very well with the general principles of religion that speak of modesty, simplicity and openness. One can say that in this situation architecture addresses the recipient, expressing the idea of its destiny.

The subject matter concerns primarily new objects, however, the area of interest also covers redeveloped buildings, or design objectives in relation to existing religious structures, including monuments. The functional approach also becomes important, where we can talk either about buildings dedicated to one function or structures in which there are also accompanying zones in addition to the guiding sacral character.

Method

The method of conducting research manifests itself in two aspects. The first, leading one, concerns the analysis of existing structures, while the second encompasses experiences from the author's own design practice.

Direct contact with buildings allows the author to analyze the most important aspects, i.e. the form, material, function or relationship with the environment. Such possibilities are offered by scientific and research trips, constituting one of the most important methods of work. The acquired material forms the basis for work based on other activities that mainly consist in systematizing and comparing objects. The literature on the subject is an extremely important aspect of this research paper. A significant role is also played by materials that come directly from the websites of the authors of the objects under study. The statements of the users of the buildings also give a large amount of information serving to obtain answers to the questions posed in the research paper. The conducted works are primarily aimed at reading and ordering design ideas accompanying these types of structures, as well as searching for and emphasizing values and the most positive features.

Elementariness is a design idea, i.e. a way of organizing space, thought leading to simplicity and the basics. It applies to architecture of all types of functions, as well as to objects of various scale. In this context, we can talk about the Basilica of the Holy Trinity in Fatima designed by Alexandros Tombazis and St. Henry's Ecumenical Art Chapel, designed by Sanaksenaho Architects. Although the buildings in question share a huge difference in cubic capacity, both express a similar idea guided by simplicity and elegance. They grow out of the same idea – elementariness. The former was shaped on the round plan, at the same time adding the second form that axially cuts the basic body of the building. The elevation that is pure in expression and the elegant and subdued material give the structure a sublime and monumental character, and at the same time correspond well with the environment of such a great religious significance.

St. Henry's Ecumenical Art Chapel is an amazing game of light. The wooden interior is precisely illuminated in one and the most important place – the altar zone. The building located in Turku (Finland) exudes mystery, resulting from the use of the simplest treatments and the role of daylight, that is, as Le Corbusier wrote: "Architecture is the masterly, correct and magnificent play of masses brought together in light" [2]. The clarity of the form of the building means that the exterior and interior create a unified design idea, which to a greater extent determines the elementary nature of the chapel.

Figure 1. The Basilica of the Holy Trinity, architect Alexandros Tombazis
Retrieved from: https://pt.wikipedia.org/wiki/Alexandros_Tombazis#/media/File:1_Alexandros_Tombazis_Bas%C3%ADlica_da_Sant%C3%ADssima_Trindade_F%C3%A1tima_img_8750_1.jpg on: 30.08.2018

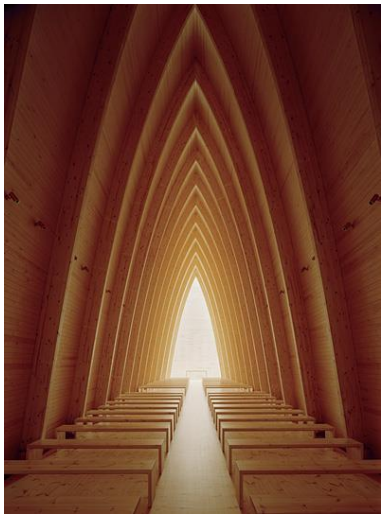

Figure 2. St Henry's Ecumenical Art Chapel, architects: Sanaksenaho Architects
Retrieved from: http://www.kolumbus.fi/sanaksenaho/ on: 30.08.2018

The author's own design practice in tasks related to this research topic constitutes a very important research method. The author of the paper also broadens his experience through the development of project designs of contemporary sacred architecture or objectives related to it directly. The buildings in which the function is complex, i.e. where, for example, a commercial zone is additionally introduced, are also very significant in the conducted research. It is very important in such a situation to determine the supremacy of sacred architecture, which, on the other hand, is able to adequately separate spaces of different purposes. The funeral chapel, café and bookshop is a design project of a multifunctional building at the Shrine of Our Lady of Consolation in Czerwińsk nad Wisłą – the Salesians. The simple form fills the space within the existing wall, referring to the structure of the object which, according to archival records, was located here earlier. The funeral chapel opens up to the square in front of the basilica on the south side. The front is characterized by three gateways that form a framework focusing on the Cross located at the entrance to the building. The modern portal emphasizes the sacral character of the object and refers to the same element in the neighbouring monument. The café and bookshop zones are served by

cloisters from the north–east side and an additional entrance from the west. A very important design objective of a multifunctional building is to preserve the spatial coherence of the interior with the exterior, primarily through the use of façade material in the interiors and taking cognisance of the existing wall that passes through the body of the building.

Figure 3. Funeral chapel, café and bookshop – view from the north–eastern side, architect: Marcin Głuchowski
Source: own materials

Figure 4. Funeral chapel, café and bookshop – view from the south, architect: Marcin Głuchowski
Source: own materials

Motivations behind the choice of the subject matter

Contemporary architecture is still an unattractive and unpopular topic for a large part of society. This observation also applies to sacred buildings. People who decide about the buildings being erected very often do not realize the importance of decisions they make. Steps taken at the stage of investor objectives or design works will have their effects for many years. Repeating old patterns, inadequate to modern times, sets back the architectural achievements developed by society. It also shows lack of professional confidence. The primary reason for the undertaken scientific activities is to show the importance of elementariness in contemporary sacred architecture. The collation, comparison and systematization of the most valuable realizations and design projects will serve to

find and present the positive features of this kind of architecture. We strive for beauty and perfection through simplicity. The research paper referred to in this article will certainly constitute a didactic aid for architects in the design of such structures. It can also have educational value for society, and in particular for decision–makers in sacred architecture. "Good original architecture depends just as much on an understanding public as on its creators" [3], and therefore improving the quality of contemporary sacred architecture primarily through building aesthetic awareness is one of the most important motivations behind the undertaken scientific activities.

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THE CAUSES, THE EFFECTS AND THE CONTROL OF POLLUTANTS OFTHE BALTIC SEA AREA

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Abstract:

The Baltic Sea plays a very important role in the live of the societies of some European countries. A relatively large amounts of plants and animals live in this reservoir. It is also, along with its beaches and the quay, a place of resting for many tourists. The Baltic Sea is an element of nature, which should be especially taken care of. Therefore, monitoring of the Baltic Sea must be carried out carefully and the pollutants reduction plans should be implemented. The aim of this work is a characterisation of the Baltic Sea pollutions and ways of prevent degradation of its natural environment, and also familiarization with the scope of control of pollutants in the Baltic Sea.

Keywords:

the Baltic Sea, pollutants, environmental monitoring

Introduction

The Baltic Sea is a shelf, inland water reservoir. Its area is approximately of 415 266 km^2, the average depth is approximately of 55 m and the volume is approximately of 21 721 km^3. It is one of the shallowest and the smallest seas on the Earth. The Baltic Sea is also the youngest sea of the Atlantic Ocean. The morphology of the Baltic Sea bottom is very diverse and it is conditioned mainly by the deep geological structure, tectonics and the activity of marine factors [1,2].

The Baltic Sea is surrounded by Denmark, Sweden, Finland, Estonia, Lithuania, Latvia, Russia, Poland and Germany. Its catchment also includes Norway, the Czech Republic and Slovakia. There are also many islands in the Baltic Sea (Fyn, Zealand, Lolland, Falster , Bornholm, Rügen, Gotland, Öland, Saaremaa, Hiuma, Usedom, Wolin, Åland Islands) [3].

The flora and fauna of the Baltic Sea are: green, brown and red algae, tapeworms, European eels, salmon, gray and ringed seals, porpoise, cod, herring, flatfish (flounder, plaice), sprats, mackerels, balsams, mussels (cockleshells, sandstones), crustaceans (shrimps, guts, giant lances, cavities). In addition, there are many raw materials in the Baltic Sea that can be used in industry and construction. At the bottom are gravels and building sands, glass sands, clays, silts and sludges. There are also minerals, such as zirconium and rutile. Under the seabed there are deposits of petroleum, natural gas, rock salt and potassium–magnesium salts [4].

Sources and effects of the pollutants in the Baltic Sea

The Baltic Sea is very vulnerable to pollutants. There is only a narrow isthmus between the Baltic Sea and salt ocean water. Because of that there are a very slow exchange of waters. Therefore, when pollutants are introduced to the Baltic Sea, they remain there longer than in other sea areas. They accumulate in water, soil and living organisms. They decompose very slowly, because of the low water temperature [2, 3].

About 150 million people in over 50 major cities live around of the Baltic Sea. It is estimated that the amount of pollutants introduced by individual countries into the Baltic Sea waters is about 1.2 million tons per year. It is a dangerously high number. This is due, among other things, to lively trade (there are up to 70 000 vessels that flow annually through the straits, a fleet fishing throughout the year and even 1000 ports and harbors). The poor sanitary condition of some beaches and bathing areas on the Polish coast is also well–known. Recently, information about toxic algae blooms and the necessity of periodic closing of popular bathing beaches is becoming more frequent [2, 5–7].

Petroleum products are one of the most dangerous contaminants of the Baltic Sea waters. Fortunately, drastic pollutions of the environment with these substances are very rare. In any case, the most contaminated are ports and shipbuilding basins. Unfortunately, we can also often encounter illegal discharges of oily water from ships, which also worsens the condition of the Baltic Sea [2, 8].

Pesticides are another type of pollutant. We receive sewages containing pesticides used in agriculture to control weeds and plant pests. That sewages finally reach to the Baltic Sea. These compounds decompose very slowly, especially in the Baltic Sea, which has a low temperature. The worst is that they accumulate in organisms (at first in planktonic plants). Then, the aforementioned compounds get into larger organisms, where they are still accumulated. They get through the entire food chain. In each next organism their amount increases, this is so–called bioaccumulation. The last element of this chain are people who eat salmon or herring. Pesticides that are in the food products also harm us [2].

Municipal and industrial pollutants also contain nitrogen and phosphorus. Phosphates and nitrates are the basic nutrients (biogenic) for plants [9–11].

The natural source of phosphorus is the geological subsoil. The processes of weathering and erosion cause that it is released from this ground. Plants absorb phosphorus from water, thus introducing it into circulation. Some of the phosphorus fall out of circulation and get into the sediments, often creating rich phosphate deposits. It is estimated that about 20 million tons of phosphorus get to the oceans annually and 2 million tons come from human activities. This is the surplus that violates the existing balance of this biogen [9–11].

Nitrogen is the second important biogen. Ocean waters contain about 22 billion tons of nitrogen and 95 % occurs nitrogen compounds. The remaining 5 % is organic nitrogen, nitrites, nitrates and ammonia. According to some sources, 78 million tons of nitrogen are released into the oceans annually, 76 % of which come from the atmosphere. About 9 million tons are deposited in sediments [9–11].

These two biogens, introduced into waters with sewage, cause their fertilization (also called eutrophication). In the fertilized waters there are growth of phytoplankton (cyanobacteria, algae), which leads to their blooms. Cyanobacteria cause turbidity of water in the surface layer, which limits the development of shallow vegetation due to lack of light. Cyanobacteria produce poisonous substances that kill animal organisms (mass fouling of seals). These substances also pose a threat to human health, when they bathing. They can cause skin irritation and illness and poisoning. After the bloom, they quickly die and sink to the bottom. With sufficient oxygen supply, this biomass decomposes and transforms into inorganic compounds, which again become the source of food for these organisms. An organic mass growth and the lack of adequate amounts of oxygen needed for its rapid decomposition leads to the deposition of this mass on the bottom. Finally, other organisms die, because they cannot tolerate the low oxygen concentration in water. At the bottom of the water reservoirs, a bottom sediment forms in the form of silt. In the absence of oxygen anaerobic processes take place and poisonous gases – hydrogen sulphide or methane – are released. The sediment accumulates more and more, the reservoir becomes shallow and transforms into a silted pond. Finally, as a result of progressive eutrophication, a swamp/peatbog is created. In natural conditions, eutrophication is very slow – hundreds, thousands of years. The emission of fertile sewage or runoff from fertilized fields to ponds, lakes and other water reservoirs accelerate this process rapidly which is a highly undesirable and harmful phenomenon. It should be noted that the Baltic Sea is particularly susceptible to eutrophication processes [10–15].

A huge problem is also poisonous warfare agents and ammunition, which usually lie in the depths of the Baltic Sea. They were sunk after the First and Second World Wars. In the 1950s and 1960s there were accidents related with the mustard agent. Nowadays, chemical ammunition is caught by fishermen and then thrown back into the sea [16].

Ways of preventing degradation of the Baltic natural environment

If we want the coastal waters of the Baltic Sea to be clean, it should be ensured that the waters flowing into it are not contaminated. Therefore, all methods of purifying groundwater from the Baltic Sea basin will be one of the ways to prevent pollution [17].

Water purifiers are used to remove harmful impurities from the water. Depending on the type of wastewater, there are three methods of purification. One of them is the mechanical method, i.e. sieving through sieves or grates to remove impurities from the water, used in the case of municipal sewage [17–19].

For the treatment of wastewater, which contain aggressive chemicals, we can use other, equally aggressive substances to dispose of those. Wastewater contains many cyanides. They are one of the most violent poisons for vertebrates. Purification consists in oxidizing cyanides with chlorine or sodium hypochlorite until obtaining carbon dioxide and free nitrogen or ammonia. This process is carried out in a very basic environment (pH~11 is optimal). Strongly alkaline wastewater must be neutralized with sulfuric acid. Heavy metals (lead, cadmium, zinc, copper) can be precipitated from wastewater, that is, they can be converted into sparingly soluble compounds [5, 14].

The third method is a biological method. Biological treatment consists in creating the best conditions for bacteria, protozoa and fungi. They reproduce and develop, and at the same time they

break down organic matter, contained in wastewater, into inorganic substances: carbon dioxide, water, nitrates and phosphates. Purified water could be considered as purified and released into the lake or river. We cannot do it, because it is still fertile. It would inevitably cause bulk algal blooms. Therefore, we also need to clean the water from dangerous excess of mineral substances. For example, we can let it in successively through a series of shallow rates. The blooms will develop in the joints, but in each next weaker and weaker. The water that will come out of the last pond will be really clean [17, 18].

The monitoring of the Baltic Sea

Nowadays, the Baltic Sea is assessed in 5–year periods, based on research carried out by the States Parties of the Helsinki Convention as part of agreed monitoring programs:

1. The Open Sea Baltic Monitoring Program implemented since 1979.
2. The Program of Monitoring of the Baltic Sea Coastal Area since 1984.
3. COMBINE program integrating the previous two, implemented in 1998.

The aim of the Baltic Sea monitoring is to learn the direction of the intensity and causes of long–term changes taking place in the Baltic Sea ecosystem. The scope of the Open Baltic Sea Monitoring Program includes: hydrological, hydrochemical and ecotoxicological measurements, including obligatory tests: temperature, salinity, density, oxygen content, nitrogen compounds, phosphorus, heavy metals, chlorinated hydrocarbons, biological studies of plankton and benthos. The Baltic Sea Coastal Area Monitoring Program includes obligatory tests: temperature, salinity, oxygen content, transparency, nitrogen compounds, phosphorus and silicon, phytoplankton, chlorophyll, benthos, heavy metals, chlorinated hydrocarbons and microbiological tests [20–24].

However, attempts to stop the biological decline of the Baltic Sea began much earlier and were initially caused mainly by concern for the good of fishing. The first agreements on the Baltic fisheries were made at the end of the 19th century. It was a convention signed by Denmark and Sweden in 1899, and this convention concerned the regulation of fisheries in the waters adjacent to these countries. In later years, many similar agreements were concluded on the protection of individual fish species against overfishing and regulation of legal issues related to the exploitation of living resources of the Baltic Sea. However, none of the agreements was in force in the entire Baltic Sea area, it was not signed by all the states and it did not entirely concern marine protection of the ecological world from destruction [25].

Nowadays, such a convention already exists. On the initiative of Poland in 1973, a diplomatic conference of the Baltic states was held in Gdańsk. The meeting was successful, the Convention on Fisheries and Protection of Living Resources of the Baltic Sea was adopted and signed. This convention, after ratification by all concerned countries, is continued to apply throughout the Baltic Sea, with the exception of internal waters. The adoption and ratification of the Gdańsk Convention opened the way for further international agreements regarding the protection of the Baltic marine environment from all kinds of pollutants. In 1974 in Helsinki, a new diplomatic conference of the Baltic States was convened. This conference was also successful. A convention on the protection of the marine environment of the Baltic Sea was adopted there [20].

This convention deals with the ways of securing the Baltic Sea against pollutants coming from all possible sources. This is very important, because the current international agreements on the protection of the marine environment regulated only the issue of discharge of petroleum and its derivatives into the sea. Under the provisions of the Helsinki Convention, contracting states are required to take appropriate measures to minimize pollution of the Baltic Sea from land. It was agreed that the removal of larger amounts of any harmful substances from the land to the sea would require special permission from the national authorities. All concerned countries will develop and adopt common criteria for issuing such permits. States of the Convention are obliged to treat municipal and industrial sewage in such a way that by their removal to the Baltic Sea there will be no significant decrease in the oxygen content in its waters. These wastewater should also not impair the hygienic conditions of the sea, nor pose an epidemiological threat [20, 25].

This convention is also connected with the prevention of sea pollution from ships. This is mainly about petroleum and oils. Thus, in the entire area of the Baltic Sea is forbidden to remove oils to water from all tankers of contracting states and other vessels. A similar prohibition applies to a number of other harmful substances (each ship carrying substances which are in the text of the Convention should keep a log of loading records and make annotations on how to remove their waste). The sewage from marine sanitary facilities has to be collected on ships in storage tanks and then removed to port reception facilities [20, 25].

However, the Convention on the protection of the marine environment of the Baltic Sea area, 1992, allowed an exception from the strict adherence to these provisions – they did not apply in the case of ensuring the safety of a ship or saving life at sea. The protection of nature of the Baltic Sea was a new obligation resulting from the signing of the 1992 Helsinki Convention. Until the nineties, this issue was not discussed, mainly because scientists did not raise these issues. It was probably the conviction that the Baltic Sea was not very attractive [21].

The 1992 Helsinki Convention raised this issue to the level of obligations of the Member States. The Baltic System of Protected Areas was established, which covers 62 regions in the Baltic Sea. Poland has proposed the simplest possible protection system, i.e. extending existing coastal national and landscape parks to coastal waters. There are still ongoing debates on extending the system to areas located on the open sea [21].

In addition to the creation of underwater reserves, other forms of nature protection are introduced, such as protection of the shore belt (100300 m wide from the water line towards the land and towards the sea), protection of rare or disappearing organisms (e.g. wild salmon, porpoise) and endangered habitat (e.g. underwater vegetation meadows) [26].

In some cases, protective activities lead to a rebirth of the population, but unfortunately conflicts with other sea users occur. An example are the cormorants at the Vistula Lagoon, which effectively compete in fishing with fishermen. Serious difficulties are also noted in Finland, where seals eat large amounts of fish from fishing nets. In both cases, it is considered to abolish the protection of these animals [26].

However, the high concentration of hazardous substances in the Baltic Sea environment is still a cause for concern, as reflected in the latest 'Fourth Periodic Assessment of the Marine Environment in the Baltic Sea Region'. Having achieved the goal of 50% reduction of pollution, the

Helsinki Commission sets another one, which will be 'the complete elimination of discharges and emissions of selected substances until 2020' [26].

Conclusions

The Baltic Sea is a dynamic ecosystem with great natural changes since the last glaciation, as well as large anthropogenic changes in the last 50 years. It is also a comprehensive network of interdependencies between physical, chemical and biological factors. Therefore, it is very dirty and sensitive to pollutants. Thanks to the fact that it is a sea whose waters belong to several countries, there is control from many sides and conventions are created to protect these important natural resources. The condition of the Baltic Sea improves and supervisors fulfill their tasks. There are also programs to make the public aware of how important this problem is, to what extent it affects everyone and how pollution can be prevented. Monitoring of the Baltic Sea is one of the points of the trip to the Gdynia aquarium, exemplary qualitative and quantitative studies of coastal water are carried out by the participants themselves.

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HYDROGEN STORAGE IN SOLID PHASE – ALTERNATIVE, INNOVATION OR THE PAST?

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Abstract:

Hydrogen is used as an alternative source of energy. This element has a large potential however, its use may be dangerous. H_2 is highly explosive, therefore, it is important to its proper storage. Currently, three ways of storing hydrogen are known and used: in the gas, liquid and solid phase. In the case of the first two methods, very high pressures (up to 800 bar) are used, and for liquid phase techniques very low temperatures (20 K), necessary to condense H_2 – which generates high costs. An alternative to these two techniques is solid phase storage. It is a new and constantly developed technique. Hydrogen in this case reacts with solids or is ab– or adsorbed on their surface. High pressures and low temperatures are not required in this case, which makes this solution the safest method. There are many types of solids used for hydrogen storage, however, very promising group are magnesium hydrides, thanks to which is it possible to store significant amounts of hydrogen up to 150 kg/m^3.

Keywords:

Alternative energy sources, hydrogen storage, storage in solid phase, magnesium hydrides

Introduction

Currently, the world is constantly looking for alternative energy sources that will effectively replace oil or natural gas, which resources are gradually running out [1–3]. One of these sources is hydrogen. It is widely accepted to say that hydrogen reserves on Earth are large enough, it can be said that this element is an inexhaustible resource [4]. During combustion in oxygen, hydrogen releases large amounts of energy, which is why it can be an ideal source of energy in home and industrial applications, but also in transport or in mobile systems. A very big advantage of hydrogen is its ecological character – during the combustion process only water is released from the reaction. The calorific value of hydrogen is high and amounts to 120 MJ/kg – for coal it is 25 MJ/kg, and for gasoline it is 47 MJ/kg. Hydrogen, unfortunately, is characterized by a small degree of energy density – about 9 MJ/l, so it must be compressed or condensed under high pressure (from about 150 to even 800 bar), which may involve the danger of explosion or unsealing [2–4].

The energy from hydrogen can be derived in two ways: as a result of the combustion reaction as well as by using appropriate fuel cells. However, in order to be able to obtain energy from

hydrogen it should be stored in a correct and effective way. Hydrogen is a very small molecule that is able to diffuse through porous materials, rubber, and at elevated temperatures even through steel. It easily leaks through even minimal gaps or leaks and cracks. Hydrogen is very light so its diffusion in the air is very fast, much faster than natural gas or gasoline. That is why it is very important to properly store hydrogen in various physical states [5–9].

Currently used and important are several hydrogen storage methods. Hydrogen can be stored in three ways: in the gas, liquid and solid phases [4, 8–12]. The first two methods have been well–known and developed for years. They have many advantages but also several disadvantages. These techniques are still considered to be quite dangerous – due to high hydrogen storage pressures. Another disadvantage is the relatively high material costs, especially for liquid hydrogen storage, because it is necessary to use very low temperatures (20 K) necessary to condense hydrogen [4, 9, 10]. The alternative and the latest solution is the storage of hydrogen in the solid phase. This is possible due to the adsorption, absorption or chemical reaction of hydrogen and solids. Hydrogen can be stored in physical metal hydrides (adsorption and absorption) and in chemical hydrides (formed as a result of a chemical reaction), as well as in carbon materials [13–15]. The use of solid materials in hydrogen storage vessels contributes to the safety of this process. Hydrogen is so strongly bound to a solid material that even during a leak, the gas slows down considerably, eliminating the risk of explosion. Therefore, it is safe to say that this method, thanks to its innovativeness, is and will be the technique of the future. There are many solids that have good hydrogen storage properties, e.g. nickel or chromium alloys, palladium, high porous carbonaceous materials or hydrobromides. However, in many respects, it is magnesium and its compounds that are the most promising materials in terms of applications as hydrogen storage. The main advantages of this type of compounds is their high ability to absorb hydrogen (up to 7.6 % by weight in the case of MgH_2) and the reversibility of hydrogen sorption reactions [8, 9, 11, 12, 15–19].

Ways of hydrogen storage – advantages and disadvantages

As previously mentioned, there are three basic ways to store hydrogen: in the gas, liquid and solid phases. In any case, other techniques for storing, compressing or hydrogen condensing are used. Various hydrogen storage vessels are used. Each of the techniques aims at the most effective hydrogen storage, thanks to which it will be possible to obtain as much energy as possible [12, 18].

Hydrogen storage in the gas phase

Hydrogen is characterized by high calorific value with low energy density – therefore, when using it as a source of energy in gas form, it is necessary to compress it. This treatment is necessary to obtain a vessel with a sufficiently large mass of stored hydrogen. This process involves a large amount of energy that needs to be supplied from outside. Unfortunately, the low density of hydrogen contributes to the fact that even under high pressure, a small amount of useful energy is accumulated – which directly affects the use of large volume hydrogen containers and increase storage costs. Hydrogen gas is stored at a temperature of about 298 K – in the pressure range of 150 to 800 bar. The pressure depends primarily on the intended use of the container. For example, for mobile systems that do not require high power, the lowest pressure values are used, but with the use of a container in buses or cars, the pressure increases to around 350 bar. In stationary applications,

pressures reach up to 800 bar. Stationary containers are mainly made of steel, however, when used in mobile applications, weight is very important, which is why containers are much lighter than steel. They are made primarily of composites based on lightweight plastics. Thanks to that, it is possible to reduce the weight by up to 50–75%. The use of such high pressures is still a psychological barrier in the aspects of safe container use, which is obviously due to the high flammability and explosiveness of hydrogen, which may occur in the event of improper storage [6, 13, 20].

Hydrogen storage in liquid phase

The introduction of hydrogen from the gas to liquid phase (condensation) increases the hydrogen energy density. The condensation process is unfortunately much more expensive than compression, because it involves a significant increase in energy expenditure – it is estimated that the energy required to condense hydrogen is 30 – 40 % of the energy value from compression [21]. As a result, the efficiency of the process is low. An additional problem is that liquid hydrogen must be stored at a very low temperature (about 20 K), which obviously increases material costs. Such containers should be constantly cooled and thermally insulated from the environment. The most commonly used coolant for this purpose is liquid nitrogen. Liquid hydrogen storage containers can also not be used in applications where hydrogen is not collected continuously – because it involves hydrogen losses due to evaporation. However storage of hydrogen in the liquid phase allows to obtain a much higher mass and volume density of hydrogen, than in the case of storage in the gas phase. The advantage of such containers is the fact that less fuel is lost – about 5–25 % less hydrogen is able to "escape" from the container when it is in the liquid phase. Currently, both stationary and mobile hydrogen containers are used in the industry. Stationary tanks usually have a cylindrical shape, are equipped with appropriately selected containers composed of two vessels isolated from each other (internal and external vessels) – these containers are characterized by a high diameter to length ratio. Mobile tanks are very similar to stationary ones, however due to their use in motor vehicles they must be characterized by greater compactness and adequate equipment. In order to minimize fuel losses to the level below 1 %, mobile containers are often covered with a special insulating foil (from 200 to 300 layers). Despite the many advantages of liquid hydrogen tanks, they are still not very economical. The cost–effectiveness of this hydrogen storage method depends mainly on the capacity and weight of the container, but also on the material that builds and insulates the storage. From an economic point of view, only large–capacity tanks are profitable [4, 20, 21].

Hydrogen storage in the solid phase

Hydrogen can be stored in physical metal hydrides (adsorption and absorption) and in chemical hydrides (formed as a result of a chemical reaction), as well as in carbon materials [13–15]. In the case of physical metal hydrides, hydrogen may adsorb on the surface of such alloys as eg nickel ($LaNi_5$) or chromium ($ZrCr_2$) alloys or absorb in powder materials – these are mainly magnesium compounds Mg_2MH_x (where M is: Fe, Co, Ni) or Mg_7TMH_y (where TM is: Ti, V, Nb) [11]. Magnesium and its compounds are the most promising materials in terms of applications as hydrogen storage. The main advantages of this type of compounds are their high hydrogen

absorption capacity (up to 7.6 % by weight in the case of MgH_2) and the reversibility of the hydrogen sorption reaction. In spite of the fact that magnesium hydride has the highest hydrogen absorption capacity, it is characterized by a slow absorption and hydrogen liberation kinetics as well as a high H_2 release (673 K), which is why ternary magnesium hydride is more popular and used. It is, for example, compound belonging to the group Mg_2MH_x – Mg_2FeH_6. This compound is characterized by a cubic crystal structure of the K2PtCl6 type, in which octahedral FeH_6 anions are surrounded by a cubic crystal lattice Mg (Figure1) [8, 16–19, 22–25]. This ternary hydride is characterized by the highest, among all known hydrogen compounds, hydrogen volume content of 150 kg/m3 and hydrogen mass content of 5,46 %, which makes it one of the most studied compounds in the aspect of hydrogen storage [26].

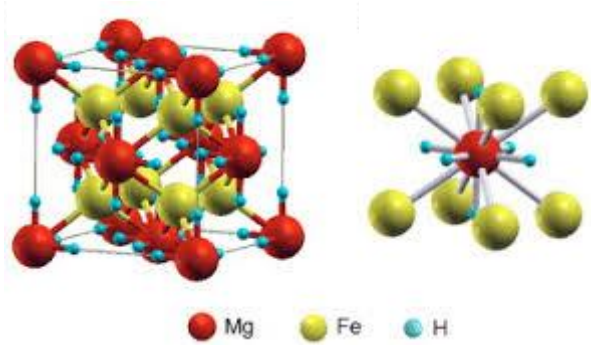

Figure. 1. Crystal structure Mg_2FeH_6 [26].

During the filling container with the solid by hydrogen, thermal energy is released, which is then usually lost. In order to recover hydrogen from the container, heat should be provided in the same way. The rate of hydrogen evolution from the tank depends on the amount of heat supplied. The current technology of physical metal hydrides, unfortunately, does not allow storage of a higher hydrogen content than 5 % of the tank's weight. In practice, this means that for a given tank to be profitable it is necessary to use a fuel cell with very high efficiency – which generates high costs [15–19].

Another of the aforementioned ways of storing hydrogen in solids is to store it in the form of chemical compounds (chemical hydrides) that are a result of chemical reactions. Thanks to this, it is possible to accumulate much more hydrogen than in the case of metal hydrides. The process of hydrogen release from such compounds is mainly due to the action of water or alcohols. An example of chemical hydrides that has already found industrial application is borohydride ($NaBH_4$). The release of hydrogen takes place as a result of an exothermic hydrolysis reaction (at room temperature). The greatest advantages of the use of chemical hydrides include the high capacity of stored hydrogen, the disadvantage being the irreversibility of the reaction. The last of the ways of storing hydrogen in bodies has been storing it in carbon materials. They are mainly highly porous materials, characterized by a large specific surface area, such as graphite, active carbon nanotubes and fullerenes. This method does not have a wider industrial application, however, many studies and experiments are still carried out in this area [8, 9, 17, 19].

Conclusion

Currently, hydrogen storage technologies are developing rapidly, but these technologies are still quite expensive and do not cause widespread trust, which is why every detail that can reduce the cost of hydrogen storage and increase the safety of such containers is important. The answer to this is certainly hydrogen storage in the solid phase. This technology use a number of physical and chemical phenomena thanks to which hydrogen can be stored in a safe and effective way. This technique is still being researched, developed and refined, but now it has high hopes.

After analyzing the advantages and disadvantages of all hydrogen storage methods, it is possible to easily answer the questions in the title of the article:

- Is this technology an alternative to two commonly used methods of hydrogen storage (in gas and liquid phase) – absolutely it is. Thanks to this method, other solutions are provided, thanks to which you can also obtain energy from hydrogen.
- Is this technique innovative – of course it is. The proposed solutions, which are already quite numerous and are constantly increasing, contribute to the development of this area of science and technology. They cause hydrogen stores that are being created to be characterized by increased safety, and the amount of energy that can be acquired is constantly increasing.
- Is this method belongs to the past – no it is not. Increasingly, we hear about the use of hydrogen storage in the solid phase in industry and automotive. This technique is and will be improved for several years and it is possible that in the future it will become a precursor in the field of hydrogen storage.

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PROCESSING CAPACITY AND CHARACTERISTICS OF CONVENTIONAL AND ORGANIC COURGETTES (*CUCURBITA PEPO L.*)

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Abstract:

In this paper characteristic of *Cucurbitaceae* vegetable (courgette) was reviewed based on currently available literature. Despite courgette is a commonly used vegetable, it is underestimated on the market. The interest in its cultivation is growing recently in European countries, including the organic farming sector. Courgette, as other organic vegetables contain typically higher level of biologically active substances in comparison to conventional ones. Processing possibilities depends on the time of fruits harvest and their physical properties (size, shape). As a result of this characteristic, it can be said that organic and conventional courgette can be widely used for processing, because of an increased production and good physical–chemical properties.

Keywords:
Cucurbitaceae pepo., courgette, organic, vegetable preserves

Introduction: courgette and cultivation system

Cucurbitaceae family includes pumpkin, watermelon, cucumber and luffa vegetables. Nowadays about 80 species of this family is cultivated around the world, with the most diverse cucurbits' shapes and colours are growing in tropical and subtropical areas of South Asia, West Africa and Madagascar [1]. Courgette, also known as zucchini (*Cucurbita pepo* L.) is a botanical variety of pumpkin and belongs to *Cucurbita* (squash) genus, having a reputation of the most important and original due to diverse shapes and fruit sizes. The terms zucchini, courgette, marrow, summer squash or young pumpkin are used interchangeably in scientific literature [2] for one botanical variety of pumpkin (*Cucurbita pepo* L.). It is an annual plant with false berry set together with a flower bed, forming the cover layer of the fruit. Edible parts are all young fruit or fleshy pericarp of physiologically mature fruit. The skin of the fruit is thin, initially delicate and shiny, coloured from yellow to dark green, depending on the variety. Among varieties cultivated in Poland dominates a green fruit colour. Physiologically ripe fruit have usually a length of up to 50 cm and a weight of up to 20 kg [3].

The market for all cucurbit species is still growing in Europe, with three main producers of Italy, Spain and Poland [2–4]. Furthermore, alongside conventional field production, the soilless cultivation of courgette is tested as well in the Mediterranean greenhouses [5]. Since, the FAO's databases do not provide information about production of courgette separately, data for whole *Cucurbita* genus can be reviewed only. Statistics from 1999 show that the highest production of cucurbits was in India and China (around 3 mln tonnes annually) and in Ukraine (around 1 mln tonnes annually) [6]. The latest statistics reveal that courgette production increased slowelly in Europe from 1.3 mln tonnes in 2015 up to 1.4 mln tonnes in 2016 [7].

The humid continental climate of Poland creates favorable conditions for thermophilic courgette, which develops best in the sun in temperatures varied between 20–25 °C. The relatively high resistance to diseases of this crop is additional advantage [3]. The fruits of courgette are yielding well after 64–85 days until autumn frosts. Harvest usually start in the second half of June or in a middle of July, and finishes as late as in the second half of September. The most often practice is harvest of fruits every other day. Single plant produces 13–45 fruits, depending on the stage of maturity in the harvest time. The fruit size determines its further use for either direct consumption (10–15 cm of length) or processing (over 15 cm of length) [3, 8, 9]. From agronomical point of view, courgette is easy in cultivation and do not need extensive plant protection, but it needs relatively high amount of water [2–10].

Organic farming and food production is growing in Europe for the last thirty years. At this time, the regulations of the organic agriculture were laid down in three Council Regulation (EEC): 834/2007, 889/2008 and 1235/2008. Organic production is defined as a system of farm management and food production, combining the best practices for the environment, biodiversity, protection of natural resources and the application of high standards for animal welfare. It is prohibited to use synthetic pesticides and mineral fertilisers, genetically modified organism and overuse of antibiotics. Instead, the use of natural fertilisers (manures and compost), natural plant protection methods (e.g. pheromone traps, glue boards) and crop rotation are allowed. These practices decrease damaging impact of agriculture on environment by reducing nitrogen and phosphorus leaching from fields, residues of pesticides in soil and plants, and by increasing biodiversity. The organic cultivation methods impact also on a metabolic processes in crop plants, increasing content of many secondary metabolites [11, 12].

As a consequence of organic agriculture practices, crops can have different content of organic compounds occurring naturally, mainly bioactive compounds [12, 13]. Moreover, the content of other substances, such as minerals, macronutrients or toxic metals seems to be different depending on cultivation methods used. Those differences in composition between plants cultivated organically and conventionally are still frequently discussed thing in scientific research, and are considered as important for human and animal health [14]. Two hypotheses that could explain the differences between plants from organic and conventional agriculture are currently considered. The first one reflects changes in plant metabolism as a result of nitrogen fertilisers application as a persistent driver inducing structural protein synthesis and plant growth. In the environment lacking in easily soluble nitrogen, as it is in organic agriculture, the plant metabolism is balanced and production of secondary metabolites (bioactive compounds, like polyphenols) is much more intensive. The second theory says, that bioactive compounds are produce in higher amounts in

organic system where pesticide use is prohibited, as a natural protection of crop plant against exposure to weeds, plant pathogens or various insects [15].

Nutritional aspects and cultivation

Nutritional value of courgette

Courgette contain a number of beneficial macro– and micronutrients and it can be consumed daily as a part of recommended well balanced diet aiming to preserve health and play the role in anticancer prophylaxis [16, 17]. *Cucurbitaceae* vegetables' chemical composition and thus nutritional value depends strongly on the genus, species and variety. For example summer squash, with around 7 % of dry matter, has 22–30 mg of vitamin C per 100 g in fresh weight (f.w.) [3] (Table1.), while other results show about 14 mg in 100 g f.w. [18] or even 9 mg per 100g f.w. of edible parts [19]. Moreover, nutrients in the plant are not distributed evenly. The vitamin C content varies in different parts of the plant. For example, in courgette flowers (which are edible as well) it is about 27 mg but in the stem might be even 130 mg of the vitamin C in 100 g f.w., what is the highest level in all parts of plant [18]. Usually, content of vitamin C is higher in fruits from young crops than in ripe fruits, and it might be up to three times lower in frozen courgette than in processed (blanched) one as well [20, 21].

Fresh summer squash fruits with skin (exocarp) contain around 2 mg of β–carotene in 100 g f.w. [20], while other tests show it is 0,2 mg per 100 g f.w. [19]. Summer squash contain also lutein and zeaxanthin (around 2 mg in 100 g f.w. of each). The content of carotenoids changes also with the treatment used in different processing methods, as shown in Table2. [20, 21]. None of α–carotene or lycopene was detected in courgette fruit however [3, 9].

In result of other researches, the content of specific components was obtained including chlorophylls and total phenolic content, how it is shown in Table1. Typical is cumulating chlorophyll in exocarp, so its content is higher in courgette with skin than in fruits without skin (respectively: 61.99 and 138.14 g of chlorophylls–a in 1 g d.w. (dry weight); 42.65 and 880.14 g of chlorophyll–b in 1 g d.w.) [22].

Courgette is also rich in minerals, such as potassium, phosphorus and calcium: 0.4 %, 0.04 % and 0.03 % respectively [3]. Profile of the macronutrients is as follows: proteins 1.2%, fats 0.14 % and carbohydrates 3.20 % [19]. Thus the caloricity of this vegetable is very low (15 kcal from 100 g f.w.) [19], and the nutritional value reflects through quantity of fiber, vitamins and biologically active compounds. The content of these compounds seems to be unique among vegetables, but still depends on cultivar, growing season, bioactive content, processing method, damage or deformation of plant cells, type of packaging, and finally the cultivation method [23 – 25].

Table 1. Dry matter, total chlorophyll a, total chlorophyll b, chlorophyll a/b ratio, total chlorophylls (a + b), total phenolic content (TPC) in exocarp and mesocarp *Cucurbita pepo* L.

Compound (unit)	Content in plant
Dry matter (%)	7.23 ± 1.92
Ascorbic acid (mg/g DW)	1.51 ± 0.19
TPC (mg/g DW)	7.94 ± 0.91
Total chlorophyll a (µg/g DW)	1373.86 ± 122.0
Total chlorophyll b (µg/g DW)	922.34 ± 84.4
Ratio a/b	1.6 ± 0.43
Total chlorophylls (a + b) (µg/g DW)	2296 ± 75.0

Source: Blanco Diaz et al. 2015

Table 2. Carotenoids content (%) in raw and cooked courgette.

	β–Carotene	Lycopene	β –Cryptoxanthin	Lutein
Raw	18.0±1.7	17.6±3.9	95.4±2.8	45.9±6.3
Boil	79.4±1.1	0.0±0.0	84.1±5.2	60.6±2.0
Grill	67.6±4.9	50.4±7.1	0.0±0.0	27.8±4.3
Microwave	56.6±3.1	49.9±11.6	0.0±0.0	50.2±4.7
Steam	56.9±12.5	3.9±0.0	77.0±5.8	57.0±8.6

Source: Ryan et al. 2008

Consumers are taking care about their health and are interested in active lifestyle. It means also choosing a diet of high nutritional value, which could have a positive effect on their health, e.g. the organic food. Similarly, lower nutritional density of intensively produced and deeply processed conventional food is increasing the consumers interest toward organically grown crops and gentle–processed organic products [26]. Therefore, the production and the market of organic food is growing year by year [27]. At the same time the nutritional differences between organic and conventional crops, and potential health effects of organic food consumption are intensively studied worldwide [14, 28]. According to many authors the most important property of organic food, in comparison to conventional ones, is a higher content of polyphenol compounds [29]. This findings were also confirmed in the recent meta–analyses of published data, which showed significantly higher antioxidant activity [11, 30], concentration of a range of individual antioxidants [11, 30, 31] in organic, compared to conventional foods. The meta–analysis results revealed also significantly lower contamination of organic food with toxic metal cadmium [11], and that conventional food are four–times more likely to contain detectable pesticide residues [11, 31].

The particularly high interests in polyphenols and other antioxidants in food are driven by increasing scientific evidence of their health benefits, including anticancer and cardioprotective effects [12, 32]. However, despite clear evidence for biodiversity and environmental sustainability–related benefits of organic farming, alongside with higher nutritional value of organic crops, there is still considerable scientific controversy over human health gains from organic food consumption

[14]. Nevertheless the demand for organic food is constantly growing, especially in Europe, North America and Oceania, and organic agriculture is gaining more and more lands and its place in the market [23, 33, 34].

Processing capacity of courgette

The period from 80s to the end of 90s, were the years of the highest interests in courgettes, but the recent 5 years has brought the big "comeback" of this vegetable. The usage of cucurbit species is strongly depended on harvest times and fruit sizes. About 30 years ago it was adjudged that fruits of 10–13 cm of length were the most suited for direct consumption and processing (e.g. marinating), and older and larger vegetables were recommended for direct consumption only. Now, the recommendations are different, and younger and smaller fruits from early harvest are usually used for direct consumption, while more mature and larger are recommended for processing. Fruits were picked from the field until first week after anthesis and sold during 2 weeks. Shapes and sizes of cucurbits are perceived as very important for acceptance of consumers, and the local market size can depends on it. Conventionally cultivated courgettes could be harvested in wide range of weighs (50–400 g). The same varieties grown in organic system are more likely to vary in sizes due to lower levels of fertilisation, and thus might be seen as less favorable for the consumers accustomed to standardisation of conventionally cultivated crops [35, 36].

Courgette is unfortunately perceived as of poor source of nutritional value because of its high water and low carbohydrates content. Nevertheless, its mild flavour makes this vegetable universally suitable for compound food preparation, together with almost every other vegetable or fruit, and herb or spice [3, 37]. Courgettes used in every stage of maturity, are also frequently treated the same way as immature pumpkin [10]. Strong correlation between sizes and treatment method was known for many years. Small, young fruits as firmer and less stringy were recommended for directly eating. The overripe, starchy and dry ones could be used to pickling and salting [3, 10]. Nowadays, when a lot more of processing methods is known, courgette can be used as a main vegetable or as a side dish in our diet. The review of processing capacity of courgette involve the popular literature or articles available online, rather than scientific or popular–scientific publications. The recipes for courgette (or zucchini), e.g. paste, pesto, adżyka, ajvar or hummus, are often traditional dishes from Asia and Middle East countries. The novelty could be chutney or ice cream made from courgette.

The most common practice for storing over the cold winter season is preservation. Because of similarity with cucumbers, courgette could be also pickled or marinated [3, 38]. It is also one of the most popular vegetable used to make frozen vegetables mix. The research focusing on changes in quality of frozen and dried courgette in different cooling conditions are well developed [36, 39–41]. It is already proved that blanching before freezing is effective practice to keep good nutritional quality of courgette fruits, except the vitamin C, which content is lowered after the use of high temperature [42]. Blanching method by microwave or boiling water does not affects sensory quality, but could damage the texture. Despite microwave radiation treatment diminishes courgette fruits structure (it looks like overcooked), it is still the most popular method used in gastronomy and mass food production [43]. The uniform and easy for blending texture of courgette is also considered to

be quality source of vegetable food recommended for elderly people, especially suffering with dysphagia [44].

Continuation of the research on the better treatment and preservation methods could give the future purpose and processing capacity of cucurbit vegetables [42, 44].

Conclusions

The scientific studies cited in this paper allows to draw the following conclusions:

1. Courgette is a vegetable that is becoming again a point of interest for producers of vegetable preserves;
2. Courgette is characterised by low caloricity, but with relatively high content of biologically active substances like β–carotene, especially in the top layer of the raw fruit
3. Courgette is a crop with low agronomic demands and easily adapts to the requirements of organic production;
4. Organically cultivated courgette maintains the appropriate sensory characteristic and it has higher antioxidant content than conventionally grown one
5. Due to the presented properties courgette has a wide range of processing capacity;
6. There still is the potential to continue research to determine the specific processing courgette fruit.

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DECEPTUS DOLO – THE NATURE OF THE DEFECT OF CONSENT IN CANON 1098 CIC 1983

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Abstract:

The article describes the process of establishing new norm in the 1983 Code of Canon Law, just before its promulgation. The historical background helps to realize why the matter of the source of the norm is still so important and open for the discussion.

Keywords:

Deceit, fraud, the natural law, the positive law, marriage

Introduction

Along with the separation of canon law as a separate discipline, the marital consensus was also a topic of discussions. In the history of the edition of canon 1098, we can observe not only the influence of the then canonical tradition being influenced by Roman law, but also the theoreticians and the canonists. By learning about the evolution of the Code work on the inclusion of the *deceptus dolo*, we can more fully understand the reasons that prompted the Supreme Legislator to introduce those norms into the current Code.

The question of its source remains an important issue for the practical application of canon 1098 as a new ground of the nullity of marriage. It raises considerable difficulties and leaves the discussion still open.

History of canon 1098 Works of the Pontifical Commission for the Revision of Canon Law and the current shape of can. 1098

On January 25, 1959, Pope John XXIII expressed his intention to revise the Code of 1917. From that moment, discussions about the scope and type of codex revisions began. The Pontifical Commission for the Revision of the Code of Canon Law was appointed by the Pope on 28th March 1963 and 70 consultants was appointed a year later. The Commission began work in 1966 and finished it with a plenary session at the end of 1981[1].

From 1st July 1968 to 13th November 1968, consultants of *De Matrimonio* group began a discussion on the formulation of a deceit as a new ground of the nullity of marriage that was not present in the Code of 1917. Interestingly, all consultors in their applications postulated its introduction. Compatibility existed also in relation to the constitutive elements of the new norm: the deceit must be serious and the law should act in favour of a deceived party [2]. However, the

question arose among the group, whether the new Code should carefully list kinds of deceit and attach errors to it, or perhaps whether it would be more appropriate to formulate an explanatory clause, which made the marriage invalid, in which qualities affecting the marital consent on the basis of deception will be defined so that jurisprudence and doctrine would decide which case and what types of cases would be included in this error. In the context of the above considerations, the group secretary suggested to concentrate mainly on the essence of deceit, and therefore indirectly also on the elements through which the attached error. During the editorial discussions, attention was drawn also to an extremely important aspect of the marital consent: whether the deceit should be considered only in the subjective aspect by fraudulent act in a serious matter, or also in objective terms, thus limiting itself to the essence of marriage. As a consequence of these considerations, the consultants choose, from among all proposed, the following formula of the new act:
Matrimonium invalidum est si quis graviter ac dolose de alterius partis qualitate magni momenti deceptus matrimonium ineat, quod re vere cognita non contraheret.
"Marriage is invalid if someone, deceived in a serious and deceitful manner as to the quality of the other party of a great importance, enters a marriage that he would not have made, knowing the truth."

This formula did not remain without the consultants' comments, which concerned the value of the quality, the strongest emphasized element of deceit, or the inclusion of a condition regarding the quality itself. Hence, there was another proposition regarding the content of the new canon:
Si quis ob dolum deceptus de alterius partis qualitate, quae consortium vitae gravite perturbet, ad matrimonium contrahendum inducitur, invalide contrahit.
"If someone is deceived regarding the quality of the other party which seriously disturbs the community of married life, is inclined to marry, is married invalidly."

Even this formula left a lot of ambiguities, because there were doubts among the consultants regarding the recognition of the effect of the deceit that would be made by third parties. The majority of consultants opted for that solution, though. Once again, the subject of meaning and value of a person's quality returned in this formula. Hence, there appeared a proposition from one of the consultants to use a more precise expression: *quae consortium vitae ex sese graviter tangat*[5]. Consequently it started a discussion about the deceit itself; the idea was to consider whether in the case of deceit in marital consent, this action would be considered only in relation to the passive subject (victim of the deceit) – then the consent would be considered invalid – or whether to the active entity (perpetrator of the deceit) – in this case, a new formula should be added: *si quis coram altera parte defectum quemdam qui natura sua aptus sit, ad consortium vitae graviter perturbandam, dolose reticuerit dum eadem persona nequit validum inire matrimonium*.

Looking at the discussion regarding the introduction of the "malice concerning some quality of the other partner" to the new Code, it can be noticed that the appropriate terms with proper diligence and accuracy were chosen for the proper recognition of the new law, and above all the noticeable concern of consultants to preserve the doctrine of the indissolubility of marriage and his sanctity, even in the perspective of recognizing the influence of the deceit on the validity of marriage. One of the examples of that concern was the attention of the sixth consultant regarding the expression *graviter deceptus* adopted in the present formula. As some of the consultants considered that that expression contained some excess should be rewritten, the consultant gave an

example that this editing was not needed: the spouse knows that his wife is infected with contagious tuberculosis, but he is in error due to a deceit about the stage of this disease. Thus, this what concerns the object is serious, but in this case the deceit itself is not of a serious nature, because the ignorance of the spouse concerning only the stage of the disease can be considered insignificant in this case. In this way, the introduction of this phrase to the scheme of the new canon has been passed. In the further course of the discussion, most of the consultants considered the malice as being silent or as not acting. In subsequent discussions, proposals were made, which in their content contained the term passive deception (silent), as well as exchanged specific attributes concerning the person (eg: venereal disease, homosexuality, pregnancy of a woman with another man)[8]. These considerations ended the following formula of the new canon:
Qui matrimonium init deceptus dolo, etiam per reticentiam patrato, circa aliquam alterius partis qualitatem, que nata est ad consortium vitae coniugaliis graviter perturbandum, invalide contrahit.

The work of the *De Matrimonio* group indicates that they did not discuss only about the content of the canon, but also other issues were raised, which ultimately determined the formula of the new law, such as: whether the deceit that hits the validity of the marriage can be caused by a third party, whether a scam could be made to enforce marriage, whether the party's admission of fraud in its favour could declare the marriage invalid, or in addition to the deceit of the person, also the fraud against the essential character of the marriage should be made, and finally whether it should be decided that the deception only violates the contract if it was concluded thanks to it. Six out of eleven consultants assumed that the deceit only disrupts consent when it gives a reason to marry. Thus, the formula of can. 1084 was extended by the matter given in the analysed doubts.

On 13th November 1968, the group of consultants defined the formula of can. 1084 bis as follows: Qui matrimonium init deceptus dolo, ad obtinendum consensum patrato, etiam per reticentiam, circa aliquam alterius partis qualitatem, quae nata est ad consortium vitae coniugalis graviter perturbandum, invalide contrahit. One of the last consultations on the final wording of the formula led consequently to the omission of the phrase *etiam per reticentiam*. The consultants decided that in this way the canon would become more understandable and easy to interpret.
In the *Schema de Sacramentis*, published in 1977, the canon on *deceptus dolo* was adopted as can. 300, in the content coinciding completely with the version adopted during the recent consultations [3]. At the meeting on 18th May 1977, four comments were made to the current proposal for the content of the new canon [4]. As a result, a small change was made to the current content of can. 300 and was accepted as can. 1052 Scheme from 1980. Its content was as follows: *Qui matrimonium init deceptus dolo, ad obtinendum consensum patratum, circa aliquam alterius partis qualitatem, quae nata est ad consortium vitae coniugalis graviter perturbandum, invalide contrahit*.

The above–mentioned content of the canon was submitted for evaluation to Pope John Paul II, who made it in cooperation with the committee appointed by him for this purpose [5]. As a result of these works, a terminological change was made. In place of *quae nata est*, was accepted *quae suapte natura*, and the term *in casu* was replaced by *potest*. Thus, the changed content of can. 1052 was accepted as can. 1098 in the Scheme of 1982 [6], and then in an unchanged form as can. 1098 in the newly promulgated Code of 1983.

The nature of canon 1098

Based on the above presented works on the new Code of Canon Law, it appears that while formulating the content of the new canon on the misleading confusion, many difficulties arose. As we can see, this defect of the marital consent was not a category easy to determinate and assess, and still seems not to be. There are also no more difficulties and positions as regards the identification of the source of the deceptive misleading, and consequently, recognition of its retroactivity or not. Now this is crucial not only in relation to the proceedings for the marriages contracted before the the 1983 Code, but it also raises a question how to apply this norm to marriages concluded between non–Catholics.

During the work of the *De Matrimonio* group, one of the consultants pointed out that the new category of consent defects introduced into the Code was a positive law, the aim of which was primarily to protect justice against the deceitfully misleading side [7].

Lack of a clear decision regarding the retroactivity of can. 1098 of the Code 1983 prompted the bishop of Freiburg / Brsg. to ask the Pontifical Commission for the Authentic Interpretation of the Code (currently the Pontifical Council for the Interpretation of Legislative Texts) for a clear and unambiguous opinion on this matter. The answer was given by cardinal C. Lara, then chairman of the Commission on 8th February 1986, and the nature of the reply was private [8]. The cardinal wrote that in the absence of an authentic interpretation regarding the confirmation of the retraction of can. 1098, and having regard to the trial *dubium*, it was necessary to apply can. 1060 and in case of doubt, pleaded in favour of the marriage [9]. The Cardinal spoke in favour of the origin of the norm from the positive law, which, therefore, does not give the possibility of its retroactive effect. However, given the huge variety of cases that are subject to the norm of can. 1098, the cardinal did not rule out the possibility that some of them could also come from the the natural law [10]. Although the answer was unambiguous, it remained an unofficial opinion. Therefore, on 25th November 1986, at the plenary session, the Commission became the problem of the source and the retroactivity can. 1098. It has been found that this problem from the point of view of the development of doctrine is not sufficiently mature, in order to be able to provide an authentic and unambiguous interpretation of this norm at that time [11].

Therefore, the definitive case was not resolved, on the contrary, it was pointed out that this matter requires a lot of analysis and research. Another answer of the Commission on 15th November 1986 was given in connection with the question about the possibility of applying can. 1103 (*vis et metus*) to a non–Catholic marriages [12]. The Commission answered positively, which indicated the source of the law in the the natural law, and hence somehow indicated that the categories of defects that limit the will of the person (and such are deceptive misleading) may have their source in the the natural law. These discussions gave several directions for the development of doctrine on the nature of *deceptus dolo*.

The natural law as a source of can. 1098

The first of the group of canonists represents a position that advocates the origin of can. 1098 from the natural law. Among her representatives, before the entry into force of the Code, was U. Navarrete. In a commentary on *Schema iuris recogniti "De Matrimonio"* was in favour of

a position that recognized the the natural character of the norm of can. 1098. In addition, the author wrote that, certainly, if the marriage was contained in terms of being a consent, it did not matter whether the error resulted from deception or not, because to the same extent everyone is protected from the machinations of the other. The author claimed that the source for this law was the natural law, because theologians and canonists did not notice differently in history. The foundation of this opinion was the canonical nature of the consensus, which in the situation of deception could not be effective, and thus could not take place mutual reciprocation and reception of spouses due to a false image of one of the parties (or both) [13]. A over a dozen years later, U. Navarrete was no longer a defender of this position, but at the same time he was not totally in favour of the positive law [14].

J. M. Serrano Ruiz advocated greater determination for the the natural origin of can. 1098. In his opinion as Christ raised the the natural marriage to the rank of the sacrament, which also emphasized his sanctity, hence the *dolus* strikes this very sanctity of marital life [15]. To the group of canonists who recognize the natural law as a source of can. 1098 belong also J.G. Johnson [16], P. Moneta [17], G. Giustiniano [18], M. Jose, F. Castaño [19], J. J. Cuneo [20] and P. J. Viladrich [21]. However, the last one pointed out that this standard in its current form was determined by a positive legislator, but it has also been the case with all the natural law norms, including *ius connubii*. In his argument he refers to the work on the reform of the 1983 Code, during which can. 1098 (but also cann. 1095, 1097 § 2, 1099, 1101 § 2, 1103) has only become a more legally orderly outcome of the previous jurisprudence. On the other hand, J. J. Cuneo, as an argument, states that the review of the law, in particular in the works on can. 1098, carried out by the Pontifical Commission, was based mainly on philosophical arguments, not on the authority of the Church in the field of establishing obstacles and defects of consent. Therefore, according to Cueno, the Commission was in favour of the opinion that what makes marriage invalid in the case of can. 1098, was a disorder of the act of will and a distorted/untrue substantial subject of the contract [22].

The positive application of can. 1103 to non–Catholic marriages (and therefore the recognition that it comes from the natural law) issued by the the Pontifical Commission for the Authentic Interpretation of the Code on 15th November 1986 was used as an argument in an opinion given by G. Ruano. In his opinion there was a deep analogy between timidity and deception – both categories limited the freedom of choice as well as the insight of the people – that was why also can. 1098 could be considered as coming from the the natural law [23].

This theory is also supported by Polish canonists. For P. Majer, the expression of support for this theory on the part of the legislator was recognized by the fact that the *deceptus* was counted as a defect of consent and not as a marital obstacle. Additionally, the author recalls that according to can. 1057 § 1, the cause of the marriage was the legal capacity of the parties to give their consent and the act of their will to marry. In the case of can. 1098 we are dealing with a certain "internal" defect of consent, which defines the defects of the Code norm in a declarative and not constitutive way. What is more, the canonist continues, the Supreme legislator's task, in accordance with the consensual principle, is to adjust the laws of positive law to the actual state of the human psyche and the relationship between the intellect and the will of the contractor [24]. According to the above P. Majer acknowledges that all defects of consent come from the natural law, because they are only a "development" of the consensual principle. Just as no human power can complete the natural defective marital consent, no human power can say that the the natural act of the will to marry is

defective and incapable of creating a marriage, which is the role of regulating the defects of a consent." The highest ecclesiastical power only through marital impediments, for exceptionally grave reasons, may take away the act of will with legal effectiveness, thereby limiting the person's *ius connubii*. Finally, P. Majer states that the conscious decision of the legislator to consider deception as a defect of consent and not an impediment, clearly indicates that it is a the natural consequence of a defect of the act of will of one or both parties, and therefore has its source in the natural law.

The thesis about the the natural law as the source of can. 1098 was also shared by some of the Roman Rota judges, but it is not a large group. The first decision in the Roman Rota was *coram* Serrano on 28th May 1982 (the year before the announcement of the Code by John Paul II, when can. 1098 was still in the Scheme). The auditor of the Roman Rota, publishing it, did not apply the law which had not been binding, but only a commentary to the standard which was to be announced soon. He stated that the marital consent expressed under the influence of deception was invalid, because in such a situation the mutual devotion of the spouses could not take place, as the giving and accepting of spouses, by the very nature of the gift of a person could only exist in trust, honesty, loyalty [25].

J. Serrano Ruiz, in a decisssion issued on 1st June 1990 referred also to the origin of can. 1098 from the natural law. In part *In iure* he refered to the abovementioned opinion of U. Navarrete from 1974 [26]. Ponens agreeded with the statement that error was the essence of a defect of consent from can. 1098 and it did not matter whether it results from a stipulation or not. And since the mistake comes from the natural law, then so does can. 1098 [27]. J. Serrano Ruiz maintained his position in the judgment on 25th October 1996. At the beginning of his observations, he pointed out that everything regarding marital consent came from the natural law [28]. Then ponens compared can. 1098 to the norm of can. 1057 – consent is a acceptation that people make to themselves. Acceptanting and the giving of self in marriage can only be accomplished through cognition. Both the deceit and the error of a person's quality completely distort cognition, it seemed obvious to the ponens that everything that seriously opposed the constitutive elements of marriage, invalidated this relationship out of the natural law [29].

Based on the aforementioned ponens's opinion, another one was written, namely *coram* Faltin dated 3rd June 1998. Although the process concerned a marriage concluded in 1988, the judge referred to the origin of can. 1098. Quoting Serrano Ruiz [30], he somehow supported the position which supports the "the naturalistic" origin of the discussed norm [31].

Analyzing Rota's sentences from 1990–2000, one can also meet one in which Ponens presented only the statement, can. 1098 comes from the natural law, without any thorough justification. The judgment of *coram* Lanversin on 17th March 1993 concerned the validity of a marriage concluded in 1978. The auditor, without carrying out any analysis, spoke in a single sentence for the origin of this norm from the natural law [32].

The fact that jurisprudence has absolute rulings that interpret the norm contained in can. 1098 as derived from the natural law, allows the use of this norm in this way also in local tribunals. Morover, the last of the judgments analyzed in this work wil be the approval of this position and perhaps also the direction of the development of research on the origins of can. 1098. The final decision *coram* Civili dated on 8th November 2000, despite the fact that it did not concern the

invalidity of a marriage concluded before 27th November 1983, referred to the issue of the origin of the canon. Pones wrote that at that time in Rota an opinion was made that the canon law 1098 *spectare ad ius the naturale* and therefore it should also be used for marriages concluded before the 1983 Code [33].

Positive law as a source of can. 1098

The majority of canonists are in favour of the non–retroactivity of the norm of can. 1098, therefore they agree that it origins from ecclesiastical law. They based their opinion on the above–mentioned response of the Pontifical Commission for the Authentic Interpretation of the Code given in 1986. However, the aforementioned U. Navarrete has shown that this group according to the constitution *Pastor Bonus*, was not competent to make definitive decisions regarding the source of this norm [34].

F. J. Urrutia, maintaining the position expressed by U. Navarrete, additionally emphasized that the attribute from the norm contained in can. 1098 was not (as in canon 1097 § 2) directly and essentially intentional, hence did not affect the validity of a legal act, which is the consent of the parties. According to can. 125 § 2, the law provides for certain exceptions, the legislator, in the author's opinion, used this option by introducing into the Code can. 1098. Since it is the intervention of the Legislator, it comes from a positive law [35]. The argument regarding the accidental character of the attribute is also shared by P. A. Bonnet [36]. In turn, F. Aznar stated that an act taken under the influence of insidious deception does not restrict the freedom of a person to the extent that it would allow the taking of a human act. The deceit, which the standard treats, must be regarded as an accidental deceit [37].

L. Chiappetta describes can. 1098 as an innovation of positive law and consistently, according to can. 9 of the Code of 1983, rejects its retroactivity. The legitimacy of its implementation is based primarily on the need to defend fairness and integrity [38]. A similar argumentation is used by P. Bianchi, stating additionally that can. 1098 is based on the the natural law in what concerns freedom in the expressed marital consent destroyed by the deceiver, but the law contained in this norm along with its implication comes from the positive law [39].

A similar opinion was expressed by J. Gressier. The Legislator stated in can. 125 § 2, as he did it earlier in can. 103 § 2 of the Code of 1917, that "an act made under the influence of grave, unjust fear, or as a result of deception is valid, unless the law provides otherwise; however, it may be resolved by a judge's verdict or at the request of the injured party, or its legal heirs, or ex officio. " "The law itself tells us that. [...] If the stratagem caused the lack of marital consent under the the natural law (which would lead to the invalidity of the concluded act), such an act would never have value. Only the positive law ("unless the law provides otherwise") [...] decides about invalidity resulting from deception" [40].

U. Tramma justifies his view in this way: "No doubt in the norm of can. 1098 is about annulment resulting from church positive law. Certainly, a new law of this kind is rooted in righteousness and justice, which affects the natural law in the way in which doctrine and jurisprudence considered it regarding fear. However, it can not be inferred from this that the invalidity of consent because of fear and deception was based directly on the natural law. In

addition to philosophical reasons (deceit, fear and error not as to the essence, which do not touch the inner being of this agreement, but concerning the path of the subject's consent, they are only a defect of consent, not a lack of it), the law itself tells us: « An act made under the influence of grave, unjust fear, or as a result of deception is important, unless the law reserves otherwise »(can 125 § 2). If the deception led to the disagreement of the natural law (which would lead to the invalidity of the act), this act would never have value. Only a positive law ("unless the law is otherwise"), which in the past has invalidated the marital consensus made under the influence of fear or – in very specific circumstances – a mistake, not from the time of the new Code decides the same void because of deception " [41].

Referring to the doctrine of the Second Vatican Council, S. Ghero stated that it did not radically change the legal concept of marriage. The deceit is not radically incompatible with the legal concept of marriage understood as *matrimonium in facto esse*, and especially with its personalistic dimension, expressed, *inter alia*, in mutual gift giving. Thus, the thesis about the natural law as the source of the norm of can. 1098 is in his view unacceptable [42].

In addition to the above–mentioned authors, L. Notaro [43] and Polish canonists: W. Góralski, M. Żurowski and G. Leszczyński also belong to the supporters of this position. In his arguments, W. Góralski refers, similarly to U. Tramma, to can. 125 § 2, thereby acknowledging can. 1098 for an exception to the general rule [44].

G. Leszczynski does not agree with the statement that the deceit breaks the marriage agreement, because it is actually done by a particular party. Moreover, the subject of marital consent is not *consortium totius vitae*, but one of the party. In addition, according to the author, the deceit does not eliminate free will, but only limits the cognitive ability enabling the choice of the spouse[45]. M. Żurowski also reffers to the intellectual cognitionof the parties, stating that through can. 1098, the Legislator protects the intellectual cognition of the victim of cunning action [46]. The vast majority of rotational decrees are in favor of the origin of can. 1098 from the positive law. There are among them there are those that do not provide us with arguments to support their opinion, but only accept the above it. In the decision *coram* Bruno on 19th November 1993, as in most judgments given in favor of a source of positive law, the basis for argumentation is can. 9 of the Code of 1983. Next, he assessed that in analyzing this defect, the consent comes directly from the errore motivato, not from the action concealing the deceit [47]. The decision *coram* Ragni on 19th December 1995 [48], deduced its arguments from the application of can. 125 § 2 and can. 9 [49]. Then, in support of the thesis of the "positivist" origin of can. 1098 cited the opinion of L. Chiappett [50], who very clearly reminds that according to can. 9 of the Code of 1983 has retroactive effects in cases expressly provided for by law. In other words, "not going backwards" is the norm, and the opposite is an exception that must be legally justified. Ponens also cited the abovementioned statements of the Pontifical Commission dated 8th February 1986 [51], as well as the one on 25th November 1986 [52]. The decision given on 4th December 1997, *coram* Defilippi, despite the fact that it concerned a marriage concluded in 1989, referred to the dispute among canonists for the source of the norm that interests us. Arguments supporting the origin of can. 1098 of the positive law were similar to the *coram* Ragni, cited above. Ponens stated, quoting the words of the judge from the decision coram Bruno [53], that the influence of deception on marital consent came directly and directly from an error motivating, and only indirectly from an insidious act.

Therefore, the thesis that the norm comes from the natural law cannot be accepted [54]. The decision on 3rd May 2012 *coram* Boccafola on the marriage contracted in 1970, ponens, in the first words of his argument, referred to the principle of l*eges respiciunt futura non praeterita*, according to which can. 1098 is not retroactive [55].

Indirect opinion

Among the opinions issued in the subject of the origin of can. 1098 both in the doctrine and in the jurisprudence, we can find positions that do not directly support any of the above, moreover, recognize that a wide range of cases subject to this norm does not allow the definitive recognition of positive or the natural law as its source.

We mentioned in the above considerations about U. Navarrete, who before the promulgation of the Code of 1983 adopted a "the naturalistic" position. However, a dozen years later his view changed a bit. He stated in 1987 that what makes a marriage void in this case is not a deceit but a specific type of error [56]. Because marriage is a deep community of life and love (its two substantive elements are the physical identity of the parties and marital consensus), and the essential qualities of one of the parties (or lack thereof) may disrupt or even prevent it from arising, therefore an error concerning these qualities should be recognized for the marriage annulment. He believed, however, that it is correct to say that the error of this quality makes the marriage invalid, even if it is not intentional, because the correctness of the natural law in this case is not to protect the contractor from the injustice of the other person, but to protect his inner freedom by marriage [57]. Thus, according to the canonist, the internal freedom of the party is limited in exactly the same way when the error is intentional and when it is not. That the cause of the error is unfair, there is almost nothing in this matter, because what restricts internal freedom is a mistake and not a cause of error, even if it is unfair. The deceit as such, according to the author, has no invalidating effect from the natural law, and the definition in can. 1098 a deceived, committed to obtain consent, should be attributed to church law. Therefore, U. Navarrete maintained that the mistakenly deceitful, made by deceit to obtain consent, e.g. regarding the infertility of the other party, makes a marriage irrelevant to the will of the ecclesiastical legislator who, if this norm fully resonates with the natural righteousness, goes beyond the natural law, protects freedom to marry against machinations and mischief of the other party [58].

Supporters of the intermediate position are also among rotatl judges, although they are in a minority. In decision on 25th October 1990 *coram* Burke ponens estimated that in can. 1098 the cause of invalidity could be explained in several ways. It can be placed in the violation of the law that the party makes a gift of marriage in truth and in fact [59]. The consequence of the violation of this right is, according to the author, the fact that the consent of the one who concluded the marriage is directed at an object which is completely different from what it thinks it chooses; therefore, the freedom and credibility of consent are distorted. Burke pointed out another reason for being nullified: it is not in accordance with the natural law to require the subject to live in marriage with a person who deliberately deceived him as to the attribute which was very important to him in view of the peaceful community of marital life [60].

On the other hand, in decision on 26th July 1996, he stated that although the prevailing opinion was that the canon law does not apply to marriages concluded before the promulgation of the 1983 Code, after careful analysis of the concept of marital agreement could be considered that the canon law is directed towards the natural law. The deceit along with the meaning of marital consent, for which the deceit is committed, seems to be a strengthening of those elements of the natural law whose absence is necessarily contaminating the very essence of the natural and holy marriage [61].

Summary

Law as a science is not constant and unchanging in its theories, assumptions and assertions. The property of every science is its progress, continuous development. Otherwise it stays in a kind of stagnation and thus loses its value. Through continuous reflection, it needs to look for deeper insights about the basic issues, paying attention to the legal procedures or damage to justice. As we can easily notice, the discussion concerning the source of the norm in can. 1098 is still open for further discussions. The final opinion has not been made. Therefore, seems to be very likely that the final decision belongs to the judges who asses every case individually.

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[8] Treśc listu jak i odpowiedź nie zostału opublikowane, stąd podaję za: M. T. ROMANO, La rilevanza invalidante del dolo sul consenso matrimoniale (can. 1098 C.I.C.):dottrina e giurisprudenza, Roma 200, 195.

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[10] „La Consulta è incline a ritenere il disposto del can. 1098 di diritto meramente positivo, e pertanto non retroattivo. Data comunque la grande varietà di casi che potrebbero cadere sotto la fattispecie ivi descritta, non si può escludere a priori che alcuni di essi possano configurare nullità derivanti dal diritto the naturale, nel cui caso sarebbe legittima una sentenza affermativa." (podaję za: M. T. ROMANO, La rilevanza invalidante del dolo sul consenso matrimoniale (can. 1098 C.I.C.):dottrina e giurisprudenza, 196; zob. też Sent. C. Stankiewicz z 27.01.1994 r., Nullitatis matrimoni, w: SRRDec., 86(1994), 65–66; oraz G. Ruano, Errore e dolo nel consensu matrimonial, w: Matrimonio e disciplina ecclesiastica, Milano 2002, s. 98).

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[48] „Ex supra relatis, quaedam autem principia omnino certa habentur, sicit, ex. gr., illud a can. 125, § 2, statutum (…); aut illud iuxta quod sub Titulo *De legibus Ecclesiasticis*, can. 9 sancit: „Leges respiciunt futura, non praeterita, nisi nominatim eis de praeteritis caveatur." (Sent. c. RAGNI z 19.12.1995 r., *Nullitatis matrimoni*, w: *SRRDec.*, 87(1998), 718).
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[50] „La consulta è incline a ritenere il disposto del can. 1098 di diritto meramente positivo, e pertanto non retroattivo. Data comunque la grande varietà di casi che potrebbero cadere sotto la fattispecie ivi descritta, non si può escludere a priori che alcuni di essi possano configurare nullità derivanti dal diritto the naturale, nel cui caso sarebbe legittima una sentenza affermativa." (podaję za: M. T. Romano, La rilevanza invalidante del dolo sul consenso matrimoniale (can. 1098 C.I.C.):dottrina e giurisprudenza, 196; zob. też Sent. C. Stankiewicz z 27.01.1994 r., Nullitatis matrimoni, w: SRRDec., 86(1994), 65–66; oraz G. Ruano, Errore e dolo nel consensu matrimonial, w: Matrimonio e disciplina ecclesiastica, Milano 2002, s. 98).
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[56] „Dixerit aliquis: Aequum est ut quis efficaciter protegatur contra iniustitiam aliorum quam secum fert dolus in materia adeo personali uti est Matrimoniüm. Cum autem remedium rescissionis in matrimonio locum habere non possit, necesse est ut matrimonium initum ex errore doloso circa aliquam alterius partis qualitatem, quae suapte natura consortium vitae coniugalis graviter perturbare potest, sit invalidum ipso iure the naturali. Quod matrimonium initum ex tali errore possit esse nullum ipso iure the naturali, admittendum esse puto. Sed ulterius, meo iudicio, est affirmandum, ut infra videbimus, errorem circa eamdem qualitatem invalidare matrimonium etsi non sit dolosus, quia ratio legis the naturalis invalidantis matrimonii in hac provincia non est defendere contrahentem contra iníustitiam aliorum, sed protegere libertatem internam ad matrimonium celebrandum." (U. Navarrete, *Canon 1098 de errore doloso estne iuris the naturalis an iuris positive ecclesiae?*, w: *Periodica* 76 (1987), 166).

[57] U. Navarrete, *Canon 1098 de errore doloso estne iuris the naturalis an iuris positive ecclesiae?*, w: *Periodica* 76 (1987), 166.

[58] „Iuri vero the naturali videtur esse omnio contrarium exigere ut quis in matrimonio vivat cum persona quae eum praestabilito consilio decepit circa qualitatem quae pro ipso coniugalis vitae pacifico consortio valde intersit." (Sent. c. Burke z 25.10.1990 r., *Nullitatis matrimoni*, w: *SRRDec.*, 82(1994), 727).

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MECHANICAL PROPERTIES OF THE IF AND DC01 STEELS AFTER APPLICATION OF THE DRECE PROCESS

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Abstract:

This paper presents the influence of the reproducible plastic forming SPD with an unconventional DRECE (Dual Rolls Equal Channel Extrusion) technique on hardening of IF and DC01 steel. The influence of number of passes on change of mechanical properties, such as tensile strength TS and yield limit YS, of tested steel was researched. The DRECE method is based on equal channel extrusion with double rolls. The forming process is based on extrusion technology with zero reduction of metal sheet thickness while achieving a high degree of deformation in the formed material, which results in a significant improvement in mechanical properties of the initial material. [1–2]. The increase of strength properties after the DRECE process in relation to the initial material was confirmed even after the first pass. For both IF and DC01 steels the highest hardening can be observed after fourth pass.

Keywords:
Sheet metal, HSS, SPD process

Introduction

Since many years The automotive industry uses cold forming processes of metal sheets to a large extent for manufacturing body elements with complex shapes. Low–carbon IF (Interstitial Free) steel and DC01 steel due to good plastic properties are currently used in the automotive industry for deep–drawing elements [3–4]. However, their low strength limits their greater use in conditions where except of high plasticity also a high strength is required. Increase of mechanical properties while maintaining good plastic properties can increase potential use of IF and DC01 steels in new areas, among others in aerospace and defence industries [5].

In recent years the interest in using unconventional SPD methods to obtain materials with ultra–fine–grained structure has significantly increased. Grain refinement favours above all increasing the strength properties of the material. Such methods include among others: DCAP (Dissimilar Channel Angular Pressing), AARB (Asymetrical Accumulative Roll Bonding) and DRECE (Dual Rolls Equal Channel Extrusion) [1, 5–9, 11]. The DRECE method is based on the DCAP method (Dissimilar Channel Angular Pressing) and ECAP – CONFORM (Continuous Forming) and is intended for forming metal sheets or bands with maximum dimensions

of 1000x60x2 mm. The material is introduced into the working space and then extruded through the feed roller by means of pressure rollers through the shaping tool without changing cross–section of the material. Multiple plastic deformations carried out this way influence the change of the structure and mechanical properties in relation to the initial material. The decisive factor for increasing mechanical properties of material after extrusion in the DRECE process is selection of the optimal forming angle in the plastic area (123°, 118° or 108°) determined by the structural arrangement of the forming tool and number of passes through the device.[1–2, 10]

SPD methods such as: DCAP, ECAP – CONFORM or AARB differ significantly from each other in the method of deformation, the impact of the tool on the deformed material and the value of deformation in a single cycle. In the DRECE method multiple plastic deformation carried out without changing the cross sectional of the material. DRECE, however, allows deformation of material in a shape of a metal sheet with much bigger dimensions than in other methods. This device is unique in Europe, since the process of structure refining in flat blanks is ate present still under development. This is vital in the context of the future use of such material. Similarly to other SPD methods the material deformed with the DRECE technique is characterized by heterogeneity of obtained structure. Currently, works to improve this method and increase the efficiency of the process are being held. [1–2, 5–9].

Experimental procedure

The material for testing were bands of IF and DC01 steel with thickness of 2 mm intended for cold forming. These steels are characterized by a single–phase ferritic structure. The chemical composition of tested steels is shown in Table1.

Table 1. Chemical composition of IF and DC01 steel

Symbol of steel	C	Mn	Si	Cr	N	Cu	Al	V	Ti	S, P
IF	0.002	0.12	<0.005	0.019	0.005	0.02	0.029	0.001	0.059	≤ 17
DC0.1	0.12	0.60	<0.003	–	–	–	–	0.001	0.05	≤ 0.045

Source: own calculations and source [12]

The SPD researches with the unconventional DRECE method were held at VŠB – Technical University in Ostrava in the Department of Mechanical Engineering. α angle in the deformed zone was 108º. The charge was metal sheets with dimensions of 8000x40x2 mm. There were eight passes of the material and each subsequent pass was carried out without changing the orientation of the metal sheet in regard to the initial position after first pass. The pressure on the feed roller was 150 bar, while on the pressure rollers (before the deformation zone) 30 bar. The pass of the material through the DRECE device was carried out at speed of 40 mm/min. The change of mechanical properties after the plastic deformation and influence of number of passes through the DRECE device on mechanical properties of IF metal sheets was researched with static tensile test. The research was carried out on a series of three samples using a conventional testing machine ZWICK with a maximum force of 100kN according to the PN–EN ISO 6892–1: 2010 standard [13].

Samples with a rectangular cross–section were used (dog–bone). Each sample was taken from a spot parallel to the direction of deformation.

Results and discussion

As a result of use the DRECE deformation the tensile strength of the IF steel has increased after the first pass to 296 MPa which is approximately 10 % growth of the tensile strength in relation to the initial state. After fourth pass it reaches tensile strength equal to 385 MPa which means that there has been over 40 % increase of tensile strength in relation to the initial material. Yield stress for the steel in the initial state is 121 MPa. After first pass it increases to 276 MPa, and after fourth pass it is 326 MPa. Tensile strength TS of DC01 steel in the initial state is 327 MPa. After the first pass through DRECE there were increase of the value of TS to 390 MPa. After fourth pass it reaches TS equal to 433 MPa which means that there has been over 30% increase of tensile strength in relation to the initial material. Yield stress for the DC01 steel in the initial state is 225 MPa. After first pass it increases to 371 MPa, and after fourth pass it is 412 MPa.
Further increasing the number of passes does not increase the mechanical properties, for both IF and DC01 steels. The obtained results of mechanical properties of IF steel after DRECE deformation are shown in Figure1, Figure 2 and in the Table 2.

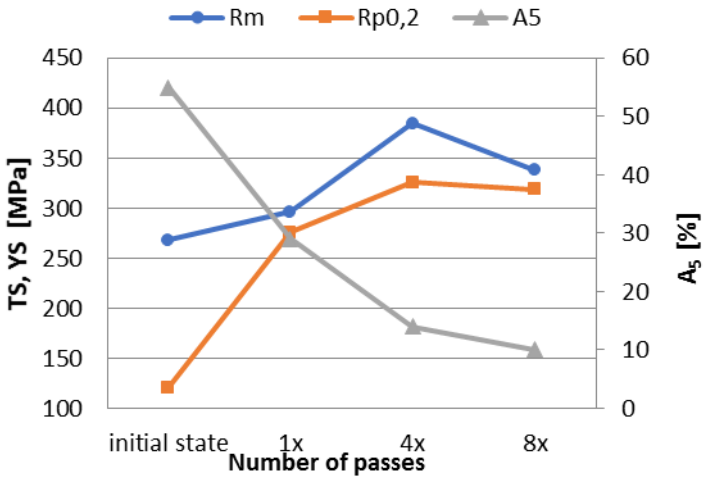

Figure 1. Influence of pass number on mechanical properties of IF steel (tensile strength TS, yield stress YS and elongation A_5); Source: own calculations

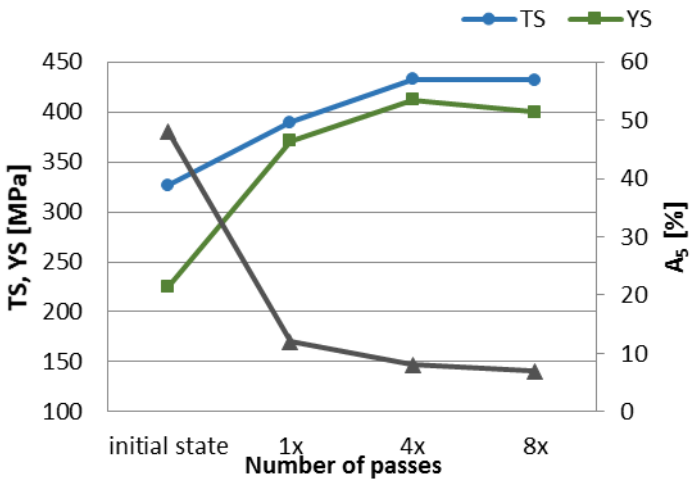

Figure 1. Influence of pass number on mechanical properties of DC01 steel (tensile strength TS, yield stress YS and elongation A_5); Source: own calculations

Also there was the indicator YS/TS calculated constituting so called reserve of plasticity. This value for IF steel in the initial state is 0.45. After first pass YS/TS increases to 0.93. This means a significant increase of the value of the reserve of plasticity of the tested steel. Similar dependence is visible in DC01 steel. Plasticity margin in the initial state is 0.69 and after the first pass through DRECE it reaches the value of 0.95. After the fourth pass the plasticity margin YS/TS for IF steel is 0.85 and for DC01 it does not change in relation to the value obtained after the first pass. Both steels – IF and DC01 – in the initial state are characterized by good plastic properties. For the IF steel A_5 elongation reaches the value of 55 % and necking is at a level of 65 %, however, with the increase of number of passes a sharp drop in ductility of the material was noticed. A_5 elongation of the material has dropped from 55 % to 29 % after the first pass and then it decreased with the increase of number of passes to value of 14 % after the 4th pass and 10 % after the 8th pass. For the DC01 steel in the initial state A_5 elongation is 48 % and necking reaches 68 %. After the first pass A_5 elongation has decrease to 12 %, and after the fourth one it is 8 %. The value of necking Z decreases with number of passes. For both steels – IF and DC01 – the highest value of necking falls to the lowest value of YS/TS ratio. Such behaviour of material after a SPD process is characteristic for most of the deep drawing low carbon steels. This phenomenon can be observed in materials deformed with the ECAP method but DRECE can be used for materials having bigger dimensions.

Table 2. Elongation, necking, and value of the reserve of plasticity of IF and DC01 steel obtained in tensile test

Symbol of steel	**Number of passes, α = 108°**	**A_5, %**	**Z, %**	**YS/TS**
IF	initial state	55	65	0.45
	1x	29	60	0.93
	4x	14	61	0.85
	8x	10	58	0.94
DC01	initial state	48	68	0.69
	1x	12	63	0.95
	4x	8	60	0.95
	8x	7	39	0.93

Source: own calculations

Conclusions

The results show positive impact of the SPD process held by the DRECE technique on mechanical properties of tested low carbon steels. Strength characteristics confirm significant improvement of mechanical properties of IF and DC01 steels after the DRECE process in relation to the initial material. In both cases the highest value of tensile strength and yield stress is observed after the 4th pass. For the IF steel the tensile strength has increased by 43,6 % in relation to the initial material and yield limit almost tripled. For the DC01 steel the value of the TS increases by 32,4 % and yield limit increases twice (approximately). Further increasing of number of passes does not cause a significant increase in mechanical properties. IF and DC01 steels in the initial state are characterized by good plastic properties but with the increase of number of passes through DRECE a sharp drop in the ductility of the material is noticeable. After 8 passes through the device A_5 elongation is 10 % for IF steel and 7 % for DC01 steel. From this point of view it seems important to use a suitable heat treatment to improve the ductility of the material while maintaining high mechanical properties. The material had the highest hardness after 4th pass through the DRECE device. HV0.1 hardness increased by over 30% in relation to the initial material.

The increase of mechanical properties after the DRECE process is attributed to the changes occurring in the micro structure (grain subdivision to an ultra–fine–grained size) after SPD, which are the subject of further research and analysis.

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CONSECRATED VIRGINS – A RENEWED FORM OF CONSECRATED LIFE IN THE CHURCH

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Abstract:

Ordo virginum – the state of consecrated virgins, is the oldest form of consecrated life in the Church. The special development of this form took place in the first centuries of the Church. However, over the ages the practice of consecration of women living in the world disappeared. The Second Vatican Council recommended a revision of the virgin consecration ritual. In modern times, the development of this individual form of consecrated life is gaining momentum. More and more women want to devote their lives to Christ, imitating Him in his everyday life rooted in the world. To meet these needs, the Congregation for Consecrated Life and Societies of Apostolic Life has issued the Instruction Ecclesia sponsae imago regarding the state of consecrated virgins. This article deals with selected aspects of the ordo virginum relevant to its understanding.

Keywords:
ordo virginum, consecrated virginity, consecrated chastity, Bride of Christ

Introduction

John Paul II at the beginning of the apostolic exhortation *Vita consecrate* [1], emphasized that consecrated life is "a gift of God the Father granted to his Church through the Holy Spirit." The Pope reminded that over the centuries there were people who wanted to imitate Christ through life according to the evangelical counsels. One of these ways of living in an individual form, which is one of the oldest forms of consecrated life as well, is the state of consecrated virgins (*ordo virginum*).

The development of the individual form of consecrated life, which is the consecration of virgins who live in the world, develops nowadays. More and more women want to devote their lives to Christ, imitating Him in His everyday life rooted in the world. The increasing number of consecrated virgins [2, 22], as well as emerging questions and problems with new ecclesiastical, cultural and social contexts gave rise to the need to issue instructions on the state of consecrated virgins entitled *Eccelsiae sponsae imago*. This instruction, constituting the base of this article, was published on 8th June 2018 by the Vatican Congregation for Institutes of Consecrated Life and Societies of Apostolic Life [3]. The article focuses only on some issues relevant to the understanding of this form of consecrated life. It is divided into four parts. In the first one is presented historical outline of this ancient form of life which is devoted to God. The second part

shows the specificity of linking the consecrated virgin with the diocese as a place of discernment and realization of its vocation. The third part discusses *sanctum propositum* of a consecrated virgin as the essence of the of a self–gift made to God. The fourth part concerns the requirements for candidates for consecration as well as the process of formation and permanent formation.

The historical outline

From the very beginning of the formation of the Church community, in various regions it developed into a form of consecrated life, which is now known as *ordo virginum*. Many women want to imitate Christ and want to lead an ascetic life, in which the most important thing was the relationship with Christ as the only Spouse. The first three centuries of Christianity were marked by the martyrdom of many Christians, including also many virgins. Hence, loyalty towards Christ was a consecration with martyrdom – at that time a total gift of yourself required also a gift from your life [3]. From the fourth century in Roman tradition was known a rite of consecrating virgins done by a bishop, through which they became consecrated persons, constituting a separate state called *ordo viginum*. Towards the community of the Church, the woman expressed her desire to live in virginity and the bishop accepted her commitment and uttered a consecrating prayer. There was also a rite known as *velatio*, which corresponded to the imposition of the virgin of the consecrated veil – the veil (similar to the placing a marital veil)[4]. Developing of the *ordo virginum* and the care of bishops for consecrated virgins are testified by the writings of many patristic authors, who gave them directions, exhorted them, but also defended the state of virginity against those who denied the value of it [5 –10].

Originally, virgins lived in their families or in their homes. Thus, they remained in their family and social environments, actively participating in the life of their Christian communities gathered around the bishop. In ancient society, the rite of women's consecration was also an expression of the Church's concern for the protection of women's rights and dignity. So it had not only a supernatural expression, but also a very clear social value. A woman who took up this state of life had more autonomy than other women depending on their families and social conditions. She could make a free life choice, and sometimes even fulfilled better her life aspirations [11].

In the fourth century, due to the large number of virgins, religious communities began to be created for them, and from the eighth century, the obligation to stay in the convent was imposed [4]. Living in the community and in accordance with the three evangelical counsels, in according to a specific rule, in obedience to the superior – this became a model of life dedicated to God. Thus, the state of consecrated virgins in its original form has been replaced by religious life. The rite of virgin consecration was used only in some convents. The institution of consecrated virgins was viable until the eleventh century [12]. In 1139, based on the decrees of the Second Lateran Council, the consecration of virgins living in the world was no longer continued. It was not until the 20th century that the consecrated life in the world was approved within the form of secular institutes. The church also returned to the ancient state of consecrated virgins. The Second Vatican Council ordered a revision of the rite of consecration of virgins. In 1970, the Congregation for Divine Worship issued a renewed rite of virgin consecration approved by Pope Paul VI [13]. The Polish translation of the *Ordo consecrationis virginum* was approved by the Congregation for Divine Worship and the Discipline of the Sacraments in 1990, and published in 2001 [14]. The state of

consecrated virgins has also found its place in the Church's legislation, namely in can. 604 of the Code of Canon Law [15]. The rite of consecration of virgins prescribes two types of consecration: the first concerns the consecration of virgins living in the world, and the second consecration of nuns connected with religious vows.

It is also worth noting that the state of consecrated virgins does not have its specific founder. It is intended for women only. The tradition of the Catholic Church does not know the consecration given to men.

The daughter of a particular Church

A place where a particular woman lives and prepares for consecration is the particular Church. As the instruction *Ecclesia sponsae imago* emphasis, the particular Church is called to accept and accompany the vocation of consecrated women in which they live. On the other hand, the consecrated woman is ought to be grateful for all the gifts she received in the communion of the saints and which she still receives through the life of the particular Church (ESI 43) [3].

The consecration of virgins takes place in the local Church. The minister of consecration is a diocesan bishop or other bishop authorized to do so. This diocese becomes a place of special belonging to the consecrated virgin. It is the bishop who allows candidates and includes them in the state of virgins. It is in the diocesan Church where they are called to serve God by performing works of mercy and a testimony of personal relationship to Christ. They are also called to be attentive to the magisterium of the diocesan bishop and to respond to his pastoral calls, and to pray for the diocesan needs, especially the intentions of the bishop (ESI 43) [3].

The rite of consecration is a public act of the Church. It is recommended that the place of consecration be the cathedral. In it the diocesan Church is revealed, in it the bishop presides the liturgy [16]. The relationship of virgins with the diocese that arises during consecration is a special kind of spiritual bond with the local community [11]. Being a part of the local church is a kind of *proprium* of that state, it is an essential feature for this form of consecrated life. However, it does not have the character of incardination, as in the case of the neo–presbyter. Therefore, the consecrated virgin has the right to change the diocese and join the new local community. The instruction *Ecclesiae sponsae imago* indicates that although the consecration establishes a special inclusion in the particular Church in which it is celebrated, it does not prevent consecrated women from moving to another particular Church, if necessary, permanently or temporarily, for example to work, to family or for pastoral reasons or other for proportionate reasons (ESI 60) [3]. In detail, this process of changing the diocese is regulated in the following numbers.

The relationship with the diocesan bishop in the spiritual dimension is really secondary, because the relationship essential for the bride who the woman becomes at the moment of consecration is her relationship with Christ and the Church [17]. This relationship – as P. Raffin writes – leads from the virgin consecrated to the Church, and only through the Church to the bishop who is the servant of the Church and the instrument of consecration [18]. The consecration of a woman takes place in the local Church, hence it is institutionally connected with the bishop's ministry, his office (at a particular moment also with a particular bishop), but through consecration it is also included in the *Ordo vigrinum* of the entire universal Church. For the whole Church, as stated in the first issue of *Praenotanda*, by the rite of consecration of virgins, shows its love for

virginity and pleads for the virgins for the gifts of the Holy Spirit [18]. Rooting in the diocese, therefore, is not related to closing only within the limits of the particular church. The consecrated virgin should open to the horizons of the mission of the universal Church and the experience of communion in the diocesan dimension.

Consecrated chastity

Virginity for the Kingdom of God is a supernatural remedy which is possible to accept only in the space of faith. It belongs to the matter of salvation, and the salvation belongs to the new order, initiated by the death and resurrection of Christ and by the sending of the Holy Spirit [11]. A person who wants to imitate Christ in consecrated virginity receives a grace of a special vocation. This person responds to Christ's previous love poured into her heart. Therefore it is a dialogue of love, a dialogue between God's grace and the person's freedom (ESI 21) [3]. God gives a special grace to the called. The charism of virginity, accepted by a woman and confirmed by the Church, is a gift that comes from the Father, through the Son, in the Holy Spirit (ESI 23) [3]. This gift protects, cleanses, heals and increases the person's ability to love (ESI 21) [3]. Virginity is not the result of an ascetic effort. It gives the person, through the sacraments, a new place in the history of salvation [11]. By engaging in God's love, the person renounces the experience of human love to unite with Him in a special bond. At the consecration ceremony, the woman publicly declares her sacred resolve (*sanctum propositum*) to persevere throughout her life in perfect chastity and in the service of God and the Church. She wants to imitate Christ to give a living testimony of love and to be a visible sign of the future Kingdom.

The consecration of virgins in the renewed rite reaches to the roots of the baptismal consecration [19]. The Second Vatican Council and John Paul II in the Apostolic Exhortation *Vita Consecrata* remind us that every religious consecration, including the consecration of virgins, is a special deepening of the baptismal consecration by which the internal unity with Christ, already established by baptism, is transformed into the gift of being like Him. It is expressed and realized more fully by the profession of the evangelical counsels [1]. The consecration of virgins is not an essential consequence of baptism as God does not command all baptized women to live in virginity. He calls only some of them [11].The consecration of virgins becomes the completion of baptism in the dimension of his virginal matrimony with Christ. Baptism gives the baptized a share in the mystery of the passion, death and resurrection of Christ, as well as participation in the mysterious matrimony of Christ the Bridegroom with the Church, his Bride [11]. Although the nuptial attitude of Christ applies to all baptisms, it can be experienced in the most characteristic and appropriate way by a woman who consecrates her virginity [11].

Discernment and formation to the Ordo virginum

Imitating Christ requires constant conversion in following Him and in fidelity. It is a continuous process that embraces all dimensions of life and extends over all life. This applies to all baptized people. Also a woman who wants to follow you and shape her vocation in the *ordo virginum* is called to engage in the process of discernment and formation. The instruction *Ecclesiae sponsae* imago indicates that it is necessary to study the signs by which the charism of consecrated

virginity is expressed with its location in the particular Church, as well as the specific way of living in a social and cultural context. It is also necessary to verify the authenticity of the vocation and purity of motivation in the light of faith (ESI 80) [3]. Formation should awaken the candidates' desire for a deeper union with Christ, to more generously respond to the Father's call, surrendering to the Holy Spirit. The true process of the formation – as the Instruction says – can take place if there is an authentic personal experience of conversion, experience of enlightenment, purification and a deeper commitment to participate in following the Lord (ESI 80) [3].

The Roman Pontiff [14] states that nuns, including women living in the world, may be admitted to consecration. According to the Pontificate, those remaining in the world should meet the following criteria:

1. they never marry or live in public, i.e. openly, in the opposite condition of chastity;
2. according to general opinion, through their age, prudence and customs gave a guarantee that they would persevere in a pure and devoted life to the Church and to others;
3. they were admitted to the consecration by the bishop of the place.

The instruction *Ecclesiae sponsae* imago basically repeats the same requirements. In the number of 82, it also mentions the age of a candidate who, starting the formation process – should be at least 18 years old and 25 when she approaches to being consecrated. It also indicates specific issues that should be addressed by verifying the candidate's spiritual experience as well as human maturity. Assessing spiritual experience, it is recommended to pay attention to the following issues (ESI 86) [3]:

1. her personal relationship with Christ and the desire to shape the whole of her being « to the Lord Jesus and to his *total self–giving* »as a loving response to his infinite love;
2. the sense of belonging to the Church, experienced through sharing in the life of the Christian community, supported by a deep love for ecclesial communion, by the celebration of the sacraments and by an attitude of filial obedience to the diocesan Bishop;
3. attention to the contemplative dimension of her life and fidelity to spiritual discipline, to times, rhythms and various forms of prayer;
4. diligence in penitential and ascetical practices and spiritual accompaniment;
5. eagerness to deepen her knowledge of scripture, the contents of the faith, liturgy, and the history and the magisterium of the Church;
6. passion for the Kingdom of God, which leads her to interpret the reality of her own times in accordance with evangelical criteria, and to respond to this reality with a sense of responsibility and a preferential love for those who are poor;
7. the presence of an comprehensive and global insight into her own vocation, which demonstrates a realistic understanding of her own history, her characteristics – her resources, limits, desires, aspirations and motivations – and which is consistent with the form of life of the *Ordo virginum.*

However, when it comes to confirm human maturity – according to the *Instruction* – the following tips will be taken into consideration (ESI 87) [3]:

1. realistic self–knowledge and a calm, objective awareness of her own talents and limits, together with a clear capacity for self–determination and an appropriate attitude towards the assumption of responsibility;
2. the capacity to establish healthy, serene and generous relationships with men and women, together with a correct understanding of the value of marriage and motherhood;
3. the capacity to integrate her sexuality with her personal identity and to direct her affective energies in a way that expresses her own femininity through a chaste life that is open to a wider spiritual fruitfulness;
4. her professional skills and capacity to work so as to provide for her own sustenance in a dignified manner;
5. a proven aptitude to reframe suffering and frustration, and to give and receive forgiveness, as possible steps towards the fullness of human nature;
6. fidelity to her word and to her commitments;
7. the responsible use of goods, of social media and of her free time.

Thus, the verification is recommended on many levels. If necessary, the Instruction shows the possibility of using in the process of discernment and formation with the help of psychologists. However, it clearly indicates that this should be done with the prior written consent of the person concerned (ESI 90) [3].

The question of the integrity of physical and moral virginity raises a lot of controversy in some environments[20, 21]. Well, according to the instruction of *Ecclesia sponsae imago*, a candidate for consecrated virgins does not have to be a virgin in a physical sense. Physical integrity is not an essential precondition for consecration (ESI 88) [3].

Ultimately, the diocesan bishop is responsible for formation, the process of discernment and the admission of candidates for consecration. He can entrust the formation process to the delegate and formators – women who have already received the consecration. However, in the final phase of the formation process, the bishop assumes responsibility for the ultimate understanding of admission to consecration. The rite of consecration does not mean that the time of formation has ended. Consecration requires growth in human and Christian maturity, but also commitment, constant care for permanent formation, which deepens and renews the reasons for the choice that it has already made. It also allows the consecrated woman to strengthen herself in her own vocation while experiencing internal dynamics (ESI 75) [3].

Conclusion

In the *Decree* of the Sacred Congregation for Divine Worship, we find that virginity devoted to God, as an exalted gift, Jesus Christ left as His Bride in heritage. Therefore, from the apostolic times, the virgins sacrificed their chastity to God, and thus became the ornament of the Mystical Body of Christ and gave them a wonderful fertility. The renewal of the virgin consecration has opened the way for many women to offer their gift to God in lifelong purity, remaining in their living environment.

Today consecrated virgins are present on all continents, in very many dioceses and they offer their own testimony of life in the Church and on every social field. The latest Vatican document, the

instruction *Ecclesiae Sponsae Imago*, is an expression of concern for the *ordo virginum* and its presence in the universal Church. The document helps to show the beauty of the Lord who transforms the lives of so many women and to discover the beauty of this vocation that consecrated virgins experience every day.

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[15] Kodeks Prawa Kanonicznego, Pallotinum 2008. Can. 604 § 1. Similar to these forms of consecrated life is the order of virgins who, expressing the holy resolution of following Christ more closely, are consecrated to God by the diocesan bishop according to the approved liturgical rite, are mystically betrothed to Christ, the Son of God, and are

dedicated to the service of the Church. § 2. In order to observe their own resolution more faithfully and to perform by mutual assistance service to the Church in harmony with their proper state, virgins can be associated together.

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PREPARATION OF NITRONES: A SHORT REVIEW

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Abstract:

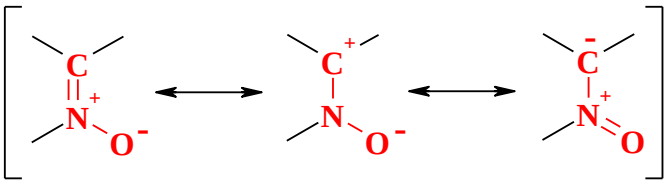
Nitrones are a group of organic compounds which are used in many reactions. To the most important application of these chemical compounds are used as 1,3–dipoles in the [3+2] cycloaddition reaction (1,3DC). In this type of processes isoxazolidines and isoxazolines are fomed [1–9]. Moreover, nitrones can be used in rearrangement reaction to oxime ethers [10], oxaziridines [11–13], amides [11–13], imines [14, 15] and ect.

Keywords:

nitrones, 1,3–dipoles

General information about nitrones

Nitrones are organic compounds consisting of an imine N–oxides. You can show them using three resonance structures.



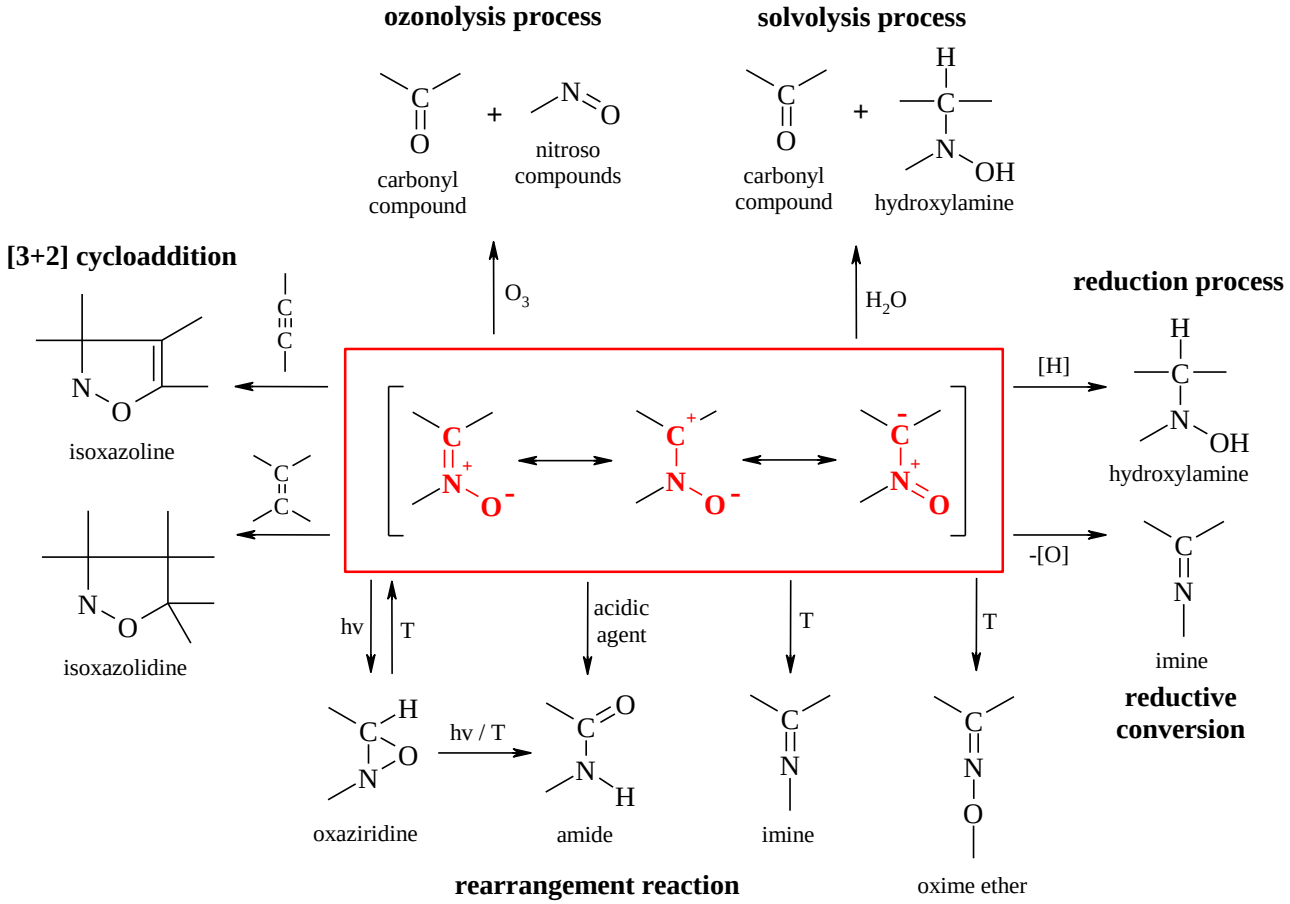
Scheme 1. Resonance structures of imines N–oxide
Source: own scheme

Conventionally, nitrons can be divided due to chemical nature of the prekursor. Therefore we distinguish aldonitrones and ketonitrones. Aldonitrones, unlike ketonitrones, have a hydrogen atom directly at carbon atom of iminoksyl group [16].

Through to the presence of a double bond in the molecule, nitrones can occur in the form of *cis* (Z) and *trans* (E) geometric isomerism. This fact was proved at the beginning of XX century by *Semper* and *Lichtenstadt* for C–phenyl–C–(4–tolyl)–N–methylnitrone [17].

Application of nitrones

Generally, nitrones are used as 1,3–dipoles in [3+2] cycloaddition reaction with alkenes and alkynes. In a course of reaction are formed isoxazolidines or isoxazolines [1–9]. Nitrones are also used in rearrangement reaction to oxime ethers, oxaziridines, amides or imines [10–15]. Another application for this class of organic compounds is synthesis of nitroso compounds, hydroxylamines, aldehydes, ketones and many other [17].



Scheme 2. The application of nitrones in chemical reactions
Source: own scheme

Methods of nitrones synthesis

Oxidative dehydrogenation Oxidation of N,N–disubstituted hydroxylamines

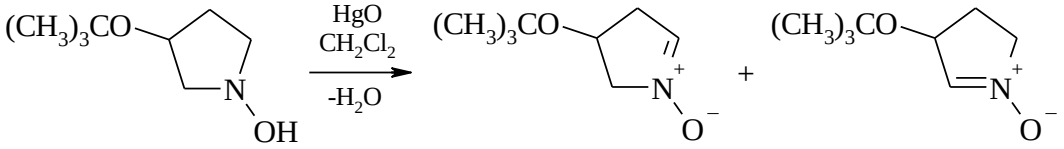
The oxidative dehydrogenation of N,N–disubstituted hydroxylamines is a method which can be used both to obtain cyclic and acyclic nitrones. In this chemical reaction as oxidizing agent are used both inorganic compounds (eg. air in the presence of solution of copper(II) salt [18], molecular oxygen [19], yellow type of mercury(II) oxide [19], "active" lead oxide [19], sodium hypochlorite [19], hydrogen peroxide [20], potassium ferrocyanide [21], potassium permanganate [22] and organic compounds (eg. *tert*–butyl hydroperoxide or copper(II) acetate [19,23]).

In practice, the most commonly used oxidizing agent are: potassium permanganate, potassium ferrocyanide and sodium hypochlorite [19, 21, 22]. These substances allow to get higher yield

performance (in contrast to air in the presence of solution of copper(II) salt) and also are characterized by relative low toxicity (in contrast to yellow type of mercury oxide and t–butyl hydroperoxide) [18,19,23]. Moreover, permanganate and sodium hypochlorite are definitely the safest of all oxidizing agent (unlike to application of peroxides and hydroperoxide compounds) [23].

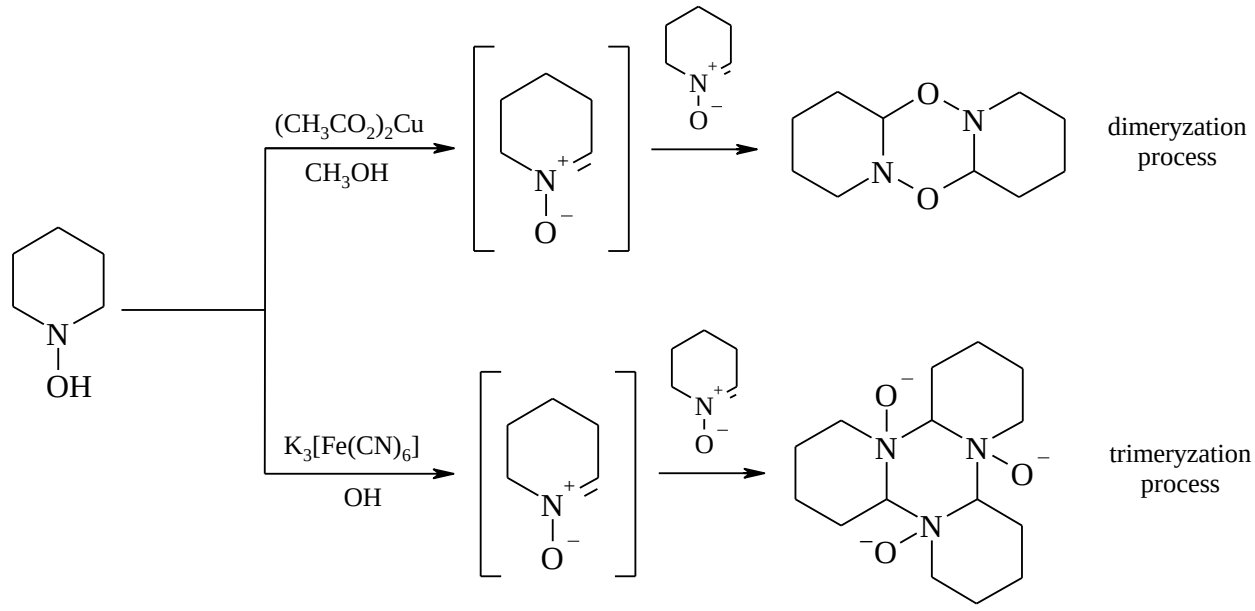
Oxidative dehydrogenation of N,N–disubstituted hydroxylamines is mainly used to prepare cyclic nitrones, which are difficult to synthesised by other methods [24].

Oxidative dehydrogenation of cyclic N,N–disubstituted hydroxylamines can be realized in competitive paths. As a result, it can lead to the creation of two regioisomeric structures. For example, by oxidation of the 3C–(tert–butoxy)–N–hydroxypyrrolidine, using yellow type of mercury oxide, two nitrones were obtained in yield 90% (ratio 9:1) [19].



Scheme 3. The oxidative dehydrogenation of 3C–(tert–butoxy)–N–hydroxypyrrolidine using yellow type of mercury oxide
Source: own scheme

Nitrones, which are obtained by this method, are not always a stable chemical compounds. For example, by oxidation of N–hydroxypiperidine are formed corresponding compound. Nitrone, depending on the oxidizing agent, can convert to other connections [24].



Scheme 4. The oxidative dehydrogenation of N–hydroxypiperidine using both compounds of copper and iron
Source: own scheme

Oxidation of N,N–disubstituted amines

Generally, synthesis of nitrones by oxidation of N,N–disubstituted amines is used more often than previous method. It is related to several factors. The first, N,N–disubstituted amines are easier to receive than their analogous hydroxylamines. And also the method is used to prepare both cyclic and acyclic nitrones [25–28]. However, in a course of reaction can form side products [29].

As oxidizing agent is most often used hydrogen peroxide in the presence of methyl–trioxorhenium [25] and sodium tungstate [26]. Other oxidizing agent usually including organic compounds for example cumyl hydroperoxide in the presence of titanium catalyst [27], dimethyl–dioxirane [28] or 4–chloroperbenzoic acid [29].

Oxidation of imines

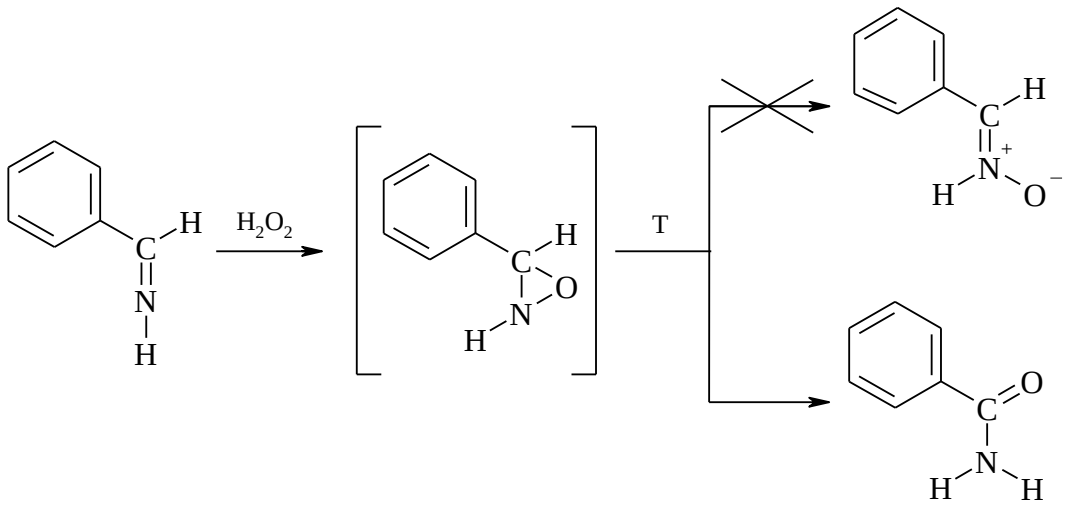
Nitrones – both cyclic and acyclic – can receive by oxidation of imines. As an intermediate product obtain oxaziridine, which are converted to nitrone by ring–opening reaction [30–33].

In practice, nitrones are often oxidized using a 30% solution of hydrogen peroxide to oxaziridines, and next rearrangement is carried out [10,30–33].

Other oxidizing agent are peracetic acid [31], titanium oxide [32], or potassium peroxy–monosulfate [33].

Rearrangement can be influenced by higher temperature [30,31], photochemically [32] or using by a strong acids (eg. 4–toluenesulfonic acid) [33].

The method is attractive due to the availability of imines. However, nitrones are not always formed during the reaction. For example in oxidation of C–phenylimine using by a 30% solution of hydrogen peroxide, during the thermal regrouping oxaziridine in a course of reaction, are formed amides instead of the expected C–phenylnitrone [34].



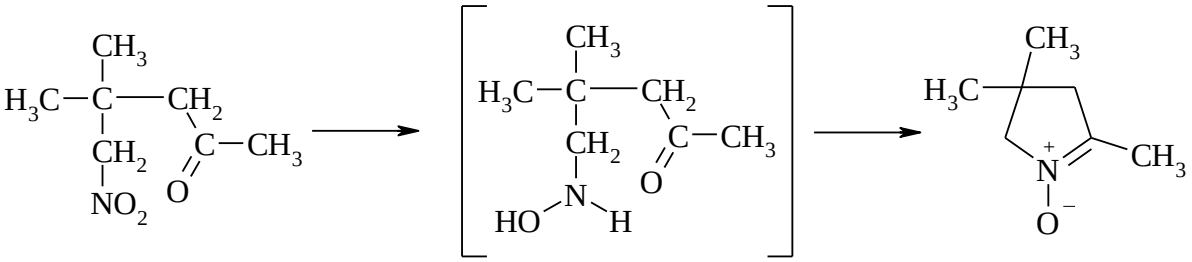
Scheme 5. The oxidation of C–phenylimines using 30 % solution of hydrogen peroxide
Source: own scheme

Condensations between N–substituted hyroxylamines and aldehydes or ketones

Another method of nitrones synthesis is reaction of condensation between N–substituted hyroxylamines and compounds containing a carbonyl group (practicly are used aldehydes or ketones) [35–40].

In a reaction can participate free hyroxylamines, or they can be generated *in situ*, from the corresponding hydrochlorides.

The method also allows to receive a cyclic nitrones. An example may be a synthesis of 2,4,4–trimethyl–1,2–dehydropyrrolidinenitrone in a intramolecular condensation of nitroketones catalyzed by zinc dust in an aqua solution of ammonium chloride [39–40].

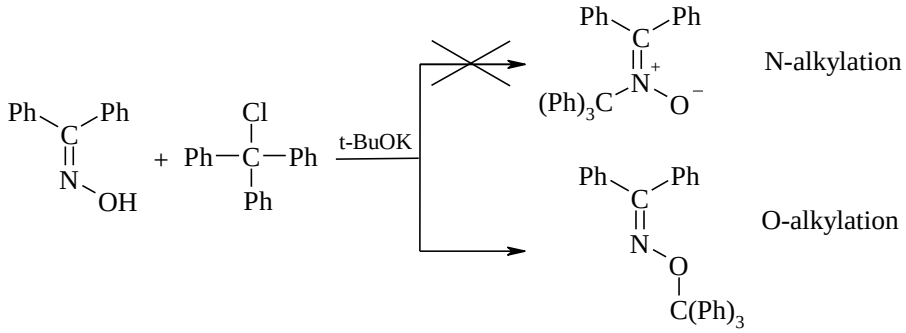


Scheme 6. Intramolecular condensation of 4,4–dimethyl–5–nitro–2–pentanone catalyzed by zinc dust in an aqueous solution of ammonium chloride
Source: own scheme

Alkylation and arylation of oximes

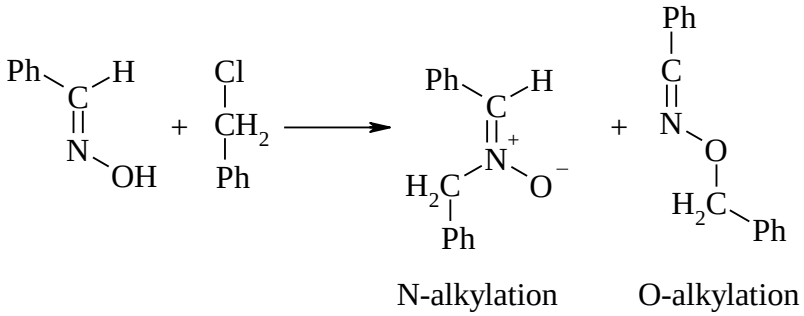
The next method of nitrones synthesis is alkylation and arylation of oximes. This technique was first time used in 1938 [16].

In oxime molecules, both N–alkylation and O–alkylation can occur. The course of the reaction depends both on the nature of the alkylating agent and on the reaction conditions [37,40–43]. When the alkylating agent and the oxime have branched substituents, they can cause steric collapse. An example can be a reaction between benzophenone oxime and trityl chloride. The reaction does not give the expected nitrone, but only oxime ether [32].



Scheme 7. The alkilation benzophenone oxime using by trityl chloride
Source: own scheme

However, most often alkylation of oximes leads to the formation of a mixture nitrone and oxime ether. An example of competition for O–alkylation and N–alkylation processes is reaction between benzaldoxime and benzyl chloride [41].



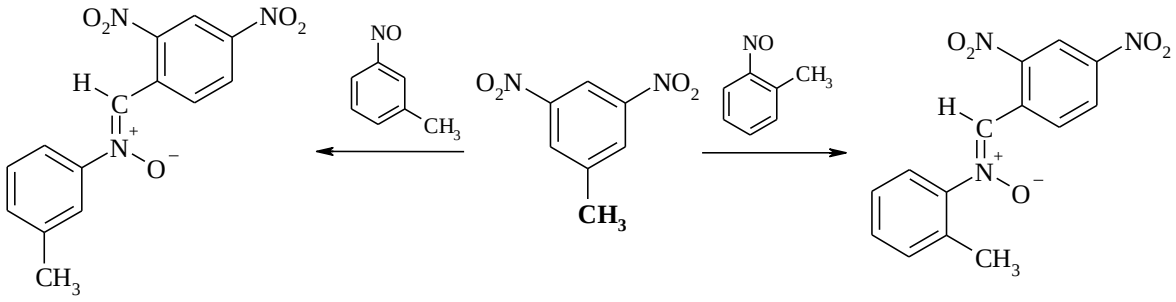
Scheme 8. The alkilation benzaldoxime using by benzyl chloride
Source: own scheme

The method is not often used due to problems with the separation of reaction products (oxime ethers and nitrones), and providing a basic environment, in order to limit tautomerisation. Moreover, the yields of obtained nitrones by this method are very small. And also, it is used to obtain acyclic nitrones, so it is not universal [40–43].

Reactions between compounds containing an active methyl (or methylene) group and nitroso compounds

Nitrones can also be obtained by reacting compounds which in their structure have an active methyl or methylene group with nitroso compounds. In a course of reaction, substrates are react to form N–hydroxylamine, which can be converted to nitrone (alternative to imine) [44]. The reaction is catalyzed by a base (eg. pirydyne [45], piperydyne [45], sodium carbonate [46] and potassium hydroxide [47]). Generally, the method is used to prepare acyclic nitrones.

An example of method is a reactions between nitrosotoluene and 2,4–dinitrotoluene (as a reagent containing an active methylene group) [47].

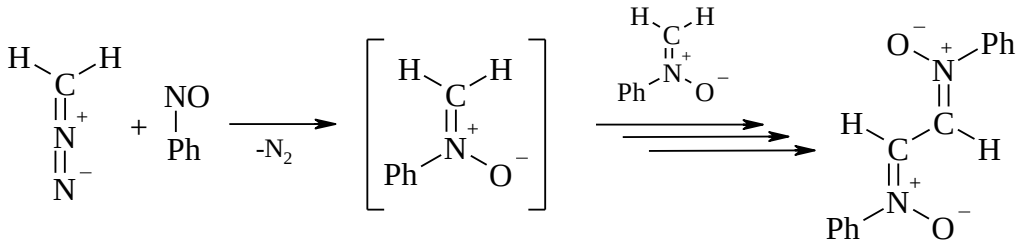


Scheme 9. The reactions between 2,4–dinitrotoluene and nitrosotoluenes
Source: own scheme

Reactions between diazocompounds and nitroso compounds

Another method of nitrones synthesis is reaction of between diazocompounds and nitroso compounds. The method is really attractive due to the possibility of obtaining three–substituted nitrones (very often with sterically expanded substituents). An example of method is a reactions between nitrosobenzene and diphenyldiazomethane [48].

In a course of the reaction it is also possible to obtain dinitrones, for example in the reaction between diazomethane and nitrosobenzene, the expected N–phenylnitrone was not obtained (it has been dimerized to glyoxal dinitrone) [48].



Scheme 9. The reaction between 2,4–dinitrotoluene and nitrosotoluenes
Source: own scheme

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FUTURE OF MEDICINE: PERSONALIZED ONCOLOGY

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Abstract:

Understanding genetic and epigenetic mechanisms of tumorigenesis allows identifying many vital mutations affected the formation of various malignancies. This led to the discovery of a new therapeutic approach, based on molecular mechanisms in the world of medicine, which is called personalized medicine (PM). This review aims to outline the state of the art of the personalized medicine in treatment, taking into account anti–cancer therapy used in selected types of tumors and the difficulties that must be faced with a PM.

Keywords:
Personalized medicine, personalized oncology, cancer

Introduction

The aging of the population and the increasing incidence of chronic diseases is associated with an increased demand for health–related products and technologies. Due to different genetic profiles and different response of patients to drug treatment one of the increasingly popular branches of medicine is personalized medicine (PM), which is a so–called "tailor–made treatment", adapting to the individual patient's needs. The approach based on understanding the differences between patients suffering from the same disease and the simultaneous recognition of the complexity of diseases may contribute to improving the effectiveness of therapy as well as minimizing the risk of side effects [1].

Personalized oncology

Personalized medicine is particularly promising in the field of oncology. Cancer cells are a problematic therapeutic target due to the racial and individual diversity of humans, heterogeneity of tumors and a variety of environmental conditions that can affect the development and progression of cancer. Genetic mutations occurring in tumors, cause their uncontrolled proliferation and often the acquisition of resistance to treatment by selective expansion of cells not responding to the treatment. Currently used therapeutic agents are often ineffective or cause several side effects. Therefore, there is a growing need for more effective and safe anti–cancer drugs, so PM seems to be one of the possible promising strategies [2].

The concept of personalized medicine in oncology should be considered in three aspects. First, it is necessary to identify people with an increased hereditary risk of cancer, which allows

determining the optimal scheme of preventive care, such as selecting an individualized prophylactic screening program, deciding on the prophylactic removal of healthy organs or chemoprevention. Determining the characteristics of molecular changes in tumor cells allows the assessment of a) diagnostic markers, i.e., supporting the diagnosis process; b) prognostic – allowing to determine the prognosis; c) predictive – allowing forecasting of responses to the applied treatment. It is equally important to determine the effectiveness of the biotransformation of the drug in the patient's body, which allows for individualizing the doses of pharmaceuticals used [3].

Genetic and molecular tests should be performed on patients with breast cancer (after immunohistochemistry), lung cancer, ovarian cancer, colorectal cancer, melanoma, chronic lymphocytic leukemia or chronic myelogenous leukemia and gastrointestinal stromal tumors (GIST), but also in the case of diagnosing other tumors of the hematopoietic and lymphatic systems. In the case of these tumors, predictive and prognostic markers are known, enabling the selection of an appropriate treatment path. Selected targeted therapies. Selected therapies are shown in Table 1. Some of them will be described below, more broadly.

Table 1.Targeted therapies for selected cancer and the predictive biomarkers used for efficacy assessment

Type of cancer	Biomarker	Drug	References
Colorectal cancer	*Expression EGFR* (epidermal growth factor); *Presence of mutations in RAS and RAF gene*	Panitumumab, cetuximab	[4]
Chronic myeloidleukemia (CML)	*Presence of BCR / ABL fusion and monitoring of BRC / ABL1 amount during treatment*	*Imatinib*	[5]
Breast cancer overexpressing HER2	Presence of HER2 Overexpression/HER2amplification	Trastuzumab	[6]
Gastrointestinal stromaltumors (GIST)	Presence of mutations in the KIT and PDGFRA (Platelet–Derived Growth Factor Receptor α) genes	Imatinib,sunitinib	[7], [8]
Non–small cell lung cancer	Presence of PD–1L overexpression	Pembrolizumab	[9]
	Presence of mutations in EGFRgenes	Gefitinib, Erlotinib	[10], [11]
Melanoma	Presence of mutations in BRAF gene	Dabrafenib, Trametinib	[12]
Ovarian cancer	Presence of mutations in BRCA1/2 genes	Olaparib	[13]

Personalized therapy in various cancers

Metastatic colorectal cancer

In the treatment of metastasis of colorectal cancer, monoclonal antibodies (MAbs) directed against the receptor for epidermal growth factor (EGFR) may be used, such as, for example, panitumumab or cetuximab. In the metastasis of colorectal cancer, EGFR is expressed, an oncogene that stimulates proliferation, migration and cell immortalization, and angiogenesis. EGFR belongs to the tyrosine receptor kinase family, which consists of EGFR/ERBB1, HER2/ERBB2, HER3/ERBB3 and HER4/ERBB4. The biological functions of EGFR are carried out by activating

oncogenes of the signal transduction pathway. An important inhibitor of AKT gene activity is PTEN. In patients who have EGFR regulated gene activation mutations (downstream genes), blocking of this receptor is ineffective, since, despite the EGFR blockade, the signal path is still active. Mutations have been shown to vary the patient's responses to therapy, not only therapies using mAbs, but also chemotherapy. Mutations in the KRAS gene are currently considered the most important predictors of response to treatment with mAbs. The study of variations in the KRAS gene before therapy with mAbs allows identification of people potentially sensitive to this type of treatment and limiting the use of mAbs only for patients without RAS mutations in cancer cells increases the effectiveness of treatment and leads to a very significant reduction in treatment costs. Although RAS mutations are currently the best–known marker of a positive response to the treatment of colorectal cancer metastasis with FGRFR inhibitors, the classification of patients for this treatment based on RAS mutational status in tumor cells increased the proportion of patients responding positively to treatment by only about 15 %. These results indicate the need to identify further markers of response to mAbs. It is clear from the current state of knowledge that such modifiers are mutations in subsequent genes from the EGFR pathway [14–16].

Melanoma

Patients with melanoma in which the activation mutation V600E of the BRAF gene was found, are treated with BRAF inhibitors such as vemurafenib and dabrafenib. Pathway in melanomas is the RTK tyrosine kinase receptor pathway. The most common mutation found in BRAF is V600E (in about 80 % of cases) and V600K (in about 17 % of cases), and less frequent are other mutations, such as the V600D and V600G mutations [17]. The presence of these mutations is a marker of an unfavorable prognosis. In addition to the BRAF mutations in the melanoma, numerous mutations activating proto–oncogenes such as NRAS, KIT, GNAQ/GNA11 are observed, as well as mutations inactivating suppressor genes (also giving the cells proliferative potential) such as, for example, CDKN2A, PTEN, NF1, BAP1. Ones of the examples may be imatinib and nilotinib as inhibitors of the KIT gene [18].

Ovarian cancer

Ovarian cancer is cancer characterized by significant genetic heterogeneity, and despite many years of research into molecular changes in ovarian cancer, no leading genetic changes have been identified that could become a therapeutic target for personalized therapy. The exception is olaparib, PARP (Poly ADP ribose polymerase)inhibitor, a drug that has been approved by the FDA, for use in ovarian cancer in carriers of a germline mutation in the genes BRCA1/BRCA2 [19]. These genes encode DNA double crack repair proteins and the loss of function of these genes results in increased cell sensitivity to PARP inhibitors. In in vitro experimental studies, the interaction of inhibitors of c–Met and PARP1 activity has been shown to inhibit breast and lung cancer cell proliferation [20].

Gastrointestinal Stromal Cancer

In the treatment of gastrointestinal stromal cancer (GIST), both in mutated forms activating proto–oncogenes KIT or PDGFRA in tumor cells and in cases without these mutations, the

therapeutic standard is the use of tyrosine kinase inhibitor imatinib. Molecular studies have shown that in the vast majority of gastric hamstrings there are either mutations activating the KIT proto–oncogene PDGFRA. Response to treatment with imatinib is various in groups of patients differing in genetic changes in tumor cells: among patients with mutation KIT in exon 11 for treatment with imatinib positively reacts about 80 %, among patients with mutation KIT in exon 9 positive for this therapy corresponds to 40 % of those treated, whereas in the group of patients without KIT mutation, only 14 % react to imatinib. Among patients with PDGFR mutations in tumor cells, about 66 % respond to this therapy, except for people with exon 18 (D842V) mutation who are completely resistant to imatinib treatment. However, even in patients who respond well to imatinib therapy, resistance to this therapy develops after about 18–36 months. This a phenomenon is associated with the genetically conditioned effectiveness of the drug metabolism and DNA repair, and with subsequent genetic changes in the genetic landscape, mainly based on the selection of cell clones that are not sensitive to the treatment. The second–line drugs (eg. those in whom resistance to imatinib has developed) are other tyrosine kinase inhibitors such as sunitinib or regorafenib [21].

Lung cancer

In the treatment of patients with non–small cell lung cancer (NSCLC), in which the mutation activating the EGFR gene tyrosine kinase is present, tyrosine kinase inhibitors such as gefitinib and erlotinib are used. Patients with NSCCL with the fusion of ALK/EML4 present in tumor cells are treated by crizotinib (approved by the US FDA)[21]. The EGFR gene activation mutation is present in NSCLC cells in 10–15 % of Caucasian, Caucasian and even 36 % of Asian patients. These are most often nonsmokers or those who smoke a few cigarettes EGFR mutations most often (in almost 90 % of cases) are in exons 18–20. The most frequent mutations are a deletion in exon 19 and L858R point mutation exon 21. Treatment with gefitinib in patients with an EGFR mutation increases the proportion of patients responding positively to treatment (from approximately 47 % to approximately 71.2 %) and prolongs progression–free survival as compared to treatment effects using chemotherapy. Very similar results were obtained for erlotinib treatment. In patients without EGFR mutations in tumor cells, the response to treatment with tyrosine kinase inhibitors is much weaker than in chemotherapy. In connection with these observations, the National Comprehensive Cancer Network (NCCN) is currently recommending molecular testing for EGFR mutations in all patients with advanced forms of NSCCL [22].

Patients who have a mutation in tumor cells, treatment with tyrosine kinase inhibitors is recommended as the first–line treatment, and in people without a mutation, as the second–line treatment. Patients treated with tyrosine kinase inhibitors inevitably develop resistance to the therapy. The most common cause of this phenomenon (in about 50 % of patients) is the appearance in the tumor, in addition to clones of cells with the above–mentioned mutations of the EGFR gene, clones of cells with an EGFR mutation in exon 20 (T790M) or overexpressing the MET or HGF path (Hepatocyte Growth Factor), which are insensitive to the treatment used [23, 24]. In 2007, the second key molecular change for NSCCL cells was discovered. It was found that about 7 % of patients (most often non–smokers, or smokers) in the tumor cells are inversions of the arm of the short chromosome 2 leading to the formation of the EML4–ALK fusion gene. Patients with this

lesion are resistant to treatment with the above–mentioned tyrosine kinase inhibitors, but they react to treatment with ALK inhibitor, crizotinib [25].

Obstacles PM

The concept of personalized medicine is becoming more and more common in the world, access to its solutions in everyday clinical practice encounters significant barriers, including inadequate knowledge and poor quality of hospital staff training, as well as need to verify and validate research techniques. Additional potential problems are related to health regulating systems (are not so flexible) and the cost of such approach (many drugs have to be introduced for the same disease).

There is a belief, that comprehensive generic research is costly. Targeted treatment reduces the risk of side effect, and therefore the need to hospitalize the patient, the final balance would be favorable because the indirect cost of treatment is reduced. Besides, PM generates indirect cost savings, since only effective drugs acting on the tumor are used, matched to the patient`s genetic profile, without selecting the appropriate treatment method trial and error, as is the case in standard treatment [4, 26].

The social problem is not the most important PM loop. The main limitation of personalized medicine is the unique genetic profiling of each patient. Changes in genes occur with low frequency, and overcoming this obstacle involves the development of genomic algorithms, and the implementation of specialized software allows forecasting at the individual patient level. Although new technologies generate costs, in the short run, the PM approach seems more economical than conventional treatment in the long run [4].

Conclusion

Personalized medicine is critical in oncology, as evidenced by still the limited research in this field. Increasing knowledge of genomics, molecular biology, toxicology, and immunology contribute to the dissemination of individualized therapy in cancer patients. However, this method of treatment is beneficial both from an economic and social point of view. The correct choice of treatment method significantly increases the number of patients who have a chance of permanent outflow with a rapid possibility of returning to life before the disease, because of shortening the treatment time and minimizing the occurrence of undesirable side effects.

PM is undoubtedly a breakthrough in oncology, and the result of investigations observed in clinical trials give great optimism and are a harbinger of the expected progress in oncology. However, this strategy to overcome cancer, requires a systemic approach, forcing coherence in the management of the treatment process. Coordination of the performance of diagnostics and its availability are, in this case, a condition for therapeutic success. Therefore, further evolution of the health care system should take into account the complexity of care and consolidation around the diagnostic and therapeutic process. Which means in case of the need for molecular diagnostics, accessibility to it and its high quality should be ensured by system solutions so that it would be delivered on time, quality and optimal economic conditions.

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ULTRA–HIGH MOLECULAR WEIGHT POLYETHYLENE (UHMWPE) AND ITS APPLICATION IN BIOMEDICAL ENGINEERING AND MEDICINE

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Abstract:

The publication is a review and has been devoted to one of polymeric biomaterials, applied in bioengineering, biomechanics, dentistry and other fields of medicine, which is ultra–high molecular weight polyethylene (UHMWPE). At the beginning of this paper the issues related to requirements for biomaterials and characteristics of basic keywords connected with them, i.e. biocompatibility, biotolerance, have been outlined. Moreover, the basic information about polymeric materials and the examples of their application in various branches of bioengineering have also been presented. The main applications of UHMWPE and its properties, which are key for implants, have been discussed in detail. Furthermore, it has also been the issues referred to forming, processing and modification of UHMWPE.
The presenting a comprehensive overview of UHMWPE applications used in biomedicine, bioengineering, biomechanics and its properties has been the aim of the article.

Keywords:
polyethylene, UHMWPE, biomedical engineering, endoprostheses, biocompatibility

Introduction

The end of the 20th and 21th century have brought advancement in the areas such as: biomedical engineering, materials engineering and medicine, which was caused by negative phenomena related to the development of civilization (i.a. an increase in the number of accidents and diseases). This, in turn, has contributed to the interdisciplinary work of specialists on solutions with regard to the reconstruction of diseased tissues or damaged human organs. Nowadays, for this purpose the transplantation of living tissues and organs and the implantation of artificial alternatives is increasingly used instead of their excision. The development of materials used not only for implants, but also for tools, supplies or medical equipment has taken place too. Polymeric materials are one of three major biomaterial groups, beside metallic, ceramic and biocomposite materials. Polymers have been playing an increasingly important role in biomedical applications since the second half of the twentieth century due to their unique properties [1–3].

Requirements for biomaterials

The development of implantology, and hence the higher demand for implants, has made greater requirements for biomaterials. First of all, these are biological requirements, because this type of material should be characterized by biocompatibility (also called biotolerance, biofunctionality), which means its proper behaviour in contact with tissues and human body. In addition, these materials (and possible wear products) should be non–toxic, i.e. they have not effect on human immune system – they can not cause any acute and chronic allergic reactions, inflammations, lead to haemolysis (i.e. the formation of blood clots) and show mutagenic and cancerogenic effects. Furthermore, biomaterials should have appropriate, high corrosion resistance in the environment of tissues and body fluids [1–4].

Further criteria, which are set for biomaterials, are mechanical (mainly strength) and tribological requirements. The following properties belong to them [2–4]:

- appropriate tensile, compression, bending and torsional strength,
- appropriate, high fatigue strength,
- good hardness and impact resistance and appropriate elasticity ,
- appropriate, high abrasion hardness,
- very good wear resistance and low coefficient of friction.

Moreover, biomaterials should be characterized by appropriate technological properties, among which the ease of processing and sterilization, ensuring the required surface and biomaterial quality and low production costs should be mentioned. Additionally, optimal physical properties of such materials, incl. the right density and viscosity, are also desirable. Furthermore, biomaterials should be characterized by a specific set of electromagnetic and thermal properties [2–4].

The above–mentioned requirements for biomaterials applied to implants, equipment or medical devices are very diverse and yet there is no material that would have a set of the above properties. However, visible development in biomedical or material engineering enables the production of increasingly better, more tough biomaterials with higher biotolerance [2–4].

Polymeric biomaterials – basic information

Polymers are chemical compounds composed of a lot of primarily organic (rarely non–organic) macromolecules, in which repeated (different or identical) structural units are connected by covalent chemical bonds. The above–mentioned macromolecules of polymers are formed as a result of polymerization of monomers. Other polymers are the effect of addition polymerization, which is progressive reaction or of polycondensation, where simple by–products (e.g. water, ammonia) are discharged. Hence polymers with linear, branched or cross–linked structure may be formed. That's why, the choice of synthesis method significantly affects obtained polymer, its structure and properties. As an example, polymer chains can form ordered, regular areas – crystalline phases or irregular, amorphous areas, whereby the occurrence of crystalline areas increases the strength properties of these materials, what makes polymers with high degree of crystallinity are more often applied in bioengineering and medicine [5–10].

Types of polymeric biomaterials and their application in bioengineering and medicine

Due to its unique mechanical and physicochemical properties (especially biocompatibility, the ease of forming, sterilization and obtaining of reproducible material quality for different batches of products) polymers have found a wide range of applications in medicine, whereby these materials can be grouped by their origin into two categories: natural and synthetic polymers [1–4]. This classification is presented in Table 1, and their application in medicine is pictured in Figure 1.

Table 1. The classification of polymer materials applied in medicine

Type of polymer	Natural polymers	Synthetic polymers	
Examples of polymer	– proteins (collagen), – polysaccharides (starch, cellulose, hyaluronic acid) – natural rubber	– polyethylene (PE), – polypropylene (PP), – polytetrafluoroethylene (PTFE), – polyvinyl chloride (PVC), – polymethyl methacrylate (PMMA), – polystyrene (PS),	– polycarbonates (PC), – polyamides (PA), – polyesters and biodegradable polymers (PLA, PET), – silicones, – polyurethanes (PUR), – epoxy resins (EP)

Source: own study based on: [1–4]

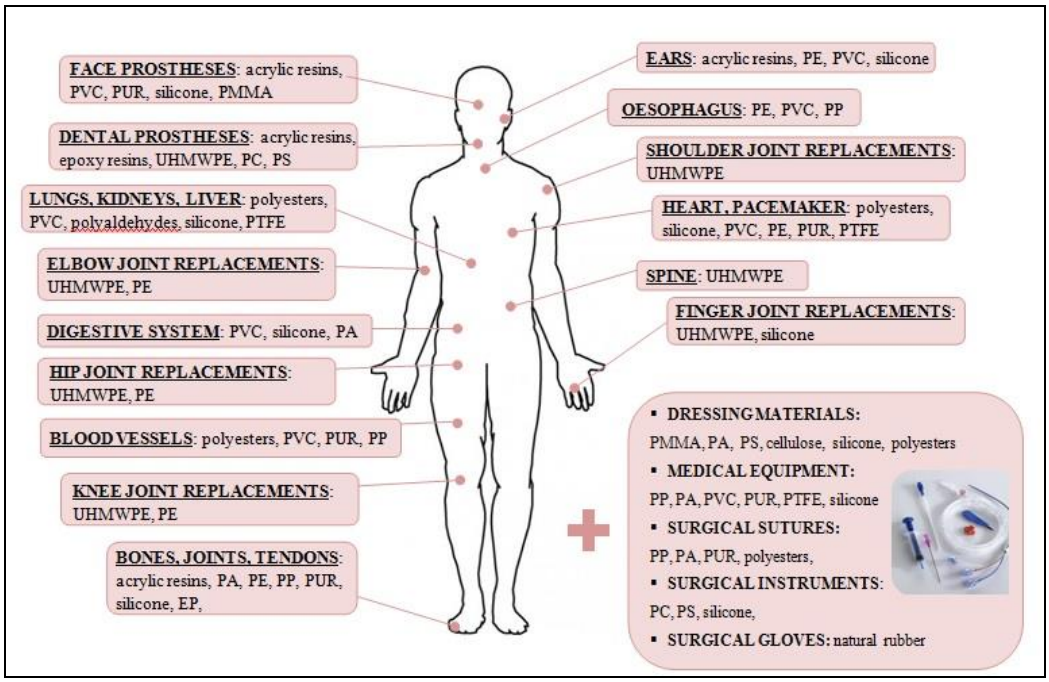

Figure 1. Polymers applied in medicine and biomedical engineering
Source: own study based on: [1–4]

Ultra–high molecular weight polyethylene (UHMWPE)

Ultra–high molecular weight polyethylene (UHMWPE), like all other PE grades, belongs to the group of polyolefins, i.e. polymers consisting only of carbon and hydrogen atoms, forming long chains by means of covalent bonds. These chains can take a linear, branched or cross–linked forms. Therefore, PE structure is very simple, as shown in Figure 2 [11, 12]. Polyethylene macromolecules

are characterized by symmetrical structure, which gives its non–polar (electrically neutral) and hydrophobic properties. In addition, this material belongs to the two–phase bodies – semi–crystalline, in which amorphous regions are visible between the crystalline regions. The number of these phases determines the degree of crystallinity [6–7, 11–13].

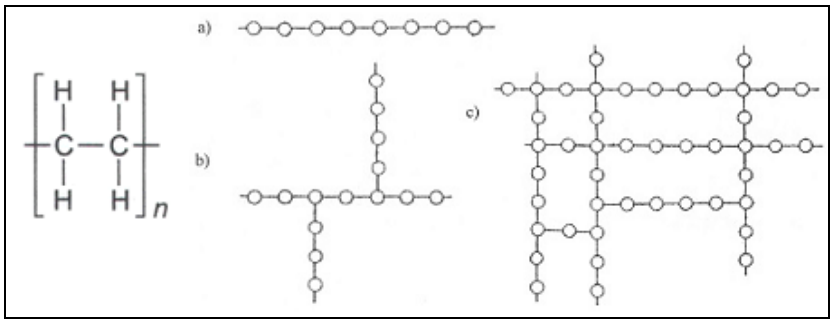

Figure 2. PE structural formula and forms of its chain: a– linear, b– branched, c– cross–linked
Source: own study based on: [6–7]

In general, polyethylene is obtained as a result of irreversible reaction – addition polymerization, during which the monomer molecules, i.e. ethylene join to form polymer macromolecules. In the case of UHMWPE, this reaction have been carried out at low pressure and in the presence of various catalysts (e.g. Ziegler–Natty–type or Phillips–type). Additionally, this process has taken place in argon atmosphere in order to protect final product against contamination [6, 7, 11–14].

Properties of UHMWPE

PE properties depend primarily on the physical structure of the material (and hence its density, molecular weight, degree of crystallinity etc.), which is influenced by the method of production. Therefore, each variety has slightly different properties [11–13]. For illustration, some properties of PE varieties have been collected in Table 2.

Table 2. Basic properties of some PE grades

Grade of polyethylene	LLDPE	LDPE	HDPE	UHMWPE
Density [g/cm^3]	0,918 ÷ 0,935	0,91 ÷ 0,925	0,94 ÷ 0,965	0,93 ÷ 0,96
Degree of crystallinity [%]	34 ÷ 60	40 ÷ 65	60 ÷ 85	39 ÷ 75
Tensile strength [MPa]	20 ÷ 26	8 ÷ 17	20 ÷ 35	22
Elongation at break [%]	> 50	> 50	> 50	> 50
Young's modulus [GPa]	0,3 ÷ 0,7	0,2 ÷ 1,4	0,4 ÷ 4,0	0,5 ÷ 0,9

Source: own study based on: [1, 9, 11–14]

In general, it is a solid in the form of powder or granulated product, alternatively semi–finished products (e.g. blocks, foils, profiles, pipes, sheets, fibres etc.), which can be transparent (whereby this property decreases with increasing density), usually white or colourless, sometimes tinted with the aim of protection against radiation. In addition, it is characterized by high biotolerance, resistance to most chemicals (with the exception of strong oxidative ones, e.g. halogens or concentrated HNO_3 and some cleaning agents) and permeability to O_2, CO_2 or most

fragrances. However, polyethylene is not weather–resistant, particularly to UV radiation and oxygen, causing accelerated photooxidation, cracking and increasing the material brittleness and it is not permeable to water and steam. In turn, taking mechanical properties into consideration, it is stated that PE is a material of low stiffness, but high ductility and good wear–resistance [11–13].

In comparison with other PE grades, UHMWPE is characterized by much better physicochemical and mechanical properties, which results from the very high molecular weight (exceeding 5 million g/mol). This variety has very good wear–resistance and crack resistance, quite good impact strength, bending or tensile strength and freeze–thaw resistance as well as very good sliding properties (abhesive surface), low coefficient of friction and damping capacity. It also has very high chemical and thermal resistance as well as good electrical and insulation properties. Lubricity and ease of processing and sterilization are other significant properties, which predispose UHMWPE to use in some medical applications [11–14].

UHMWPE modifications

Ultra–high molecular weight polyethylene is generally chemically or physically modified by actions minded to change properties or give new ones, whereby this process is carried out during the production of the material or its processing (i.e. forming the pilot product). Typically, the modification is aimed at reduction of production costs, improvement of strength properties, chemical, thermal resistance and resistance to ageing (mainly influenced by UV radiation) and obtaining better processing properties. In the case of UHMWPE, this process involves addition of processing aids (antioxidants, light stabilisers, mineral or powder fillers of metals) or crosslinking by means of organic superoxides or radiation [15].

Crosslinking is the process of joining of two or more different molecular chains by means of cross–links of three–dimensional space lattice, whereby properties of crosslinked polymer depend on these cross–links (their type and amount). As a result of this kind of modification, strength, wear–resistance and resistance to ageing have been improved. Radiation crosslinking takes place in usually in properly adapted electron accelerators and this is x–ray of polymer by electron beams or gamma rays. In addition, this type allows to sterilize the material in single and bulk packs. [1, 15–17]. UHMWPE is crosslinked in two ways:

- firstly, it is radiated with a dose of 50÷100 kGy (kilograys), followed by melting process, which leads to elimination of free radicals;
- the material is radiated with using two doses of gamma radiation (firstly a dose of 75 kGy), which brings the development of free radicals in polyethylene, taking part in forming of cross–links; then the temperature is raised in order to anneal the material and additionally homogenize it and improve its mechanical properties; free radicals are eliminated during sterilization with using gamma radiation.

Chemical modification of UHMWPE is typically carried out with using different processing aids, primarily stabilizers (e.g. soot), increasing polymer resistance to ageing and weather conditions (ozone, oxygen, changing temperature, luminous energy etc.) and hence protecting against oxidation, depolymerization and decomposition. Recently, UHMWPE have been also modified by addition one of the stabilisers, i.e. vitamin E (α–tocopherol), which result is a new polyethylene grade – E–Poly (ePoly). Typically, the stabiliser is added prior to the production step,

mixing it with the PE powder, after which the material is subjected to radiation crosslinking. In turn, the second method involves the mixing vitamin E into the previously crosslinked UHMWPE, which is typically used in the production of endoprostheses elements. In general, studies carried out so far have shown that vitamin E protects against oxidative degradation and improves the strength, fatigue properties and abrasive wear of UHMWPE, but it is not known, how these properties change in the case of long–time using of these elements [1, 12–15, 18–20].

Sometimes, ionic implantation is applied, in which the surface layer of the material is modified by bombardment with high energy ions, It leads to the incorporation of atoms of metals or non–metals (e.g. argon, argentums, helium, carbon) in the polymer structure, which affects the change of optical (e.g. roughness), mechanical (increase in hardness), tribological (increase in wear–resistance, decrease in coefficient of friction) and chemical and thermal resistance. However, these changes depend on the structure of polymer, type of applied ions, dose and energy of the beam [21].

UHMWPE production for medical applications

Chemical, physical and mechanical properties of ultra–high molecular weight polyethylene, used in production of implants, significantly depend on production process and polymer sterilization. The choice of appropriate conditions of these processes allow to obtain medical products with the highest quality and desirable parameters [13–14].

UHMWPE production for implants consists of some stages. Firstly, the UHMWPE must be polymerized from ethylene gas, which leads to obtaining PE resin powder (Figure 3a). Then this powder needs to be consolidated into sheets, rods or near–net shaped implants (Figure 3b). Semi–finished products are developed during ram extrusion, direct compression molding or hot isostatic pressing, which are carried out under elevated temperature and pressure. Finally, UHMWPE implants need to be machined into their final shape (Figure 3c and 3d). Then, these components need to be sterilized and packed in appropriate conditions, whereby currently the most popular methods are gas sterilization with using ethylene oxide and sterilization applying bactericidal activity of radioactive radiation. After that, these elements of implants can sit in surgery [13, 14].

Figure 3. Processing steps in the manufacture of UHMWPE implants: A– obtaining the resin powder, B– consolidated semi–finished rods, C– machining of the UHMWPE rods on a lathe, D– UHMWPE acetabular components
Source: own study based on: [14]

The application of UHMWPE in medicine

Ultra–high molecular weight polyethylene (UHMWPE) is widely used in medical applications because of its unique properties (especially biocompatibility, low mass, resistance and other appropriate technological, strength and tribological properties). It is mainly applied in joints replacement and surgery. The most common applications are [1, 3, 13, 14]:

- components of hip and knee endoprostheses,
- components of endoprostheses of shoulder, elbow and ankle joints,
- prostheses of fingers,
- implants of spinal discs,
- bone plates for osteosynthesis,
- meshes for reconstruction of large hernias etc.

Hip joint endoprostheses

Hip joint replacement has been one of the most often made operations in the last few decades and UHMWPE has been applied in these endoprostheses since about 1960s. It is usually used to treat degenerative changes of the hip and injuries such as transcervical fracture or fracture of trochanter area. [1, 22, 23].

These procedure involves entering metal part into femoral bone and artificial acetabulum into pelvic bone, hence hip joint endoprosthesis consist of three basic components, i.e. acetabular cup anchored in the pelvic bone and stem implanted in the medullar cavity of femoral bone, which may belong together with the head of prosthesis (sometimes they are separated elements). In some types, an additional component is metal basket (cover), in which cup is placed. The construction of hip endoprosthesis and methods of its attachment in the human body is shown in Figure 4 [1, 14, 22, 23].

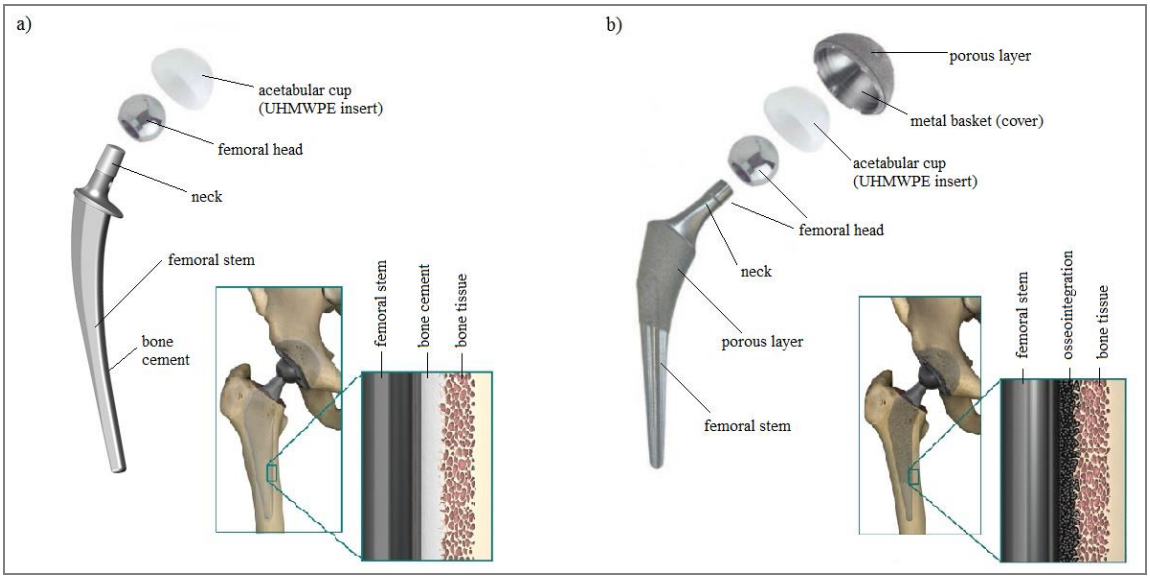

Figure 4. The construction of hip endoprosthesis and methods of its attachment – cement–fixed (a) and cementless (b)
Source: own study based on: [1, 14, 22, 24]

Elements of cementless endoprosthesis are fixed by pressing or screwing in, whereby these components are covered by porous layer (e.g. hydroxyapatite – HAp, sputtered titanium or mixture of these materials) on the whole surface or its part. These fixations are based on osseintegration of bone and porous layer, whereby speed of these process and the durability of the fixation depend on the type of porous material (layers based on titanium are overgrown slower than those based on HAp). Cement–fixed endoprostheses, in turn, are attached by bone cement (PMMA), which is strong fixation and allows to incompletely load pelvic limb on the first day after alloplastic surgery. Sometimes hybrid endoprostheses, in which stems are fixed by bone cement and cups by pressing, are used [1, 14, 22, 23].

In this case of endoprosthesis UHMWPE is used in acetabular cups (inserts), which directly cooperate with femoral heads, hence friction node (femoral head – acetabular cup) is the basic component of implant. These element are made of different types of materials, whereby their selection belong to factors having significant influence on frictional resistance, wear–resistance and finally on the durability f the endoprosthesis. The most popular material combinations (Figure 5) for wear couples *femoral head – acetabular cup* are [1, 14, 22, 23]:

- ceramic – ceramic (e.g. Al_2O_3 or ZrO_2),
- ceramic – polyethylene (UHMWPE),
- metal (mainly CoCrMo, ferrous or titanium alloys) – polyethylene (UHMWPE),
- metal – metal.

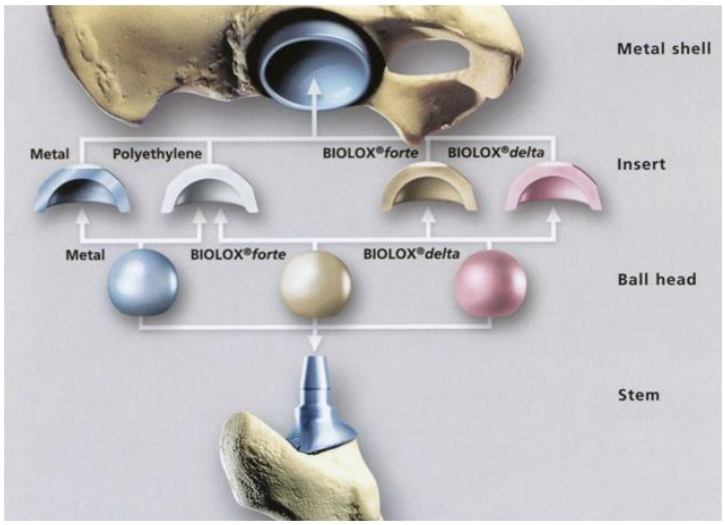

Figure 5. Material combinations applied for hip endoprotheses
Source: own study based on: [25]

In turn, femoral stems are made of metal materials (e.g. stainless steel – 316L, titanium alloys – Ti6Al4V or cobalt and chrome alloys – CoCrMo). Both metal heads and ceramic heads can cooperate with UHMPWE cups [22, 23].

Acetabular cups made of UHMWPE are characterized by low wear–resistance, hence they fast wear (which is related to loss in mass and change of inner cup diameter) and lastingly deform, what can lead to vertical and horizontal migrations of cups, loss of endoprosthesis stability, forming wear products and their migrations. Additionally, large number of them can lead to bone resorption, inflammations in the joint and eventually to loosening elements of the endoprosthesis. In turn,

cumulation of frictional wear, creep and ageing processes leads to reduction in the thickness of UHMWPE cup and its strength properties, which can cause reduction in its lifting capacity and eventually its fracture. And this is reason for reimplantation operations [1, 22–23, 26].

Knee joint endoprostheses

Knee joint replacement has been used in the treatment of degenerative changes of this joint and inflammations related to rheumatoid arthritis and its main aim is reduction of pain and restoration of basic joint functions and its mobility. However, it is done rarely because of complex structure of this joint and higher costs, although recently there has been increasing number of knee replacement surgeries [13–14, 22].

Total knee joint endoprosthesis usually consists of three elements: metal component fixed in tibial bone, polyethylene insert, being moving part, and metal component fixed in femoral bone (Figure 6). Usually these elements have or no small stems (Figure 6a), but due to large deformations or ligaments injuries, long stems fixed in these bones are used (Figure 6b). This implant can be fixed in the same way as hip implants, i.e. by bone cement cementless or hybrid method. In turn, the most often used materials are metal alloys (mainly CoCrMo, titanium alloys) to production of tibial and femoral parts and UHMWPE to mowing inserts, whereby these elements and hence whole models are individually adjusted to patients [13–14, 22].

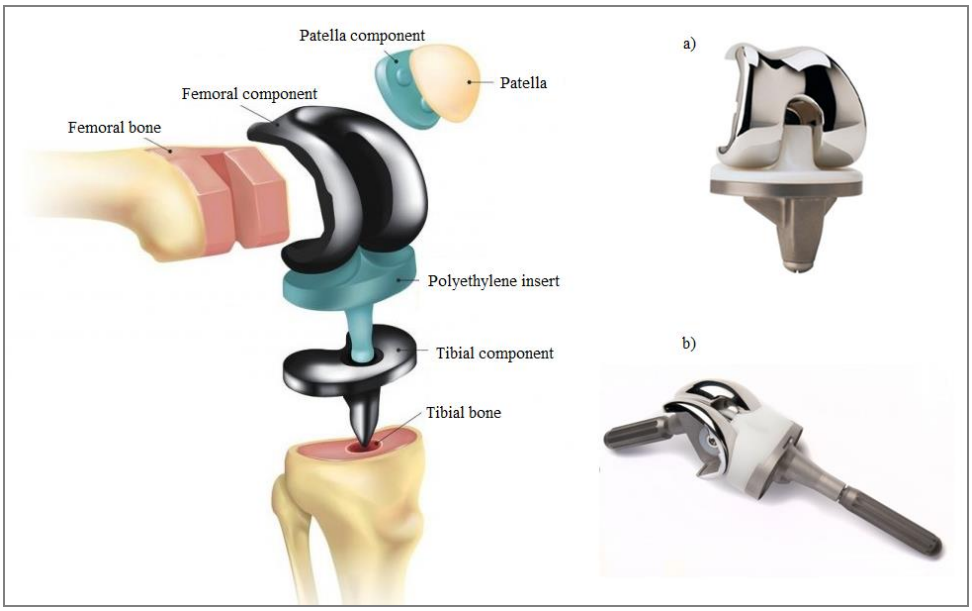

Figure 6. Material combinations applied for knee endoprostheses and their types: with small stem (a) and long stems (b)
Source: own study based on: [14, 22, 27–28]

As in the case of hip endoprostheses, knee implant's life span is reduced, which is affected by such factors as level of patient's activity, his body weight and general health. Wear concerns in particular polyethylene inserts, which can be destroyed influenced by carrying loads during the work in environment of the human body. In general, the following adverse phenomena occur in them:

- their frictional wear and fatigue, which lead to loss of material, forming of wear products change UHMWPE roughness and consequently to loosening of implant

- change of macro–geometry of their surface, which is caused by plastic deformations, scrapings, and creep of material,

All these negative changes lead to loss of endoprosthesis functionality and revisions, hence over–engineering of biomaterials used in production of implant's elements is very significant [14, 22].

Other medical applications

UHMWPE is also applied in other joint implants, e.g. shoulder (Figure 7a), elbow (Figure 7b) or ankle joint (Figure 7c), but these surgeries have been rarely done, hence the development of these prostheses has not been intensive. Furthermore, in these types of endoprostheses polyethylene parts are used as sliding elements and are destroyed after long time of exploitation [14, 22].

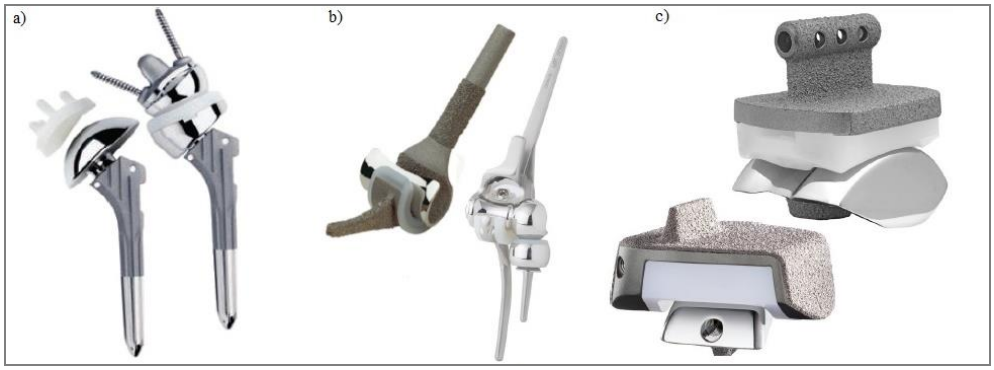

Figure 7. Examples of shoulder (a), elbow (b) and ankle (c) joint endoprostheses
Source: own study based on: [14, 22]

UHMWPE is also used in artificial spine discs (Figure 8a), which are implanted between two health adjacent ones. Usually, it consists of two metal endplates and core made of polyethylene (Figure 8b) [14, 22].

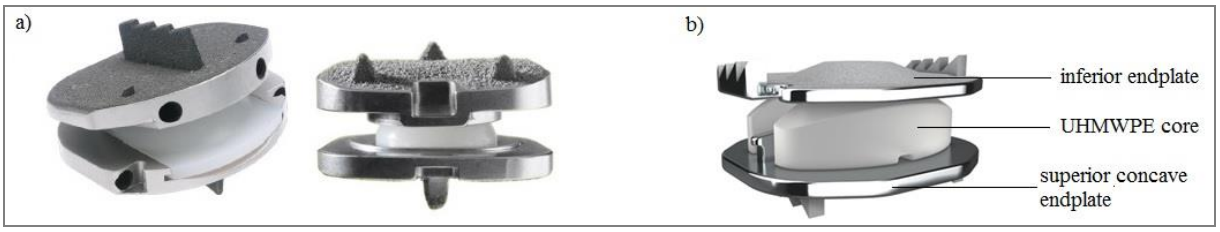

Figure 8. Examples of implants of spine discs (a) and their construction (b)
Source: own study based on: [14]

Summary

Ultra–high molecular weight polyethylene (UHMWPE) is the biocompatible material, which has been successfully used in medical applications for over half century. It is most often applied in production of bearing elements of hip and knee joint endoprostheses as well as artificial spine discs. Shoulder, elbow and ankle implants are less popular.

UHMWPE properties are strictly related to methods of production, machining and sterilisation, but they change influenced by the environment of human body. As an example, elements made of this material can be destroyed as a result of frictional wear, abrasion, plastic deformations, creep or fatigue wear. Currently, numerous research studies on UHMWPE development have been carried

out. Their aim is to improve wear–resistance and hence extend period of exploitation after implantation to human body.

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THE SELECTED TOOLS AND TECHNIQUES USED IN DESIGN THINKING METHODOLOGY

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Abstract:

Design Thinking is the methodology, which is aimed at creation of innovative, sometimes original solutions, i.e. new products or services. This publication refers to tools and techniques applied during design process carried out in accordance with assumptions, rules and the spirit of DT. The examples of them have been given below. In turn, these selected tools (e.g. empathy maps, brainstorming etc.), which are the most popular and used, have been described in detail. Additionally, in this paper, the notion of this method and five stages of Design Thinking (empathizing, defining the problem, generating ideas, prototyping and testing solutions) have been concisely discussed. Summarizing, basing design process on structured form, basic rules and application of different DT tools stimulates creativity of team group and drives effectiveness of their members. This, in turn, leads to generation of sometimes unconventional, abstract ideas and hence innovative solutions.

Keywords:

Design Thinking, Design Thinking tools, innovations, creativity, brainstorming

Introduction

Design Thinking is the methodology, which supports innovations, stimulating creativity in making new original, sometimes abstract and unconventional solutions. They are response on various complex problems, to which companies, entrepreneurs or other institutions and organizations have to face up during running their business [1–2].

But it is asked where in general DT came from and when it appeared? Well, its beginnings go back to the 1960s, however the real and rapid development of DT took place in the 1980s and 1990s. Then, first ventures accordant with this concept and corresponding to more and more bigger demand of entrepreneurs from Silicon Valley, were created at Stanford University in California. Hence DT facilitated the transfer of creative ideas, visions or other solutions from the world of science to business [1, 3–7]. Here, it should be mentioned that Professor at Stanford University David M. Kelley largely contributed to the creation of this methodology. Then, with other scientists, he founded design office – IDEO, which currently excels in its field, developing innovative solutions and cooperating with such brands as e.g. Apple, IKEA, Microsoft or Toyota.

Additionally, then two design centers – *d.school*, i.e. Institute of Design at Stanford University and HPI School in Potsdam were set up respectively in 2004 and 2007 in order to develop and popularize this methodology among students as well as to allow them to carry projects out (in according to this conception) [1, 4–9].

What is Design Thinking? – its notion, basic assumptions, rules and stages

Design Thinking has no single, clear definition. As an example Tim Brown's (CEO of IDEO) words can be given: *„Design thinking is a human–centered approach to innovation that draws from the designer's toolkit to integrate the needs of people, the possibilities of technology, and the requirements for business success."* Therefore, it can be said that DT is firstly organized way of approach to solving different problems as well as an intellectual framework for innovative, original and unconventional ideas. Secondly, it can be determined as an intuitive method of work, in fact workshop cooperation and teamwork. And thirdly, DT also means a set of various characteristic tools, techniques and working methods, which are applied in business [3, 7–9].

What is Design Thinking based on?

Basing the design process accordant with DT methodology on detailed understanding of future clients, i.e. their problems and needs, allows to achieve high effectiveness and success, which is desired by customers solution. In addition, it is necessary to apply a few key and essential elements, which can be defined as core of DT. These basic assumptions and rules are [1, 4–5, 7–12]:

- ***concentration, focus on the other person, user, future client*** – by looking through user's eyes, from his perspective, going beyond some familiar frames (i.e. *out of the box*) – experience and habits, which allows to understand conscious and unconscious needs of customers and their problems and hence stimulates creativity in generating various ideas;
- ***interdisciplinarity*** and ***teamwork*** – which allows to obtain a broader overview of a given problem, view from many various perspectives and also stimulates the creativity, exchange of experience and drives effectiveness of team members, leading to generation of innovations, sometimes very abstract solutions;
- ***experimentation and hypotheses testing*** – which allows to check obtained prototypes if e.g. they meet the user's needs, solve his problem or bring expected effect; in addition, it enables to get quite significant feedback from potential users – because they can tell us what should be changed, improved or thrown out, becoming valuable source of information about the given solution;
- ***human rule*** – which means that the nature of design process is social, hence this process is aimed at satisfying human needs or solve problems, with which users come up against in everyday life;
- ***the rule of ambiguity*** – which put emphasis on experimentation, looking at problems from different perspectives and going beyond limits or learned schemes and patterns, because this approach positively affects creativity and innovative;

- ***the rule of tangibility*** – which dictates to visualize an idea, makes it tangible, e.g. through simple prototypes due to the possibility of gathering feedback from users, facilitating communication with them, checking and testing given solution;
- ***the rule of putting emotions*** – according to which products and services not only speak functionally, but also evoke positive emotions in people and they can achieve significant success on the market.

This basis of design process allows to create solutions, which meet the following criteria, i.e. are desirable by future customers, technically workable and economically justified [1, 7].

Stages of Design Thinking

Design Thinking, defined as structured process of creation and development new solutions, consists of five stages, which allows to carry out project from problem diagnosis to looking for devising solutions. Appropriately determined sequence of phases, which is pictured in Figure 1, enables all of the time to improve the final result, whereby it is necessary to go from the first phase, through all subsequent ones to last, not omitting any of them and not changing their order. Because these actions can lead to start the process from the beginning as well as cause a waste of time and increased costs [1, 3–5, 7–15].

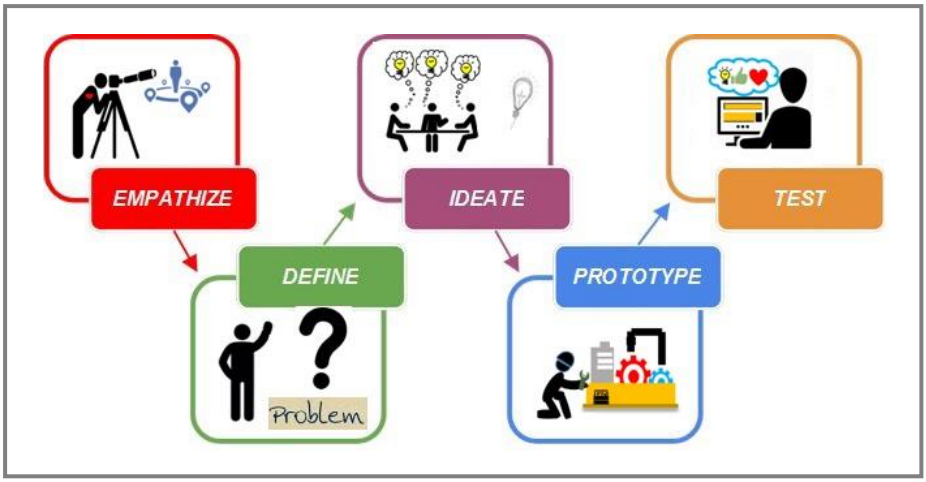

Figure 1. The stages of Design Thinking
Source: own study based on: [1, 3, 7]

The first stage – ***empathizing***, has cognitive, observational nature. It is connected with focusing on potential client and entering his shoes, skin, i.e. looking at problems from the point of his view, hence it is essential to get to know and understand his own habits, needs, problems, intuitive motivations or implicit premises, determining human choices and affecting generating solutions. In this phase it is very important to overcome existing pattern thoughts, stereotypes and prejudices, because they can *muddy the issue.* In addition it is necessary to make out market and technological conditionings of project. This stage ends with collecting of research material (qualitative and quantitative data), which should be so comprehensive to recognize, identify proper, real problem in the next steps [1, 3–5, 7–15].

The next phase – ***diagnosis of needs*** and ***defining the problem*** – is related to the synthesis and analysis of obtained earlier information. It is aimed to accurately diagnose right problem and

answer the questions: *what are the user's needs? what is important for him? how can other help him?* This is the biggest and most difficult challenge for many project teams, because requires primarily a broad view on given issue and turndown of standard thought frames (habits, learned schemes) as well as a large amount of time and very precise analysis of gathered data [1, 3–5, 7–15].

The third step – called also as ***ideation*** – is the most creative in the whole DT process and is connected with generating as many ideas as possible, which enables to obtain a wide range of potential solutions (whereby the their number is most important, not their quality). For this purpose it is necessary to cast out all limitations, be open–minded, audacious in creating abstract ideas and willing to teamwork as well as not to judge, criticize or reject other ideas, because this kills creativity and does not conduce to inspiriting other team members to the further sometimes crazy, out–of–the–box ideas. Additionally, for creative work, pleasant atmosphere and setting should be provided. This step ends with selection the best idea from other ones, usually in a democratic way – by voting. On its basis the prototype will be developed [1, 3–5, 7–15].

The fourth phase – ***prototyping*** – has key importance in the whole process, reducing the risk of failure. It is aimed to sketch the visually and functionally model, not complex prototype, precisely reflecting the final product, whereby it is essential to give significant details in order not to draw conclusions based on guesswork, but only on observed facts. Hence at this stage it is necessary to obtain first, preliminary opinions, which sometimes allows to modify the direction of further work, saving the time and money and bringing closer to the market success [1, 3–5, 7–15].

The last step – ***testing created solutions, their improvement*** and ***evaluation*** – has continuous nature and is connected with presentation of prototype to customer in its real environment in order to obtain opinions about it, feedback and unbiased assessment. It enables to modify that model, leading to desired effect and eventually to its implementation [1, 3–5, 7–15].

Selected tools and techniques applied in Design Thinking methodology

Design Thinking uses various types of tools, techniques or methods. It should be mentioned that because of multidisciplinary approach of this methodology they have been adapted from different kinds of fields of knowledge such as: art, engineering, anthropology, psychology, design, management etc. Using of these tools and techniques is aimed at streamline the process of solving problems and communication with business partners [1, 8, 13].

At the beginning, i.e. at the stage of empathizing, various tools and methods, which enable to get to know and understand the other person, future client, get and deduce a lot of interesting information about the recipient, are used. Additionally, they should support preliminary analysis of observations and favour unexpected insights and conclusions. In turn, implementation of the second Design Thinking stage requires techniques, which streamline further analysis of gathered data and consequently help to appropriately define, diagnose real problem and its whole image. The third DT phase applies methods, which – as the name suggests – are aimed to generating ideas, whereby each of them is only a starting point to determine further directions of action. Then, at the prototyping stage, used techniques and tools enable to visualize earlier selected ideas, create example simplified model of product or service and lay it before other people.

Table 1. Example tools, techniques and methods applied in DT methodology

DT stage	Example tools, techniques and methods
Empathizing	– interviews, group interviews, – conversations with specialists, – surveys, – questionnaires, – photojournals – help to prime interviews, create basis for richer discussion and better understand a person's context, the people who surround them, community dynamics, etc., – immersion – talking to potential recipients in place, where they live, work, lead their lives and spending day/s shadowing them, observing their behavior etc., – consumer personas, – empathy maps, – journey maps, – moodboards, * ~~focus groups~~ – are not used, because people average their responses against the background of the other survey participants, which leads to the avoiding of negative opinions and to the drawing false conclusions,
Defining problem	– 5×why? (5×W), – 5×W and 2×H (5W2H), – re–framing the problem, allowing to change the perception of the issue, – mapping problem: how? vs. what for? – which helps in understanding the differences between this questions + using tools from the first stage (moodboards, empathy maps)
Generating ideas	– brainstorming, – brainwriting, – Six Thinking Hats method – mind–mapping, – analogies, – the pyramid of associations ,
Prototyping	– 3D prototypes, models – built from the various, simplifiest materials with using of simply tools, e.g.: paper, cardboard, foam, plastic, polystyrene foam, wood, plasticine, glues, scissors and other available resources, existing products, which can be cut, glued, painted, stapled etc., } PRODUCTS – computer simulations or 3D prototyping, models from Lego, Play–Doh – comics, maquettes, } SERVICES – storyboards, storytellings – layouts, – user's path drawings – stagings – flow diagrams – present the way, how e.g. mobile apps are working
Testing and evaluation	– evaluation sheets, – evaluation surveys, – SWOT analysis, – SCAMPER method,

Source: own study based on: [1, 3–5, 7–9, 12–15, 17–25]

It is necessary to be mentioned that the way of visualization should be other than a verbal description. This step is connected with the last one, i.e. testing and evaluation, which applies tools helping to gathering feedback (suggestions, clues, comments, advice, opinions etc.) from potential

recipients. This feedback is guidelines for creating next, improved prototypes. The examples of tools, techniques and methods applied in projects carried out with Design Thinking methodology have been collected and presented in Table 1, whereas selected of them have been discussed below [1, 3–5, 7–13, 23–25]:

Customers, buyers personas

One of tools applied during implementation of empathizing stage is technique called as persona, whereby it means visualization, model of potential customers, buyers, making them real. In a word, it represents a character, with which clients, design teams can engage and use efficiently in the whole design process, usually during the empathizing or defining phases of DT. Persona is created and completed on the basis of earlier conducted interviews and observations, hence it contains such information as: demographic data (e.g. age, name– usually fictional, dwelling place, educational background etc.), issues relating to job, family life, hobby, skills, ways of spending free time, typical planner, behaviour, attitudes, patterns, motivations, values, goals, challenges, things, which are enjoyed or made him sick and his quotes. Thanks to these personal data it is easier to empathize with him and understand his needs, not only in the context of one topic. This method simplifies communication, project decision and work in the next stages, because thanks to it teams have constant insight into the needs and expectations – everything is in one place. Additionally, it should be noticed that for any given projects creating only three or four personas is the best, because the aim of this method is not to represent all audiences or address all their needs, but to focus on the major needs of the most important user groups. Example pattern for creating personas is presented in Figure 2 [1, 3, 7–8, 12–13, 17–25].

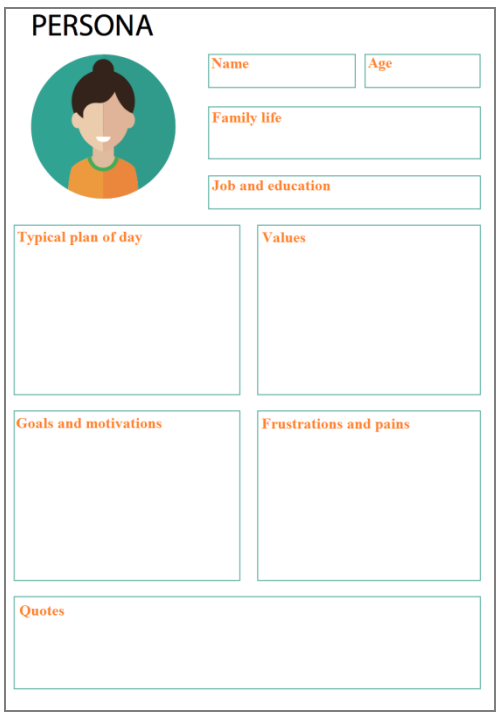

Figure 2. Pattern of personas used in empathizing
Source: own study based on: [21]

Empathy maps

Other tool applied during in fact empathizing and defining the problem is empathy map, which helps to systematize gathered knowledge about potential client, analyze it and sometimes conduce to noticing unexpected insights and conclusions. It is completed based on conducted earlier interviews and observations – just as persona. In this case information is grouped in the form of four main field of map, where each of them answers on these questions:

- ***what says and does?*** – i.e. the totality of behaviour in different circumstances, attitudes to surrounding, expressed opinions, e.g. information about job, daily activities, hobby, practices, habits etc.;
- ***what thinks and feels?*** – i.e. issues important to client – his worries, challenges, feelings, opinions about given problem, conclusions from observing of world, which are characterized and determined him;
- ***what sees?*** – i.e. customer's way of looking at surrounding, events, places as well as characteristics of the his environment, including analysis of competition, key people from the immediate environment and problems he encounters;
- ***what hears?*** – i.e. heard (positive and negative) opinions of other people about project problem, him and different issues, whereby these question helps to assess who has the most impact on the client and how it affects him;

Additionally, except these four standard fields, two extra parts are marked on the map:

- ***pains*** – e.g. problems, barriers, fears, worries of potential customer;
- ***gains, aspirations*** – i.e. his desires, dreams, motivations, profits, which are derived from life, key values and his notion of success.

These fields are very significant, because they can then be example arguments during creation of solutions. Additionally, thanks to these all six parts of map, it is possible to view on future client from very wide perspective, it gives the full spectrum of subject, which helps to work in the next stages of design process. The pattern for creating empathy maps and already completed example are presented in Figure 3 [1, 3, 7–8, 12–13, 17–25, 27].

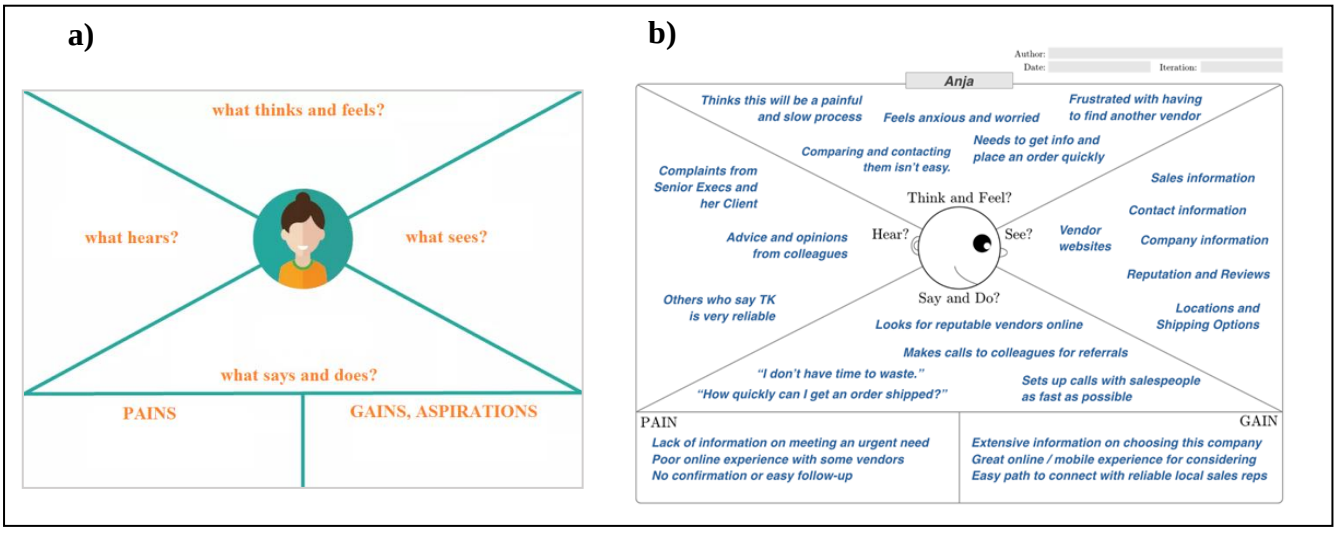

Figure 3. Pattern of empathy map (a) and its completed example (b) used in empathizing
Source: own study based on: [21, 34]

5x why? method

During the second stage of Design Thinking a tool called as 5×*why*, whom author is Sakichi Toyoda, founder of Toyota Industries Co., is used. It is an iterative technique, which aim is analysis of casual connections of a given problem and determination its source, initial reason that should be detected (thanks to the next questions: *why?*) and eliminated it. In a word, it makes it possible to answer questions about the cause of given problems, thanks to which their nature and solution become obvious, clear and understandable. Before, it is necessary to gather all available information about found problem, issue as well as describe it clearly and precisely, which allows to concentrate on a correct theme. Then, it is time to ask subsequent questions: *why*? about five times, which allows to find basic cause, source of problem and eliminate it. This method is seemingly easy, but this in some cases can be a catch. It happens that the wrongly formulated question *"why"* at any of the stages will lead us to wrong, erroneous solutions or to a dead end. Hence, when using the 5×*why* method, it should be stopped asking further questions at the moment of looping in the answers or when the conclusions are not logical, are mutually exclusive and start to look wrong. Then, the whole process should be started again and it is necessary to try to correct this question which led us in the wrong direction. The example scheme of this technique is presented in Figure 4 [1, 3–5, 7–9, 12–15, 17–25, 28, 35].

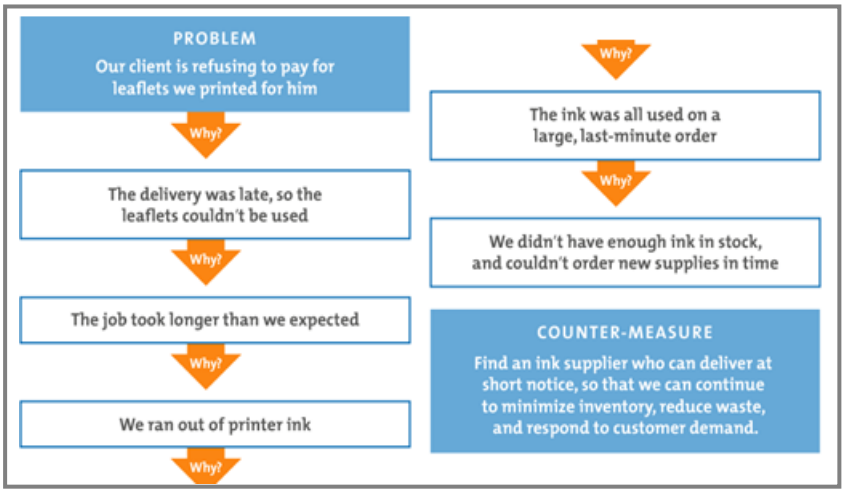

Figure 4. The example scheme of 5×why technique
Source: own study based on [28]

Brainstorming

One of the basic tools applied in ideation stage is *brainstorming*, which uses collective thinking, involving a multidisciplinary group to listen and draw ideas based on other solutions. In this method, coloured sticky–notes, post–its are used, on which each idea is saved. Then, post–its are pinned to a wall, blackboard or flipchart in various configurations, but sometimes they are attached in another place, deleted or changed to other, which reminds that this process requires a lot of flexibility and distance to one's own ideas. Brainstorming is carried out in not big groups (10÷12 members) in according to determined schedule, lasting about 15÷20 minutes, whereby the main challenge is to follow its basic rules, which are described below in Table 2. The effect of each brainstorming

session is the list of ideas, sometimes shorter, sometimes longer, in which similar ideas can occur and other will not meet users needs. Hence it is important to discuss them, sort and select the best, the most interesting, promising ones, whereby each of team members can take a vote on e.g. 2–3, projects and in democratic way the most interesting ideas will be chosen. Summarizing, well carried out brainstorming can quickly push the process forward. Examples of carried out brainstorming session are presented in Figure 5 [1, 3–5, 7–9, 12–15, 17–25, 29–33, 35].

Table 2. The clues and rules for brainstorming

No.	The rule
1.	***Create an interdisciplinary team.*** ***Define aim and theme of brainstorming session.*** ***Choose a moderator (who will conduct a session, monitor the rules and animate the participants).*** ***Provide accessories: boards, markers, post–its, caffeine.***
2.	***Provide the right amount of time – brainstorming is not a race.*** Set a time by which the session should end. This helps to keep the pressure on, forcing more ideas to be generated.
3.	***The voice is given by the person leading the session.*** ***Everyone has the right to submit any number of ideas.***
4.	***The quantity is important, not the quality of ideas.*** Hence ideas can be controversial, crazy, bold, ridiculous, abstract. Additionally, it should be remembered that as many ideas as possible = the wide range of potential solutions.
5.	***Save all ideas!*** Additionally draw solutions – it stimulates creativity.
6.	***Do not criticize, comment, reject and asses other ideas, do not yammer!*** Criticism kills creativity and discourages less brave people to further activities, hence it should be remembered that at this stage of brainstorming each idea is great.
7.	***Look for inspirations!*** It is important to listen carefully and improve the ideas of others people – borrowing, modifying and refining someone else's ideas is most desirable. Additionally you can search for inspirations in different line of works and benefit from analogies, associations.
8.	***Get rid of all restrictions, be courageous in creating solutions, be unconventional –out of the box, and willing to cooperate in a team .***
9.	***Stay focused on topic***! To get more out of your session, keep your brainstorm question in sight.
10.	***One conversation at a time.*** All ideas need to be heard, so that they may be built upon.

Source: own study based on: [1, 3–5, 7–9, 12–15, 17–25, 29–33, 35]

Figure 5. Brainstorming used in generation ideas stage
Source: own study based on [28]

Six Thinking Hats Method

Other technique, which streamlines the generation of ideas is Six Thinking Hats method, also called as DeBono method (from its author). It is based on the parallel thinking model, which allows to obtain as many opinions about research problem as possible, whereby these different potential solutions are discussed, looking at them from various angles, perspectives. It should be mentioned here that these six mental hats symbolize six different states of mind, thanks to which teams look at everything a bit differently. During session of generating ideas in order each of team members "*dresses hat*" in appropriate colour, thanks to which all participants focus on a specific approach at one time. Then, team better cooperates than if one person were to evaluate ideas emotionally (*red hat*), another person tries to be objective (*white hat*), and yet another person were critical of everyone ideas (*black hat*). Usually, firstly people in *blue hat* comment on the aim of a meeting and main problem, then members, dressing *white hat* describe situation and present facts, after which participants in *red hat* describe their feelings accompanying a given problem. Then, it is time to dress *green hat* and give some solutions, after which one of them is being chosen. At this stage *blue hat* watches on this choice and *white hat* summarizes information about obtained solution, after which members in *yellow hat* and *black hat* indicate its respectively positive and negative aspects, while *red hats* describe feelings. Finally, *blue hat* sums up results. Table 3 presents factsheet of these hats, their explaining and example used leading questions [1, 3–5, 12–15, 17–25, 35].

Table 3. Six Thinking Hats method and its explanation

Applied Hat	Explanation	Example leading questions
Red Hat 	– symbolizes emotions, feelings, impressions, intuitions; –is strong associated with expression, emotions, passions, impulsiveness and emotional exaggeration of reality;	*How do you react to it?* *What emotions do you feel?* *How do you feel about this topic?*
White Hat 	– is representation of objectivity; – a person in white hat deals with facts and figures, there is no feeling or emotion in it how he perceives reality and there is only what for him he can rationally present;	*What facts do you know?* *What do you know about …?*
Black Hat 	– symbolizes blackness, pessimism, risks and dangers; – represents logically thinking pessimist, who has negative attitude, warns against dangers, criticizes reality and bodes fails;	*What do you dislike in…?* *What do you see wrong in this?* *Will it work?* *What weaknesses do you see?*
Yellow Hat	– represents optimism curiosity, pleasure and seeking joy; – a person in yellow hat is an total optimist who only sees positive aspects of solutions;	*What can be done?* *What good pages do you notice?* *Why is it worth doing?* *What positive qualities do you see?*
Green Hat 	– represents opportunities, possibilities, creativity; – a person in this hat has fresh look and finds new ways, does not stick to the rules and acts differently than patterns, he has a full head ideas and creative approach to forming solutions;	*What else may develop from…?* *How can I do it more effectively?* *What else can I do?* *What to change to make it different?*
Blue Hat 	– is representation of organizing, process control; –person in this hat is distant, neutral impartial observer and his main task is control of the thinking process and imposing discipline;	*What kind of thinking does this matter require?* *What should be done next?* *What has been done so far?*

Source: own study based on: [1, 13, 32, 35]

Prototyping

Prototypes of innovative products are usually obtained during building them from various, simplifiest materials with using of simply tools, e.g.: paper, cardboard, foam, plastic, polystyrene foam, wood, plasticine, glues, scissors and other available resources or existing products, which can be cut, glued, painted, stapled etc. Additionally, more and more popular prototyping with using 3D or computer simulations are also used for this purpose. In turn, in the case of services or mobile and web applications there are applied different types of visualization ideas, which are other than a verbal description. These are, among others, comics, storyboards, storytellings, layouts, user's path drawings, stagings, maquettes, whereby some examples of them are pictured in Figure 6 [1, 3–5, 7–9, 12–15, 17–25].

Figure 7. Examples of protypes
Source: own study based on [30]

SWOT analysis and SCAMPER method

At stage of testing tools, which supports gathering feedback from potential clients and sort their opinions, suggestions, comments, clues, are applied. Hence one of these methods is SWOT analysis, adapted from management, which allows to evaluate ideas and their prototypes, providing for four main perspectives:

- their ***strengths (S)***, i.e. advantages of new product or service, which can affect increasing sales and demand;
- ***weaknesses (W)***, i.e. their disadvantages, minuses, reducing sales;
- ***opportunities (O)***, i.e. market needs, national politics, sociocultural changes, macroeconomic matters, technological changes etc.;
- ***threats (T)***, connected with e.g. potential or current competitors or users,

whereby (S) and (W) are internal factors whereas (O) and (T) are external factors. They help to understand market viability of future product or service. Example table used for SWOT analysis is presented in Figure 8a [13, 20, 26].

Other type of tools used in the last DT stage is SCAMPER technique is aimed at reasserting ideas based on seven factors and pushing them further using these following factors:

- ***substitute (S)*** – focuses on the parts in the product, service or solution, idea that can be replaced with another;
- ***combine (C)*** – gives the possibility of merging two ideas, stages of the process or product in one single more efficient output;
- ***adapt (A)*** – aims to adjust or improve product or service for a better output;
- ***modify, minify or magnify (M)*** – refers to changing the process in a way that unleashes more innovative capabilities or solves problems;
- ***put to another use (P)*** – concerns how to put the current product or process for another aim or application or how to use the existing product to solve problems;
- ***eliminate (E)*** – refers to remove unnecessary, weak parts of products or simplify process;

- ***reverse (R)*** – i.e. changing sequence, arrangement, configuration.

This tool is also applied during the third DT stage – generating ideas. Example diagram used for SCAMPER method is pictured in Figure 8b [20].

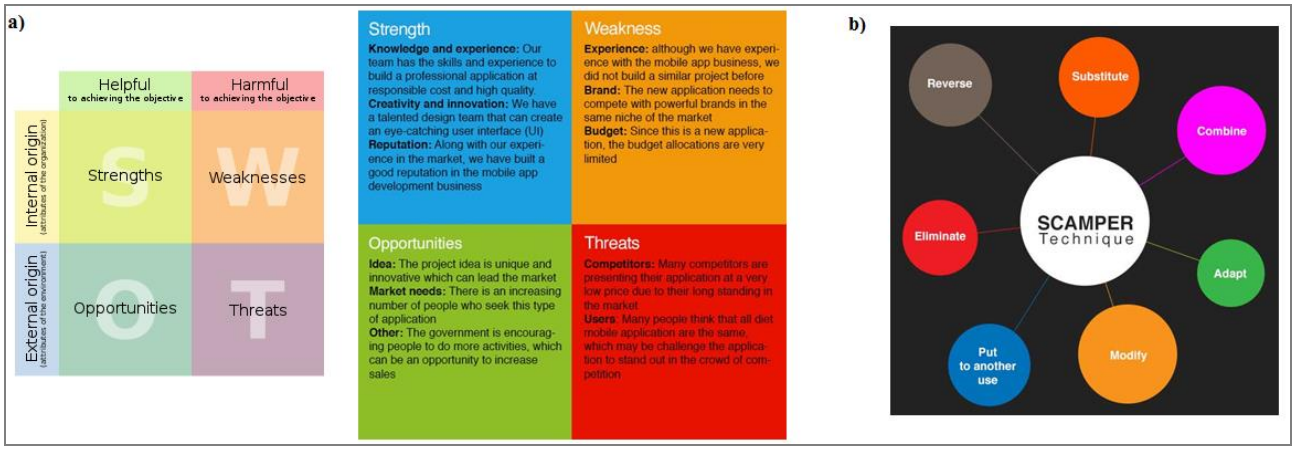

Figure 8. Examples of diagrams for SWOT analysis and SCAMPER method
Source: own study based on [20, 26]

Summary

Design Thinking methodology leads to creating solutions complying with the needs and expectations potential customers. It rises in people and ends with innovative solutions tailored to their needs, hence it combines empathy, intuition and understanding people with analytical competence and sometimes engineering skills. Based on five very important stages (i.e. empathy, defining the problem, ideating, prototyping and testing) methodology uses various types of tools and techniques, which have been adapted from different fields of knowledge, both these connected with hard and soft competences. These tools are characterized by simplicity and ease of use in order to help the users' focus on the method. Thanks to them DT is multidisciplinary and cooperative, which aids multipronged, comprehensive looking at a given problem, from different perspectives. In turn, using of e.g. brainstorming affects aspect of experimentation, assuming that there is not one concrete problem solution – there are many possibilities. These all factors make for the creation of dedicated, useful solution in every real – local government, business, social or scientific.

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TOWARD SPATIAL AWARENESS FOR STAND ALONE MOBILE DEVICES

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Abstract:

The growing number of mobile devices in our environment leads to development of various technologies, including spatial awareness, which provides information about positioning of a device. The most popularly used in positioning are two branches of devices, one uses antennas in respect to which the device is positioned, second takes an advantage of environment features that are acquired by sensors like camera or LIDAR. Those methodologies are described, together with examples of those technologies. The article presents a review of chosen positioning technologies with regard to incorporated algorithms. Each approach requires specific algorithm to determine the localization, which principle is described shortly.

Keywords:

Localization, Spatial awareness, Algorithms

Introduction

Spatial awareness is one of basic human abilities, healthy people are able to state their position in the scene. It is possible because of signal processing performed by brain. Impulses from receptors are aggregated with prior knowledge into information about localization of the body in respect to surroundings. Humans are not only aware of their localization in scale of room or building, but also in scale of city or country. However the further from the body the more memorized information predominate signals from sensors in order to deduce localization. For example it is possible to state that someone is in the classroom which probably is in school, basing only on the visual information. But to state in which country the person is more information is needed as where he was previously or in what language are books in classroom. Similarly some algorithms require information about initial position in order to determine localization in the future.

The ability, to determine position in the world, is useful for mobile devices, as they are also changing their position. Similarly to humans a position of a device might concern local environment such as building or greater one as city or country. Spatial awareness of a device is a feature that allows to localize it in its specific environment. Different technologies are used to position a car on a road and different to localize phone precisely on a table.

Ability to localize oneself is useful in many scenarios. The localization of a lost phone, surely facilitate finding it, position of a vehicle enables using navigation systems and supports

development of autonomous vehicles. However there is no technology that is appropriate for all possible scenarios, usually one must balance costs and performance according to specific requirements. Sometimes one system is used for many different purposes but as accuracy of couple meters is enough to navigate vessel on open sea, it can result in serious accident if applied to a self–driving car, without support of other systems. For that reason different methods and devices are often combined to reduce imperfections of single technology.

Modern mobile phones are one of the best equipped devices in this term, as they are able to localize themselves using variety of technologies: satellite based radio–navigation, LTE signals, Wi–Fi or other Bluetooth devices. Therefore mobile phones are a perfect example in which many technologies might be connected together. Such systems composed of various technologies can complement themselves in order to obtain the most accurate information. Combining satellite based radio–navigation with BLE (Bluetooth Low Energy) beacons allow to localize device as well outdoors as indoors (in buildings equipped with BLE devices).

The paper briefly presents the most popular and interesting technologies from new point of view. They are presented according to group of used algorithms, the aim is to show similarities between seemingly completely different technologies. Algorithms were divided into three groups basing on source of information: Received Signal Strength (RSS), signal's Time of Flight (TOF) and cloud of points.

Fundamental applications of localization systems

Despite variety of localization technologies, some of them have similar objectives to achieve. The information about position of a device may serve to plan future actions or to analyse past behaviour. One of the most known applications of localization is navigation system that is planning a route from device's localization to specific destination. Those systems are tracking the device's position and verify if it is on designated path, reporting outcomes. Tracking a vehicle movement allows also to charge a fee for road usage.

Sportsmen are often taking advantage of recorded activities in order to track progress and modify training plan. Some rescue teams are using positioning systems to find victims of accidents or natural disasters [1]. In USA emergency services are allowed to use global navigation satellite system (GNSS) data to localize the calling phone.

As the technology for localization is handy and cheap it is also used for entertainment purposes. Games such as geocaching take an advantage from user's localization to allow him to play hide and seek.

Information about localization can be used to build maps of the environment, such approach is used in OpenStreetMap project [2]. Simultaneous localization and mapping algorithms are using localization to build a map in form of 2D or 3D cloud of points.

In army localization can be used not only to navigation but also to guide missiles to target. Government can also use localization to track criminals that are under house arrest or sex offenders that cannot approach certain areas.

The information about clusters of identifiable devices and their movements are useful for business. The companies use localization to place new branches and to present specific advertisements.

Algorithms Based on Received Signal Strength

Localization can be calculated basing on the phenomena that the signal strength is declining as the distance from the source increases. An example is presented in Figure 1, the transmitter is broadcasting a signal, which is received by devices A, B and C. Both devices A and B receive signal of equal strength, because their distance from the transmitter is also equal. On the other hand device C is receiving much weaker signal, because it is further from the transmitter than devices A and B.

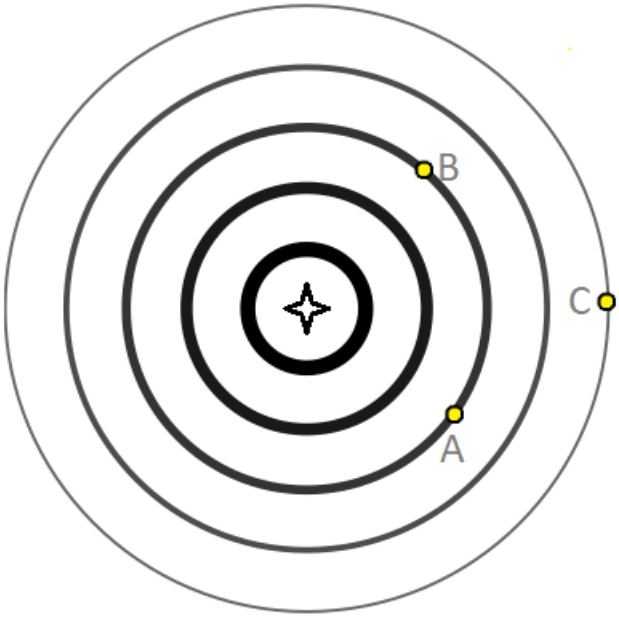

Figure 1. Visualization of received signal strength. Transmitter is in the centre, A, B and C are receivers.
Source: Personal collection of author

The relationship between distance from receiver to transmitter and signal power is nonlinear and can be described with equation:

$$\frac{P_R}{P_T} = \left(\frac{\lambda}{4\pi r}\right)^2 \tag{1}$$

P_R is power of received signal, P_R is power of signal generated by a transmitter, λ is the wavelength of the signal and r is the distance between sender and receiver. The formula (1) works in ideal conditions – without noise or signal reflections. Thus a formula with introduced loss γ of signal was developed:

$$P_R = P_0 - 10\gamma \log_{10}\left(\frac{r}{r_0}\right) \tag{2}$$

P_0 is a reference power of received signal in the environment where the transmitter was in distance r_0. Value of γ is obtained during calibration. Finally based on the distance r from at least three transmitters it is possible to calculate the position of a receiver, for example by triangulation.

Bluetooth Low Energy

Bluetooth device can broadcast a signal in range of dozens of meters, which can be used to determine position of a device. Bluetooth Low Energy (BLE) is a technology that reduces power consumption, size and cost of the device [3]. Usually the positioning system is composed of a set of Beacons and a receiver. Beacons are devices that broadcast their unique id. Receiver detects Bluetooth signal and restore sender id. The system can be constructed in two ways either the receiver is fixed and Beacons are mobile or beacons are fixed and receiver is mobile. In both cases the fixed device must have determined exact position which cannot be change while functioning. It is advised to perform calibration measurements that allow to determine reference values for the equation (2).

Triangulation is a method that allows to determine the localization of the device basing on signals from three different sources of known position [4]. Assuming that a device is in unknown position (x, y) and the distances d_A, d_B, d_B from the devices are known as well as their positions $(x_A, y_A), (x_B, y_B), (x_C, y_C)$ following formulae can be used:

$$\begin{cases} (x - x_A)^2 + (y - y_A)^2 = d_A^2 \\ (x - x_B)^2 + (y - y_B)^2 = d_B^2 \\ (x - x_C)^2 + (y - y_C)^2 = d_C^2 \end{cases} \tag{3}$$

Solving the equation (3) a localization of the device can be determined. The method can be extended in case of more devices with fixed position are available [4].

There exist an alternative method for localization based on BLE, that is supported with compass and accelerometer [5]. It uses Monte Carlo localization method which is also known as particle filtering. The method initially creates a set of hypothetic localization of a device, usually with use of pseudorandom generator. As the device is moving the hypotheses are corrected or rejected in order to preserve only the best one. The algorithm converges to solution that is close to real position. The requirement for the method is to feed it with map containing localizations of fixed BLE devices.

Wi–Fi fingerprinting

Omnipresent Wi–Fi signal can be used for localization as well as other signals. The main concept of Wi–Fi fingerprinting is to use a Wi–Fi map of a certain region and match signals acquired locally by the device to derive its position [6]. Initially a map of the region must be created as there is no resource for such a new approach. The map is made by moving by the roads and recording id of Wi–Fi signal and its strength. Then an object can be localized basing on information about available Wi–Fi networks and their strength, matching can be done by using for example kNN classifier [7].

Algorithms Based on Time of Flight

The signal sent by transmitter does not immediately appear in the receiver, it needs time to travel the distance. The branch of technologies which exploits the duration of time that is necessary for signal to reach its destination is referred to as Time of Flight or Time of Arrival.

The transmitter is sending a time in which the broadcasting of the signal starts. Similarly the receiver records at what time the signal arrived, those information can be used to calculate the distance between the two devices. The distance δ between receiver and transmitter can be calculated with use of the following formula:

$$\delta = c(t_R - t_T) \tag{4}$$

where c is the speed of light, t_R is the time when the transmission was received, t_T is the time when transmission was broadcasted, given by the transmitter.

Global navigation satellite system

Satellite radio localization is a system that was originally developed and exploited for military purposes [8]. Currently, the army and other public agencies are providing public access to the satellite signal without any charges. As a result the GNSS is frequently used to localize a device outdoors with accuracy of a few meters.

A satellite is broadcasting a radio signal that carries information about its ephemeris. It is an information that enables to calculate position of the transmitter at any given time. Based on that information a receiver is able to compute the distance from the transmitter and by means of communication with other transmitters it can determine its own position.

As the device measures the signal fly time and transmitter is responsible for broadcasting current time, in the ideal case those two should be synchronized. If the devices are not synchronized the created time deviation is causing an error. What is more, in multi–satellite system where each transmitter has its own clock that should also be synchronized (GPS, Galileo, GLONASS). Because all satellites in one system are synchronized the receiver will be desynchronized by the same time Δt with every satellite. The signal is affected also by other means like atmospheric conditions and electromagnetic storms. Finally the position of a receiver can be calculated with use of:

$$\delta = \sqrt{(x_T - x)^2 + (y_T - y)^2 + (z_T - z)^2} + c\Delta t + \sigma \tag{5}$$

where (x_T, y_T, z_T) is the position of the satellite retrieved from received message, $(x,\ y,\ z)$ is the position of the receiver which is unknown. σ is an error that is caused by all other factors but desynchronization. In order to resolve the equation with three unknown variable, at least three equations are needed, hence three satellites are the hypothetical minimum. Thus signals received from more than three satellites allows to estimate not only the position but also the overall position error σ. The problem can be resolved in many ways, e.g. with Bancroft algorithm [9], Newton Raphson method, Kalman filter and least–squares method [10].

Ultra–Wideband

Ultra–Wideband (UWB) is an emerging technology that uses high–bandwidth communication. It enables sending data with high–rates (up to 2Gb/s) [11], with low energy consumption but on

small distances, up to 10m. The technology uses very short impulses to transmit the data, what results in high bandwidth, which allows to transmit large portions of data.

The localization algorithm using UWB was proposed [12, 13]. It uses time of signal's arrival combined with triangulation method to obtain the localization of a device inside a coal mine.

Other

Mobile phone signals are present in almost every denser urban areas, so it can be used to localize as well [14, 15]. The LTE (long–term evolution) signal carries information about time and positioning, which can be extracted and processed to calculate position of a receiver. The solution is less accurate than e.g. GNSS, but may be a key helper in places where GNSS signal is dim or unavailable.

Algorithms Based on Cloud of Points

A position can be deduces also from a more complex datasets than signals from transmitters. Some methods process images or scans of environment in order to determine localization. The variety of sensors that can be used have resulted many sophisticated algorithms that are dedicated to specific device and environment thus only the most essential will be described.

Data in a cloud of points form might be acquired by a camera in as a RGB or infrared image. Information about distance from the object can be obtained by pairing and infrared diode and a camera or by a laser beam fly time, e.g. LIDAR (*Light Detection and Ranging*). Those datasets describing local relative distances between the device and a surrounding can be matched to deduce what path a device was following in terms of displacement and rotation. Another idea is to match current view of environment with a reference map in order to localize a device on such map.

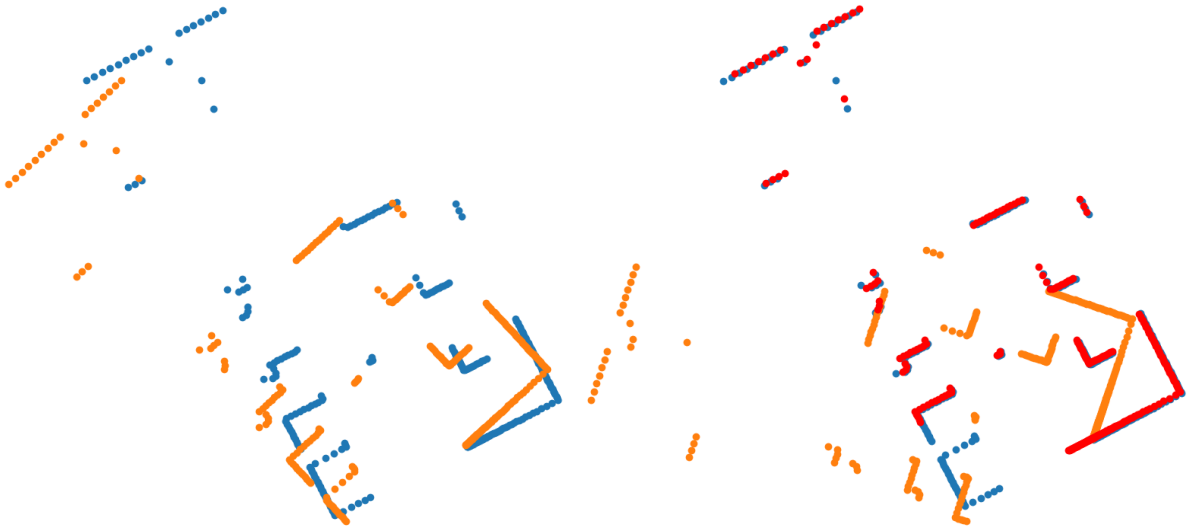

Figure 2. On the left two clouds of points (blue and orange) that are similar but not aligned. On the right the orange cloud of points is rotated and translated (red) to match blue points.
Source: Personal collection of author

The example of two clouds of points alignment is presented in **Figure 2**. Both sets of points are scans acquired by LIDAR and presented in Cartesian coordinate system. The environment was not changed between acquisition of scans, but the position of the device was changed, what results in misalignment of data. Finding the best alignment (red points in Figure 2) is equivalent to calculating translation and rotation of the device. As a results a sequence of device displacements can be a base for reconstruction of whole path that device moved through.

Iterative Closes Point

Iterative Closes Point is an algorithm that minimizes the distance between two clouds of points and is most commonly used to process data acquired by a LIDAR. The algorithm uses optimization, in which the objective function is minimized. The function minimizes the distance (6):

$$D = \sum_{j=0}^{n} \min(d(x_{ij}, x_{i+1})) \tag{6}$$

D is the measure of similarity/distance between scan i and $i+1$. d is an Euclidean distance between two points, n is the number of points. x_{ij} is *j*–th point form scan i and x_{i+1} is any point form scan $i+1$. In other words for each point from scan i the distance to closest point from scan $i+1$ is taken as a part of overall alignment measure.

The parameters which are changed during optimization are rotation and translation of scan $i+1$ in comparison to scan *i*. When the desired alignment is reached then a proper translation vector and rotation angle are known. Those values, accumulated along the path, can inform us about position of the device and path that it went along.

Bathymetric positioning

Positioning and navigation in under–water environment pose an interesting problem. Such environment is practically lacking any landmarks and the surface of an ocean itself is too huge to place some underwater lighthouses or other markings. What is more, due to the physical reasons there is no GPS signal available underwater.

One of solutions proposed in available literature is the bathymetric positioning [16], which uses echo–sounder. The concept is to scan bed of a reservoir and comparing it with stored data that describes the observed terrain's properties. There are available databases describing bathymetry maps that cover large parts of seas. One of constrains of the technology are limited resolution of databases and of echo–sounder used for data acquisition.

To localize a device under water an algorithm that compares captured data with stored map is essential. Those algorithms might be similar to described previously like ICP or particle filtering [17].

Algorithms Based on Inertial Navigation Systems

Another concept for localization is to use known initial position and analysing information about movement in order to deduce the displacement. The idea was implemented as well on the ground [18] as underwater [19]. The key is to gather signals from devices such as accelerometers,

gyroscopes and sometimes magnetometers, usually placed on three orthogonal axes. The signals are gathered by device called Inertial Measurement Unit (IMU). Analysis of acquired signals allows to calculate displacement and rotation of an object in three dimensional space. Using previous position and time elapsed it is possible to calculate a new position. A drawback of such method is that all measurement noise and errors are accumulated and cause a drift of the computed position that will grow over time. Despite the high precision of measurement devices that are being produced [20] the presence of a drift is unavoidable. Therefore frequent verifications of position and additional correction algorithm are unavoidable.

Summary

An abundance of algorithms and techniques allow find appropriate one for almost any purpose. Many interesting and promising technologies are still in development as Bluetooth Low Energy and UWB, what suggest that their performance might be improved. However there are still methods to be created, as current research is focused on merging and applying compliment technologies to achieve better performance.

Facing the spatial awareness of a device problem one should weight all the advantages and disadvantages, like accuracy, costs, speed, dimensions, of a technology to be chosen. Even though the desired solution will not be possible with the use of a single technology or algorithm. Available literature shows that a combination of different approaches lets get closer to satisfactory results.

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JUVENILE OFFENDERS. CAUSES AND WAYS OF UNDERSTANDING THOSE OF CRIMINAL BEHAVIOR

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Abstract:

Wanting to understand nonconformist attitudes of children and youth and try to see the cause of their criminal behavior should be referred first to their upbringing. One should focus on the basic social cell which is the family, find out which families they come from, where they were born, how they grew up. Only this knowledge can allow us to understand some of the problems they faced and the desires that they had when they grew up. In every anti–social behavior of children and young people there is even a substitute of their internal pain, suffering or hate with which they had to contend, often growing up in pathological families. On socialization, person learns social behavior, shapes his values so necessary for functioning in adult life. This is not an attempt to justify their criminal acts, but an empathic, objective and real look at their behavior through the prism of their past, negative experiences.

Keywords:

nonconformist attitudes, anti–social behavior, pathological family, socialization

Family in the child's socialization process

Socialization [Lat. s*ocialis* – "social"], the process of taking over by the unit of knowledge, communicative competence, psychosocial skills, as well as the system of values and norms resulting from the impact of the social environment; supports the integration of the individual with the community and its adaptive (adaptive) way of behaving in a social environment. Socialization thus understood lasts throughout life, but most often the term is applied to the process that occurs mainly in the earlier period and consists in instilling in the child socially recognized values and norms and teaching social roles to it. On the basis of sociology, socialization is defined in terms of learning and adopting by the individual cultural traditions and patterns that determine its behavior (the process of growing into culture) and acquiring skills to properly play social roles, within which internalizes the values and norms necessary for effective action in these roles. Specialized institutions play an important role in socialization, especially the school. The effect of socialization is also the acquisition of specific behaviors characteristic of sex and age. A similar meaning to the term "socialization" has the concept of socializing, understood as an adaptation to society. On the basis of psychology, socialization is understood as a process of changes taking place in the course

of the social development of the individual under the influence of social interactions, thanks to which the individual develops through interaction with other people, social patterns, behavior and experience. Socialization, although it primarily occurs in children and adolescents, also occurs in other periods of life as shaping the so–called development in the process of development and upbringing. social personality. It means developing within the unit specific, socially and culturally determined, internal patterns of actions and behaviors, the rules of cognitive recognition of individual experience, its emotional survival and valuation. As a result of socialization, the acquisition of appropriate social competences takes place. (Knowledge, skills), development and shaping of attitudes, feelings, internalization of principles and norms, enabling an individual to participate in a group of companies. and society. The effect of socialization is the socialization of the individual (otherwise – socialization). The indicators of the stage of social development and the level of socialization achieved by the unit are pro–social activities and motifs. The result of social development is the achievement of the unit of social maturity. Sometimes socialization and socialization are expressed as synonyms, meaning, on the one hand, embracing culture (acculturation), and on the other, acquiring social maturity. Therefore, socialization in the understanding of the process of growing into culture and shaping the social personality can be treated as two aspects of the same phenomenon [1].

The family is a fundamental factor that determines life, tradition, social value and many others so important, reflected in the adult life of each of us. In it, he learns about social life. Here man has the greatest chance of self–realization. It is also a treasury of knowledge and experience, which consists of ethical, cultural, spiritual and material values that determine human development [2]. We base our experiences, actions and intentions on our experience. How we were brought up, in which family we grew up has a huge impact on our further life decisions. Often without knowing this, we subconsciously rely on our experience by making different decisions, looking for a way out of a given situation, or trying to solve a problem that bothers us.

Socialization thus becomes an indispensable and decisive factor in the education of everyone in our lives. The problem arises when it is downplayed by parents for various reasons. The psychological development of the child determines the external environment to a large extent (peers, the media, the Internet). An external environment that imposes its trends, a way of behaving. Whether we will be susceptible to often negative factors and temptations depends only on us. Our decisions will be based on "ethical values" raised from the family home and will be a determinant for our decisions. The shortcomings and shortcomings of the social educative environment either will create a social attitude of children and youth, or contribute to the formation of an anti–social attitude [3]. The problem in question will concern social maladjustment, and hence the inability of the individual to adapt to the requirements of the social group; non–recognition and non–compliance by the individual of commonly accepted norms and behavioral patterns in a given community [4].

Researchers dealing with the problem of social maladjustment state the diversity and interdependence of the determinants of this phenomenon. They also emphasize the fact that limiting ourselves to stating and analyzing only symptoms, instead of looking for the causes of social maladjustment, is inappropriate in every respect. Without determining the conditions, it is impossible to proceed effectively to an unadjusted unit. A special place in considering the

etiological aspect of social maladjustment is occupied by the family environment, because it is the first and basic social, educational and caring environment of the child. There are many factors inherent in the family that lead to anti–social behavior of children and young people.

B. Hołyst states that the main cause of social maladjustment is the pathology of emotional ties in the family in terms of the child's relations with parents, relations between parents, as well as between the child and siblings. The process of creating emotional ties is related to satisfying primarily the mental needs of: security and security, solidarity and communication with close relatives, the need to accept recognition. Not meeting any of these needs causes fear, insecurity and insecurity. Simply satisfying the child's basic needs does not automatically testify to the kind and loving attitude of parents. Unmet psychic needs the child tries to compensate outside the home. He usually goes to a peer group in which he finds understanding and acceptance. It is not uncommon, however, that youth groups are destructive [5].

The socialization of a child always takes place within a specific social world, under the influence of "significant others" whom he encounters in this world and who are imposed on him by this world. In primary socialization, the child can not choose significant others, he or she is placed before a predetermined group and must accept them. For each child the first significant other are parents and the closest family. Also, and perhaps above all, these significant other children do not choose, because there is no choice.

This fact results in serious consequences. First of all, the identification of a child with parents is automatic. Secondly – for the same reason – the internalization of the specific reality of parents is inevitable. Parents as significant others give the child their definitions of the world as an objective reality and in a situation of lack of choice, it internalizes this world as the only existing and the only one that can be thought of. It is not difficult to notice that if the family space of the child's socialization is filled with violence, internalization of this is inevitable. Children can strengthen themselves in the conviction that the world whose representatives are their parents is evil and threatening, and violence – in its various forms and forms – is a necessary means to achieve its goals.

Using violence against children, parents build in them a belief that it is a widely accepted attitude in the world, what more – provides children with patterns of aggressive behavior. In addition to the immediate consequences of the use of violence against children, it also seems important to their indirect consequences in time, taking the form of aggressive or anxious attitudes directed to people and the world, anti–social or criminal behavior. The use of violence ceases to be a transitional state or a one–time action, forced by circumstances, it can become their way of life. An example may be the so–called "street fighters", recruited among the youth, for whom there are only two types of people: strong and powerless, killing and killing.

Family violence is often accompanied by the previously mentioned phenomenon of poverty, from which children try to go out and use violence. It is more difficult in these family environments affected by anomie, where poverty takes the form of deficits in the sphere of values and where violence does not find strong moral counterparts. It appears as a retaliation against perpetrators, as a way of acquiring goods unattainable by another way and a way of satisfying the needs that the family does not provide to children, as a form of rebellion against the world in which they build identity, exist and suffer as an attempt to realize themselves in struggle with the reality that

surrounds them. In extreme cases, children's violence against the world and people is a "cry of despair", a cry for help and even an elementary attention to it [6].

The dysfunctional family and its impact on the personality development of the child

The dysfunctional family is, to put it shortly, a family that does not perform its functions. It is a family that through disrupted relationships, rules, roles or communication does not ensure its members the possibility of healthy and full functioning. The term dysfunctional family is often defined as a family, where one or more people are addicted (e.g. from alcohol, drugs, drugs, work, food, etc.) in which violence occurs or one of its members can not fulfill its role due to the mental disorders experienced. Regardless of whether one or many people are disturbed, the whole family is affected because the family functions as a whole and is more than just the sum of the parts. Family members interact with each other [7].

In contemporary families, the emotional ties that connect its members (spouses, children with parents) are weakened, and the parents' lack of authority. The realities of life in the capitalist economy system, increasing unemployment requires the individual to constantly adapt to the high demands placed by him, new professional tasks, which often results in neglect in the sphere of family life, inability to provide adequate care and control over minors. Adaptation mechanisms, which have so far fulfilled their role, do not seem sufficient to meet the requirements of functioning in new economic and social conditions. The individual is forced to learn again the behaviors, rules of functioning, build new types of interpersonal relationships, necessary in the process of social communication, learn the rules of the new law. Family structure, the origin of a minor, its material and living situation, adopted system of values, children's competence to act and transmitted in the intergenerational transmission belt patterns of social roles exert a profound influence on the formation of the offspring raised in the family, his personality and identity. It has been proven that the family can have a destructive impact, not fulfilling its assigned functions, and have a significant share in the process of derailing a minor. Hołyst reports that the majority of registered juvenile offenders come from families with negative cumulative factors, such as: criminal behavior patterns, parental or sibling alcoholism, lack of emotional family ties, aggressive behavior, abandonment of the family, lack of positive patterns of work and social roles [8].

Many studies show that the aggressiveness of children is primarily the effect of negative parental attitudes. Two such groups are distinguished: attitudes close to emotional distance, rejecting, unacceptable and those that restrict the freedom of the child through excessive control, excessive interference in the child's affairs, physical violence or imposing certain activities.

The emotional distance of parents in their relationships with children is accompanied by their aggressiveness, argumentative behavior, negativity, hostility, manifestations of rebellion and outbursts of anger. In the weave of negative factors in extreme cases, emotional rejection is conducive to criminal behavior, that is, aggressiveness, aggression, cruelty and manifestations of sadism.

Consideration of the influence of parental attitudes obliges you to take up the subject of compliance or the absence or even opposition of maternal and paternal attitudes. It is beneficial to

educate in a situation in which the attitudes of both parents are positive, taking into account, however, the natural differences associated, for example, with their social role. Children raised in such a family are less aggressive. If the parental attitudes show differences, but they are not contradictory, it may slightly increase the aggressiveness of children, which increases more under the influence of extremely different mothers and fathers, for example: positive–negative or negative–positive, however, the most aggressive are similarly negative attitudes. Analysis of diversity, difference or opposition of parents' educational attitudes emphasizes the importance of the emotional aspect of these attitudes in shaping the aggressiveness of children [9].

Intercultural research indicates the lack of uniform, universal boundaries set for the period of adolescence. On one hand, such a situation results from cultural and social factors, and on the other hand from the processes of biological maturation of an individual and the tasks that culture and society assign to an adolescent. Thus, both the individual aspect (the process of biological maturation and psychological adolescence) and external (cultural, economic and social) influences the development of people in adolescence. Economic prosperity and wealth of citizens can accelerate maturation (so–called acceleration), while poverty, limited access to goods and the labor market can lead to a worse economic situation, poorer nutrition and delayed processes of biological maturation (deceleration). Lack of work may result from the lack of adequate education, it may lead to the extension of dependence on the parents, and thus to the lack of independence, independence and autonomy.

The tasks resulting from adolescence processes are: the transition from the position of emotional dependence to independence, from the lack of controlling emotional impulses to their control, from immediate gratification of needs to their postponing, the transition from egocentrism to sociocentrism. At that time, the individual should go from the stage of specific to abstract thinking. In social life, a qualitative change involves the development of interpersonal relationships (peer relationships and adults), while in the moral aspect, the individual from the moral heteronomy stage (morality based on the fear of punishment) should go to moral autonomy. The moral development of the youth is – according to L. Kolberg – addicted to the contact of young people with people more mature than them – moral attitudes are significant for moral development. The highest stages of moral development (postconventional morality), according to the author, reach 10% of young people. A. Brzezińska emphasizes that the common risks of the adolescence period include: loss and moral anomie – especially during the transformation periods [10].

Aggressive behavior of children and adolescents resulting in breaking the law

The growth tendency of the occurring crime, and in fact criminal acts committed by minors has been at a similarly high level for years. The negative premise is that the age of people who violate the law is constantly decreasing. The statistics show that some people commit punishable offenses at the age of 11 or 12. The forms of behavior of children and adolescents are becoming increasingly antisocial, these people are violent, aggressive and any attempts to draw their attention only intensify their anger and hostility. In many cases their behavior seems relatively easy to explain. These people have a command for such behavior from their parents who are not able to find their fault in the negative behavior of their child, to teach, to talk, to react. The parent currently does not allow the thought that his child is guilty of something. He repels the "attack" often in a vulgar

manner, thus giving quiet consent to the next anti–social behavior for his child. The parent blames everyone around him (school, peers) seeking in this justification for both his child and himself. Such behavior of the parent is the beginning of violation of legal norms by the child, and in the future a premise for criminal behavior and brutality towards themselves. Of course, the crime figures of minors are different, often their behavior is trying to be explained by the progressing globalization, economic and social status, consumerism and other social factors such as the threat of social exclusion. In spite of some correctness and the consent of these statements, which can not be disagreement, attention should be paid to the frequent lack of socialization, which is the basic factor for all social classes that enables prudent and proper decision making in accordance with accepted legal and moral standards.

The majority of children in the course of normative development, before they start school education, acquire the ability to run in times of anger or frustration alternative to aggression, socially accepted behavior. It can be noticed, then, that they are "unleashed" by the use of aggression. Only disturbances in the process of developing the ability to regulate: anger and aggressive impulses can lead to the consolidation of the tendency to aggressive behavior. In younger children, the manifestation can be frequent aggressive interactions with peers or with close relatives, or caregivers [11].

Social maladjustment is expressed in two aspects. The first, essential, has a sociological dimension and comes down to action. We can only infer maladaptive behavioral symptoms based on its behavior that violates social norms and antagonizes social relations and systems. As has been said, these are uncontrollable and impulsive behaviors, and that is why it is necessary to consider the quality of teaching and thought that is related to the nature of behavior. In this way, we penetrate the second, psychological aspect of maladjustment. The feelings and thoughts accompanying maladjusted acts of behavior have a primitive character and can be compared to those that were proper to the primitive man. Although at the beginning of the evolution of the human race they played a fundamental role and still have a big role in the life of every human being, in the process of this evolution, effective mechanisms were created to control their activation and course. Modern man must be aware of experiencing irresistible feelings and thoughts from primitive, instinctive reactions. Man must be aware of the effects that these instinctive reactions can cause. Without this awareness and the ability to control the instinctive feelings, thoughts and behaviors that consequently bring damage to other individuals, it would be impossible for society to live together, civilization, culture and society "in general". The failure to develop such control mechanisms is a major cause of non–compliance. The role of these mechanisms is expressed in censoring or avoiding potentially dangerous impulses. It is so important for human nature that without it human society would be impossible. Most often the role of control mechanisms is associated with the control of negative feelings, and therefore anger and hostility, which directly lead to destructive acts.

In fact, their functions, which boil down to controlling the sense of fear and fear, are equally important, which limit our actions or even make it impossible to achieve goals, especially those that are far–reaching and involve the need to interact with other people. In the first case (controlling hostility), the lack or weakness of control mechanisms creates an externalizing type of maladjustment, in the second (inability to control fear) leads to an internalizing type, equally

important, expressed in subordination, subordination, dependence, in morbid concentration on oneself. The latter behaviors are also acts against their own interests [12].

Police and court procedures in relation to minors committing criminal offenses

Minors, the right person who committed an act prohibited by criminal law before the end of a certain age (in Poland 17 years) [13]. In the understanding of criminal law, a person who at the time of committing a prohibited act is under 17 years of age. It shall be punished only in special cases referred to in Article 10 § 2 of the Penal Code and in art. 13 and art. 94 of the Act on Juvenile Justice in 1982. The Act on juvenile delinquency proceedings qualifies the age of a minor: up to the age of 18 – preventing and combating demoralization; from 13 to 17 years of age – proceedings for criminal offenses; no longer than until the age of 21 – implementing educational measures and corrective measures. Applying any educational or corrective measures, the court should be guided by the good of the minor [14].

A minor in the light of the juvenile delinquency law may display demoralized behaviors, i.e. behaviors that are inconsistent with certain social norms and are not crimes such as alcohol consumption, cigarette smoking, prostitution and other related things. In relation to such juveniles who display these behaviors, the Police conduct a disciplinary conversation in the presence of a legal guardian (mother, father, other person who looks after the minors). Information from the conversation in the form of a note is sent to the Family Court in accordance with the local jurisdiction in order to take appropriate action against such a person by the Court. If, on the other hand, a minor commits a crime, correctly called an offense, the procedure looks different here. Of course, it is necessary to cooperate with the Family Court, which is based in the first place on the Police sending all collected materials related to the offense committed by the minor (description of the offense). After getting acquainted with the Family Court, this one issues or not, the decision to initiate proceedings against the person. After issuing such proceedings, the necessary materials necessary for the further course of the proceedings should be collected, such as: accepting the notification, hearing witnesses or establishing the circumstances of the event and performing other activities that bring something important to the case. After performing these activities, a juvenile person is again called to the given Police unit in relation to which the proceedings are conducted along with the legal guardian. The person is given appropriate instructions: the rights and duties of a minor and the charge is presented with the permission of the Family Court, to which the person has to respond. The minor is prejudiced about his or her rights; he may submit explanations or refuse them, only by lodging them before, for example, the Family Court. All activities involving the minor are held in the presence of his legal guardian. The legal guardian himself is not a party to the proceedings and does not speak on behalf of a minor, but it is to constitute a kind of "compensation", support for a minor, for whom interrogation activities due to his age (sometimes 13, 14 years) can be certain kind of traumatic experience, cause fear or uncertainty. Whether the minor submits explanations or is not, recorded in the relevant protocol. In this protocol, also the legal guardian briefly refers to the activities carried out by a police officer, taking into account his possible reservations as to the form, activities of conducting proceedings against a minor. Subsequently, all collected documentation is sent to the Family Court, who becomes familiar with the materials of the proceedings and makes decisions about assigning a probation officer. The tasks

that the curator is facing in relation to a minor are, among others: examining the situation regarding the minor, his functioning in the school and family environment, living conditions and other necessary influencing the shaping of his social attitudes. The interview takes the form of a note and is forwarded to the Family Court. The hearing in the Family Court takes on a different character than in the Penal Department itself and may take place without the participation of the person concerned himself, it is a minor (depending on the practice of the Court). The Family Court decides to apply a minor legal measure against a minor. Such information about the application of a given legal remedy is sent to the Police unit.

Proceedings in matters of minors are regulated by the Act of October 26, 1982. on proceedings in juvenile cases.

The measures applied to the juvenile and the powers of the family court are set out in art. 5– measures applied to a minor and art. 6– the powers of the family court in matters of minors.

Art. 5– the juvenile may use educational measures and a corrective measure in the form of placement in a correctional facility; punishment can be imposed only in cases provided for by law, if other means are not able to ensure resocialization of a minor.

Art. 6– for juveniles, a family court may:

1) give a warning;
2) to commit to a specific procedure, in particular to remedy the damage caused, to perform specific work or services for the victim or local community, to apologize to the victim, to study or work, to participate in appropriate activities of an educational, therapeutic or training nature, to refrain from being in certain environments or places or to stop using alcohol or other substance in order to enter into a state of intoxication;
3) establish supervision responsible for the parents or guardian;
4) establish supervision of a youth organization or other social organization, workplace or trustworthy person – providing guarantees for a minor;
5) apply superintendent's supervision;
6) refer to a probation center, as well as to social organization or institutions dealing with work with minors of an educational, therapeutic or training character, after prior consultation with that organization or institution;
7) to pronounce a ban on driving vehicles;
8) order forfeiture of things obtained in connection with the commission of a punishable offense;
9) adjudicate placement in a youth educational center or a professional foster family who have completed a training course to provide care for minors;
10) adjudicate placement in the correction center;
11) apply other measures reserved in this Act to the jurisdiction of the family court, as well as apply the measures provided for in the Family and Guardianship Code, with the exception of placement in a foster family, foster family, family children's home, day care facility, care and education institution and a regional care and therapeutic institution [15].

A minor is usually responsible before the Family Court, whereas there are premises when the criminal court decides that the juvenile will decide about the next. These premises are defined in art. 10 § 2 of the Penal Code:

1) when a juvenile committed a deed punished with an adult,

2) when it is necessary to examine the case jointly,

3) when the proceedings were initiated after the minor's 18th year of age [16].

Art. 10 §. 2 of the Penal Code: Minors, who after the age of 15 commits a prohibited act specified in art. 134, art. 148 § 1, 2 or 3, art. 156 § 1 or 3, art. 163 § 1 or 3, art. 166, art. 173 § 1 or 3, art. 197 § 3 or 4 art. 252 § 1 or 2 and in art. 280, may respond to the principles set out in this Code, if the circumstances of the case and the degree of development of the perpetrator, its characteristics and personal conditions speak for it, and in particular, if the previous educational or corrective measures have been ineffective.

Art. 134 – Whoever assassinates the life of the President of the Republic of Poland shall be punished by imprisonment for a period of not less than 12 years, imprisonment of 25 years or imprisonment for life.

Art. 148 § 1. Whoever kills a man shall be subject to the penalty of deprivation of liberty for not less than 8 years, imprisonment of 25 years or imprisonment for life. § 2. Whoever kills a person: 1) with particular cruelty, 2) in connection with taking a hostage, rape or robbery, 3) as a result of motivations deserving special condemnation, 4) with the use of explosives, subject to imprisonment for a shorter period of time from the age of 12, punishes 25 years imprisonment or punishment for life imprisonment. § 3. The penalty specified in § 2 is subject to who, by one act, kills more than one person or was previously validly convicted for murder and the perpetrator of the murder of a public official committed during or in connection with his duties to protect people or protect people's safety or the protection of public safety or order.

Art. 156. § 1. Who causes severe damage to health in the form of: 1) depriving people of sight, hearing, speech, ability to beget, 2) other severe disability, serious incurable or long–term disease, a real life–threatening disease, permanent mental illness, total or significant permanent incapacity for work or permanent, significant disfigurement or deformation of the body, is punishable by imprisonment from one to 10 years. § 3. If the consequence of the act specified in § 1 is death of a person, the perpetrator shall be subject to the penalty of deprivation of liberty from 2 to 12 years.

Art. 163 § 1. Who brings an event that threatens the life or health of many people or large–sized property, in the form of: 1) fire, 2) collapse of a building, flooding or landslides, rocks or snow, 3) explosions of materials explosive or flammable or other rapid release of energy, the spread of poisonous substances, asphyxiant or burning, 4) violent release of nuclear energy or the release of ionizing radiation, subject to the penalty of imprisonment from one year to 10 years. § 3. If the consequence of the act specified in § 1 is death or serious injury to many people, the perpetrator subject to the penalty of deprivation of liberty from 2 to 12 years.

Art. 166. § 1. Whoever, by using a deception or rape on a person or the threat of direct use of such a rape, takes control of a watercraft or air, shall be punished by imprisonment from 2 to 12 years. § 2. Who, acting in the manner specified in § 1, brings direct danger to life or health of many people, subject to imprisonment for a period not shorter than 3 years. § 3. If the consequence of the act specified in § 2 is death or serious injury to many people, the perpetrator is subject to the penalty of deprivation for a period not shorter than 5 years or 25 years imprisonment.

Art. 173. § 1. Anyone who causes a disaster in land, water or air traffic that threatens the life or health of many people or large–sized property, is punishable by imprisonment from one year to ten

years. § 3. If the act referred to in § 1 is death of a person or serious damage to health of many people, the perpetrator is subject to imprisonment from 2 to 12 years.

Art. 197 § 3. If the perpetrator commits a rape: 1) jointly with another person, 2) against a minor under 15, 3) towards a preliminary, descendent, adopted, adopter, brother or sister, shall be subject to the penalty of deprivation of liberty for a period not shorter than that 3. § 4. If the perpetrator of the act specified in § 1–3 acts with particular cruelty, he shall be subject to the penalty of deprivation of liberty for a period not shorter than 5 years.

Art. 252. § 1. Whoever takes or holds a hostage in order to force a state or local government body, an institution, an organization, a natural or legal person or a group of persons to a particular behavior, shall be punished by imprisonment for a period not shorter than 3 years. § 2. If the act specified in § 1 is connected with the particular hostage's torment, the perpetrator shall be subject to the penalty of deprivation of liberty for a period of not less than 5 years or punishment of 25 years imprisonment.

Art. 280 § 1. Whoever steals, using violence against a person or threatening to use it immediately or leads a man to unconsciousness or vulnerability, shall be punished by imprisonment from 2 to 12 years. § 2. If the perpetrator of the robbery uses firearms, knives or another similarly dangerous object or means of overpowering or acts in another way directly threatening life or together with another person who uses such a weapon, object, means or manner, is punishable by imprisonment for a period not shorter than 3 years.

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STUDY ON DISSOLUTION CONDITIONS OF MANGANESE OXIDE AND SILVER FROM TANTALUM CAPACITORS SCRAP

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Abstract:

The selective dissolution of MnO_2 and Ag from tantalum capacitor scrap at various process conditions has been studied. The research materials were properly prepared various types tantalum capacitor scraps in pyrolysis, grinding and sieving processes and were characterized. Solutions of H_2SO_4 and organic acids such as acetic, ascorbic, citric and oxalic give better dissolution yields of manganese than only H_2SO_4 (72÷94 vs 90÷99 % for H_2SO_4 and acids mixtures, respectively). Silver dissolution, which occurs in more intense conditions, is also possible using H_2SO_4 and H_2O_2 solutions. Dissolution yields of silver are achieved at 26÷38 %. These studies prove that it is possible to use only reagents from utilization stages and green chemical compounds to enhance of tantalum recycling from WEEE. Due to the selectivity for manganese and silver, it is possible to recover them simply.

Keywords:

tantalum capacitors, tantalum recycling, eco–friendly recycling, transition metals recovery

Introduction

Periodical publishing of a list of critical raw materials (CRMs) for the European Union (EU) during the years 2011÷2017 [1, 2] show that among the CRMs is tantalum. Tantalum is a key component of tantalum capacitors (TC) characterized by high electrical capacity, which are crucial to the development of the electrical and electronic industry, especially in portable devices manufacturing (like mobile phones and laptops) and energy control and storage systems. Tantalum is mostly imported to EU, and, despite its presence in the list of CRMs, end–of–life recycling input rate is very low – about 1÷4 % [1–4]. It is understandable that it is necessary to improve the efficiency of current tantalum recycling processes or to develop new recycling methods.

About 40 % tantalum world demand falls on electrical and electronic applications (i.e. TC) but it is predicted that this demand will be decreasing, due to the possibility of substitution (e.g. high capacity ceramic capacitors or supercapacitors) [3, 5] or reducing the content of tantalum (thin film capacitors) [6]. The current waste electric and electronic equipment (WEEE) contains conventional TC for through–hole assembly (which can be considered as old tantalum scrap) and for surface

mounting to devices. These TC can contain up to 50 wt. % Ta [7], which means that they are an important secondary source of this metal.

Study topic description

Types of capacitors, their composition and construction

Due to the method of assembly to the electrical system or on printed circuit board (PCB), the following types of TC are distinguished: for though–hole technology (THT), among which the most numerous are leaded tantalum capacitors (LTC) (Figure 1.A and C), and for surface–mounted technology (SMT or SMDTC – surface–mounted device tantalum capacitor) (Figure 1.B and D) which is used in mass production. They differ in their external construction, but are similar in internal structure (Figure 1.E). Typical TC consists of an sintered metallic tantalum anode covered with tantalum (V) oxide (Ta_2O_5) dielectric layer. A cathode is manganese (IV) oxide (MnO_2) powder. The whole is covered by the following layers: graphite, silver (Ag) and epoxy resin (ER). The anode, dielectric and cathode have a porous structure to increase the surface area and thus the electrical capacity.

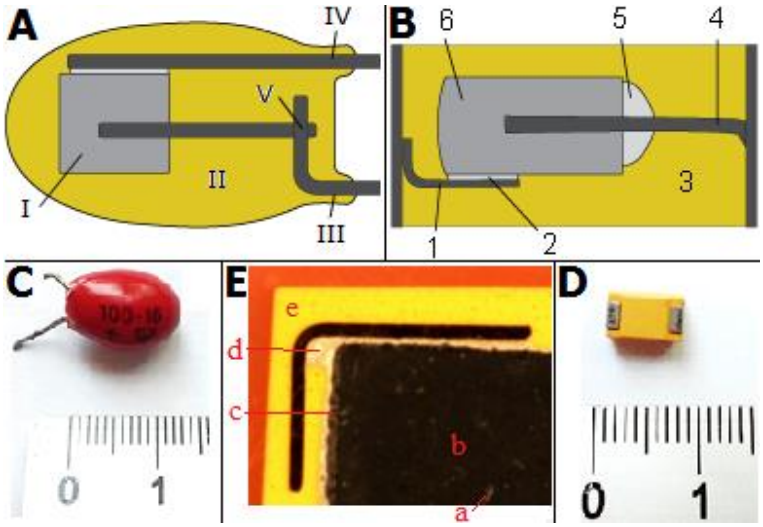

Figure 1. A and B – schemes of the construction of TC: LTC (I – anode, II – epoxy resin encapsulant, III – positive lead, IV – negative lead, V – weld) and SMDTC (1 – leadframe, 2 – silver filled epoxy, 3 – epoxy resin encapsulant, 4 – anode wire, 5 – teflon washer, 6 – anode), C and D – TC scraps used in this work (LTC and SMDTC respectively), E – optical microscope image of internal structure of SMDTC fragment: a – metallic tantalum particles, b – Ta– Ta_2O_5–MnO_2 layers, c – carbon ink, d – silver paint, e – epoxy resin
Source: [8] (A and B) and own (C, D and E)

It is currently carrying out research to replace MnO_2 by polymers to increase the TC efficiency [9]. Another reason is the removal of the strong oxidant (which is MnO_2) from the capacitor composition, which can cause failures and increase the electrical resistance (as a result of the reaction with Ag) [10]. The predicted trend of substitution of conventional TC for polymer capacitors will cause an increased share of tantalum in WEEE.

Tantalum recycling from WEEE

Many studies on the tantalum recycling from WEEE show that it is possible to recover tantalum and other associated metals. There are many methods to recycle tantalum: alkali and acid treatment with earlier mechanical–magnetic separation [11], oxidation treatment with mechanical and chemical treatment [12], method using solubility of tantalum in Cu–Fe alloy [13], exfoliation process of PCB [14], chlorination tantalum by iron chlorides [7, 15, 16], chemical reduction of oxidized tantalum by magnesium [16, 17], recovery with ionic liquids [18], supercritical water treatment [19], vacuum pyrolysis of organic materials combined by physical separation [20, 21] and other. Only few work concern the removal of MnO_2 and Ag from TC scrap. This is due to several facts: the research material in the novel works are polymeric TC that do not contain MnO_2; a small amount Ag, up to several percent, is not as interesting as tantalum. From the previous work [17] it follows that incomplete removal of Mn can contaminate the end product, giving phases with Ta, oxygen and reducing agent, thus lowering the reduction process efficiency.

Dissolution of manganese oxide and silver in sulfuric acid solutions

The simultaneous removal of Mn and Ag is possible by leaching via using sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) [22]. It is critical to use H_2O_2 as an oxidizing agent for Ag and reducing agent for MnO_2. Under conditions of high temperature and low concentration of H_2SO_4 and H_2O_2 (150 ^{0}C, both 1.5 M) it is also possible to leach Ag [23]. Dissolution of Ag in H_2SO_4 (without oxidizing agent) occurs only at high concentration and at high temperature with release sulfur dioxide [24]. The method described in [25] requires using a temperature of 200 ^{0}C to react, but a by–product is hydrogen.

The dissolution kinetics of MnO_2 in H_2SO_4 was described in [26]. It is known [27] that MnO_2 interacts with H_2SO_4 and H_2O_2. The work [28] presents the results of study on the MnO_2 removal from TC by reducing leaching reaction of H_2SO_4 + H_2O_2 and hydrochloric acid (HCl) + H_2O_2. It follows from [22, 28] that it is possible to easily remove MnO_2 on hydrometallurgical way. However, as a result of the reaction with HCl + H_2O_2, unstable $MnCl_4$ is formed, which decomposes with release of chlorine. In addition, in both cases, collective leaching occurs, which may complicate the subsequent separation of Mn and Ag. Studies on dissolving MnO_2 with using H_2SO_4 also containing organic acids (OA) such as oxalic [29, 30], ascorbic and citric acids [30] were made. Manganese removal proceeds by reducing leaching, in which OAs are reducing agents. In comparison to removing Mn only by H_2SO_4, the addition of OA improves the removal efficiency [30]. The work [30] refers strictly to recovery of zinc and manganese from spent batteries, but this idea can also be implemented to remove manganese from TC.

Study motivations and objectives

The main objective of this work was to study the possibility of removing MnO_2 and Ag from the TC scrap by dissolution process according to pro–ecologically recycling in the context of good small– and large–scale practice and cost–effectiveness. This term is understood as a process in which only by–products, utilized (cheap H_2SO_4 from utilization of SO_2) or derived from microbiological processes (organic compounds) reagents are used. The practical objective was to obtain a concentrate of tantalum (in both form: metallic and oxide), without other metallic

impurities, on the hydrometallurgical way, that is possible for further recycling (e.g. by magnesium reduction).

Laboratory tests of MnO_2 dissolution were carried out by reducing leaching using only H_2SO_4 and solutions of H_2SO_4 with following organic acids: acetic ($C_2H_4O_2$), ascorbic ($C_6H_8O_6$), citric ($C_6H_8O_7$) and oxalic ($C_2H_2O_4$), or in some cases with H_2O_2, and tests of Ag dissolution – by oxidative leaching using H_2SO_4 and H_2O_2. The chemical composition of initial materials (IM): LTC and SMDTC scraps were characterized. Research materials (RM) were prepared by pyrolysis, grinding and sieving of TC scraps. Each of these steps were described, and the chemical composition and particle size distribution of RMs have been characterized. The effect of such parameters as acid(s) and H_2O_2 concentration(s) (c_x), time reaction (τ), temperature (t), liquid–to–solid ratio (l/s) on the dissolution yield of Mn and Ag were determined.

Experimental

Initial and research materials, reagents

IMs were LTC and SMDTC scraps (Figure 1.C i D) from domestic source. Because the electrical leads (EL) and metal pads are also integral part of TC (in particular LTC, in which their share is significant), the IM has not been deprived of them. There were also other electrical parts, such as solders and leadframes.

The RMs (both types of TC separately) were prepared in the following order: first IMs were pyrolyzed, then the solid residues after pyrolysis were grinded, and finally were sieved, and parts such as ELs were separated. These prepared RMs were used to study on dissolution of MnO_2. The RMs for study of selective dissolution of Ag in H_2SO_4 were obtain by completely removing MnO_2 (and other impurities) in H_2SO_4, without attacking Ag.

Solutions were prepared with 95 % H_2SO_4, 30 % H_2O_2, 99.5 % $C_2H_4O_2$, $C_6H_8O_6$, $C_6H_8O_7 \cdot H_2O$ and $C_2H_2O_4 \cdot 2H_2O$, and for rinsing was used 92 % ethanol (all mentioned reagents are p.a. and from Avantor Performance Materials Poland). For dilution of H_2SO_4, dissolution of OAs and rinsing was used distilled water. In the pyrolysis step, the inert atmosphere was obtained by injecting of 99.2 % nitrogen (Air Liquide Group Poland).

Study on dissolution

Chemical interactions between MnO_2 and H_2SO_4 with/without H_2O_2 or OAs are given by these reactions [26, 27, 29, 30]:

$$MnO_2 + H_2SO_4 \rightarrow MnSO_4 + \frac{1}{2}O_2 + H_2O \quad (1)$$

$$MnO_2 + H_2SO_4 + H_2O_2 \rightarrow MnSO_4 + O_2 + 2H_2O \quad (2)$$

$$MnO_2 + H_2SO_4 + \frac{1}{4}C_2H_4O_2 \rightarrow MnSO_4 + \frac{2}{3}H_2O + \frac{1}{2}CO_2 \quad (3)$$

$$MnO_2 + H_2SO_4 + \frac{1}{10}C_6H_8O_6 \rightarrow MnSO_4 + \frac{7}{5}H_2O + \frac{3}{5}CO_2 \quad (4)$$

$$MnO_2 + H_2SO_4 + \frac{1}{9}C_6H_8O_7 \rightarrow MnSO_4 + \frac{13}{9}H_2O + \frac{2}{3}CO_2 \quad (5)$$

$$MnO_2 + H_2SO_4 + C_2H_2O_4 \rightarrow MnSO_4 + 2H_2O + 2CO_2 \quad (6)$$

and between Ag and H_2SO_4 with/without H_2O_2 by the following reactions [23]:

$$2Ag + H_2O_2 + H_2SO_4 \rightarrow Ag_2SO_4 + 2H_2O \quad (7)$$

The amounts of added OAs and H_2O_2 were stoichiometric in relation to H_2SO_4 according to reactions (2–6 and 9).

The solutions were heated with a laboratory hot plate. After reaching the given temperature (measured with a thermocouple), the RM was added into the beaker. Mixing was carried out using a magnetic stirrer and the mixing speed, constant in all cases, was 200 rpm. After the reaction time had elapsed, the mixture was filtered (on a paper filter, in cases of concentrated and hot acids on a glass funnel), the solid residue was rinsed with distilled water and ethanol (because the silica and pyrolytic coke contained in RM are hydrophobic and the remainder of AO is well dissolved in ethanol). Composition analysis was done for the solid residue after dissolution.

Materials preparation and analysis methods

The pyrolysis, which was aimed at removing the most of ER (by releasing mainly volatile carbon compounds and halogens), was carried out in a horizontal electric furnace at 400 ^{0}C in nitrogen atmosphere for 45 min (as reported [20]). Yield of solid residue (R), which was used to evaluate the pyrolysis, is given by the formula [20]:

$$R = \frac{m_{SR}}{m_{IM}} \cdot 100\% \quad (8)$$

where: m_{SR} – mass of solid residue after pyrolysis, m_{IM} – mass of initial material – both in g.

To increase the homogeneity of the RMs, the surface contact between material and leaching solution and allow the sieving of ELs and other unnecessary parts of TC, materials were grinded in a laboratory grinding machine for 5 min. ELs were removed from grinded materials by sieving and the particle size distribution of RMs was determined. Materials were manually sieved on square mesh sieves for 10 min – in this way sieve analysis were performed.

Content of each component for IMs and RMs (LTC and SMDTC) was determined by energy dispersive X–ray fluorescence analysis (EDXRF, MiniPal4 PANalytical) and X–ray powder diffraction analysis (XRD, Rigaku Miniflex II) and additionally by mechanical dismantling. The dissolution yield (η) was determined by formula below:

$$\eta_x = \frac{C_{p,x0} - C_{p,x,\tau}}{C_{p,x,\tau}} \cdot 100\% \quad (9)$$

where: $C_{p,x,0}$ – initial concentration (x is Mn, Ag or other), $C_{p,x,\tau}$ – concentration after process (both in %) – also determined by EDXRF analysis.

Observations, results and discussion

Components content determination in materials, dismantling, pyrolysis and sieving

Table1. shows the components mass fractions of the IMs, which are conventionally divided (on a macroscopic scale) into: ER, ELs with other electric components and anode (containing Ag, graphite, MnO_2 and tantalum). For LTC, the largest share (over 57 %) has an anode, and a small (5 %) have ELs. However, in SMDTC, the share of epoxy resin and anode is more or less similar (about 38 %), but electrical components (metal pads and leadframes) have a large share. This is explained by the internal structure of SMDTC and large participation of copper in these parts. The

presented mass fractions are not universal because they will depend on the size of TC; they concern only those TC scrap used in this work.

Table 1. Components mass fractions of the TCs used in this work (a detailed description in the text above)

capacitor type	epoxy resin	electical leads/metal pads and leadframes	anode
	wt %		
LTC	37.1	5.1	57.8
SMDTC	36.9	23.2	39.9

Source: own calculations

Yield of solid residue of pyrolysis process (as R) are resented in Table2. Whereas the results of this parameter for SMDTC can be compared with literature data [20,21] and correspond with them (despite the content of MnO_2 in SMDTC used in this work), there is no data about R for LTC. The higher R value for SMDTC can be explained by the high quality of the ER, which contains more silicon and is doped with halogens (increasing the decomposition temperature). Also the shape of the TC could have been significant – LTCs have the "beads" shape, so they have a large surface area, which enhances the pyrolysis process.

Table 2. Yields of solid residue after pyrolysis

capacitor type	mass of initial material m_{IM}	mass of solid residue after pyrolysis m_{SR}	yield of solid residue R
	[g]		[%]
LTC	139.492	122.812	88.0
SMDTC	16.678	15.848	95.0

Source: own

The grinded materials after pyrolysis were dark brown fine powders with fine shine metallic flakes. This color was caused by a high content of pyrolytic coke and graphite, MnO_2 and metallic tantalum. The sieve analysis results (Table3.) show that particle–size classes above 0.315 mm are small (in both cases) – there are ELs with the wire shape and which classified as waste. Undersize fraction 0.315 mm (RM) is 92÷99 % of the sieved materials. Some of the ELs were grinded too and also found themselves in the RM.

Table 3. Sieve analysis results (a detailed description in the text above)

particle–size class [mm]	capacitor type	
	LTC	SMDTC
	passing [%]	
>0.4	7	0
0.315÷0.4	1	1
0.125÷0.315	52	33
0.090÷0.125	30	23
<0.090	11	44
average particle size [mm]	0.127	0.055

Source: own calculations

SMDTC scrap was more susceptible to grinding – in this case, the average particle size is 0.055 mm. Particle–size class 0.125÷0.315 mm of LTC is the highest, over 50 %, and subsequent classes are linearly decreasing; the average particle size is greater and amounts to 0.127 mm.

The chemical compositions of RMs are presented in Table4. Due to the amorphous nature of pyrolytic coke, the carbon content is not include into account. The tantalum content has been converted to Ta_2O_5, but it should be remembered that tantalum is also present in the metallic form. While in LTC the main component is tantalum – 39 %, in the SMDTC it is SiO_2 – 33 %. In addition, there is a lot of SiO_2, MnO_2 and Sn in the LTC, and too Cu in SMDTC but no Sn. The content of tin and lead in LTC is explained by the presence of old type solder (Pb–Sn alloy). The materials of both types also include Fe and Ni from fine grinded ELs. The Ag content in LTC and SMDTC is similar and amounts to approx. 6.6 %. There are also small amounts of TiO_2, BaO and CaO: their presence is explained by compounds such as barium titanate and calcium titanate, which may be part of the ELs or dielectric layer (due to the high relative permittivity).

Table 4. Chemical compositions of RMs for study dissolution of MnO_2 – results of EDXRF and XRD analysis (a detailed description in the text above)

capacitor type	SiO_2	TiO_2	MnO_2	Fe	Ni	Ag	Ta_2O_5	Sn	BaO	Pb	CaO	Cu
	wt [%]											
LTC	13.50	0.607	13.54	3.08	0.45	6.41	39.10	14.71	0.40	8.28	nd	nd
SMDTC	33.24	0.690	12.87	3.58	0.12	6.83	22.41	nd	nd	nd	0.65	19.61

Source: own

Dissolution conditions of manganese oxide

In any case, it was observed that during the dissolution studies a part of the RM floated on the free surface. There were probably hydrophobic silica and pyrolytic coke particles. After leaching, the filtrate after some time took on a light flesh color, which indicates the presence of Mn in the solution. The SMDTC leaching tests gave a slightly blue filtrate due to the presence of Cu^{2+} ions. Other RMs components were also dissolved, primarily Fe and Ni. Due to the Fe content of a few percent in RMs (look at Table4.), it was important to include the dissolution yield of Fe. Ingredients such as Sn, Ob, TiO_2, BaO and CaO under MnO_2 dissolution conditions did not dissolve. In the case of SMDTC, Cu was simultaneously dissolved, which was also included.

Analyzing the effect of H_2SO_4 concentration on dissolution yields (with other constant parameters described in the description in Figure 2.) it is noted that both Mn and Fe pass into solution at low c_{H2SO4}. In the cases of Mn and Fe, the equilibrium is set at c_{H2SO4} about 2 $mol \cdot l^{-1}$. For these and higher c_{H2SO4}, η are maximum 94 and 90 %, Mn and Fe respectively.

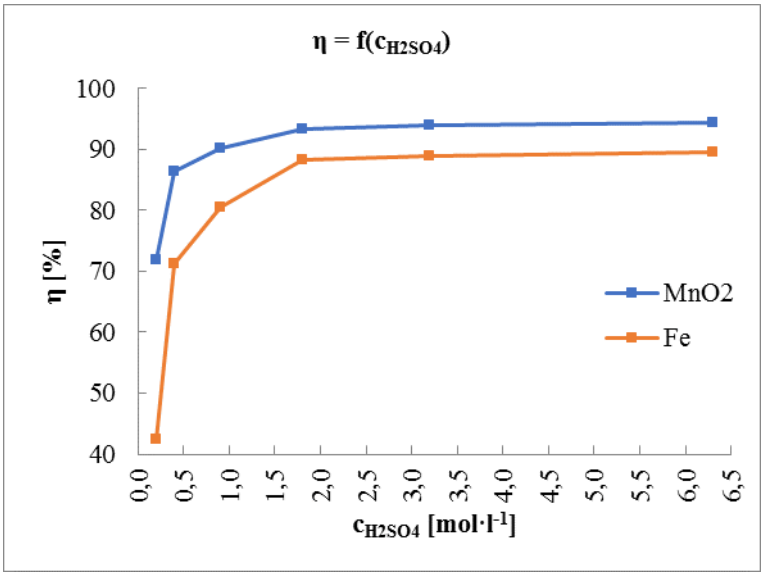

Figure 2. Effect of H_2SO_4 concentration on dissolution yields of MnO_2 and Fe, H_2SO_4 concentrations: 0.2, 0.4, 0.9, 1.8, 3.2, 6.3 mol·l^{-1}, constant parameters: τ = 120 min, t = 30 ^{0}C, l/s = 20 ml·g^{-1}, RM = LTC
Source: own calculations

The effect of τ on η_{Mn} is insignificant (Figure 3.A); for τ = 180 min and more η_{Mn} reaches a maximum value 98 %. In the time reaction range 60÷120 min, a significant increase in η_{Fe} is observed, and practically after 120 min, most of Fe is dissolved. As shown in Figure 3.B, in the temperature range 30÷60 ^{0}C η_{Mn} is constant, while η_{Fe} increases by twenty percentage points. At 80 ^{0}C, η_{Mn} reaches 98 % (five percentage points more than at 60 ^{0}C).

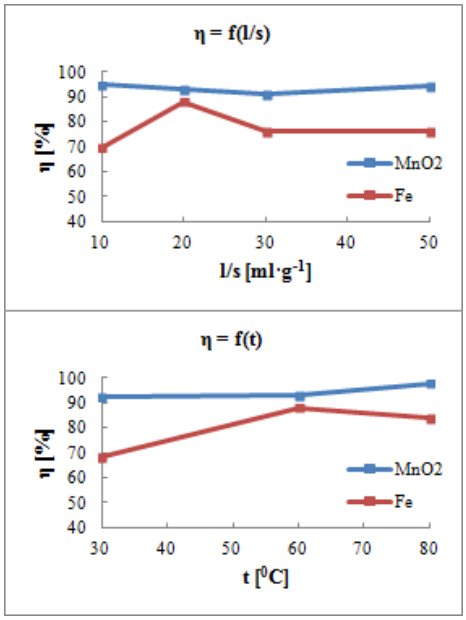

Figure 3. On the right – Effect of time reaction on dissolution yields of MnO_2 and Fe, reaction times: 60, 120, 180, 240 min, constant parameters: c_{H2SO4} = 1.8 mol·l^{-1}, t = 30 ^{0}C, l/s = 20 ml·g^{-1}; on the left – Effect of temperature on dissolution yields of MnO_2 and Fe, temperatures: 30, 60, 80 ^{0}C, constant parameters: c_{H2SO4} = 1.8 mol·l^{-1}, τ = 120 min, l/s = 20 ml·g^{-1}, RM = LTC
Source: own calculations

In the studied l/s (Figure 4.A), this parameter has no effect on the η_{Mn}. The highest value of η_{Fe} is reached for l/s = 20 ml·g^{-1}. Figure 4.B shows η depending on capacitor types (LTC and SMDTC). In the case of SMDTC the results are low. This is due to fact that acid reacts with Cu too. For this reason, a test with H_2O_2 was also carried out (results in the third diagram in Figure 4.B). The addition of H_2O_2 drastically decreased η_{Mn} and η_{Fe}, slightly increasing η_{Cu} (from 23 to 25 %). This may be due to the following reasons: the H_2SO_4 + H_2O_2 mixture is so strong oxidizing agent that reactions have occurred with the organic matter that has been after the pyrolysis process (which in RM may be over 30 %), resulting the solution loss; in addition, MnO_2 has the catalytic decomposition of H_2O_2 properties (which was manifested by intensely bubbling gas), which should increase the leaching ability, but only a minor part of H_2SO_4 and H_2O_2 reacted with Cu. Proving this would require study, but it practically demonstrates that in this case the addition of H_2O_2 does not work satisfactorily.

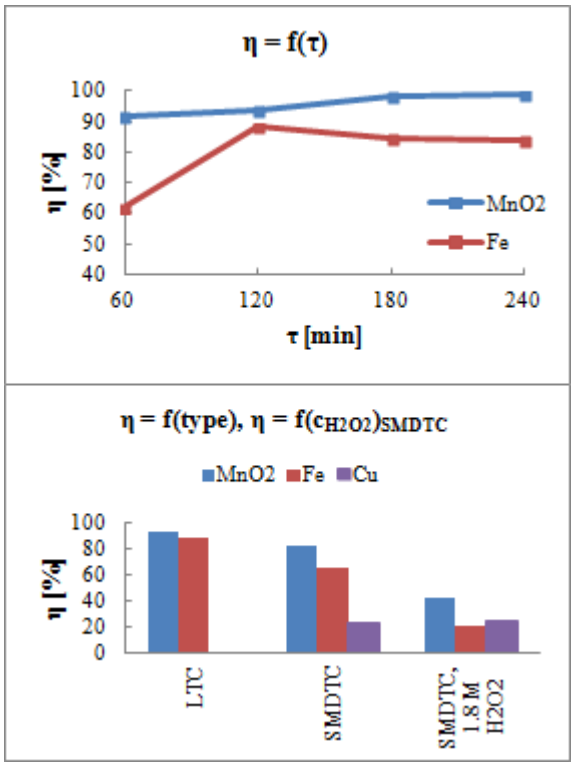

Figure 4. On the left – Effect of liquid–to–solid ratios on dissolution yields of MnO_2 and Fe, liquid–to–solid ratios: 10, 20, 30, 50 ml·g^{-1}, constant parameters: c_{H2SO4} = 1.8 mol·l^{-1}, τ = 120 min, t = 30 ^{0}C, RM = LTC; on the right – Dissolution yields of MnO_2 and Fe for: LTC, SMDTC and SMDTC with H_2O_2, constant parameters: c_{H2SO4} = 1.8 mol·l^{-1}, c_{H2O2} = 1.8 mol·l^{-1}, τ = 120 min, t = 30 ^{0}C, l/s = 20 ml·g^{-1} (a detailed description in the text)
Source: own calculations

Figure 5–8 show the results of reductive leaching via using OAs: $C_2H_4O_2$, $C_6H_8O_6$, $C_6H_8O_7$ and $C_2H_2O_4$ respectively. In almost all cases, the equilibrium of manganese dissolution was set at an acids concentration of about 1 M, expect for the $C_2H_2O_4$, where already at 0.2 M η_{Mn} it reaches a constant value. The maximum η_{Mn} were 98, 99, 97 and 99 % for $C_2H_4O_2$, $C_6H_8O_6$, $C_6H_8O_7$ and $C_2H_2O_4$ respectively, and in comparison to leaching with H_2SO_4 only, they are almost always higher by few–several percent (see Figure 2). η_{Fe} values for c_{C2H4O2} and c_{C6H8O7} are similar to those of leaching with H_2SO_4 only and oscillate at 70÷91 %. The lower η_{Fe} values (71÷76 %) are in the case

using $C_6H_8O_6$, where the equilibrium is set in the whole range of concentration. Whereas the situation is different when using $C_2H_2O_4$: η_{Fe} decreases with increasing of c_{C2H2O4}. The reason for this is very low solubility of the formed iron oxalates, which, despite rinsing the solid residue with water and ethanol, did not dissolve. Hence, and due to the very good results of manganese dissolution in the entire concentration range, it is recommended to use low concentrations of this acid. Especially, so that the solubility of $C_2H_2O_4$ in the aqueous solutions is the lowest in comparison with the other OAs.

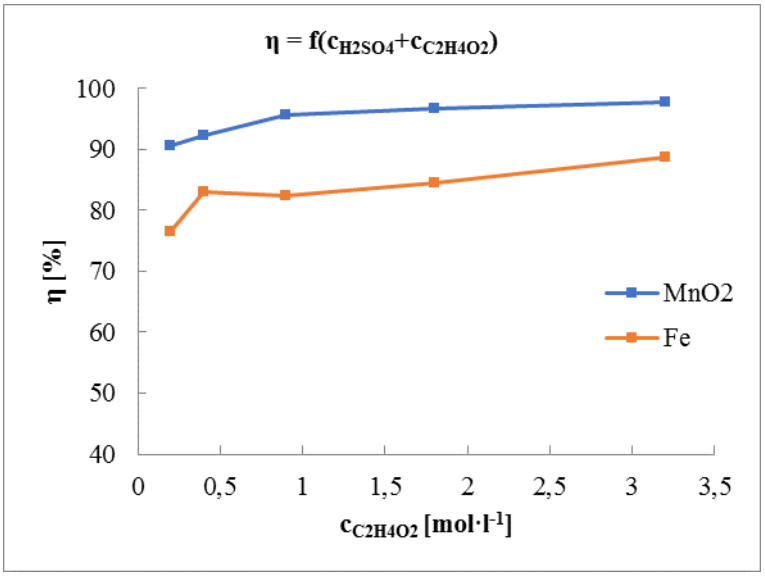

Figure 5. Effect of $C_2H_4O_2$ concentration on dissolution yields of MnO_2 and Fe, H_2SO_4 concentrations: 0.2, 0.4, 0.9, 1.8, 3.2 mol·l^{-1} and $C_2H_4O_2$ concentrations are stoichiometric in relation to H_2SO_4 according to reaction (3), constant parameters: τ = 120 min, t = 30 ^{0}C, l/s = 20 ml·g^{-1}, RM = LTC
Source: own calculations

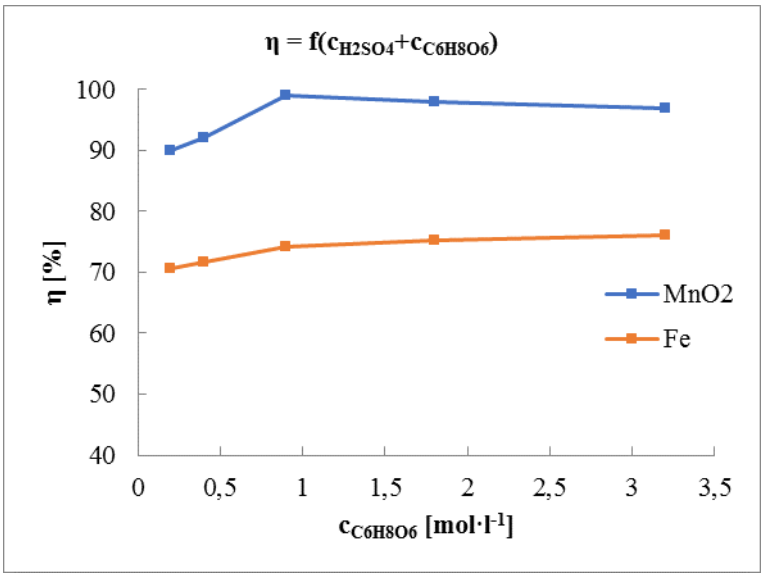

Figure 6. Effect of $C_6H_8O_6$ concentration on dissolution yields of MnO_2 and Fe, H_2SO_4 concentrations: 0.2, 0.4, 0.9, 1.8, 3.2 mol·l^{-1} and $C_6H_8O_6$ concentrations are stoichiometric in relation to H_2SO_4 according to reaction (4), constant parameters: τ = 120 min, t = 30 ^{0}C, l/s = 20 ml·g^{-1}, RM = LTC
Source: own calculations

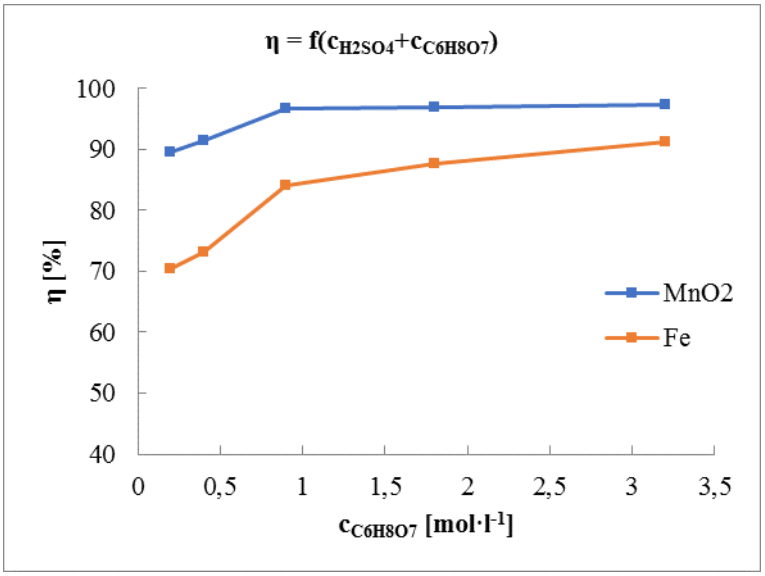

Figure 7. Effect of $C_6H_8O_7$ concentration on dissolution yields of MnO_2 and Fe, H_2SO_4 concentrations: 0.2, 0.4, 0.9, 1.8, 3.2 mol·l^{-1} and $C_6H_8O_7$ concentrations are stoichiometric in relation to H_2SO_4 according to reaction (5), constant parameters: τ = 120 min, t = 30 ^{0}C, l/s = 20 ml·g^{-1}, RM = LTC
Source: own calculations

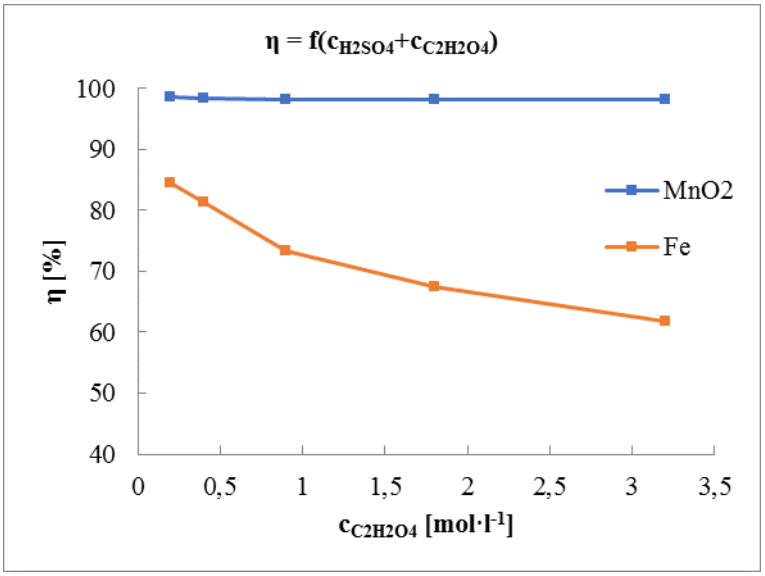

Figure 8. Effect of $C_2H_2O_4$ concentration on dissolution yields of MnO_2 and Fe, H_2SO_4 concentrations: 0.2, 0.4, 0.9, 1.8, 3.2 mol·l^{-1} and $C_2H_2O_4$ concentrations are stoichiometric in relation to H_2SO_4 according to reaction (6), constant parameters: τ = 120 min, t = 30 ^{0}C, l/s = 20 ml·g^{-1}, RM = LTC
Source: own calculations

Dissolution conditions of silver

In order to completely remove MnO_2 and other impurities from IM to prepare RM for dissolution study of Ag, based on the preparation process presented in Experimental and results presented above, there were carried out following preparation steps: pyrolysis, grinding and sieving, and at the end also leaching under conditions: c_{H2SO4} = 6.3 M, τ = 180 min, t = 60 ^{0}C, l/s = 20 ml·g^{-1},

for both LTC and SMDTC scraps. The composition of the RMs thus obtained was examined by X–ray methods. This data (Table5.) was used to calculate η_{Ag}. As can be seen in this table, practically all the Mn, Fe and Ni are removed. The silver concentration increased to the forecasted value 8÷9 wt %.

Table 5. Chemical compositions of RMs for study dissolution of Ag – results of EDXRF and XRD analysis (a detailed description in the text above)

capacitor type	SiO_2	TiO_2	MnO_2	Fe	Ni	Ag	Ta_2O_5	Sn	BaO	Pb	CaO	Cu
	wt [%]											
LTC	23.56	0.472	0.06	0.67	0.13	8.41	38.93	7.76	0.32	15.84	nd	nd
SMDTC	29.99	0.971	0.16	0.43	0.07	9.43	37.22	nd	nd	nd	0.55	11.34

Source: own

The use of hot H_2SO_4–H_2O_2 solutions causes the solution after the Ag leaching process to take a brown–orange color, which causes the presence of chlorine and bromine. Figure 8 and 9 show the results of dissolution yields. Tin is also leached; thus, simultaneous removal of Ag, halides and Sn occurs. The highest η_{Ag} = 38 % was achieve for τ = 240 min. A similar result was achieved for l/s = 30 (η_{Ag} = 34 %). Parameters such as τ and l/s, in the studied ranges, do not significantly affect η_{Ag}. Although these are not very high η, however, it has been proven that it is possible to remove Ag with H_2SO_4 and H_2O_2. Good results of η_{Sn} were achieved (37÷78 %). However, the co–leaching Ag and Sn mean that the conditions were not maximized under Ag removal point.

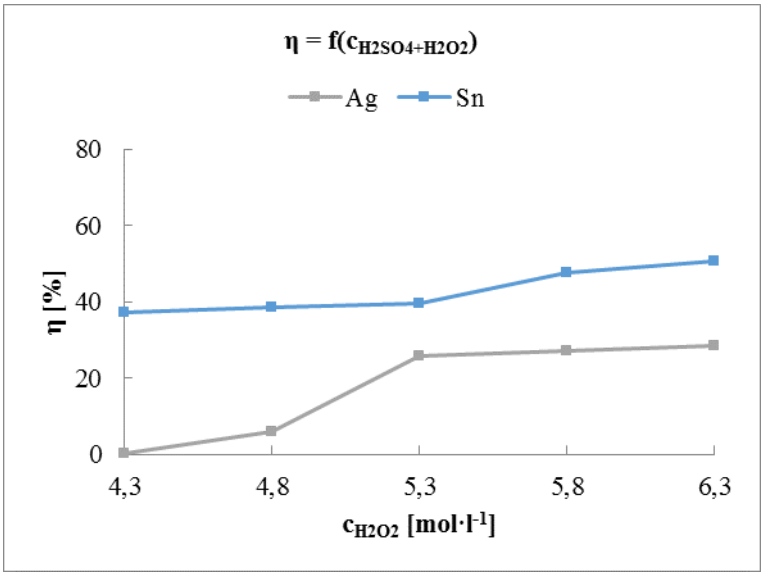

Figure 9. Effect of H_2SO_4–H_2O_2 concentration on dissolution yields of Ag and Sn, H_2SO_4–H_2O_2 concentrations: 4.3, 4.8, 5.3, 5.8, 6.3 mol·l^{-1}, constant parameters: τ = 120 min, t = 95 ^{0}C, l/s = 10 ml·g^{-1}, RM = LTC
Source: own calculations

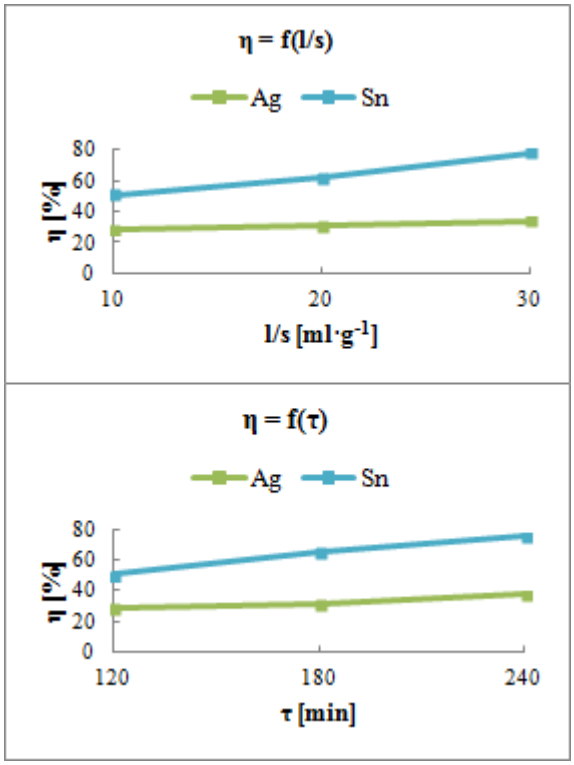

Figure 10. On the left – Effect of time reaction on dissolution yields of Ag and Sn, reaction time: 120, 180, 240 min, constant parameters: c_{H2SO4} = 6.3 mol·l^{-1}, c_{H2O2} = 6.3 mol·l^{-1} t = 95 ^{0}C, l/s = 10 ml·g^{-1}; on the right – Effect of liquid–to–solid ratios on dissolution yields of Ag and Sn, liquid–to–solid ratios: 10, 20, 30 ml/g, constant parameters: c_{H2SO4} = 6.3 mol·l^{-1}, c_{H2O2} = 6.3 mol·l^{-1} t = 95 ^{0}C, τ = 120 min, RM = LTC
Source: own calculations

Proposal for the recovery of manganese and silver from the leaching solutions

Manganese sulfate ($MnSO_4$) can be used in a variety ways, e.g. for the preparation of other manganese salts. Electrolytic manganese oxide (EMD) or activated manganese oxide (AMD) are produced on an industrial scale by the electrolysis of manganese salts, including also $MnSO_4$ [31, 32]. Thus, the above–obtained manganese salts (organic salts too, especially manganese acetate [32]) can be used for the manganese oxides production. However, due to the fact that manganese nitrate ($Mn(NO_3)_2$), not $MnSO_4$, is used for the tantalum capacitors manufacturing [10], EMD and AMD can be used to produce other electronic components, e.g. dry–cell batteries or supercapacitors. Solution after TC scrap treatment can be reused in different process, e.g. for the spent batteries recycling [30] (if the potentially free acid remains). Simultaneous leaching of multi–type WEEE can also be taken into account, however it can complicate the extraction and purification of tantalum.

Silver sulfate (Ag_2SO_4) is dissolved in a hot H_2SO_4 solution, but precipitate at room temperature. Therefore, hot filtration of the solid residue of TC scrap after treatment is indicated, otherwise, Ag_2SO_4 dissolution in hydrochloric acid [23] or ammonia solution [25] needs to be used.

The mentioned examples of by–products recovery obtained from hydrometallurgical treatment of TC scrap will be more efficient if there are no impurities such as Fe and Pb–Sn in the material.

Thus, mechanical, magnetic or other separation method (see subsection Tantalum recycling from WEEE) should also be implemented to a greater extent.

Conclusions

The following conclusions can be drawn from this work:

- tantalum capacitor is a complex electronic subassembly in terms of structure and composition, consisting of parts such an epoxy resin encapsulant, terminals and anode. The anode has a multi–layered structure, and they consist of: metallic tantalum, Ta_2O_5, MnO_2 (or polymer), graphite and silver. The above–mentioned factors make tantalum recycling from WEEE a challenge;
- after pre–treatment processes such a pyrolysis, grinding and sieving, the processed TC scraps consists mainly Ta_2O_5, MnO_2, SiO_2, as well as Fe, Cu, Sn and Pb, and are relevant methods of tantalum enrichment. From the economic point of view, the silver content is also important, which should be taken into account. In order to more efficiently recycle tantalum from WEEE, other impurities should be removed;
- dissolution of MnO_2 in H_2SO_4 is an effective method to remove this compound, but the use of additional organic acids, such as $C_2H_4O_2$, $C_6H_8O_6$, $C_6H_8O_7$ and $C_2H_2O_4$, improve η_{Mn}. In the studied ranges of various parameters, the concentration of acids has a greatest influence on the dissolution yield. There is also the removal of other impurities, in particular Fe;
- selective dissolution of Ag by using H_2SO_4 and H_2O_2, but under other conditions that occurs after initial removal of MnO_2, is an effective method of Ag leaching;
- it is possible to process TC scrap according to "green" recycling technology, using only utilization products (H_2SO_4) and organic compounds (OAs). The dissolution conditions studied are also suitable for the processing of other types of WEEE, such as spent batteries and silver–bearing material.

Literature

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THERMO–OPTIC PROPERTIES OF HIGH ALKANES FILLED MICROSTRUCTURED FIBER

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Abstract:

Nowadays one of interesting applications of a fiber optic sensor is dedicated to measuring temperature. This is due to the unique properties of a transducer based on a photonic crystal fiber (PCF). This has a great influence on sensitivity, temperature and time responses of the environmental disturbances. Infiltration to the air holes of the PCF by higher alkanes allows to design a fiber optic threshold temperature sensor. There have been observed hystereses of temperature and time responses when the sensor is tested in a cycle of heating and cooling and switching temperatures are different. This class of materials (alkanes) are very good candidates for manufacturing a multistage temperature threshold sensor. Therefore, in the future, we will carry out the research in order to introduce higher alkanes nanoparticles to reduce these phenomena.

Keywords:

high alkanes, photonic crystal fiber, fiber optic threshold sensor

Introduction

Research on the use of glass as a medium for transmission of information began at the end of the 19th century. After nearly a century, in 1966 researchers Charles Kao and George Hockhman of Standard Communications Laboratories in Great Britain described it in their publication [1] on fiber optic. They presented it as a coaxial, cylindrical structure of the core and glass jacket on the border of which there is a one–percent difference in refractive indices. This event initiated a rapid development of research aimed at developing a method for manufacturing fiber optical glass fibers with the lowest possible optical losses with regard to the path of signal transmission [2, 3].

Obtaining low optical losses at the decimal decibel level was possible due to the development of the method of producing glass with a very high degree of purity. At present, the material used for fiber production can contain several atoms of pollution per 1 million particles of glass. The optical fiber of this material is currently the best transmission medium. It allows for the transmission of signals in the band exceeding 1 THz, with the attenuation of 0.2 dB/km.

Optical fiber is defined by contemporary scientists as a dielectric waveguide constituting a system of transparent centers with different refractive indices n (the refractive index of the core

is higher than the index of refraction of the jacket), which can lead optical radiation due to the effect of a total internal reflection at the boundary of these centers [4].

The development of a relatively new technology related to the production of photonic fibers has created new research fields for the work on fiber optic optical sensors. Easily shaping of a photonic fiber microstructure allows to control optical parameters of this type of fibers [5].

Optical fiber sensors have many advantages over other types of sensors. These include:

- high sensitivity and large capacity,
- small size and low weight,
- resistance to electromagnetic and environmental interference,
- no impact on other devices' work,
- very wide range of working temperatures (much wider than of many electronic devices),
- design based on electrically insulating materials – application in, i.e., a high–voltage environment or explosive,
- design based on chemically passive materials, non–polluting and non–corrosive, possibility of coupling with telecommunication systems,
- possibility of using in places where using other sensors is hard or impossible.

A number of advantages and applications of fiber optic sensors make them displace traditional sensors [6, 7].

There are many types of fiber optic sensors on the market that can be classified as follows [6, 8]:

- according to their construction:
  - internal sensor (single–mode or multimode) – factor disturbing propagation of a signal works directly on the optical fiber;
  - external sensor (single–mode or multimode),
    - factor disturbing propagation of a signal works on a modulator to which an optical signal is supplied and discharged using an optical fiber.
- according to their use:
  - physical sensor (e.g., measurements of temperature, pressure, deformation value);
  - chemical sensor (eg, pH measurement, gas composition analysis, spectroscopic studies);
  - biological sensor (e.g., in medical research).
- according to their area range:
  - single–point sensors;
    – single measurement at the end of a fiber, information from a single source (similar to electric sensors);
  - multipoint sensors
    – measurement at multiple points along a single fiber optic line;
  - distributed sensors;
    – continuous measurement along the optical fiber along its entire length.
- due to the modulated parameter we distinguish sensors with modulation: polarization; phase; amplitude; wavelength; frequency and several of the above parameters.

Fiber optic sensors that are currently widely used are sensors designed to temperature measurement. This technology is used in both manufacturing and industrial processes, in civil engineering, as well as in scientific research and everyday life.

The biggest advantage of these sensors is the ability to perform precise temperature measurements (with the accuracy of 0.3 K) for thousands of control points, located at distances of up to several kilometers, using only one optical fiber. The measuring system, which is a part of the sensor, controls and registers temperature of a tested factor or environment and compares it with the developed algorithm. The sensor can be configured depending on the needs. There is also a possibility of entering multiple alarm thresholds depending on the areas of potential danger, an alarm can be generated, e.g., when:

– exceeding the set temperature threshold;
– temperature drops below the set threshold;
– local temperature exceeds the set value relative to the average/desired temperature;
– and others.

Such operation allows for immediate localization and removal of, e.g., failure or error in the operation of the equipment or system. This prevents development of undesirable events and ensures maintenance of the safety status. Added bonus of optic fiber sensors is a possibility to work in difficult conditions (pollination, dust), resistance to corrosion, UV and water, as well as no impact on monitoring systems, nor environment.

Research

In the tests conducted, a temperature sensor based on an LMA 10 special fiber was prepared into which openings higher alkane (Figure 1.) [9–12] was introduced.

Transducer	MP [°C] *	T_{ON} [°C]	T_{OFF} [°C]	ΔT [°C]
T1 (n – nonadecane)	26 – 29	32.5	31.1	1.5
T2 (n-heneicosane)	39 – 41	41.0	38.6	2.4
T3 (n-tetracosane)	49 – 52	51.1	49.5	1.6
T4 (n – octacosane)	57 – 62	61.8	60.8	1.0

* Data from Sigma Aldrich Internet web site

Figure 1. Catalog data of melting points used filling materials and experimental ON and OFF temperatures for tested sensor [13].

Thus obtained filled fragments of LMA–10 fiber were welded at both ends with sections of a standard single–mode fiber ending on one side with FC/APC optical fiber connectors. Permanent welding of a special and standard fiber and creation of a so–called cordura patch are made with the FERTILE FFS–2000 fiber optic welder from Vytran [13].

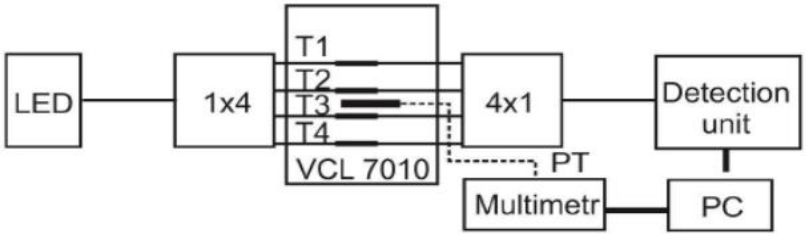
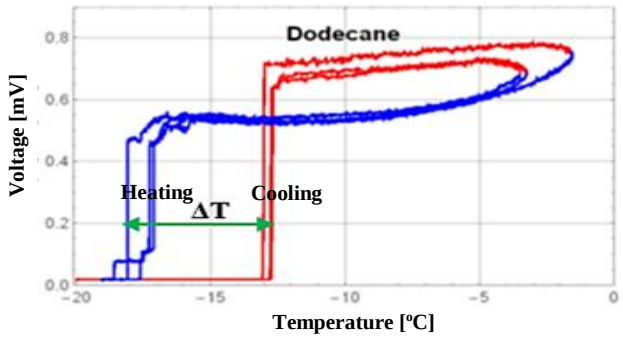


Figure 2. Scheme of a multilevel optical fiber sensor with four transducers [9].

The prepared patch–cords were subjected to thermal–optical tests and a special stand was prepared for this purpose which consisted of: light source, 1x4 coupler, climate chamber, detector set, thermocouple or thermo–resistor, multimeter and computer (Figure 2).

a)



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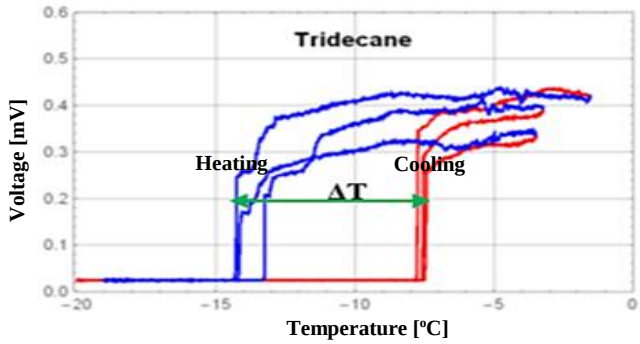

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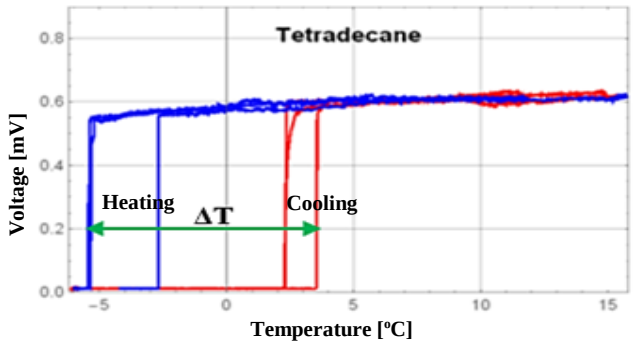
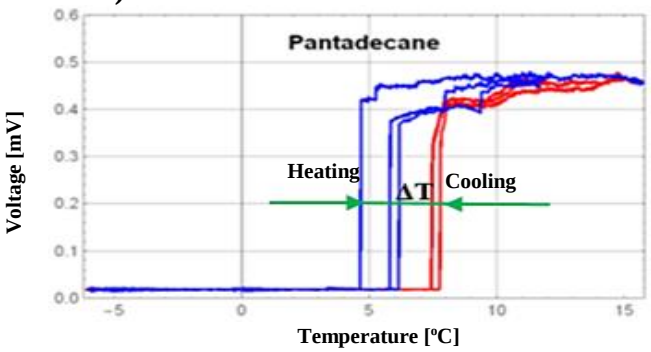


d)



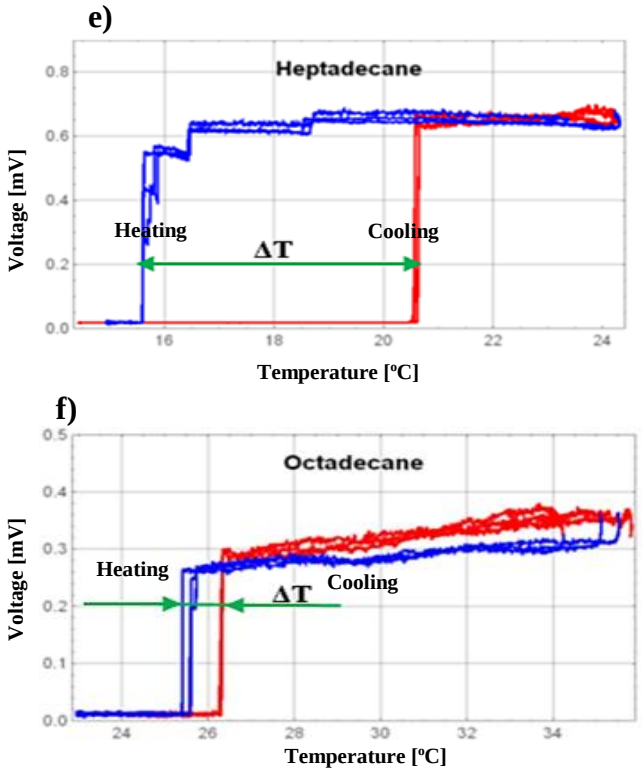


Figure 3. Graphs showing dependence of voltage on temperature for selected n–alkanes: a) dodecane, b) tridecane, c) tetradecane, d) pentadecane, e) heptadecane, f) octadecane [9,10].

The optical signal from the LED source with a wavelength of about 850 nm was introduced into the coupler where it was separated into four outputs. One of the ends of the prepared patch cord was attached to all output ends and was connected to the detector. Signals from detectors were given to the card of analogue–digital converters. The patch cords were placed in a climatic chamber, the application of which enabled measurements to be taken at given temperatures and appropriate heating and cooling cycles. To improve the operation of the station, and to ensure adequate control of the temperature prevailing in the climatic chamber, a thermoresistor connected with a multimeter was used, which, through the control software passed the current resistance value converted to the temperature value. Data obtained from the detectors and the multimeter were collected and processed by a designed software written for need of the conducted research in a LabView graphic programming environment.

Each of the manufactured converters placed in the discussed station was tested as a threshold temperature sensor. For each of them, measurements of changes in the voltage recorded by the detector as a function of time of reading the signal value from the analogue–digital converter and the thermal characteristic showing the voltage changes as a function of temperature of the resistor have been made. Taking into account their previously discussed thermo–optical properties and the proposed application of these transducers, their most important property is the transducer's transition temperature between the ON and OFF states.

By analyzing the above graphs (Figure 3.), it can be concluded that all selected n–alkanes allowed to make transducers that change their state from off to on, or vice versa. Unfortunately, in each case the diagrams showing dependence of the output signal on temperature show discrepancy

between transition temperatures when the transducer "turns on" (heating process which is marked in red) and when it "turns off" (cooling process which is marked in blue). Such changes in the measured quantity are called hysteresis of the transducer state change.

For each of the materials, the so–called dead area (ΔT), which is the difference of extreme values of transitions and is marked in the above graphs by green arrows.
This area defines the temperature range for which the sensor transition from on–off state to off state or vice versa will only allow to estimate the temperature at which the sensor is located.

For most of the tested n–alkanes, there is a so–called effect of supercooling, i.e., liquids of high purity (purity of the tested substances was at a level of 98 %) during the cooling process they do not clot at the same temperature, but usually lower. In addition, the transducers are activated at temperatures lower than the melting temperatures of individual n–alkanes. Additionally, the level of the output signal at cooling and heating reaches different values or, if these values are similar, there are quite significant fluctuations. Particular attention is paid to the alkanes dodecane and heneicosane which are characterized by visible "loops" that arose during the transitions from heating to cooling (dodecane) and from cooling to heating (heneicosane). This may indicate that crystallization and melting do not occur in the entire volume of material in the same way. In addition, heneicosane is the only one showing a surprising property which is the inclusion of the transmitter in heating process at temperatures lower than during the cooling process. The remaining transducers behave as standard – the transition temperature during cooling is lower than the transition temperature during heating [14].

Conclusion

Photonic optical fibers differently microstructured are waveguides currently used in many specialized and everyday applications (including broadband light sources, fiber optic sensors, e.g., smoke, pressure etc., as well as in access elements of telecommunications' networks). These are fibers usually made of a homogeneous material (e.g., silica glass), often a periodic pattern of holes in the area of the fiber optic skirt, and the lack of openings (i.e., a uniform material) in the core region.
We have shown a group of fiber optic transducers based on a partially filled LMA10. For six compounds: dodecane, tridecane, tetradecane, pentadecane, heptadecane and octadecane have been selected to be used as transducers which are useful for our experiment. By analyzing their thermo–optic properties, we observed that for all samples the melting points are close to product information. For all samples we have had hysteresis between melting and crystallization points, which makes us believe that a high purity grade of the used materials and a small number of crystallization centers are the major problems in this case. These materials are very good candidates for manufacturing multistage temperature threshold sensor on which we will report in the future work.

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FREE RADICAL IN THERMALLY STERILIZED OPHTALMIC DRUG – EPR SPECTROSCOPY EXAMINATIONS

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Abstract:

EPR spectroscopy was used to examination of free radicals in thermally sterilized pilocarpine. Conditions of thermal sterilization were chosen according to the pharmaceutical norms. The aim of this work was to determine concentration and free radical properties of thermally sterilized pilocarpine. EPR spectra were recorded in the range of microwave power of 2.2–70 mW. g–Factor, amplitudes (A), integral intensities (I), and linewidth (ΔB_{pp}) of the spectra were determined. Free radical concentration (N) in the heated samples was determined. EPR spectra were not obtained for the non heated pilocarpine. EPR spectra were detected for the all thermally sterilized samples. The spectra revealed complex character, their asymmetry depends on microwave power. The lowest free radicals concentration was found for the pilocarpine sterilized at temperature 180 ^{o}C during 30 minutes. EPR spectroscopy is proposed as the method useful to optimization sterilization process of drugs.

Keywords:

free radicals, thermal sterilization, pilocarpine , EPR spectroscopy

Introduction

Electron paramagnetic resonance (EPR) spectroscopy was used for examination of free radicals in thermally treated pilocarpine. Thermal treatment in hot air as sterilization process was tested. Sterilization is expected to exterminate microorganisms in drugs [1, 2], but chemical structure and therapeutic interactions of drugs with tissues should not be modified. Conditions of thermal sterilization are described in the pharmaceutical norms [3–8]. It is expected that thermal sterilization breaks chemical bonds and produces free radicals in drugs depending on temperatures. A lot of our works about formation of free radicals in organic pharmaceutical substances at high temperature are known [9–12].

The aim of this work was to determine concentration and free radical properties of thermally sterilized pilocarpine. It is not found in literature information about free radicals in this drug. The EPR measurements are proposed by us to use to optimize sterilization process. The optimal temperature and time of heating of the drug are those that produce the lowest amount of free radicals in the sample.

Free radicals have influence on a lot of diseases such as atherosclerosis, diabetes, and cancer, as well as to accelerate the aging of the body [13].

Free radicals should not exist in drugs, because they may cause a lot of toxic effects in tissues. The presence of free radicals in the body causes oxidative stress. It has many negative effects. Free radicals may lead to peroxidation of membrane lipids. As a result of this process, which consists of three stages: initiation, propagation and termination, short fragments of carbon chains are formed. Aldehydes and hydroxyaldehydes, such as malondialdehyde (MDA), are very often formed. Lipid peroxidation is easier as more double bonds contain a fatty acid particle. Reactive oxygen can also destroy proteins. They trigger the modification of side chains of amino acid residues, change the spatial structure of proteins, their aggregation or cracking. This is especially dangerous for proteins that are permanent and their exchange in the body occurs very slowly. Despite of the greater stability, nucleic acids can also be modified by free radicals. The effects of their action are: phosphodiester bonds and DNA or RNA strand breaks, modifications of nitrogenous bases, among which the most sensitive is thymine, as well as damage to sugar residues [13].

Under the influence of free radicals, the sugar molecules that make up glycoproteins and proteoglycans can change their antigenic properties. In turn, their effect on hyaluronic acid leads to its depolymerization and dysfunction of joints [13].

Reactions mentioned above have serious effects on the cell. They lead to dysfunction of the cell membrane, intracellular proteins (enzymatic, signaling or transport) and changes in genetic information, leading to mutations. They can also interfere with the functions of the mitochondria, and have the effect on the metabolic activity of the cell, lead to lysis of erythrocytes, stimulate platelet aggregation, disturb calcium metabolism, and degrade the cytoskeleton [13].

Experimental

Sample

Pilocarpine is an alkaloid with a parasympathomimetic effect. Pilocarpine has similar effects to acetylcholine [14]. The most common source of pilocarpine used industrially are plants of the genus *Pilocarpus*, originating from northern Brazil. Under optimal in–vitro environment conditions, incubated in the dark, callus tissue of *Pilocarpus microphyllus* produces large amounts of pilocarpine [15]. Pilocarpine causes overstimulation of exocine glands, for example sweat, lacrimal, salivary, gastric glands. It also induces miosis (narrowing of the pupils) [16]. Pilocarpine lowers intraocular pressure by facilitating the outflow of intraocular fluid that is why pilocarpine is used locally in glaucoma. In addition, pilocarpine is used in the Sjögren syndrome, xserostomia and in atropine and other cholinolytics intoxication [14]. In pediatrics pilocarpine is used in sweat test which is important in cystic fibrosis diagnostics [17]. It can also have an effect cardiovascular system [16]. Chemical structure of pilocarpine is presented in Figure 1 [18].

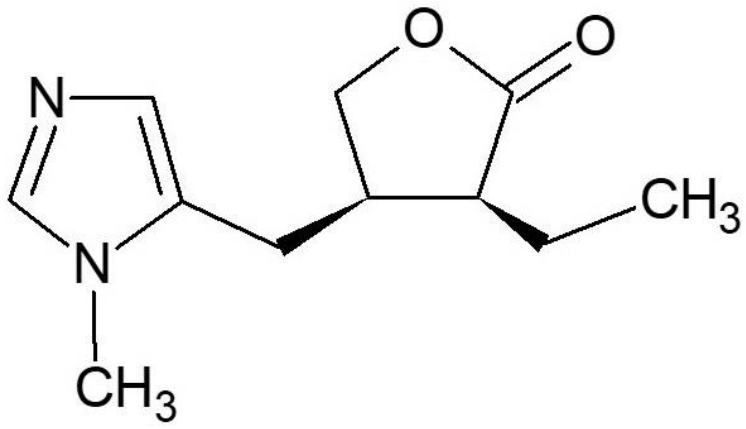

Figure 1. Chemical structure of pilocarpine [18].

Pilocarpine was sterilized according to the norms [3–8] at the following temperatures: 160 °C for 120 minutes [3–5, 8], 170°C for 60 minutes [6–8], and 180 °C for 30 minutes [6– 8], respectively. Sterilization process was performed in professional sterilizer Memmert company (Germany) with hot air.

The powdered samples of pilocarpine were measured in the thin–walled glass tubes. EPR signals were not obtained for the empty tubes, they do not contain paramagnetic impurities.

Pilocarpine was purchased from Sigma–Aldrich company.

EPR Measurements

The electron paramagnetic resonance (EPR) measurements were performed 15 minutes after sterilization. The samples were examined at room temperature. The first–derivative spectra were recorded by the use of an X–band (9.3 GHz) EPR spectrometer of Radiopan company (Poznań). Magnetic modulation was 100 kHz. Microwave frequency was directly measured by MCM 101 recorder of Eprad company (Poznań).

The first–derivative EPR spectra were measured with microwave power in the range 2.2–70 mW. g–Factor, amplitudes (A), integral intensities (I), and linewidth (ΔB_{pp}) of the EPR lines were analysed (Figure 2). The parameters A_1–A_2, and B_1–B_2 of asymmetry of lineshape of EPR spectra were determined (Figure 2).

g–Factor was calculated from the resonance condition according to the formula (1) [19]:

$$g = h\nu/\mu_B B_r \quad (1)$$

where:

h – Planck constant,

ν – microwave frequency,

μ_B – Bohr magneton,

B_r – resonance magnetic induction.

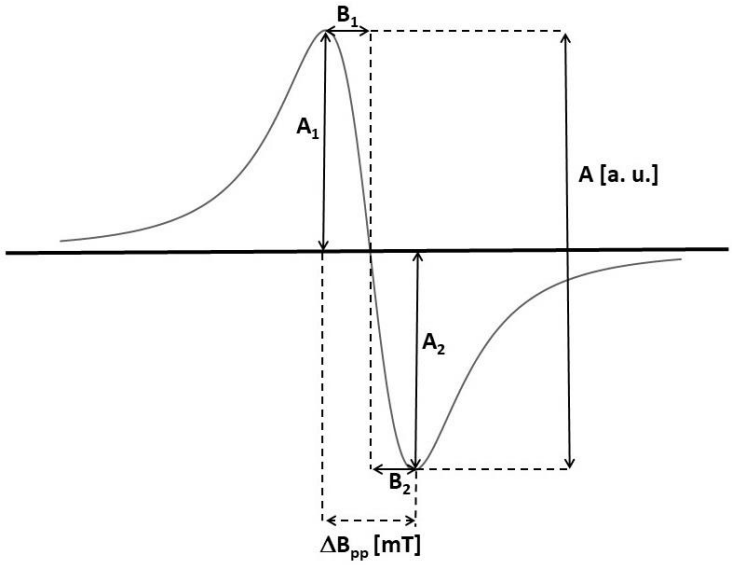

Figure 2. The analysed parameters of the EPR spectra: amplitude (A), linewidth (ΔB_{pp}), and the asymmetry of lineshape parameters: A_1, A_2, B_1, B_2.

Continuous microwave saturation of EPR lines was applied to examination of spin–lattice relaxation processes [19, 20].

Free radical concentration (N) in the samples was determined as follow (2):

$$N = N_u[(W_u A_u)/I_u] \bullet [I/(WAm)] \quad (2)$$

where:

N_u – number of paramagnetic centers in ultramarine (reference);
W, W_u – receiver gains for the tested samples and ultramarine;
A, A_u – amplitudes of ruby signal for the tested samples and the ultramarine;
I, I_u – integral intensities for the tested samples and ultramarine,
m – mass of the pilocarpine sample.

Ultramarine with the strong stabile EPR line was the reference for free radicals concentration in the samples. A ruby crystal ($Al_2O_3:Cr^{3+}$) was permanently placed in the resonance cavity, and it was used as the secondary reference during measurements of the concentration.

Results and Discussion

EPR spectra were not measured for the original, non–heated samples. EPR spectra were obtained for all the variants of temperature and time of thermal sterilization, that were tested. The original samples are free of paramagnetic impurities. Free radicals were found in pilocarpine sterilized at 160 °C for 120 minutes, 170 °C for 60 minutes, and 180 °C for 30 minutes. The EPR spectra of the sterilized pilocarpine are present in Figure 3. Free radicals are formed in pilocarpine as the result of thermolysis. Thermal energy break chemical bonds in the tested drug. It is expected that thermal transformation change the therapeutic interactions of this drug. The interactions of free radicals of pilocarpine and tissues may be the source of toxic effects. The EPR spectra changed with temperature of sterilization. The parameters of the EPR spectra of the samples sterilized at different temperatures and times are shown in Figure 3 a–c.

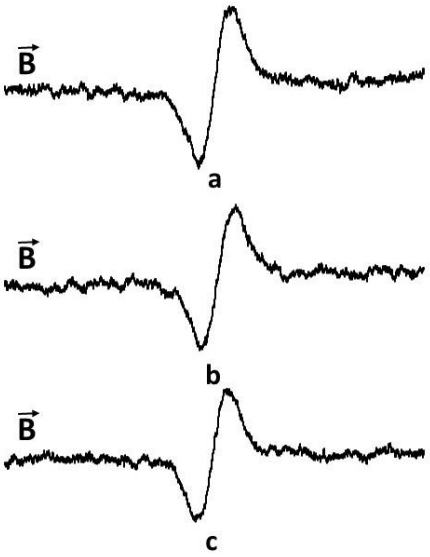

Figure 3. EPR spectra of pilocarpine sterilized at 160 °C for 120 minutes (a), 170 °C for 60 minutes (b), and 180 °C for 30 minutes (c). The measurement was done 15 minutes after sterilization with microwave power of 2.2 mW.

Concentrations (N) of free radicals, g–factors, and linewidths (ΔB_{pp}) of EPR spectra of pilocarpine sterilized at different conditions are presented in Table 1. The tested EPR spectra were broad lines with linewidths in the range 0.56–0.57 mT. Dipolar interactions are probably responsible for such line broadening. The apparent g–factors 1.9995–1.9998 indicate that unpaired electrons in the heated pilocarpine are located on carbon, nitrogen, and oxygen atoms. The high free radical concentration (~10^{18} spin/g) characterizes all the samples. The lowest free radicals concentration was obtained for pilocarpine sterilized at 180 °C for 30 minutes. Such conditions of sterilization are proposed as the optimal for pilocarpine.

Table 1. Free radical concentration (N) in the sterilized pilocarpine, integral intensity (I), g factor and linewidth (ΔB_{pp}) of its EPR spectra.

Temperature of sterilization [°C]	N x 10^{18} [spin/g]	I [±0.1 a.u.]	g [±0.0002]	ΔB_{pp} [±0.02 mT]
160	14.5	5.0	1.9998	0.56
170	13.2	4.4	1.9996	0.57
180	11.8	3.8	1.9995	0.56

Several types of free radicals are formed in pilocarpine during sterilization. Free radicals system in thermally sterilized pilocarpine was complex. Line shape of EPR spectra changed with the increasing of microwave power. The changes of the asymmetry parameters A_1–A_2, and B_1–B_2 of the EPR spectra of pilocarpine sterilized at 160 °C for 120 minutes, 170 °C for 60 minutes, and 180 °C for 30 minutes, are shown in Figure 4–5 a–c, respectively. The correlations presented in

Figure 4–5 resulted from the different changes of the individual EPR component lines with increasing of microwave power.

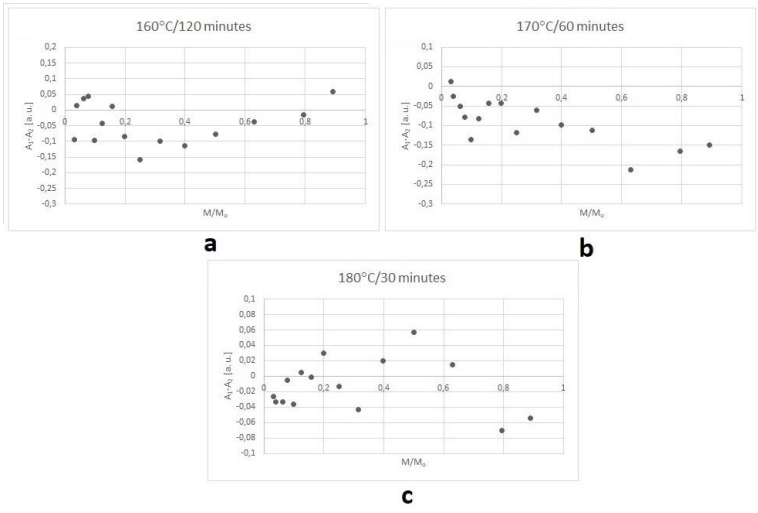

Figure 4. Influence of microwave power (M) on the asymmetry parameter A_1–A_2 (a–c) of EPR spectra of pilocarpine thermally sterilized at different conditions. The measurement was done 15 minutes after sterilization. M – microwave power used during the measure of the EPR spectrum. M_o – total microwave power produced by klystron (70 mW).

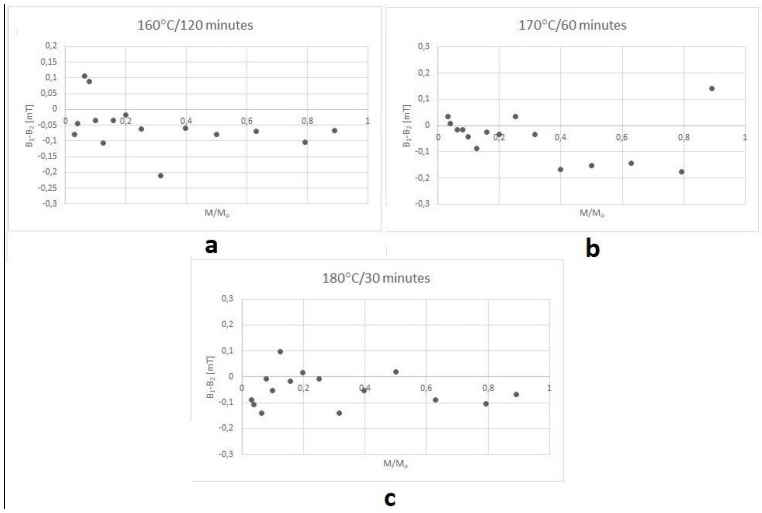

Figure 5. Influence of microwave power (M) on the asymmetry parameter B_1–B_2 (a–c) of EPR spectra of pilocarpine thermally sterilized at different conditions. The measurement was done 15 minutes after sterilization. M – microwave power used during the measure of the EPR spectrum. M_o – total microwave power produced by klystron (70 mW).

The changes of amplitudes and linewidths of the EPR spectra of pilocarpine with increasing of microwave power are shown in Figure 6 and 7, respectively. The amplitudes reached the maximum at low microwave powers, so it can be concluded that slow spin lattice relaxation processes exist in the analyzed samples. EPR lines of all the sterilized pilocarpine samples increase with increasing of microwave power and for the higher microwave powers amplitudes decrease (Figure 6). The slowest spin–lattice relaxation processes exist in pilocarpine sterilized at the all tested temperature

and times of sterilization process. The slow spin–lattice relaxation processes were also found in thermally sterilized rosuvastatine [21], drotaverine [22], famotidine [23], and pharmaceutical base – *Vaseline album* [24]. The EPR spectra of pilocarpine are homogeneously broadened. The increase of linewidths (Figure 7) with the increasing of microwave power was observed.

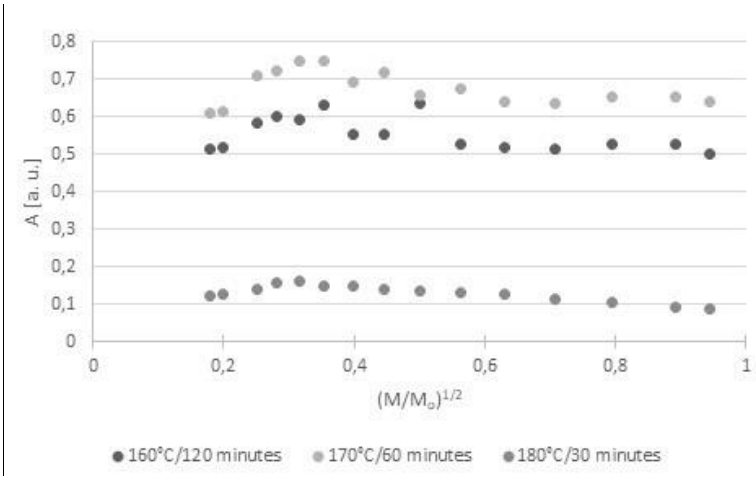

Figure 6. Influence of microwave power (M) on amplitude (A) of EPR spectra of pilocarpine sterilized at different conditions. The measurement was done 15 minutes after sterilization. M – microwave power used during the measure of the EPR spectrum. M_o – total microwave power produced by klystron (70 mW).

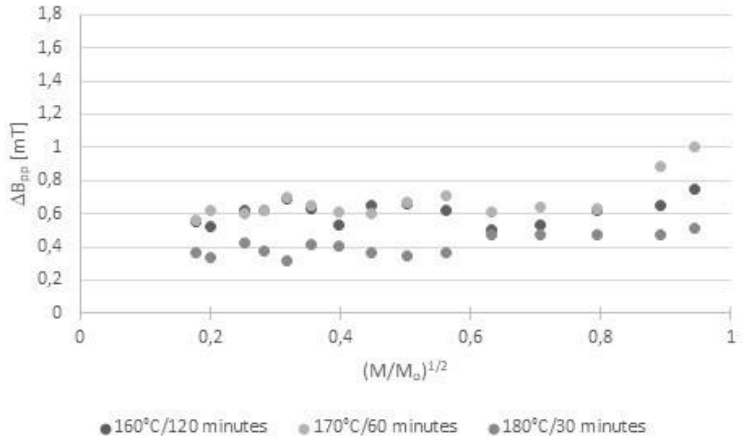

Figure 7. Influence of microwave power (M) on linewidth (ΔB_{pp}) of EPR spectra of pilocarpine sterilized at different conditions. The measurement was done 15 minutes after sterilization. M – microwave power used during the measure of the EPR spectrum. Mo – total microwave power produced by klystron (70 mW).

The obtained results indicate usefulness of electron paramagnetic resonance (EPR) studies to optimization of sterilization process. The EPR analysis of drugs should be done during the production of drugs. The Pharmaceutical norms [3–8] should be respected and the lowest amount of free radicals should be formed in drugs.

Conclusions

EPR studies of thermally sterilized pilocarpine pointed out that:

1. Free radicals (10^{18} spin/g) are formed during thermal sterilization of pilocarpine at all tested conditions.
2. Thermal sterilization conditions of pilocarpine with the lowest concertation of free radicals are temperature 180^{o}C and time of heating 30 minutes.
3. Complex system of free radicals exist in thermally sterilized pilocarpine.
4. Slow spin–lattice relaxation processes and strong dipolar interactions exist in thermally sterilized pilocarpine.
5. Continuous microwave saturation of EPR lines of pilocarpine indicated that the spectra are homogeneously broadened.

Acknowledgements

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HOW DOES THE CHANGE OF THE OPEC CARTEL'S SUPPLY POLICY INFLUENCE THE GLOBAL PRICES OF CRUDE OIL – AN EVENT STUDY ANALYSIS

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Abstract:

The aim of the article was to examine the impact of the OPEC cartel decisions taken in November 2016, specifically the transition from a strategy of maximizing market share toward that reducing the supply of raw materials, on the global prices crude oil. The countries of the oil association have decided for such a move following two factors translating into drop in oil prices, specifically a significant increase in global oil stocks and a strong increase in production of raw materials among countries outside the OPEC cartel (mainly in the US). The research methodology comes down to the analysis of events as one which is usually applied in the literature to assess the impact of extraordinary unexpected event, which cause significant fluctuation in prices of financial instruments. As a result of the conducted research, it was found that the decision taken by the cartel to introduce restrictions on production finally led to increase in the price of the crude oil.

Keywords:

event study, crude oil, cartel OPEC, the US shale revolution, trade war

Introduction

Crude oil, besides natural gas and hard coal, is currently the most important energy raw material in the world and accounts for generating about 40% of energy consumed globally [1]. As a result, changes in its price have a significant impact on the shaping of the economic situation in most countries around the world. However, the problem arises from the fact that many places of oil production do not match with the location of the largest centres of its processing and consumption, which consequently might lead to the possibility of artificially inflating its prices.

Two oil crises, both taking place in the 1970s (aimed at limiting the amount of power raw material supplied), made crude oil the most important commodity in global trade and contributed to achieving by the commodity the status of "political raw material" describing the fact of using it by the largest producers to meet non–economic goals [2].

During recent years relatively strong fluctuations in oil prices have been recorded. This was mainly driven by the member states of the OPEC cartel, which tried to strengthen their market position in the global production of the commodity. As a result, members of the cartel led to the outbreak of a trade war with oil producers from the United States (US companies using hydraulic fracturing caused a significant increase in the production of power raw material). This consequently led to an increase in overall volatility in the market (Figure 1), which could cause serious

consequences for maintaining the stable preserving of the economies heavily dependent on oil imports [3].

Given the above, the aim of the article is to examine the markets impact of decisions taken in November 2016 by the OPEC members and Russia in respect of transition from the strategy of maximizing market share to the strategy of reducing the supply of raw material.

Figure 1. WTI oil prices (USD per barrel)
Source: Bloomberg

The research is conducted on the basis on database collected from two main sources – the Bloomberg terminal and analytical materials of the US Energy Information Administration (EIA). The research methodology, in turn, is based on the analysis of events. This kind of modelling is widely used in the literature to analyse among others the impact of announcements on company's profits or turnover or, in general, to assess the impact of extraordinary events, which cause significant changes in the quotations of financial instruments. Importantly, the study assumes that the research method is applied to the informationally effective market.

As a result of the study, it was found that the decision made by the members of the OPEC+ association caused significant changes in the market prices of crude oil. The analysis does not exhaust the possibility of further research, which comes mainly from the fact that the cartel continues its strategy and subsequent steps, unexpected today, may cause necessity for further study. It is also worth considering issue that percentage increase in the share of world oil production among Americans. In addition the breaking of the nuclear agreement with Iran by Donald Trump should be raised. These additional events complicate the developments on the crude oil market and adds to the possibility of further bouts of volatility in financial markets.

Changes in the supply policy achieved by cartel OPEC in 2016

For many years, crude oil has been recognized as the most important power commodity in the world that has an impact on many aspects of politics as well as the global economy. At the same time, the largest share of this commodity has been in possession of countries that could have been

characterized by a high risk of economic destabilization and, consequently, the possibility of rapid reduction in supply. To counteract such a scenario, world strongest countries competed to gain control over the areas rich in oil reserves.

In the years of 1950s to 1960s, the world average of crude oil prices fluctuated between 2 – 4 USD per barrel. Such low prices on one hand enabled fast development of highly developed countries, but on the other hand they pushed Arab producers toward striving to raise the prices and thus achieve higher revenues from exports. In that way the Organization of the Petroleum Exporting Countries (the OPEC) was founded, initially created by five countries: Saudi Arabia, Kuwait, Iraq, Iran and Venezuela. The cartel was established in Baghdad during a meeting of the signatories from 10 to 14 September 1960 [4] in order to:

i) coordinate and harmonize Member States' fuel policy, so as to be able to ensure fair and stable prices for raw material producers;
ii) providing efficient, economical and regular crude oil transport to its consumers;
iii) obtaining decent profits for entrepreneurs, who invest their capital in the oil industry [5].

Initially, the OPEC was ignored by both, the major crude oil corporations and the biggest importers of the raw material. It was widely expected that it will work inefficiently and, therefore, quickly cease to exist. However, following years brought a further increase in the share of OPEC countries in the global structure of crude oil supply. In the 1990s and at the beginning of the 21st century, these countries were responsible for around 40 % of global oil production, which gave a significant impact on pricing at the oil market.

At the turn of the century, a significant effort aimed at improvement in efficiency of the oil production taken by the USA turned into the so–called shale revolution. This led to a strong increase in production in this country and, at the same time, to a significant reshuffle in the global structure of raw material producers[1]. The Americans, given their own production, wanted to reduce the impact of the cartel OPEC on the development of global oil prices and to liberate their economy from importing energy commodities.

The increase in both the oil production and exports from the United States, which has taken place after 2010, led to an intensification of oil exploit also among countries of the OPEC, aiming at maintaining their market share. The primary country that was in charge of these activities was Saudi Arabia, which efforts led to a rapid decline in prices (Brent crude prices in 2014 fell by 46.81 % to 57.33 USD per barrel and WTI crude oil by 44.18 % to 53.27 USD per barrel) and translated into a significant reduction in the production profitability among countries that had higher extraction costs (e.g. Venezuela, Russia and the United States). As a result, American producers have gradually decreased their production and conducted activities aimed at maximizing its efficiency.

The higher production of Saudis was consequently counteracted by other countries belonging to the cartel, which could have no longer balance their budgets with revenues from the sale of oil[2]. In

[1] In February 2018 year, the Americans set a new record in the production of crude oil breaking the level of 10,044 million barrel per day achieved in November 1970 (currently, the production at the end of June 2018 year is already 10,900 million barrel per day).
[2] According to estimates of the US Energy Information Administration (EIA), revenues from oil exports in the OPEC countries in 2016 year fell to 433 billion USD – the lowest level since 2004 year. This means a 16% decrease compared

addition, the slowdown in economic growth, which affected developing countries (including China) as well as the appreciation of US dollar driven by monetary policy tightening in the United States (initiated in December 2015), was continuously influencing the demand on crude oil and intensifying losses facing by the exporters of the raw material.

Table 1. Agreed volumes of crude oil production and reference levels among the OPEC countries

Country– the OPEC member	Reference production level (barrel thousand per day)[3]	Reference production level from January 2017 year (barrel thousand per day)	Agreed limit on production volume from January 2017 year(barrel thousand per day)	Production level in May 2018 year (barrel thousand per day)	Limitation of production volume after May 2018 year (barrel thousand per day)
Algeria	1089	1039	–50	1020	–69
Angola	1751	1673	–78	1530	–221
Ecuador	548	522	–26	520	–28
Equatorial Guinea[4]	–	–	–	120	–30
Gabon	202	193	–9	180	–22
Indonesia[5]	–	–	–	–	–
Iran	3975	3797	+90	3810	+165
Iraq	4561	4351	–210	4480	–81
Kuwait	2838	2707	–131	2710	–128
Libya[6]	–	–	–	990	
Nigeria[7]	–	–	–	1620	
Qatar	648	618	–30	600	–48
Saudi Arabia	10544	10058	–486	10010	–534
UAE	3013	2874	–139	2870	–143
Venezuela	2067	1972	–95	1440	–627
Total	31236	29804	–1164	31900	–1766

Source: own study, data from the Bloomberg platform, the OPEC Secretariat, http://www.opec.org/opec_web/static_files_project/media/downloads/publications/MOMR%20December%202016.pdf (27.11.2017).

Against this background, on 30 November 2016 in Vienna, the OPEC cartel met with ten additional countries willing to support the association's activities and signed a contract aimed at reduction of oil production by a total amount of about 1.8 million barrel per day (Table 1). In addition, the purpose of the newly created OPEC +[8] group was to reduce oversupply of crude oil to

to 2015 year and about 63.5% compared to 2012 year. In addition, the EIA in May 2017 year predicted that in 2017 year cartel revenues would amount to 539 billion USD, and in 2018 595 billion USD.. EIA, *OPEC revenues fact sheet* https://www.eia.gov/beta/international/regions–topics.cfm?RegionTopicID=OPEC (03.01.2018).

[3] The production levels of crude oil were set for October 2016 year, with the exception of Angola, for which data concern to September 2016 year.

[4] Equatorial Guinea became a member of the cartel on May 25, 2017 year. The level of oil production in this country at the end of May 31, 2017 year amounted to 150.000 barrel per day.

[5] Indonesia has suspended its membership of the cartel OPEC. It was a member the OPEC from 1962 to 2008 and from January to November 2016 year.

[6] Country temporarily excluded from the agreement by March 2018 year.

[7] *Ibidem*.

[8] OPEC+ – is a group of countries that in November 2016 year joined an agreement aimed at limiting crude oil production. Apart from the OPEC cartel countries, these were also: Azerbaijan, Bahrain, Brunei, Kazakhstan, Malaysia, Mexico, Oman, Russia, South Sudan and Sudan.

the five–year average calculated for OECD countries. The contract was to enter into force on January 1, 2017 year and initially was set for half a year.

The introduction of restrictions on crude oil supply resulted in a significant jump in oil prices: Brent crude oil prices on November 30th, 2016 gained as much as 6.88 % (increase to 53.94 USD per barrel) while WTI crude oil almost 3.28 % (increase to 51.06 USD per barrel – Figure 2).

The period of reduced production lasted for seventeen months from 1 January 2017 to 30 June 2018 (despite the fact that on 30 November 2017, during 173th meeting of the OPEC cartel, members of the association extended the period of agreement until the end of 2018). On June 22nd, 2018, during meeting in Vienna, the OPEC+ countries decided that from July 1, 2018 year they would strive to increase the extraction of the crude oil in such a way that the level of production restrictions reach the level defined by the agreement signed on November 2016 (in May 2018 the level of adjustment among the cartel OPEC countries increased to level of 152 %). However, no exact value on potential increase in oil production was given (Figure 3).

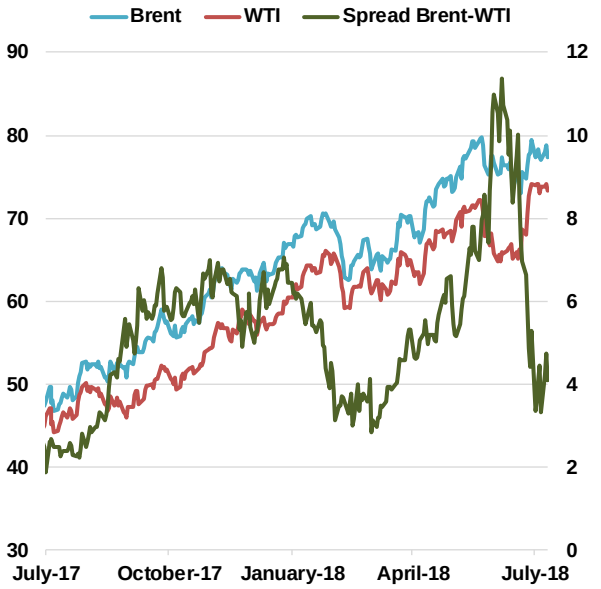

Figure 2. WTI and Brent oil prices (USD per barrel) and their spread (right axis)
Source: Bloomberg

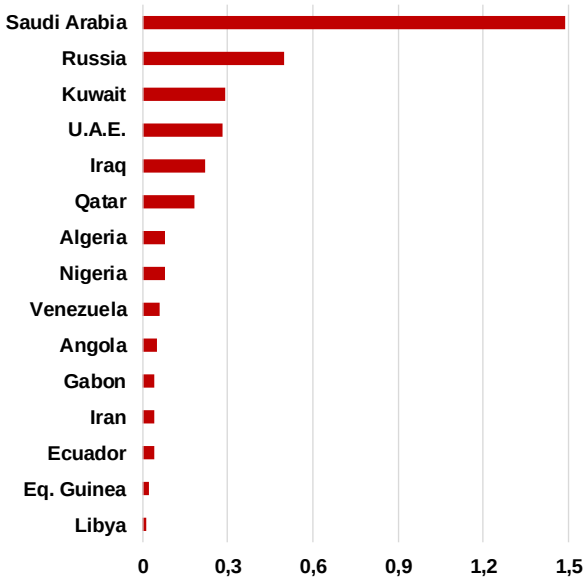

Figure 3. Spare capacity in the OPEC countries (in million barrel per day)
Source: Bloomberg

Methodology event studies analysis

In behavioural finance, the event studies analysis is one of the widely–implemented tools toward analysis of the impact of various types of extraordinary political and economic events on the quotations of financial instruments. Such a type of analysis usually helps to assess the impact of splits on quotations of share prices, or the consequences of the announced dividend payment on share prices and amount turnover.

In practice, to be able to use it, the market should met an assumption of informational efficiency. The efficient market, according to the above, confirms the scale development and efficiency of the economy as a whole, which the analyzed market is an element of. The basic definition of the efficient market hypothesis was proposed by Eugene Fama in 1970. According to that definition, an efficient market is a market that fully reflects all available information [6]. The essence of the original definition has been shifted from the immediate adjustment of financial instruments prices under the influence of new information toward full reflection of the information in the prices of these instruments [7]. In addition, Fama has defined the conditions that must be met in order to particular capital market could be considered an efficient market (however, it should be emphasised that these are not necessary conditions, but at most sufficient for the given capital market to be considered efficient). He enumerated here [8]:

i) information efficiency as a situation in which exist a widespread availability of information for all participants of the capital market (failure to meet condition results in charging fees for access to information that could be used in the process of making investment decisions);
ii) no transaction costs in stock trading (the occurrence of transaction fees on financial markets leads to a situation in which investors will invest their funds only if the expected rate of return is higher than the transaction costs necessary to be incurred);
iii) compliance of market participants with regard to the direction of particular information impact on price of the asset (for example, a drop in oil production should increase its prices or central banks' interest rate increase should contribute to an appreciation of a given currency).

In this article and in scientific studies in which the method of event analysis is used, one should assume an efficient market hypothesis leading to the conclusion that if a given event is significant, it should almost immediately be reflected in the price of a financial instrument.

The direction of changes in the prices of financial instruments can be deducted from the behaviour of a rational investor. The assumption of the rational behaviour of market participants is a basic element of the efficient market hypothesis. According to this assumption, all market participants take rational action under access to full information and disposal of identical tools for assessing current and future events. In addition, it is assumed that all investors should be characterized by coherence of decisions made in the purchase or maintenance of instruments in the investment portfolio at the time of obtaining "positive" information, as well as the sale or non–purchase of instruments when obtaining "negative" information. Ultimately, also the rationality of investors will be expressed in the desire to maximize profit against a predetermined level of risk or to minimize risk at a predetermined level of profit [9].

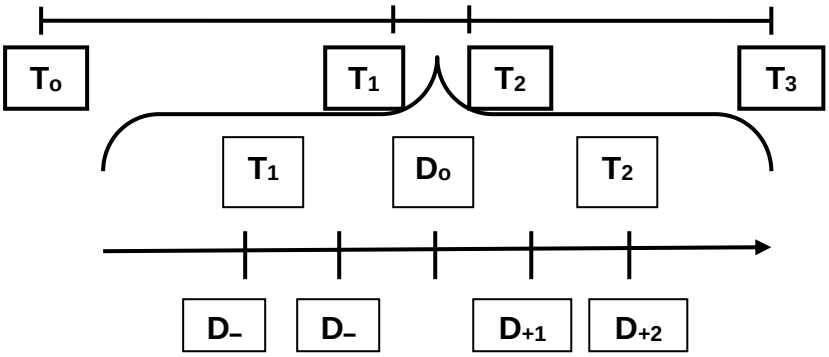

Figure 4. Windows in event study
Source: S. Kujawa, E. Ostrowska, Analiza zdarzeń i jej zastosowanie w finansach behawioralnych, (2016), Vol. 4, 191 – 200.

Explanations:

- $(T_o, T_1]$ – estimation window,
- $[T_1, T_2]$ – event window,
- (T_2, T_3) – post–event window,
- D_o – event day,
- D_{+1} – the first day after the event,
- D_{+2} – the second day after the event,
- D_{-1} – the day before the event,
- D_{-2} – the two day before the event.

After discussing the initial assumptions, the basic stages of the analysis should be presented. This principles in the methodology of event analysis were developed by C. J. Campbell [10] and Elton and Gruber [11]. According to them the study should consist of the following stages:

i) definition of an event and the determination of the event window,
ii) specifying the criteria for selecting companies/components for the sample,
iii) the selection of measures determining the level of expected (normal) and upward (extraordinary) rate of return,
iv) estimation of the model describing the expected rate of return, after prior determination of basic parameters, such as the length of the event window and the location of the estimation window relative to the event window,
v) verification of initial hypotheses,
vi) presentation of aggregate results being the basis for generalizations,
vii) interpretation of results and formulating conclusions.

The figure above graphically shows the location of the event window relative to the estimation window. The estimation of the results that will be used to calculate the expected rates of return can be made on the basis of quotations from the estimation window T0 – T1 or even T2 – T3, that is, data after the period of the event. The estimation window in literature is most often identified with the period immediately preceding the event window, but never adhering to the day of the event. This means that the last day of the estimation window cannot coincide with event window. In

addition, the length of the event window compared to the estimation window should be relatively short. Nevertheless, it should be individually determined given the specification of component to be tested. It should also be noted that in the case of a significant expansion of the window's length, it should be analyzed in great detail whether during the appearance of the estimation window there is no additional disturbances that could trigger significant changes affecting the price of the analyzed financial instrument [12].

For the purposes of this study, it is also worth clarifying that in each case D_o is the day of the event, for example the day of the economic event (close at a given day a given instrument) and for D_o was calculated daily percentage change in the value of a given asset[9]. In addition, when using the event analysis method, assets that are subject to daily valuation/price changes should be used. Only under such an approach we are able to demonstrate the impact of extraordinary event on the behavior of investors, and thus on the quotations of a specific financial instrument.

Empirical verification of the event analysis on the basic of OPEC cartel's supply policy change in 2016

In order to check whether the selected event has affected the valuation of the financial instruments, the additional rate of return should be calculated as follows [13]:

- Calculation of the additional rate of return in the event window, which has been adjusted by the actual rate of return from the independent period.

$$AR_{it} = R_{it} - E(R_{it}) \quad (1)$$

where:
AR_{it} – an additional rate of return on shares *i* achieved in the period *t*,
R_{it} – actual rate of return on shares *i* achieved in the period *t*,
$E(R_{it})$ – expected rate of return on shares *i* in period *t*, if the event did not occur,
t – day or month depending on the data and window unit used for calculations events.

- Calculation of the actual rate of return based on data from the estimation window.

$$E(R_{it}) = K_i \quad (2)$$

where:
$E(R_{it})$ – expected rate of return on shares *i* in period *t*,
K_i – average rate of return on shares *i* in the independent period.

- Calculation of the cumulative abnormal rate of return in the event window [14].

$$CAR_{it} = {}^{T}\sum AR_{it} \quad (3)$$

[9] Calculation of the daily percentage change in the value of a financial instrument: Change (Z)% = (Index (Z) / Index (D) –1 x 100%, where: Index (Z) – closing value of the share at the session on the OPEC decision date, Index (D) – closing value of the instrument on the previous one session (reference value). *Podstawowe algorytmy indeksów giełdowych* https://docplayer.pl/44043112–Podstawowe–algorytmy–indeksow–gieldowych.html (30.08.2018).

t=1

where:

CAR_{it} – cumulative abnormal rate of return on shares i achieved during the observation period T,

T – observation period, time interval measured in days or months,

$^{T}\sum AR_{it}$ – the sum of abnormal rates of return.

- Calculation of average cumulative abnormal rate of return.

$$ACAR = (^{T}\sum AR_{it})/N \quad (4)$$

where:

ACAR – cumulative average abnormal rate of return,

N – number of components of the studied population,

$^{T}\sum AR_{it}$ – the sum of additional return rates.

In this article, to calculate the actual rate of return, one of the main models based on the average rate of return from the independent period was used. Average rates of return from the estimation period were calculated according to the universal model described in the formula number 2. The analyzed instruments in the study were[10]:

i) Brent crude – is a high quality grade of crude oil, which is classified as a sweet type It is extracted in more than a several fields located in the North Sea and is the most important oil type on the European market, priced in the US dollar [15].
ii) West Texas Intermediate crude oil – is one of the types of crude oil that is traded on the New York Mercantile Exchange (NYMEX). It is also used as an oil benchmark for the valuation of other varieties [16].
iii) S&P 500 index – is one of the most popular US stock market indices, which groups companies listed on the Stock Exchange New York Stock Exchange and NASDAQ. This index is managed by the Standard & Poor's rating agency [17].
iv) currency pair EUR/USD – is the most popular currency pair in the world. It owes its popularity primarily to the dollar, because most countries in the world has a large part of the foreign exchange reserves denominated in this currency. In addition, the most important benchmarks describing the value of crude oil are valued in the dollar [18].
v) USD/RUB currency pair – is another important currency pair on the oil market, because Russia is the largest producer of energy raw materials in the world. In addition, changes in oil prices have a significant impact on the value of this currency pair and on revenues from sale of oil.
vi) gold valued in USD – is a raw material that has always been one of the forms of capital investment and played an important role in the monetary system. Gold as an investment has been steadily used to protect the real value of money. In addition, it is part of the foreign exchange reserves of many countries in the world [19].

[10] The quotations of the analyzed financial instruments come from the Bloomberg platform.

The analysis of events was made on the basis of reactions of financial instruments mentioned above for the decision of the OPEC + to introduce production limits for crude oil that were to enter into force at the beginning of 2017. The main criterion influencing the choice of the analyzed event was primarily its global dimension as well as the significance of the decision in terms of long lasting consequences which as many oil producing countries (which have not cooperated with each other) have decided to simultaneously reduce the volume of their production.

In the study, the actual rates of return were determined based on the independent periods preceding the event of 30 November 2016 year. Their calculation was based on the daily rates of return from 30 trading dates (from October 18 to November 28, 2016), within the so–called estimation window (period from T_0 do T_{+1}). On the basis of thirty daily returns, the arithmetic mean of return rates for any given financial instrument was calculated. The spread of the event window extends from day D_{-1} do D_{+3}, that is from the day preceding the decision to the third day after the OPEC+ members decided to reduce oil production by approximately 1.8 million barrel per day.

Table 2 presents daily abnormal rates of return for individual financial instruments. In the case of WTI crude and Brent crude, the daily abnormal rates of return for D_{-1} (the day before the announcement of the decision) was respectively –4.10 % and –4.06 %. On the day of announcement of the decision to introduce reduction of extraction (D_0), the value of the abnormal rate of return (AR) increased accordingly to the levels of +9.14 % and +8.62 %. The cumulative abnormal rate of return (CAR) for WTI species from day before the announcement of the decision (D_{-1}) to three days after the publication of the message (D_{+3}) was +9.23 % and for Brent +12.68 %. This means that in the analyzed period, as a result of the publication of information on limiting the extraction of the raw material, the oil indices significantly gained in value. Analogous calculations were also carried out for other instruments, but in their case no such strong changes were noticed.

Table 2. Daily abnormal rates of return in the event window as a result of OPEC+ decision to reduce oil production (%)

Day t		Financial instruments					
		WTI crude oil	Brent crude oil	EUR/USD	Gold	Index S&P500	USD/RUB
The period of the event	–1	–4.10	–4.06	+0.22	–0.64	+0.25	+0.50
	0	+9.14	+8.62	–0.69	–1.43	–0.15	–1.40
	+1	+3.11	+6.68	+0.56	–0.29	–0.23	–0.17
	+2	+1.04	+0.76	–0.09	+0.33	+0.16	–0.04
	+3	+0.04	+0.68	+0.82	–0.76	+0.70	–0.04
CAR		+9.23	+12.68	+0.82	–2.79	+0.73	–1.15

Source: own calculations.

Conclusion

In the modern world, crude oil has been established as one of the most important source of energy and one of the most popular investment raw materials. Over the decades following the discovery of oil, the economic its importance has been intensively increasing. Currently, it also poses a function of political raw material often used for numerous international battles.

The strong dependence of many countries on crude oil imports, combined with the increased volatility of its quotations in recent years after the 2007 crisis, led to an increase in risk aversion among investors and the strong conflict among the largest oil producers. In addition, the trade war,

which started in 2014 between producers of raw materials from the United States and Saudi Arabia, led to a sharp decline in oil prices in the world, which in turn translated into a decrease in sales proceeds and losses of previously accumulated foreign exchange reserves, especially for producers which were characterized by higher production costs (for example: for Russia and Venezuela). As a result, many oil–producing countries tried to exert pressure the Saudis to stop applying the policy of unlimited production of the commodity. Ultimately, this was done in November 2016 year. Member states and additional non–cartel producers have committed to significantly reduce production. The signed agreements entered into force in January 2017 and led to an outflow from the market of approximately 1.8 million barrel per day (due to difficulties with extraction in Venezuela and other technical problems with production, the introduced limit exceeded the levels set in the first half of 2018).

Using the event studies analysis, the research of these decisions was carried out and confirmed that the signed agreement by the members of the OPEC+ association caused strong changes in crude oil prices in the world. On the day of the decision (D_0), the value of the abnormal rate of return (AR) was respectively +9.14 % for WTI crude oil and +8.62 % for Brent crude oil. Instead, the cumulative abnormal rate of return (CAR) for the WTI crude oil from day before the announcement of the decision (D_{-1}) to three days after the publication of the message (D_{+3}) was respectively +9.23 %, and +12.68 % for Brent oil. The value of other instruments that participated in the study did not change so significantly.

The analysis does not exhaust the possibility of continuing further research, because the cartel still maintains its strategy, which means that its further steps may be the subject of additional studies. In addition, it is also worth developing the approach toward breaking the nuclear agreement with Iran by Donald Trump. This event complicates the already tense situation on the crude oil market and causes the possibility of further bouts of volatility on commodity market. Moreover, investors are also waiting for November this year, when new restrictions will enter into force. Their primarily prohibit the purchases of Iranian oil under the threat of sanction imposed by the USA. The introduction of such restrictions may seriously disrupt the global structure of oil prices, which, if prices increase, will translate into a weakening of global economic growth. In this situation, the supply policy of the OPEC + association may also change.

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MARINE VIRUSES IN THE GLOBAL ECOSYSTEM AND PREVALENCE OF NOVEL CHAPERONINS IN THE VIRIOPLANKTON

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Abstract:

Marine viruses are the most abundant forms of genetic material in the ocean. It was estimated that there are 10^{30} viruses in the seawater and their concentration in the surface waters is approximately 10^{10} per liter. Thus, they have the greatest contribution to the genetic diversity among other biological particles. The current state of knowledge of marine viruses shows that we should take them into consideration to understand biological and biochemical processes in the ocean since they have influence on nutrient cycling and the evolution of host organisms. Viral biology and ecology depends on the successful replication during which viruses rely on protein–folding machinery composed of chaperonins. This group is still poorly characterized and only a few phages are known to encode chaperonin genes. However, it was shown that chaperonin–carrying viruses are ubiquitous and widespread in marine ecosystems. The question is how chaperonins are linked to the biological features of virioplankton.

Keywords:

Marine viruses, virioplankton, chaperonins

Introduction

Many studies have confirmed the presence of viruses in marine ecosystems [1–3], but initially their role was underestimated. Not until the first report in 1989 about their great abundance was published [4], were marine viruses disregarded. Marine virology, being relatively new area of oceanography, has been intensely studied and it is now considered to be the field of a great importance. In recent years it turned from estimating viral abundance and spatial distribution to studying viral diversity and now it is moving towards the detailed analysis of viral evolution and ecology. Since the revelation about the high concentrations of viruses in seawater, researchers have been focused on developing accurate techniques to analyze viral communities. Methodological advances contributed to the significant interest in this discipline that led to a notable progress in evaluating and quantifying effects of viruses on marine ecosystems [5–6].

With total estimates of 10^{30} viruses in the ocean they are the most abundant biological entities and have the greatest contribution to the genetic diversity in the sea, which is still poorly explored [5, 7]. The term viral "dark matter" was coined to describe the existence of abundant uncharacterized viral lineages, which had been revealed by metagenomic approaches [8–11] . Viruses are key players in

global ecosystem and have the impact on ecological, biogeochemical and evolutionary processes in the ocean (reviewed by [5, 12–14]. They presumably infect all organisms and are the main agents responsible for mortality and diseases. Viral infections can lead to evolution of host organism as well as virus particles by introducing new genetic information [15]. Moreover, viruses are the major components of the marine food webs and thus play a role in nutrient and energy cycles as well as in controlling diversity and distribution of microbial communities [4, 16–18]. Importantly, viruses can contribute to termination of algal blooms [12, 19–22]. Their movement between marine and terrestrial environments can lead to emergence of pathogens [23].

The current state of knowledge of marine viruses shows that one should take them into consideration to understand biological and biochemical processes in the ocean. With their significant roles in oceanic ecosystems, it is important to understand the characteristics of marine viruses and their distribution. Despite the progress in comprehension of marine viruses, studying them is still challenging. One important aspect of the biology and ecology of virioplankton is protein folding in replication process, which is guided by protein–folding machinery comprised of chaperonins, chaperones and folding catalyts. Metagenome sequence data revealed that chaperonin–carrying viruses are ubiquitous and widespread in ocean [24]. The question how chaperonins influence the biological features of virioplankton is still to be answered.

This review is divided into two sections. The first part provides the general information about marine viruses (their abundance, diversity, role in the marine ecosystem), whereas the second one focuses on viral chaperonins and their role in virioplankton.

General information about marine viruses

The abundance of marine viruses

Since the discovery of first marine viruses, they have been studied for several decades [25, 26]. Initially plaque assays of pure cultures were used, which do not allow to estimate the total abundance of viruses in the sample. This is why viruses were not regarded as quantitatively important particles in the marine ecosystem. However, with total estimates of 10^{30} viruses in the ocean they are by far the most abundant biological agents in the marine environment and majority of them are phages [5, 7, 27, 28] . It was shown that typical number of viral particles varies from 10^7 to 10^{10} per liter in the water column, which exceeds typical bacterial abundance (from 5– to 25–fold) [4, 17, 19, 29]. Prokaryotes are the second most abundant biological group [28], however, viruses are very small in size (~100 nm; 10–200 fg) and thus constitute only approximately 5 % of the prokaryotic biomass. This makes viruses the ocean`s second largest biomass [7]. Viral abundance in marine sediments ranges from 10^7 to 10^{10} per gram of dry weight and it is much greater than observed in the water samples [30–36].

Transmission electron microscopy (TEM) was used in early studies on viral abundance. It requires special procedures to concentrate viruses from seawater, but it is the only method that at the same time provides the data on morphology of virus–like particles [4, 17, 29]. However, estimates of abundance using this technique were proved to be variable and inaccurate [37]. Moreover, it is relatively expensive and time consuming. In many cases TEM has been replaced by epifluorescence microscopy (EfM) [19, 38–40] and significant differences in results obtained by TEM and EfM have been reported [41]. EfM is high–throughput method, more accurate than TEM

and is now the most popular technique used to estimate the total abundance of viruses. Methodological errors in sample fixation have resulted in notable underestimations in many studies. However, when the protocol is carefully followed the estimation by EfM is accepted to be accurate [7, 42]. Flow cytometry (FC) is the latest approach used to estimate abundance of virus particles and their distribution [43, 44]. It is accurate high–throughput method which enables to quantify subpopulations of viruses and their potential host cells. It allows many samples to be analysed quickly. Current estimations of viral abundance in water column are quite accurate and reproducible. Nonetheless, it is still hard to estimate abundance of viruses present in a great number in marine sediments [45, 46].

Marine viruses have the greatest abundance in coastal, low–salinity waters [47, 48] and it decreases with distance from the shore from coastal waters (nutrient rich) to oligotrophic (nutrient poor) ocean [30, 49, 50] as well as it decreases exponentially with the depth from euphotic zone to deep waters (with some exceptions of subsurface maxima observed) [28, 51–54]. In marine sediments the greatest number of viruses is present in surficial coastal sediments and there are much less viruses in deep–sea sediments lacking the continental material inputs [35, 36, 55]. Similarl to bacteria, there are many more viruses in sea ice in comparison with the water beneath it [56] and in sediment pore water than in overlying water [30, 32].

Marine viruses are dynamic group with seasonal variations in abundance and degree of lysogeny. Studies have shown that viral abundance changes in a short time and with the distance [35, 48, 57]. The number of viral particles as well as distribution depend on physiochemical characteristic of water masses [13, 28] and our knowledge about those controlling factors is still poor. In surface waters viruses are destroyed and damaged by sunlight and other factors [58–62]. Viral dynamic is particularly influenced by changes in ecological conditions (e. g. algal blooms) [18, 63]. Noticeable alterations in viral abundance over minutes to hours indicate synchronized lysis of host cells and rapid degradation of a large portion of the progeny viruses. Viruses and bacteria follow the same general abundance patterns and viral production takes place at microbial hot spots. Marine viruses` abundance is correlated with the abundance of their host and to less extent with the system productivity (chlorophyll *a* concentration), which indicates that most of marine viruses infect prokaryotes [13, 28, 30, 36, 49]. The ratio of viral particles to prokaryotic or bacterial cells (VBR) varies between different marine environments [15, 28, 64].

The diversity of marine viruses

Despite the fact that viruses are extremely abundant not only in marine ecosystems, but also in lakes, the current state of knowledge of the composition of viral assemblages (viral groups) is not sufficient. In particular, the distribution of bacteriophages` genotypes is poorly explored. Viruses are reservoirs of enormous genetic and biological diversity with many morphotypes and complexity of host resistance and susceptibility [2, 4, 65]. However, assessing their genetic diversity and thus phylogenetic and taxonomic relationships has been challenging since they do not have universally conserved marker gene such as ribosomal DNA genes in prokaryotic organisms [66]. Moreover, many viruses mutate very fast. Therefore, official viral classification is not based on sequence data, but rather on characteristics of the virions and host range [67]. Viral morphology is essential for

modern viral taxonomy [68], but it is correlated with whole–genome–derived taxonomy and the biology of viruses [66].

Viral morphological characteristics (morphotype, capsid diameter and tail length) can be compared using a quantitative transmission electron microscopy (qTEM) method [69]. The most frequently isolated marine phages are viruses with contractile tails (e. g. myoviruses and T4–like viruses) and long flexible tails (e. g. siphoviruses and lambda–like viruses) [70–72]. Nevertheless, global ocean qTEM analyses showed that non–tailed viruses are dominant, but nearly unexplored group. Moreover, the ratio of observed morphotypes (myoviruses, podoviruses, siphoviruses and non–tailed viruses) was very similar in each oceanographic region, which indicates that the relative abundance is maintained by controlling factors [69].

The great obstacle in examining viral diversity is that majority of viral hosts are unculturable. To study diversity of marine viruses without culturing restriction fragment length polymorphism (RFLPs) and hybridization analyses were first used and followed by denaturing–gradient gel electrophoresis, pulse–gel electrophoresis and hybridization [71, 73, 74]. Culture–independent approaches (whole–community genome sequencing i. e., metagenomics) have been adopted to compare viral assemblages from marine environments [75–77]. The metagenomic of viruses started in 2002 from using shotgun sequencing in genomic analysis of two uncultured marine viral communities. The study has shown that most of the diversity was uncharacterized [78]. Many following studies have revealed that viral diversity is underrepresented in existing databases like GenBank. For example, metagenomic analyses of assemblages from four major oceanic regions (from the Arctic Ocean, the coast of British Columbia, the Gulf of Mexico, and the Sargasso Sea) showed that majority of the viral sequences were not similar to those available in the extant databases [76]. Global diversity of viruses was found to be tremendous (presumably several hundred thousand of species), but local diversity can be nearly as high due to viral migration [76]. There are more than 5,000 viral species or genotypes in 100 liters of seawater [78]. The diversity of marine–sediment viral communities is also very high (more than 10^4 viral genotypes per kilogram of sediment) and most likely they are one of the greatest pools of unexplored sequences on Earth [79]. It was shown that viruses are widely dispersed (everything is everywhere), but in different marine environments certain viral types are enriched probably through selective pressure [76].

Although there is no universal gene in viruses, there are some genes that allow to distinguish specific subsets of the viral community. Recently, sequence–based alternative classification of viruses have been proposed [60, 80] and usually a single gene locus is used to characterize specific viral group. Single–locus approach can possibly work in the case of particular groups of viruses, however, horizontal gene transfer can impede interpretation of obtained data [81]. Sequence analysis of DNA polymerase genes of *Phycodnaviridae* revealed the great genetic variation not represented in culture and also showed that very similar sequences were prevalent in distant geographic locations [74, 82]. Moreover, analysis of viral capsid assembly protein gene g20 found in some cyanophages (myoviruses) has led to the conclusion that enormous genetic diversity can occur on large and small spatial scales [83, 84]. Nearly identical sequences recovered from the freshwater and seawater environments suggest that similar hosts and viruses infecting them are widely distributed or that there is a broad horizontal gene transfer of g20 among phages [85, 86]. Similarly to studies on DNA polymerase genes most of the sequences represented no cultured

viruses [85, 86]. Mentioned studies indicate that viral genes are passed through successive organisms and host cells are vessels for viral sex.

The role of viruses in marine ecosystems

Most of viruses in the ocean waters appear to be infectious [62] and some of them maintain infectivity in sediments for many years [81, 87] . It was estimated that circa 10^{23} viral infections occur in the ocean per second, which are major source of mortality and disease within a wide range of organisms. Most marine viruses infect the dominant organisms in seawater (prokaryotes and microalgae) and thus, they have a great influence on the world`s ocean [17, 19]. Ultimately, their impact is divergent depending on phage–host interactions (intracellular phage coexistence in the case of temperate phage or cell death caused by lytic phage). Although, many approaches have been used, quantifying impact of virus–mediated mortality on host community remains difficult [7]. Viruses remove approximately from 20 to 40 % of the standing stock of prokaryotes in surface waters everyday and mortality of prokaryotes caused by viruses in water column and sediments is often in the range of 10–30 %, but can reach 100 % [28, 58, 88–91]. Viral lysis is considered to be as important cause of microbial mortality as grazing by protists [89]. Moreover, the relatively restricted host range of many viruses defined by the virus–receptor interactions suggest that they have an important role in controlling composition of microbial communities by 'killing the winner' [13, 28]. Studies show that viruses have a role in termination of phytoplankton blooms, which was termed control by 'reduction' [12, 19–22, 59]. During bloom events there is high cell abundance and the probability of collision with host is increased. Viruses propagate rapidly and it can lead to bloom collapse.

In the view of the mortality caused by marine viruses, they have a significant role in nutrient and energy cycling. The effect of viral lysis depends on the quantity and composition of released material. The process diverts microbial biomass away from higher trophic levels, since products of the lysis such as amino acids and nucleic acids are available to bacteria [12, 18, 92]. The viral–mediated transfer of material from living organisms to pools of the particulate and dissolved organic matter (POM and DOM) is called viral shunt (Figure. 1) [7, 93]. Much of this material is converted to CO_2 by respiration and photodegradation [7, 12, 13, 93].

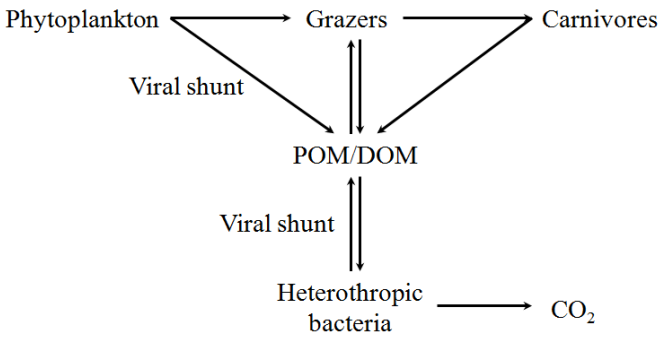

Figure 3. Viral shunt. Viruses cause the lysis of cells, converting them into particulate and dissolved organic matter (POM and DOM).
Source: own study based on [7]

Other effects can include the release of the organically complexed iron that limits primary production in much of the world`s oceans [94]. Transfer of organic material to the dissolved pool affects the biological pump and increases the amount of carbon it transports to the deep ocean (the viral shunt releases 0.37–0.63 Gt carbon per year on global scale) [7, 36]. Virus–infected cell can have accelerated sinking rates, which leads to sequestration of more carbon and other organic molecules [95].

Viruses (especially phages) can carry and transfer many genes of their hosts [15, 96]. It may have negative but also positive effect on host physiology, distribution and evolution. It was reported that the rate of transduction in marine environment is very high and it was extrapolated that 10^{24} genes are transferred from virus to its host every year in the oceans [97, 98]. However, this number is possibly greater due to the action of generalized transducing agents (GTAs) [99]. Genra *Synechococcus* and *Prochlorococcus* are responsible for about 25 % of global photosynthesis [100]. It was shown that their photosynthetic genes (e. g. *hli*, *psbA*, *psbD*) are very often carried in phage genomes [101–103] . It has apparent implications for horizontal gene transfer between specific ecotypes of *Prochlorococcus* that thrive at different depths in water column [104] and for which phages serve as reservoirs utilizing changes in ecological niches [105]. Expression of viral auxiliary core photosystem genes can have a substantial impact on oceanic productivity [103].

Transformation of host can also have dramatic effects on humans. Metagenomic studies conducted on large scale showed that viruses contain many virulence genes (e. g. antibiotic resistance, toxicity, host adhesion, host invasion genes) that can be taken up by bacteria, which extend their ecological niches. Marine example is a common nontoxigenic near–shore bacterium *Vibrio* cholerae. Emergence of toxigenic strain involves horizontal gene transfer of phage cholera toxin (CTX) genes [23]. Apart from virulence genes marine viruses are reservoirs of genes involved in metabolic and functional pathways. It was surprising that genes involved in vitamin and cofactor synthesis, stress–response genes like those encoding chaperones or bacterial motility and chemotaxis genes were found to be more common in viromes than in their corresponding microbiomes [77]. Viromes can serve as a novel gene banks with unique host–adaptation genes as it was shown for deep–sea hydrothermal vents viral communities that store genes involved in microbial adaptation to extreme conditions (high pressure, high temperature, high concentration of inorganic chemicals) [106]. Viruses have relatively narrow host ranges, but viral–like particles can transfer genes between Archaea, Bacteria and Eukarya [107]. Not only do viruses move genes from one host to the other, but also between ecosystems [108]. Hence, viruses contribute to a global genetic pool.

Chaperonins

General information about chaperonins

Viral reproduction depends on the host organism, which supplies substrates and apparatuses for viral propagation. Infection induces changes in cellular gene expression and physiology of the host. Due to host stress and production of viral proteins protein–folding activity is increased. Thus, genes encoding chaperones and other stress–inducible proteins are the most highly induced [109]. Molecular chaperones have a general and essential function in the cell [110]. They are upregulated under stress (e. g. heat shock), but most of them are constitutively expressed. They are involved in

numerous cellular activities such as protein folding/unfolding, disaggregation of protein aggregates, oligomeric assembly/disassembly, protection of nascent polypeptide chains from premature aggregation, polypeptide transport across biological membranes and protein degradation. Chaperones are found in all three domains of life and they are exploited by viruses. Chaperonins are molecular chaperones found in mitochondria, chloroplast and prokaryotes [111, 112]. They are universally conserved proteins that mediate the folding process of nascent or misfolded polypeptides and thus they are important for successful replication of viruses. There are two main classes of chaperonins. Group I is found in Bacteria and eukaryotic organelles and is comprised of GroEL and its co–chaperonin GroES working in complex. Group II is found in Archaea (thermosomes) and Eukaryotes (TRiC/CCT) [113–115]. Chaperonins are one of the many host proteins that viruses utilize during their lifecycle. In fact, the *groE* genes were first discovered in *E. coli*, since cognate mutant strains were unable to support the growth of bacteriophage λ [116–117] and bacteriophage T4 [118–120]. It was shown that *groES* and *groEL* mutations in *E. coli* block assembly of the bacteriophage particles (e. g. head assembly or tail assembly), but the mechanism of blockage depends on the bacteriophage [116, 118, 120–122].

Viral–encoded chaperonins

Many diverse viruses utilize chaperone machinery provided by the host, which allows to keep their genomes to a minimal size [123]. However, chaperonins are essential in phage assembly and the necessity of protein folding machinery for successful replication probably selects for the gain and evolution of viraly–encoded chaperonins or other folding machinery. Viral chaperonins have rarely been observed in sequenced viral genomes (only within few viruses) and thus they are still poorly described, but it is striking that most of analyzed environmental viral genomes (EVGs) contained chaperonin genes [124]. It may be caused by the fact that cultivated phages do not represent the abundance of phages in the environment [125] or there likely are proteins having chaperone function that are unrecognized within viral genomes [126].

Several co–chaperone proteins that are able to replace GroES in the GroEL/GroES complex have been identified from different bacteriophages. For example protein Gp31 of bacteriophage T4 and protein CocO of phage RB49 are necessary for folding the major capsid protein, which makes them essential for productive infection [127, 128]. There are putative Gro–EL–like proteins in viruses of which protein gp146 of bacteriophage EL – an GroEL–ortholog – have been described [127, 129, 130]. Additionally, the gene–product 39.2 of phage RB69 was found to alter the conformation of GroEL into a more favourable form for the phage and similar homologues are present in phages T4, RB43 and RB49 [126]. There are many more unidentified phage–encoded proteins that are suspected to change the chaperone complex. Recently, the first virally encoded chaperonin – phiEL chaperonin form phage EL – was proposed to work separately from host chaperonins [123].

Marine and coworkers conducted analysis of data obtained by metagenomic approaches [24]. They found out that chaperonin–carrying viruses are prevalent in marine ecosystems and the unexpected abundance and diversity of Group I and II viral chaperonins was revealed. These chaperonins were evolutionary distinct from cellular counterparts. It was shown that viruses commonly encode co–chaperonin GroES since the putative GroES genes were more widespread

than GroEL genes. However, it was suggested that aquatic viruses encoding GroEL will most likely encode their own co–chaperonin as well. The presence of thermosome sequences in surface water samples indicates that there are euryarchaeal viruses [24]. Viruses of archaea are very enigmatic and only recently chaperonins have been detected within them. Metagenomic approaches revealed three distinct viral groups of marine group II Euryarchaeota (MG–II) viruses denoted as magroviruses [131]. MG–II are one of the most abundant microbes in ocean surface waters and so are mangroviruses [132–134]. Heretofore no representatives of MG–II have been cultivated. It is unique for some magroviruses that apart from the replicative and structural–morphogenic proteins their genomes also encode either a bacterial–type chaperonin GroEL or a thermosome subunit, the archaeal homolog of GroEL, which are highly similar to their homologs. In magroviruses chaperonin genes were shown to be located in the replicative gene cluster and thus they possibly facilitate the folding process of the replicative proteins and replisome assembly [131].

Conclusions

Marine viruses represent the greatest resources of genetic diversity on Earth, which is much greater than prokaryotic one, but it is still less sampled and relatively uncharacterized. However, with the lower Sanger sequencing costs and utilization of large–scale pyrosequencing, we should be able to reveal global viral sequence diversity in a relatively short period of time [76]. However, development of infrastructure and analytical tools will be necessary to analyze enormous datasets obtained by these studies and to infer from viral diversity. In particular, genetic richness of viral community (viral taxonomy) can provide information on the impact of viruses on their hosts [77]. Many new datasets are revealed, but most of the sequences represent previously unknown 'viral dark matter' [8–11]. Thus, despite the fact that viruses are remarkably important, our understanding of how they shape the ecosystem is limited and it remains a bottleneck in the development of predictive models. However, chaperonin genes can serve as excellent phylogenetic markers due to their deep evolutionary conservation and prevalence in the virioplankton. They are good targets for studies on ecology of chaperonin–encoding viruses.

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INFLUENCE OF THE GROOVE ON STRESS DISTRIBUTION AND DEFORMATIONS IN THE CASE OF A SINGLE INCISOR IN REMOVABLE PARTIAL DENTURE METAL FRAMEWORK

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Abstract:

Partial denture metal framework is a specific kind of prosthetic restoration where Dental Technician has a problem with breaking off of single incisor from the dentures. It happened because in this part is a smaller area to put acrylic resin than for example in part with molars. A popular solution to improve connectivity between false acrylic tooth and acrylic denture base plate is to make a groove in the central area of the tooth. This paper focuses on this kind of solution.
The static numerical analysis was performed to check how the stresses and deformations distributed. To this analysis, the ANSYS program was used. The results show that most stresses concentrate on the part where acrylic resin don't have enough thickness. So this stresses can happen to break out the tooth. Groove doesn't influence on improving the bond in case of addition force at an angle to the incisal edge of the tooth. In the case of tensile analysis, grove makes that the largest deformation show on the groove.

Keywords:

removable partial denture metal framework, finite element method, stress distribution, PMMA, incisor

Introduction

One of the methods of prosthetic reconstruction is the removable partial denture metal framework. This is a special type of denture which in its construction contains a metal framework. This framework makes it possible to reduce the surface of the prosthesis and increase its strength. However, this type of reconstruction is associated with a large number of difficulties in its construction. For example, the patient must have enough durable teeth and they must be well set in the alveolus. In addition, the shape of the teeth must be appropriate or be prepared by the dentist. But this article is about another aspect. And it is lack of space and size of elements of the denture.
So, this article focuses on the case of a single incisor in removable partial denture metal framework. Because in conversations with dental technicians and dentists, a significant problem appears. Patients having in their prostheses (both upper and lower) single incisor (first or second)– it means that the neighboring teeth are the natural teeth of the patient– they report the need for repair after only a few months. The reason is the fallen out acrylic incisor. Each repaired place is no longer a homogenous product, so further repairs of the faulty place are only a matter of time. This is an important problem because this kind of dentures aren't refunded by the Polish National Health Care Fund [1]. So the patient paying for the denture, which should suffice for about 4 years, receives

a defective product. The time of about 4 years is the period in which happened the maintenance deteriorates of removable partial denture metal framework caused, among others abrasion of abutment teeth and/or lowering of the alveolar process bone [2].
In addition, this problem is quite a common occurrence. Articles inform, that up to 33 % of repairs carried out by a dental technician are associated with the incisal breaking off from the dentures [3, 4]. Researchers analyzing the connection between acrylic false teeth and acrylic denture plate base they don't take into account important factors. It's the occurrence of a metal framework that reduces the surface area for the acrylic denture plate and incisor teeth, which due to their structure have a smaller area of contact with the acrylic plate than the molars [5–8].
There are many methods to improve the connection between acrylic teeth and the acrylic denture plate. A popular solution is to make grooves [9–11] or a diatoric cavity [6, 12] on the tooth surface from the side of contact with the plate. It's a kind of way to develop the surface and make an acrylic hook.

Methods

This paper focuses on the method of improving the bond by the groove and its effect on the distribution of stresses in the acrylic resin surrounding the metal framework and the filling groove. Comparing it with no preparation surface of the tooth.
3D models were made that differ the only occurrence of a groove or lack of it. The created tooth is the upper central incisor. Dimensions have been taken from the literature [13]. The model has been simplified to perform the numerical analysis. The whole model consists of three main parts (Figure 4, Figure 5). The element colored with pink it's the denture plate, gray is a metal framework and the yellow is an artificial acrylic tooth.

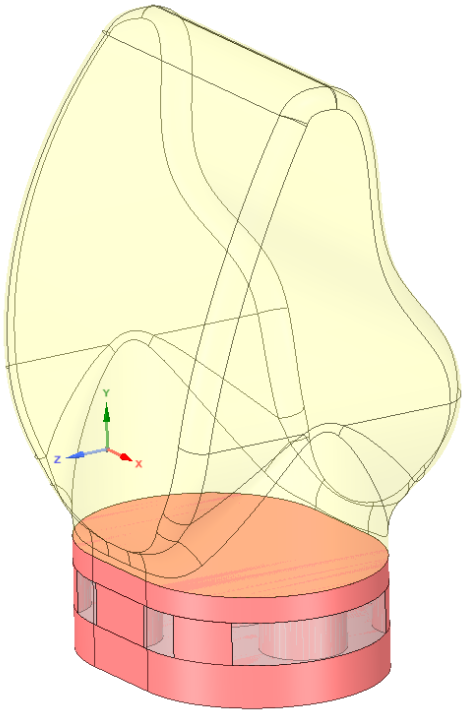

Figure 4. Created 3D model of a fragment of a metal frame denture without a groove
Source: own picture

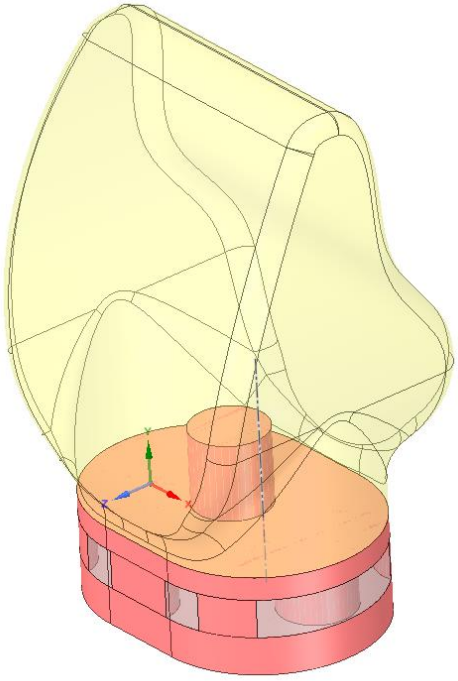

Figure 5. Created 3D model of a fragment of a metal frame denture with a groove
Source: own picture

The dimensions of the frame and acrylic are the same as the real elements used for the production of dentures. The suggestion of dimensions was instruction how to make denture metal framework by Renfert and their products [14]. Because a dental technician uses prefabricated elements when making a frame denture (for example– from Renfert company). Then a waxy framework (like this shown in Figure 6) is turned into a metal one.

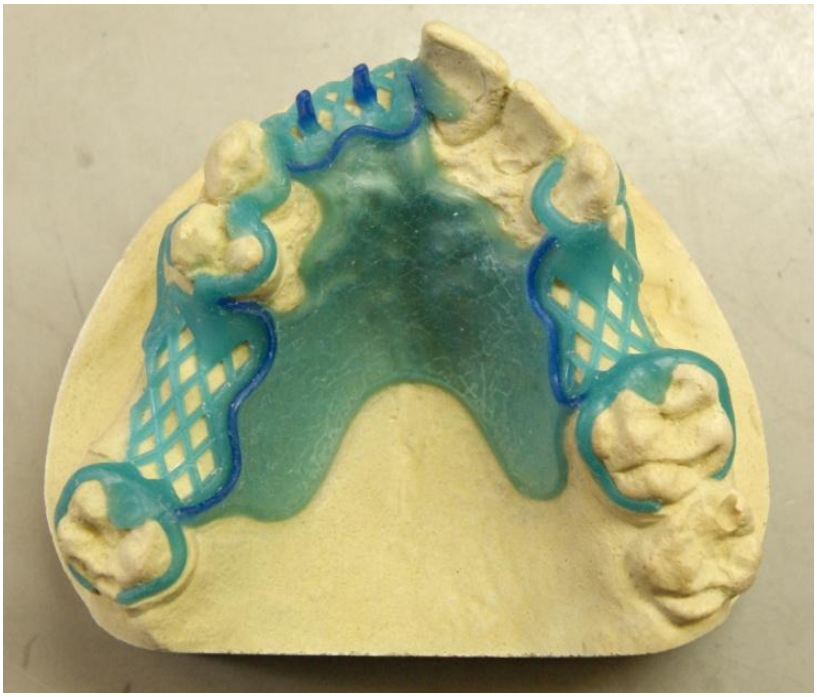

Figure 6. An exemplary waxy framework of the upper denture
Source: own picture

So, the thickness of the metal framework is the same as dimensions of the wax retention grid with round holes (thickness 1.0 mm, hole diameter: 2.0 mm), acrylic under the skeleton has the dimension of the self–adhesive wax plate (thickness 1.0 mm). The thickness of the acrylic layer between the teeth and the framework was 0.6 mm to show a small amount of acrylic resin in this part.

Groove values were taken from the publication [10]. So a dimension of diameter and height of the groove is 2.0 mm in the central part of the tooth was made.

The ANSYS program was used to perform numerical calculations (Ansys Inc., USA) with the 3D SpaceClaim design module.

First, the program material database was created with the physical properties necessary to perform numerical calculations. In Table 1 all used values are included. The created model consists of 2 materials: poly(methyl methacrylate) and Co–Cr–Mo alloy. PMMA is used for the production of artificial teeth and a denture base plate rebuilding soft tissues. The properties of both elements differ slightly (Table 1). It's because the mixing ratio between the monomer and the polymer, the production method, additives (such as dyes) in every product can be different. Individual parameters were applied according to information found in the literature. The used alloy is Remanium GM 800+ (Dentaurum GmbH & Co. KG, Germany). It is a material designed for the production of framework dentures. It consists of:

- 58.3 % Co
- 32.0 % Cr
- 6.5 % Mo
- 1.5 % W
- 1.0 % Si

Table 1: Values of mechanical properties of materials used from a numerical simulation
The value marked * comes from tests used nanoindenter

Properties	**Unit**	**Material Value**					
		PMMA (base plate)		**PMMA (tooth)**		**Co–Cr–Mo alloy**	
		value	**source**	**value**	**source**	**value**	**source**
Density	g/cm^3	1.19	[15]	1.19	[15]	8.2	[16]
Young's Modulus	MPa	2 940.00	[15]	4 760.30	*	230 000.00	[16]
Poisson's Ratio	–	0.44	[17]	0.44	[17]	0.29	[18]
Yield Strength	MPa	51.70	[15]	51.70	[15]	720.00	[16]

The next step was to create a mesh needed to perform the numerical analysis. Near to surface of connecting between the false tooth and acrylic resin the inflation was created. It was created on the top and walls of the grove too. This was important to more details analysis in this part. Because of a complication of the shape of the tooth geometry in this part tetrahedrons mesh was created. On other parts mesh is hexagonal. So mesh of 3D model of geometry with grove consist of 487 290 elements and without preparation– of 446 773 elements. So mesh was created the best for this kind of numerical simulations.

Then 2 tests have been carried out. Both were static linear analysis. Because this research wasn't important exactly the value of the stresses and deformations, but to check where are the defective points which could happen break out of the tooth. The investigation was carried out to find the answer to the question: is grove change anything in the connection between tooth and base plate?

In first tests were added force at an angle to the incisal edge of the tooth. As the value was chosen 120 N from the literature [19]. Articles show that in the front part of the teeth (like on incisors) the loads are around 120 N but on the distal teeth (like molars and premolars) it can be even 420 N [19]. And because to the analysis, it is important to fixed geometry– model in both tests had fived support on the lower part of acrylic (which connect in the mouth with soft tissues) and on the cut off parts of the metal framework (Figure 7, Figure 8).

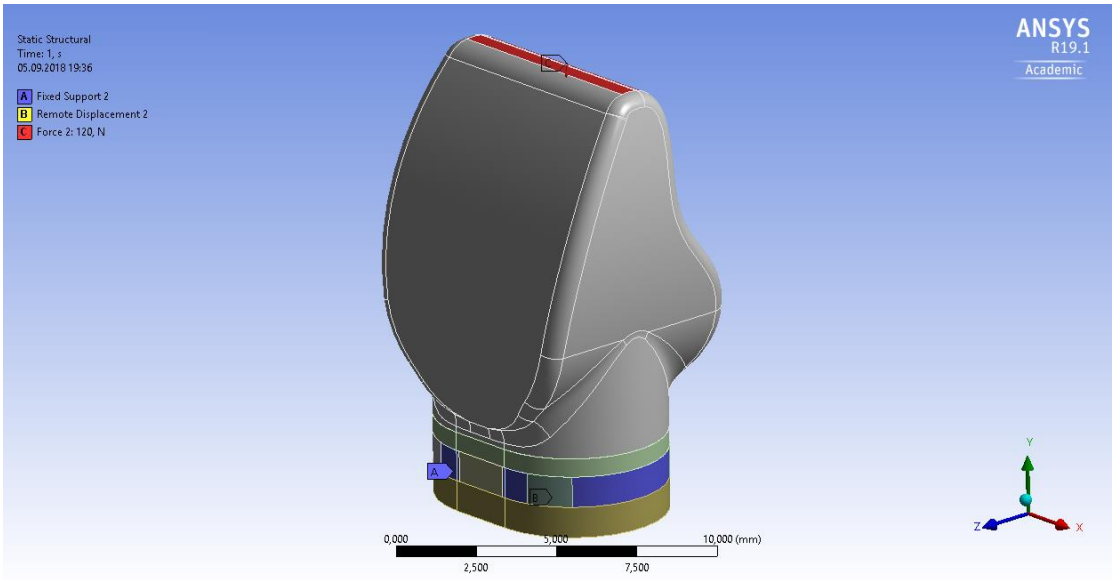

Figure 7. Supports and loads in case of both models– with grove and without in first tests
Source: own picture

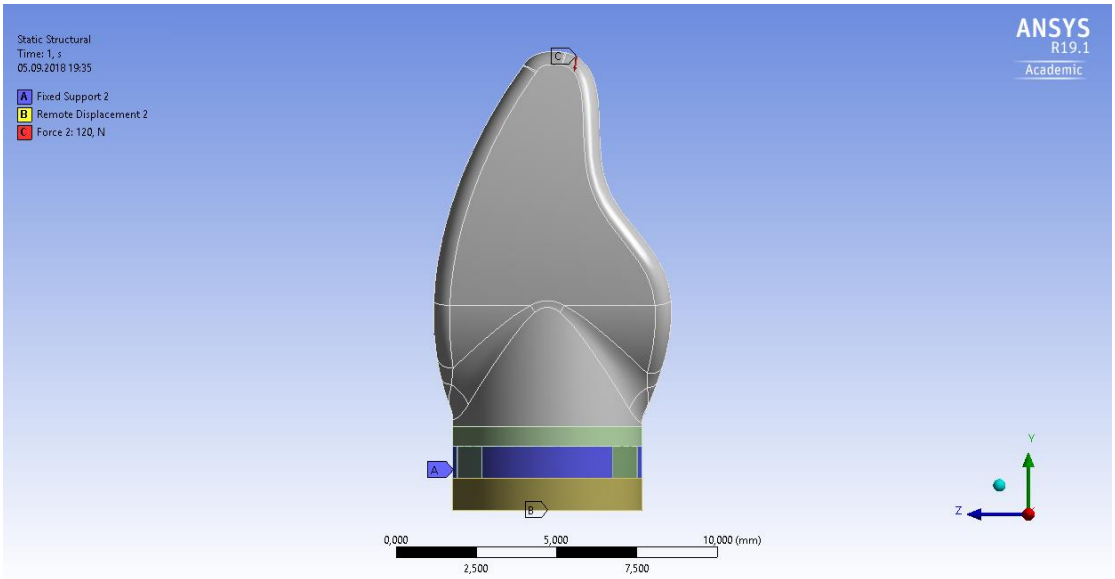

Figure 8. Supports and loads in case of both models– with grove and without in first tests
Source: own picture

Second tests were a static linear tensile test. Supports were almost the same as in case of first tests, but here instead of fixed support displacement was used. But the parameters of this have been set in such a way that this support worked just like fixed support. However, the force with which the tooth was pulled was aligned along the y–axis (Figure 9). Also, this one had a value of 120 N.

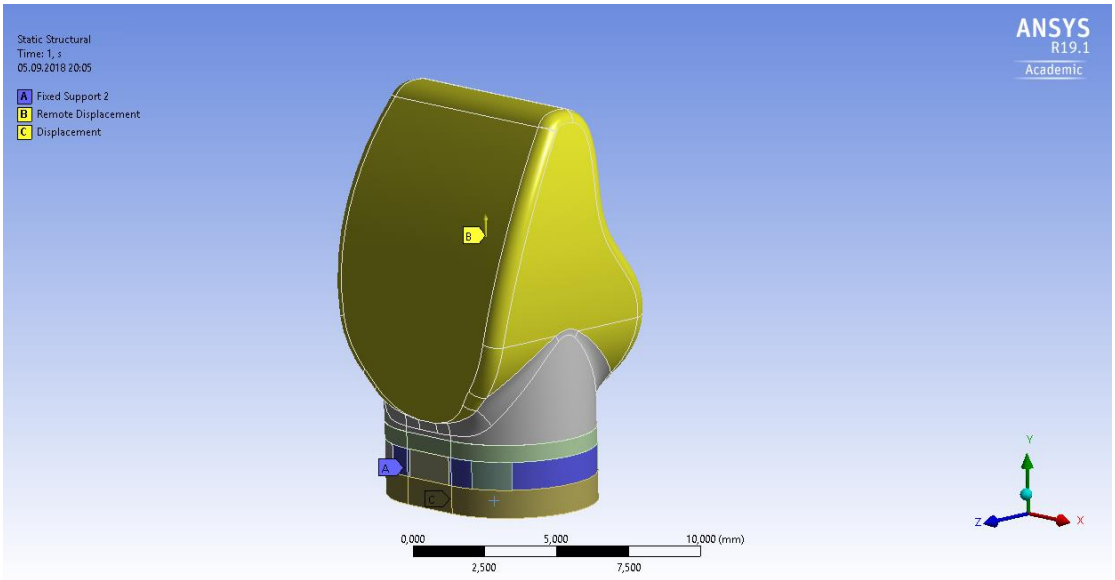

Figure 9. Supports and loads in case of both models– with grove and without in second tests
Source: own picture

Results

Results of stress distribution of first tests are visible in Figure 10, Figure 11.

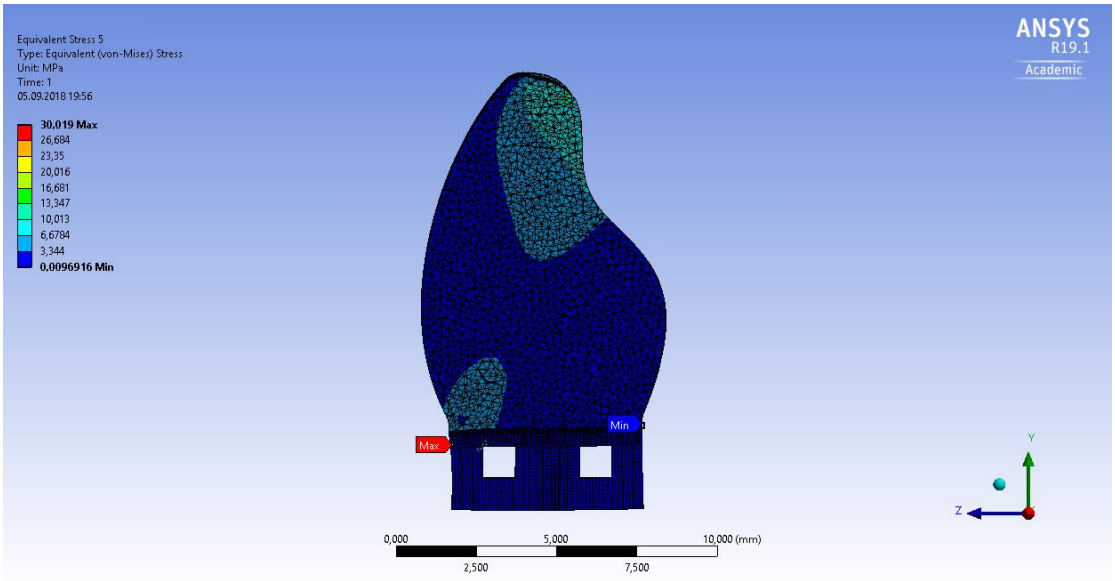

Figure 10: Stress distribution in case of the model without a grove in the first test
Source: own picture

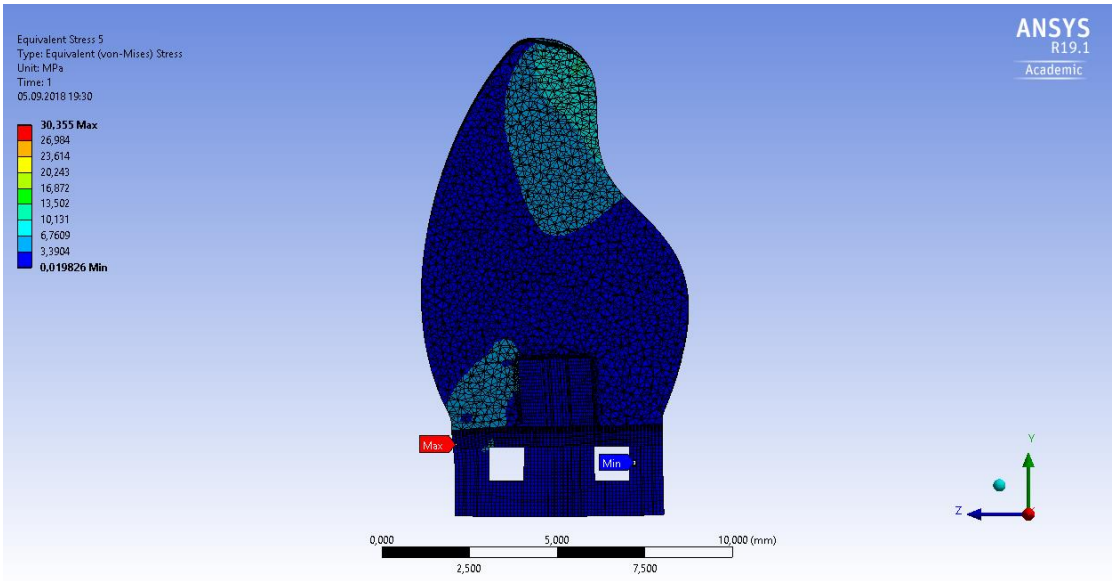

Figure 11. Stress distribution in case of the model with a grove in the first test
Source: own picture

Figures show that in both cases– with and without grove– the higher stress is in the area of the thinnest layer of acrylic base plate and existence of grove nothing change. Even the values are almost the same.

But grove happened different distribution of the deformation (Figure 12, Figure 13) in the same test.

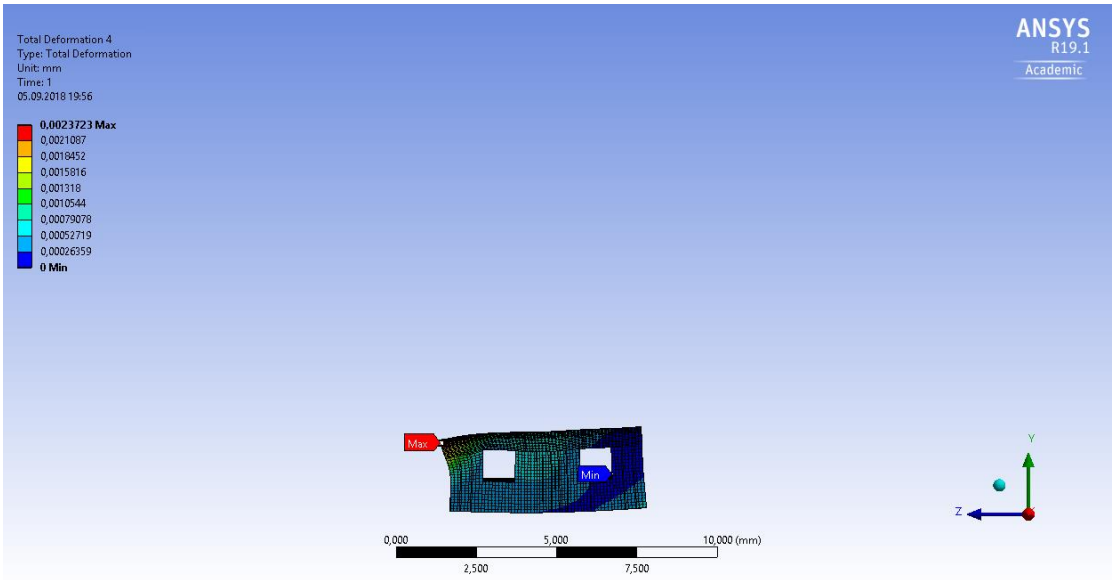

Figure 12. Deformations in case of the model without a grove in the first test
Source: own picture

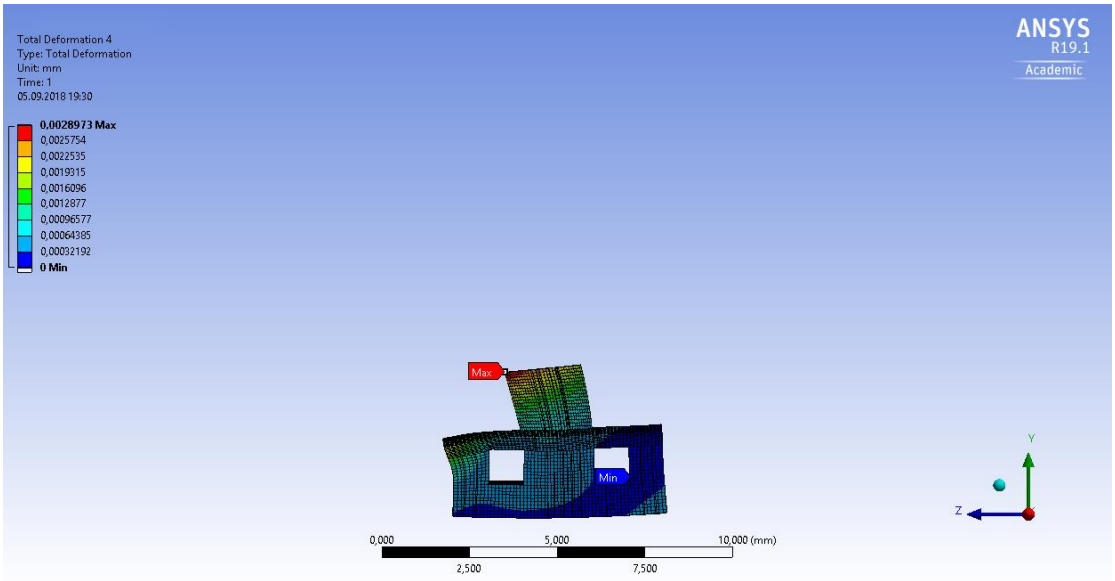

Figure 13. Deformations in case of the model with a grove in the first test
Source: own picture

Figures show that in part of the thinnest layer of base plate deformations still exist, but are a little smaller. The highest deformations are on the top of the grove.

In the second tests following results of the stress, distribution was obtained (Figure 14, Figure 15).

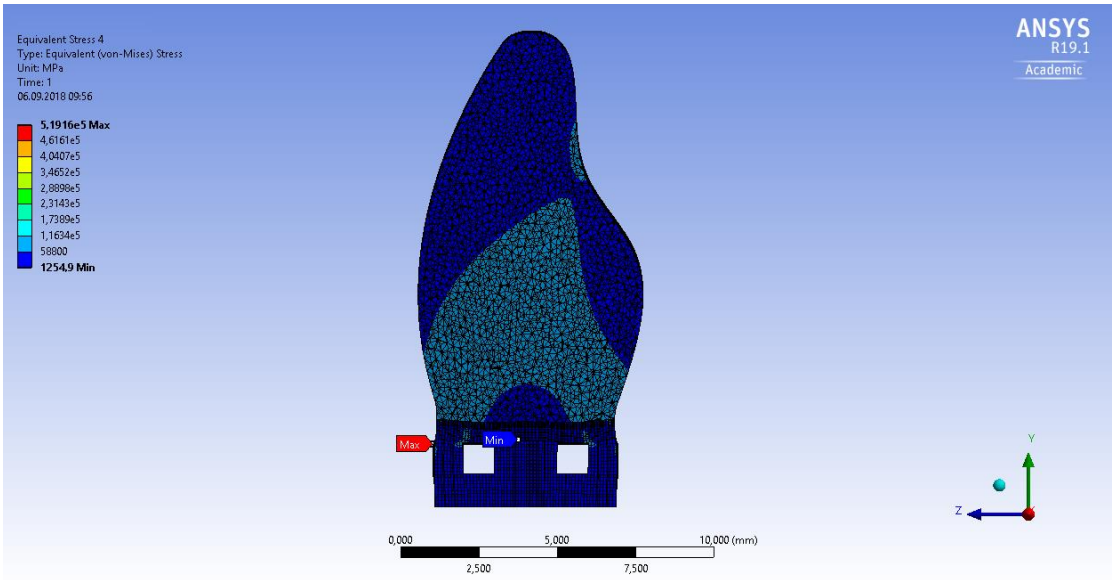

Figure 14. Stress distribution in case of the model without a grove in the second test
Source: own picture

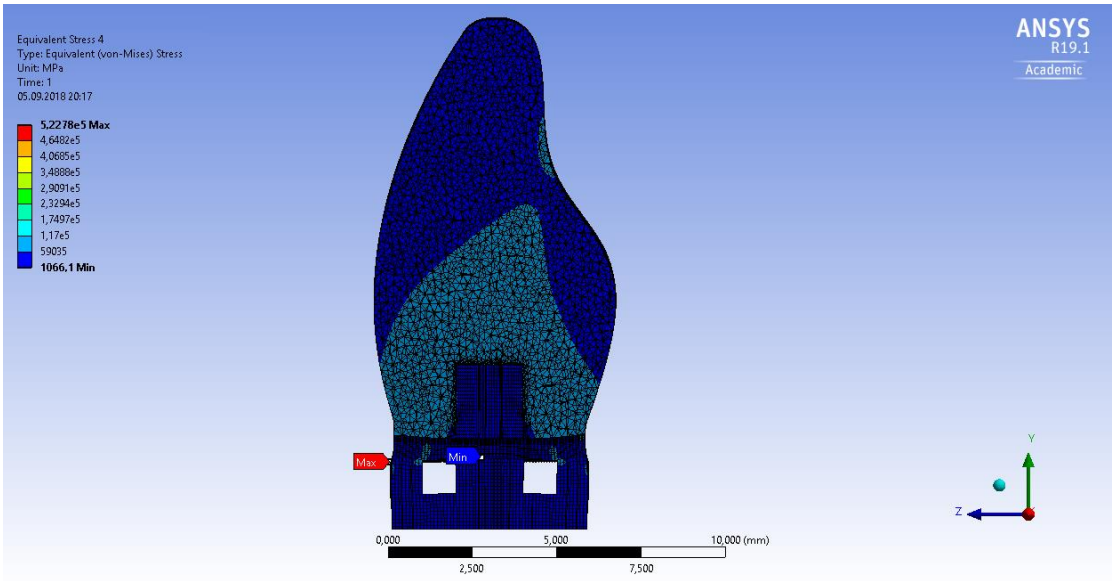

Figure 15. Stress distribution in case of the model with a grove in the second test
Source: own picture

Stress distribution is almost the same case like the first test. The highest values are on the thinnest area of acrylic resin. So grove doesn't have a big influence on this.
However, Figure 16, Figure 17 shows some changes of deformations.

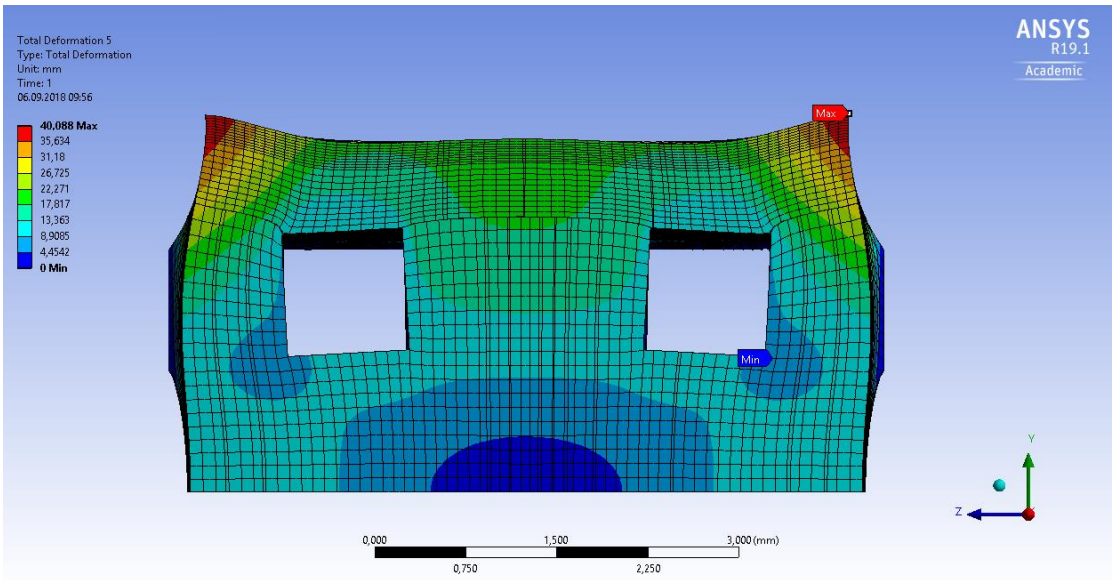

Figure 16. Deformations in case of the model without a grove in the second test
Source: own picture

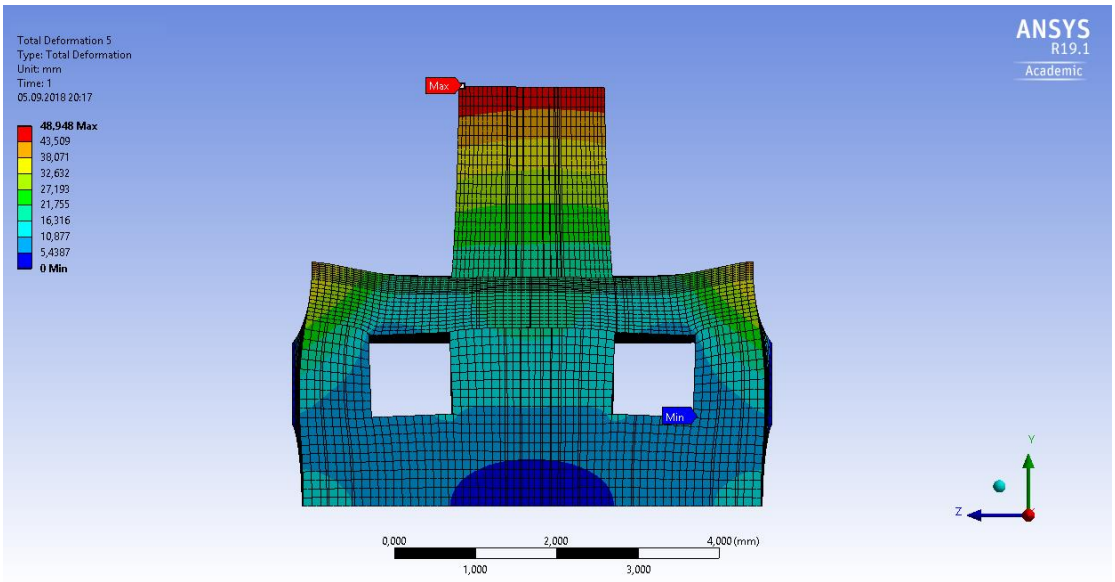

Figure 17. Deformations in case of the model with a grove in the second test
Source: own picture

This analysis shows that the highest deformations are on the top of the grove, but without it, the highest values are on the area of the thinnest base plate.

Conclusion

Tensile strength of PMMA is 58.50 MPa [15] and compressive is 81.40 MPa [15]. So even the highest values of deformations still don't exceed the strength of PMMA. So even the deformations changed because of grove it still doesn't help. Because the highest stresses are in the area of the thinnest layer of acrylic resin regardless of the existence of grove or not. And that's the most defective place in the removable partial denture metal framework. This part could break out after multiple dynamic loads which cause worst support of the tooth and then the tooth will break out.
In future research, the different shapes of the grooves should be compared. Because maybe different shape could change the distribution of stress in the acrylic resin of base plate. The dynamic analysis should be executed too, to compared values.

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ULTRASONOGRAPHIC IMAGING OF CARPAL JOINT IN DOGS

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Abstract:

Ultrasound examination of joints in small animals is not as well developed and studied as in human medicine. The aim of the study was to visualize the structures of the carpal joint in the group of seven healthy dogs. In each animal a linear probe was placed on the medial, lateral and palmar side of the carpus in order to locate the bones, tendons and ligaments. On the transverse sonograms, the distal row of the carpal bones with the accessory carpal bone, and the superficial and deep flexor tendons were visualized. These tendons were also visible on sagittal sonograms as intermediate echogenic structures. The collateral and accessory metacarpal ligaments have been identified only on the sagittal ultrasound images. The study shows the possibility of using this technique to examine the ligamentous apparatus and tendons of carpus in healthy dogs. In conclusion, these results suggest that ultrasound examination may be useful in diagnosis of diseases and trauma of these structures in dogs.

Keywords:

canine, carpus, ultrasonography

Introduction

Ultrasonography is quick, widely available and cheap method of diagnostic imaging in veterinary medicine. This imaging tool is not as commonly used for detecting joints as in human medicine. It is used in human patients for diagnose joint disease, injury, abnormalities and to guide percutaneous procedures to treat conditions. There were described procedures with ultrasound around human wrist and hand structures. The radio–carpal joint, small carpo–metacarpal joints and wrist tendons could be detected [1]. Ultrasonography is especially well studied to evaluation of soft tissue structures in small animals. Tendons and ligaments made up of many closely aligned parallel fibres, for that reason abnormalities are easily recognized as either high or low signal areas in otherwise uniform structure, This imaging modality can also be used in evaluating the amount and character of joint fluid as well as the thickness of synovium and articular cartilage, and in localizing periosteum, soft tissue tumors invading bone, and in some instances, fractures and sequestrations [2].

Examination of the musculoskeletal system in dogs is often conducted using a 10–12 MHz linear ultrasonic probe. A canine patient should be placed in the lateral position while the examined limb is raised [3]. In dogs, the ultrasonography examination is often used for assessment a lager limb joints such as shoulder, elbow, hip and stifle joints structures [4]. When it comes to the canine

carpal joint, it is not commonly visualized using ultrasound by veterinary surgeons. This is the result of the lack of adequate knowledge and a small amount of research carried out and described.

The most frequent disorders of the carpal joint in dogs are ligamentous injury, fractures of bones, epiphyseal separations and dislocations. Growth plate defects, osteoarthritis, ischemic necrosis of bone and neoplasm are less frequent diseases of carpal joint [5, 6].

The canine carpal joint includes antebrachiocarpal, middle, carpometacarpal and intercarpal joints. This joint consist of two rows of bones. The intermedioradial, ulnar, and accessory bones constitute the proximal row. The bones of the distal row are first, second, third and fourth carpal bones. Long collateral ligaments for the main joints of the carpus are lacking in dogs. However, in comparison to other species the dorsal and palmar parts of the joint capsule are much thicker. A modification of the palmar parts of the carpus is called the flexor retinaculum and it is well developed in the dog. The stabilization of carpus is formed by ligaments such as short medial collateral, short lateral collateral, palmar ulnocarpal, palmar radiocarpal and two accessory metacarpal ligaments. Many amount of short intercarpal ligaments connect the carpal bones transversely and hold these bones in the two rows. The extension and flexion of carpal joint in dogs are the purpose of extensor carpi radialis, extensor carpi ulnaris, flexor carpi radialis and flexor carpi ulnaris muscles. Flexor digitorum superficialis is a strong and flat muscle in dogs. It is located directly deep to the skin and antebrachial fascia in the caudomedially part of the antebrachium ant it covers the musculus flexor digitorum profundus. The muscle becomes tendinous a short distance proximal to the carpal joint and its final attachment is the accessory carpal bone. It is a flexor of the metacarpophalangeal and proximal interphalangeal joints. Whereas the musculus flexor digitorum profundus consists of humeral, radial and ulnar heads whose tendons unite to form the thick digital flexor tendon. It is a flexor of the carpus and digital joints [7].

These structures are exposed to injuries caused by excessive physical activity or accidents. Damage to the ligaments and tendons of the canine carpal joint is often not diagnosed because radiography does not show these injuries. Ultrasonography could be a complement to diagnosing lameness in dogs in veterinary medicine.

Materials and Methods

Seven healthy crossbreed dogs, 4 female and 3 male, weighing on average of 26.8 kg (range 21–37 kg) were used in this research. The mean age of studied dogs was 10 years and ranged between 7 to 13 years. Each dog was sedated with 0.5 mg/kg xylazine intramuscularly (Vetaxyl, Vet–Agro, Poland) during ultrasound examination. Animals were placed in right lateral recumbency, the left carpal joint of each dog was examined in neutral and flexed positions.The hair around the left carpal joint was clipped, and the sagittal and transverse ultrasonographic scans were received. Ultrasonographic examination was performed with a 7.5–12 MHz linear probe (MyLab^{TM}Five, Esaote). The transducer was placed on the medial, lateral and palmar side of the carpal joint between the two rows of the carpal bones.

Results

Ultrasound examination of group of dogs showed the possibility of imaging the musculoskeletal system and several ligaments of the canine carpal joint. The study failed to locate the deeper and smaller structures build the discussed joint.

Bones

In each of the examined dogs the transverse ultrasonographic images of carpal bones of the distal row were obtained. The image of the joint surfaces of first, second, third, fourth carpal bones and joint spaces with the probe placed on palmar side of joint was visualized (Figure 1). Better image quality was obtained in flexed position of exanimated joint in each animal. Ultrasound examination also allows for the assessment of the accessory carpal bone of all examined joints (Figure 2). The image of all bones was hyperechoic to the environment.

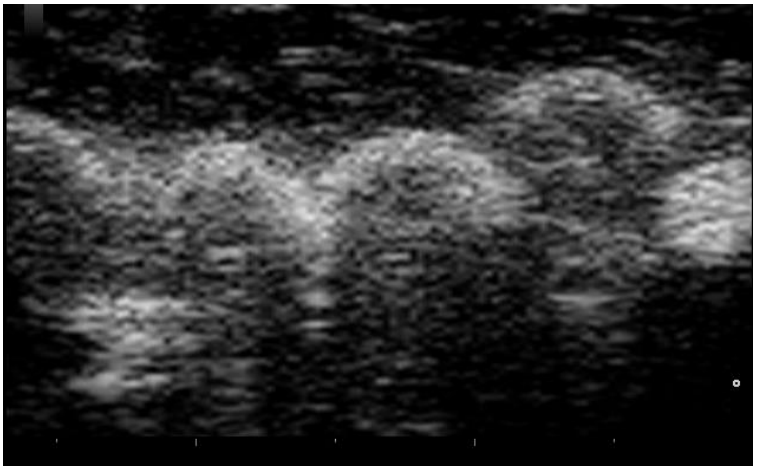

Figure 1. Ultrasonographic image of first, second, third and fourth carpal bones
Source: own study

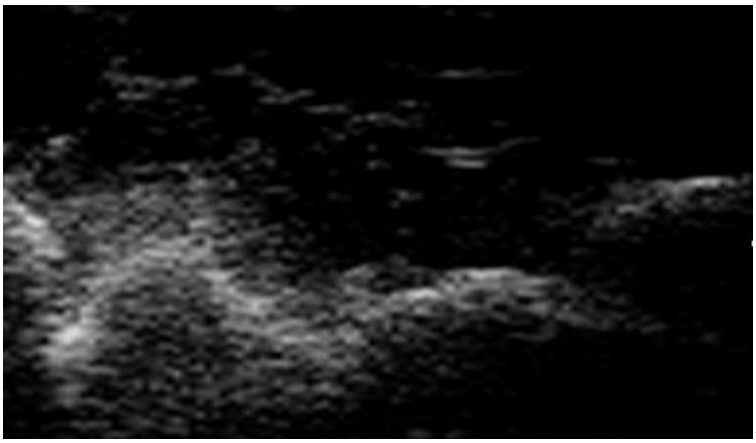

Figure 2. Ultrasonographic image of accessory carpal bone
Source: own study

Tendons

The superficial and deep digital flexor tendons were visualized on sagittal (Figure 3) and transverse sonograms in each examined dog. These tendons were seen as intermediate–grade echogenic structures with inhomogeneous areas. On the transverse sonograms the deep digital flexor tendon was seen like a comma shape, while the superficial digital flexor tendon was oval

shape (Figure 4). These tendons were imaged with the probe placed on the palmar side of the carpal joint above carpal pad in neutral position.

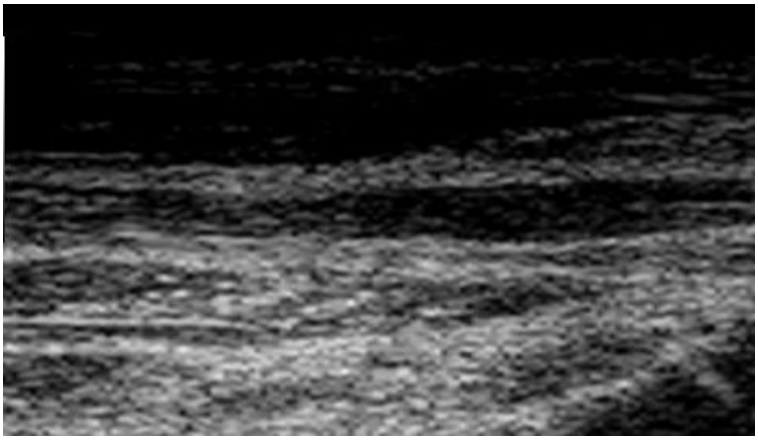

Figure 3. Ultrasonographic image of sagittal section of superficial and deep digital flexor tendons
Source: own study

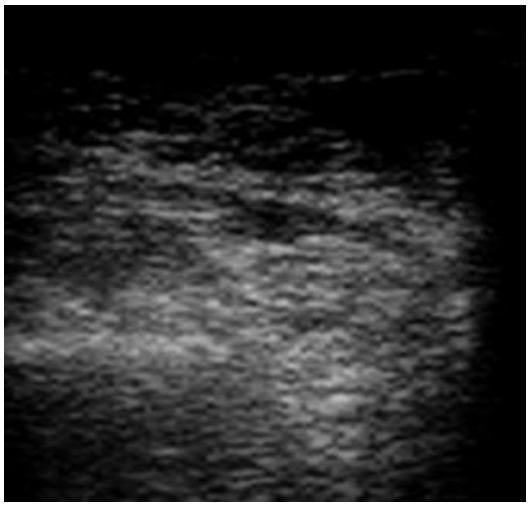

Figure 4. Ultrasonographic image of transverse section of superficial and deep digital flexor tendons
Source: own study

Ligaments

A short medial collateral, a short lateral collateral and accessory metacarpal ligaments were identified and imaged on sagittal and transverse ultrasonographic scans in each of examined carpal joint. Ultrasound image of ligaments in sagittal section exposed their filamentous structure consists of homogeneous, linear hyperechogenic brands (Figure 5). However, scans in the transverse section were more difficult to assess and identify. Collateral ligaments were visualised by place the ultrasound probe respectively to the medial and lateral surfaces of the carpus in neutral position. In the same position, on the palmar side of carpus, under accessory carpal bone, accessory metacarpal ligaments were detected.

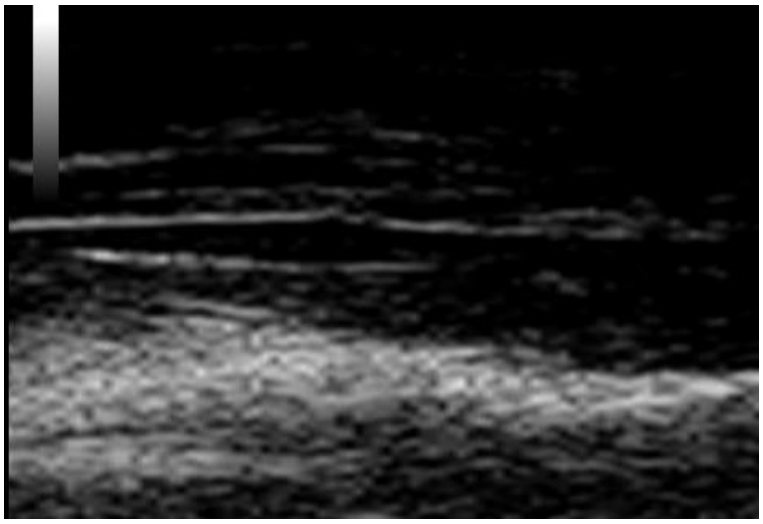

Figure 5. Ultrasonographic image of sagittal section of short lateral collateral ligament
Source: own study

Discussion

Ultrasonography is a diagnostic imaging method generally used in human and veterinary medicine. In humans, it is often used as a supplement to orthopaedic diagnosis, even in the case of complaints of small joints such as wrist or hand joints [1]. The commonly used radiography in diagnosing the causes of lameness in dogs does not show all joints injuries. Due to the small size of the carpal joint in a dog, its imaging diagnosis is limited only to radiographic examination. Complementing the diagnosis with ultrasound examination could provide information about the condition of the ligaments and tendons of the canine carpal joint.

This study was shown that the visualization of tendons and ligaments of the carpal joint of a dog by ultrasound is possible. The tendons of the superficial and deep digital flexor muscles were revealed on sonograms. The preformed ultrasonographic examination were also visualized the short medial collateral, short lateral collateral and accessory metacarpal ligaments of canine carpus. These tendons and ligaments are often exposed to injury because of their functions and localizations. The study also showed localization of first, second, third, four and accessory carpal bones on sonograms. The group of tested dogs was selected in terms of weight, which was above 20 kg for each animal. However, it would be necessary to perform tests for the smaller size of dogs in order to compare and determine the sensitivity of the USG examination of carpus.

Studies in veterinary medicine describe the use of ultrasonography in imaging of shoulder [8], elbow [9], hip [10] and stifle [11] joints in dogs. Research shows a small number of examples of the use of ultrasonography to diagnose carpal joint injuries and diseases in dogs. Diagnosis of stenosing tenosynovitis of the abductor pollicis longus muscle in dogs has been described according to radiographs of the carpus. Radiographic images showed tubular bony proliferation distally to radial groove, deeper radiolucent medial sulcus than opposite limb and soft tissue swelling medial to the carpus. Research shows that ultrasonographic examination can be helpful to differentiate between injuries of the tendon or tendon sheath of the abductor pollicis longus. This muscle fixes the carpus medially and it is an adductor of canine carpal joint. Establishing of fluid content, thickness of tendon and presence of mineralization in the connective tissue can be possible using

ultrasonography [12]. In one clinical case, the authors described a dorso–medial luxation of the radial carpal bone in a dog. Radiographs of the carpus in this study showed medial luxation of the radial carpal bone with its radial articular surface oriented medially and a tiny fracture of the fourth carpal bone on its latero–distal aspect. Therapy was carried out by a closed reduction of the luxation and conservative treatment. Conducted ultrasound examination on a dog with dorso–medial luxation of the radial carpal bone have shown tenosynovitis of the tendons of extensor carpi radialis and common digital extensor muscles [13]. The present the studies showed possibility of ultrasonographic examination of carpal canal in dog. The median nerve can be seen like ovoid shape with bright punctuate echoes during US examination. It is also located on the posteromedial side of median artery which can be recognized by colour Doppler imaging [14].

In conclusion, results of this study showed that ultrasonographic examination of canine carpal joint was an easily adequate technique for visualised normal tendons and ligaments. The study showed the advantages of using this method to assess the structure of some anatomical structures of the carpal joint. It can be suggested that ultrasound will detect abnormalities associated with damage and diseases of these tendons and ligaments. However, more research on these structures in both healthy and sick dogs are necessary to conducted. It would allow for more accurate use of this method to assess the canine carpal joint in veterinary medicine.

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DIGITAL IMAGE CORRELATION USED IN ANALYSIS AND MONITORING OF MECHANICAL BEHAVIOR OF MACHINE ELEMENTS

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Abstract:

The presented work shows additional possibilities offered by the up to date research methodknown as Digital Image Correlation (DIC), which becomes more and more popular in mechanical investigations of materials properties and machine components. Tensile tests of ultra–ductile steelareconducted byStrength Testing Machine – MTS Landmark 370.10. The samples are covered by the system of special pattern of pots (speckle patterns) and the change of the pattern set is registered by the photo–camera during the test.The registered pictures are analyzed by GOM–Correlate Softwarein order to obtain displacements and strains maps of the tested element. The purpose of the analysis is the verification and comparison of data received from the Strength Testing Machine (MTS 370.10) and by means of the research method (DIC). The displacements and strains are compared in selected measurement steps. Performed investigationsare the first step before the assessment of static and fatigue behavior of thin isotropic and anisotropic plates with various shapes of notches.

Keywords:

DIC, GOM–Correlate, experimental, investigations, analysis

Introduction

Reliable construction elements made of different types of materials are under constantmonitoring, what is very important in engineering practice and exploitation.Each of material groups (metals, ceramics, polymers, glasses, elastomersand hybrid materials) has different mechanical properties and this causes variousfailure behaviors under applied loadings [1]. At present, most of experimental investigationslike tensile, compression, shear or bending tests are monitored by the additional non–destructive research methods such as thermography, strain gauge measures or image analysis techniques (EPSI or DIC).Such combination of different methods is very helpful in analysis and verification of obtained results –allows to make an assessmentof deformations, degradations and localization of crack zones in investigated elements. The Digital Image Correlation (DIC) is good example of these methods. DIC is the non–destructive optical measuring method used in material researches.The main purpose of the DIC is to obtainthe results in the form of displacements and strains maps.Using the DIC itis also possible to indicate the weakpoints in investigated element and the expected crack nucleation points during the performed tests. This is particularly important in case of constructional elements with notches.

In the presented work the results obtained in the tensile tests of ductile steel are compared with these obtained bythe DIC method [2].

Material and specimens geometry

The material studiedin this paper isan ultra–ductile steel, which belongs to low–carbon group of steels.The subgroup of the investigated material is additionally described with two letter code DC, which is dedicated for plastic forming for elements with very high ductility. The results of average chemical composition measured in the spectroscopy investigation are listed in Table1. Specific contents of chemical elements such as C, Mn, P and S provide excellent flexibility during the cold–plastic forming.Characteristic properties for this type of steels are high deformability and elongation achieves around 40 % [3].

Table1. Chemical composition of ultra–ductile steel obtained by spectroscopy investigation

C	Mn	P	S	Si	Fe
0,05	0,17	0,01	<0,15	0,03	res.

Source: Author's investigation

The material is available in the form of cold rolled metal strips and sheets with thickness of 2 mm. The dimensions of the samples used in the tests comply with PN–EN 10002–1: 2001 standard. Samples are obtained by machining process. In the Figure 1 the shape and detailed dimensions of samples are presented (L_0=70mm). Such dimensions of the used samples are intentionally chosen to take into account the measuring range of the testing machine and the size of grips. Also the increase of the observation area makes the results of the DIC more reliable.

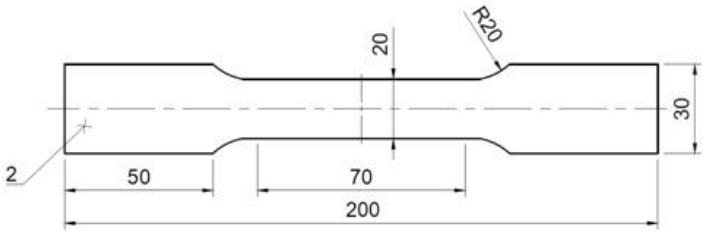

Figure 1. Technical draw with dimensions of tensile test sample
Source: Author's draw

Test description

The performedtensile testismade by means of the Strength Testing Machine MTS Landmark 370.10 200Hz with dedicated software used for registration of force as a function of imposed vertical displacement. In parallel photo–camera with interval timer is used to registered changes in speckle pattern during the tension test. The Figure 2 shows scheme of the experimental stand – Strength Testing Machine and DIC system. Specific and more detailed information is provided in the sub–sections below.

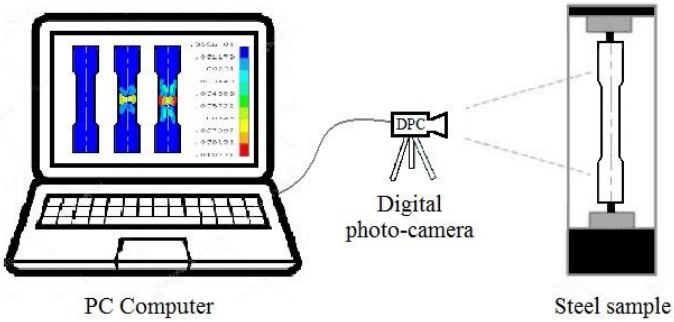

Figure 2. Scheme and visualization of the experimental installation
Source: Author's work

Strength Testing Machine

The strength testing machine MTS Landmark 370.10 200Hz is versatile, high–performance servo–hydraulic system forstatic and dynamic material and component testing. This type of machine is floor–standing and ideal for testing of componentsand materials such as plastics, elastomers, aluminum, composites, steel, super alloys, and etc.Using this machine it is possible to perform the tests such as: tension, compression, bending, stress relaxation, component strength and durability, crack propagation, fatigue crack, high cycle fatigue, low cycle fatigue and other [4]. Selected specifications of the equipment usedare shown in Table 2.

Table 2. MTS Landmark 370.10 floor–standing specifications

Specifications	**Units**	**Model: 370.10**
Force capacity	kN	100
Available actuator ratings (nominal)	kN	15, 25, 50, **100**
Actuator dynamic stroke	mm	100, **150**, 250
Working height	mm	922
Stiffness	N/m	467 x 10^6
Weight	kg	635

Source: [4]

The tensile tests of the investigated specimens were divided on 2 stages. In the beginning the speed of extension was set to 0.1 mm/minin order to registeryield limit very precisely in the first phase of test. In the second phase, after the exceeding the yield limit, the speed of extension test was increased 1mm/min. This was caused by expected very long time of the test. Such procedure does not have important influence on the obtained results. During the test time, elongation and force were register with frequency 5 Hz.

Digital Image Correlation

DIC method was developed in the early 1980's for measuring surface displacements and deformations [5]. Digital Image Correlation (DIC) is a non–contact whole–field imaging technique that employs tracking and image registration for accurate deformation and strain measurements. Method can be divided on two types: two–dimensional (2D) and three–dimensional (3D) [5]. In the case of two–dimensional (2D) type it is enough to use one camera, while in three–dimensional (3D) type of analysis minimum two cameras are recommended – usually three or more [7]. This method requires a digital imaging system to optically record images of the surfaces before and after deformation. It is a technique based on surface analysis methods, which involves monitoring and

identifying of changes in a speckle pattern applied to the surface of objects under observation, which have been subjected to some form of mechanical load. The pair of gray level functions of theimages was then compared using advanced image correlation and processing algorithms to determine thedisplacement and deformation gradients [5].

Principle of DIC working is as follow.Each picture, taken with a digital photo camera, corresponds to a different load step. Resolution of images is segmented into 2446x3264 arrays of individual light–sensitive cells, also known as photo–sites or pixels. Images were taken with a chosen time–interval. Each pixel stores a certain grey scale value ranging from 0 to 255, in accordance with the intensity of the light reflected by the surface of the tested specimen. Two images of the specimen at different states of deformation are compared by using a pixel and its signature in the undeformed image, and searching for the pixel in the deformed image in order to maximize a given similarity function. A single grey–value is not a unique signature of a pixel; hence, neighboring pixels are used in practice. Such a collection of pixels is called a subset or correlation window. The displacement result, expressed in the centre point of the subset, is an average of the displacements of the pixels inside the subset. The step size defines the number of pixels over which the subset is shifted in x– and y–direction to calculate the next result. The size of a subset can be, e.g. 7x7, 11x11, 15x15 pixels, etc.; the step size can be 3, 5, 7 pixels, etc.The uniqueness of each signature is only guaranteed if the surface has a non–repetitive, high–contrast pattern. Subsequently, the software determines the displacement values of the centers of the subsets, which yields an entire displacement field [6].

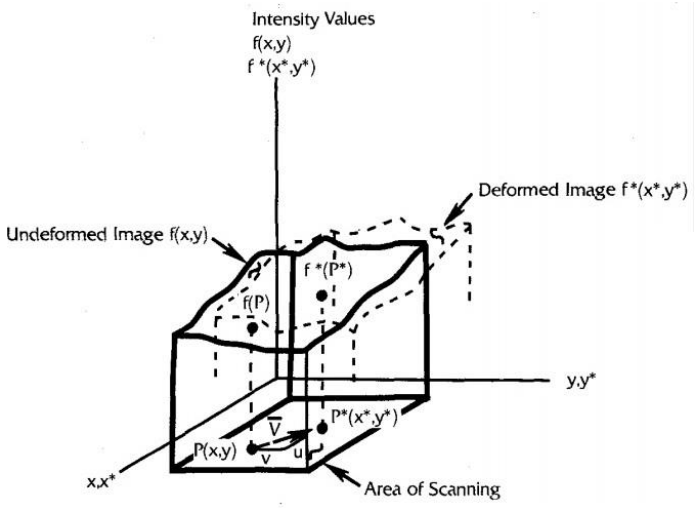

Figure 3. Gray–level representation of deformed and undeformed digital–speckle images
Source: [8]

Idea of digital image correlation is shown in the Figure 3. Let us consider changesinthe dimensions and position of short segments determined by the position of two points in the state before (P, Q) and after deformation (P1, Q1), Figure 3, described by the following equations in a three–dimensional, rectangular Cartesian coordinate system (3D) [2]:

$$P_1 = (x_1, y_1, z_1) = [x + u(P), y + v(P), z + w(P)] \quad (1)$$

$$Q_1 = (x_1 + dx_1, y_1 + dy_1, z_1 + dz_1) = \begin{bmatrix} x + u(P) + u(Q) - u(P) + dx \\ y + v(P) + v(Q) - v(P) + dy \\ z + w(P) + w(Q) - w(P) + dz \end{bmatrix} \quad (2)$$

where: u, v, w – are respectively displacement components in the direction of the x, y, z axis.

The lengths of segments PQ and P_1Q_1 are expressed as follows [2]:

$$|PQ|^2 = (ds)^2 = dx^2 + dy^2 + dz^2 \tag{3}$$

$$|P_1Q_1|^2 = (ds_1)^2 = dx_1^2 + dy_1^2 + dz_1^2 \tag{4}$$

For use in digital–correlation work, one notes that the observed intensity pattern is a two–dimensional projection of the object onto a plane. Therefore, the form of the finite–strain equation that one would employ to compute the strain is given by [2,9]:

$$\varepsilon_{xx} \cong \frac{\partial u}{\partial x} + \frac{1}{2}\left[\left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial v}{\partial x}\right)^2\right] \tag{5}$$

$$\varepsilon_{yy} \cong \frac{\partial v}{\partial y} + \frac{1}{2}\left[\left(\frac{\partial u}{\partial y}\right)^2 + \left(\frac{\partial v}{\partial y}\right)^2\right] \tag{6}$$

$$\varepsilon_{xy} \cong \frac{1}{2}\left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right) + \frac{1}{2}\left[\frac{\partial u}{\partial x}\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\frac{\partial v}{\partial y}\right] \tag{7}$$

In the DIC system procedure, the undeformed area is subjected to the analysis consisting in the assignment to individual, small coordinate areas of their position. Then, the undeformed reference zone is separated and changes in its shape and position are analyzed during the loading history and recorded in the coordinate system [2].

Every image loaded to softwareconsists of many pixels – it does not include any information about specific length. Before the analysis of image in GOM Correlate, calibration of real dimensions on reference image should be set.High–resolution images allow formore accurate analysis but produces bigger size of image, which causes slower and longer analysis process.The user of the method should always consider how precisely results must be [2, 5–8]. Influence of speckle pattern set is more advance case and it is described in other paper [6].

Results of experimental tests

In the present study, the uniaxial tensile tests coupled with the DIC technique are used to investigate behavior of steel sample. The Figure 4 shows one of the force–displacements curves

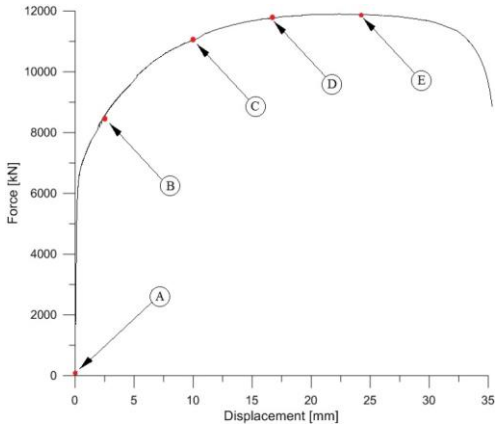

Figure 4. The force – displacement curve for sample included synchronized points equated to DIC
Source: Author's result

during the test. On this curve certain characteristic points are chosen. In these points the results from the strength testing machine with those obtained by means of the DIC method are compared. The received data from Strength Testing Machine and results from GOM–Correlate are matched to letters from force–displacement curve by the registered time of the tests. Synchronized in time results in fit points illustrated in Figure 4 are presented in Figure 5 and 6.
Additionally in Table3 the results of average mechanical properties are presented.

Table 3. Average mechanical properties of the steel samples

Investigated material				
Parameter	**Symbol**	**Result**	**Unit**	**Standard deviation**
Yield Stress	$R_{0,2}$	195	MPa	± 15,5
Tensile strength	R_m	312	MPa	± 10,4
Fracture strength	R_u	247	MPa	± 13,4
Strain	A	45	%	±3,1

Source: Author's results

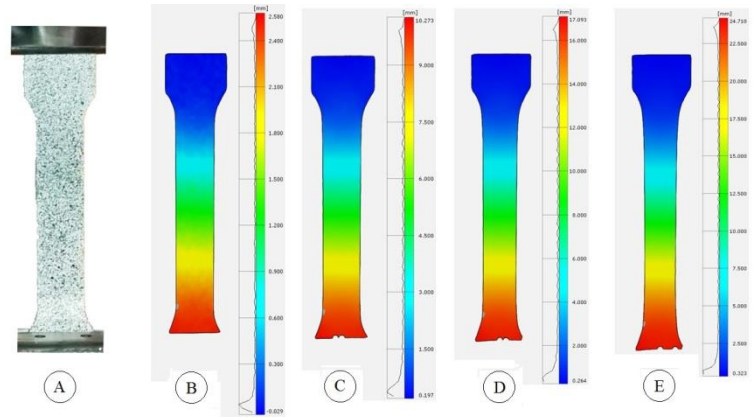

Figure 5. Digital Image Correlation results of axial displacement fitted to characteristic points from Figure 4
Source: Author's results

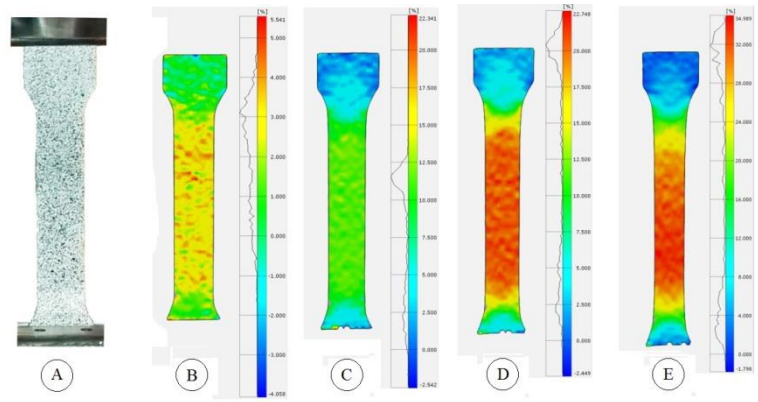

Figure 6. Digital Image Correlation results of axial strain fitted to characteristic points from Figure 4
Source: Author's results

In Table 4 and 5differences between Strength Testing Machine and Digital Image Correlation results are presented. Data from GOM – Correlate strains are taken from histogram.

Table 4. Differences between MTS Landmark 370.10 and GOM Correlate results of displacements synchronized in time

	Point A	**Point B**	**Point C**	**Point D**	**Point E**
Time [s]	0	1500	3750	4070	4360
Force [N]	0	8564	11023	11785	11880
MTS 370.10 Displacement [mm]	0	2,508	10,014	16,943	24,091
GOM Correlate Displacement [mm]	0	2,580	10,273	17,093	24,210
Displacement difference [mm]	0	0,072	0,259	0,150	0,119

Source: Author's results

Table 5. Differences between MTS Landmark 370.10 and GOM Correlate results of strains synchronized in time

	Point A	**Point B**	**Point C**	**Point D**	**Point E**
Time [s]	0	1500	3750	4070	4360
Force [N]	0	8564	11023	11785	11880
MTS 370.10 Strain [%]	0	3,583	14,286	24,204	34,416
GOM Correlate Strain [%]	0	3,257	12,218	21,687	34,989
Strain difference [%]	0	– 0,326	– 2,068	– 2,517	–0,573

Source: Author's results

Concluding remarks

The main purpose of the study was to use and test the digital image correlation method, which was donein a simple experimental study which was a tensile test. Attached additional research method as Digital Image Correlation provided information about behavior of material under tensile load and finally gives the distribution of displacements in the whole testing area. Obtained results coincide to a great extent withdisplacements and strains obtained by means of the strength testing machine.

- Mechanical properties (Table 3) of investigated samples have a large spread of results. It is probably caused by a faulty technological process during production. Check and verification will be possible after the microstructure analysis.
- The displacement maps from DIC are shown in the Figure 5. The obtained results are compared with displacement data from strength testing machine (MTS 370.10). The discrepancy between them is shown in Table 4 and seemsto be not significant.
- The strainmaps from DIC are shown in the Figure 6. These maps open a possibility ofstructure monitoring and can helpto identify zone exposed to the possible damage (the red areas in the pictures). On that base the place of possible destruction can bepredicted (red zone of map "E").
- In specific step of test displacements and strains can be compared. Results displacements and strains presented in Table 4 and 5. Maximum displacement difference between methods is 0,259

[mm] and maximum strain difference between methods is – 2.068 %. The discrepancy of results can be attributed tothe human mistake orbrightness illuminating sample, or speckle pattern, or software settings.

Those methods are successfully applied in mechanics. DIC is a proven technique both in terms of the technical advancement and in terms of the applications for which it is applied. This one successfully is used in many branches of industry, inspections of technical condition and during research and development of new technologies [5]. The combination of the above–mentioned methods gives the opportunity to compare the results with Finite Element Method (FEM) or active–thermography. Steel plates with various notches will be taken in the field of interests in future considerations (static and fatigue).A current example of the use and combination of monitoring (DIC) and simulation (FEM) research techniquesis the proposal of A. Muc et al. – Figure 7.

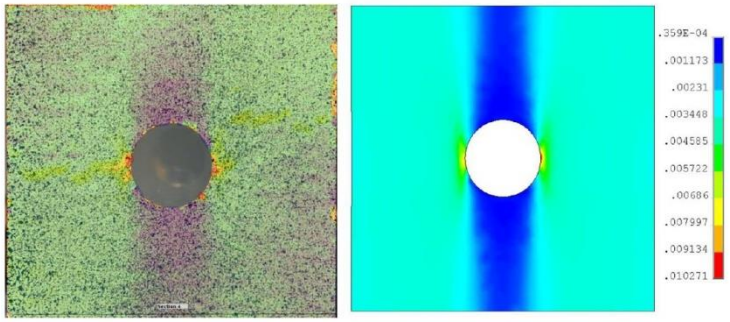

Figure 7. Monitored area of construction element by DIC (left) and FEM simulation (right) – woven roving composite. Source: [9]

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AMALGAMS – TOOTH FILLINGS OF THE PAST IN THE MODERN DENTISTRY OF THE 21ST CENTURY

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Abstract:

Together with the dynamic development of science and technology, there has been a huge progress in the field of dental conservative treatment, which is linked, among others, with the improvement and discovery of new dental materials. Despite a wide selection of tooth fillings from various types of materials, amalgam continues to be used to reconstruct the dental hard tissue, because this kind of material is covered by the social insurance in Poland.
Amalgams are metallic materials – an alloy of silver with mercury – which are the basic materials in conservative dental treatment. Silver alloy is a fine powder mostly composed of silver, copper and tin. After mixing the silver alloy with mercury, a dental amalgam is formed.
Currently in dentistry silver alloys are used with high copper content (13–30 %). Amalgams are the most frequently used fillings of dental cavities. When placed in tooth cavities, they undergo two disadvantageous reactions: tarnish and corrosion
Low price of the amalgam fillings, quickness of their application and no added costs for the dental surgery (e.g. expensive binding systems for light–cured composite fillings) causes that it is only the amalgam that is the material refunded by social insurance to fill side teeth.
The aim of the paper is to present the amalgam fillings and show their benefits as well as potential side effects.

Keywords:

amalgam filling, dental materials, metal alloys

Introduction

Amalgam is a general name for metal alloys with the main component of mercury. Patients associate it with a silver filling of metallic shine therefore it is often referred to as a silver tooth filling.

21st century, together with a dynamic development of science and technology, brought a giant leap in the field of dental conservative treatment. It was associated with improving and discovering new dental materials. Amalgam is the oldest material used to fill hard tissue of teeth. These types

of materials find their application on occlusal and proximal surfaces in the molars and premolars, in which the cosmetic aspect is not a major issue [1–3]. Apart from many advantages, like high hardness and durability, good flexibility and insignificant change in shape and volume, they also show a significant number of disadvantages. For a proper filling of the tooth with amalgam material, it is necessary to remove not only the decayed parts of the tooth, but also a part of the healthy tooth tissues in order to give the cavity a proper shape. A significant drawback of the amalgam fillings is their high heat conductivity which can cause oversensitivity of teeth [4–6].

Together with the dynamic development of science and technology, there has been a huge progress in the field of dental conservative treatment, which is associated, among others, with the improvement and discovery of new dental materials. Despite a wide selection of tooth fillings from various types of materials, amalgam continues to be used to reconstruct the dental hard tissue, because this kind of material is covered by the social insurance in Poland.

Aim of the paper

The aim of the paper is to present the amalgam fillings and to show their benefits as well as potential side effects.

Amalgam

Amalgams are metallic materials – an alloy of silver with mercury – which are the basic materials in conservative dental treatment. Silver alloy is a fine powder mostly composed of silver, copper and tin. After mixing the silver alloy with mercury, a dental amalgam is formed.
There are two types of amalgams:
–low–copper which contain less than 6 % of copper, and high–copper, containing 15–30 % of copper [1].

Currently in dentistry silver alloys are used with high copper content (13–30 %). Each of the components plays a specific role, and their percentage share decides on the physical properties of mercury [2, 3]. Silver, tin, gold increase the plasticity of the amalgam, while copper and zinc reduce it. Zinc and copper increase the volume of the alloy, while tin reduces its elasticity. Other metals such as palladium, platinum, gold, indium or copper were added to improve resistance to corrosion and to enhance the mechanical properties of the finished amalgam mass. Although innovations have eliminated zinc from most alloys, studies show that small amounts of this metal in high–copper amalgams improve their quality by reducing brittleness.

Amalgams are the most frequently used fillings of dental cavities. In addition to the properties associated with reconstruction of the hard tissue of tooth, that is: proper colour, shine, transparency, adhesions and marginal tightness, invariable volume, resistance to chewing forces, abrasion, crushing, proper hardness and flexibility, they should be neutral to the whole organism (chemically and physically stable, resistant to moisture, biological factors, be corrosion–proof and the surface layer should not degrade, not cause electro–galvanic or allergic reaction). According to the studies by Hajdug [6], filling a cavity with a silver amalgam causes an increase of the mercury and lead content in the tooth tissue, not only of the one with the filling, but also of the adjacent teeth. After

measuring the level of mercury in dental hard tissue, its higher content was proven in the dentine than in the enamel [7–11].

Attention should also be paid to the possibility of adverse effect of the metal elements of fixed and removable orthodontic appliances and of dentures. The releasing metal ions can cause local changes, such as:

discoloration, inflammation of the tongue or angles of the mouth or redness or erosion of the oral epithelium.

Metallic taste and burning of the mucous membrane surrounding the fillings may occur. Some patients report oversensitivity to sweet, salty foods or spices, as well as burning of the tongue and lips, dryness or excessive salivation [11–16].

Amalgams placed in tooth cavities undergo two disadvantageous reactions: tarnish and corrosion. Tarnish occurs in the form of a thin film causing discoloration of the amalgam. The discoloration of those surfaces can be easily removed by polishing off the amalgam filling. Corrosion, on the other hand, is a surface and subsurface form of the filling damage, caused by a chemical or electro–chemical reaction.

Chemical corrosion usually appears on the incorrectly polished surface of the amalgam, where unevenness and cavities facilitate the accumulation of food debris, thus initiating corrosion. Electrochemical corrosion is caused by the contact of fillings made of various metals, e.g. gold and amalgam or several amalgams in adjacent teeth [12–16]. Corrosion of amalgam affects not only the quality of the filling, but can also cause changes in the oral mucous membrane in the direct neighbourhood of the filling or reactions of a general inflammation of the oral mucous membrane caused by galvanic currents [4, 5, 7, 17–22].

An important, although not appreciated by dentists, problem of patients using more than one amalgam filling is a change in the taste of the eaten food [23, 25, 26].

Hygiene of work with amalgam is important as mercury is potentially toxic, therefore special care should be exercised in reducing the exposure of the patient and medical personnel. Strict obedience of regulations enables taking advantage of the wonderful benefits of new amalgams [7, 9, 11]. Amalgam causes poisoning in a small number of patients. Factors that may be contributing to the condition are: allergic, psychological and toxicological components. However, correct application of the amalgam by the dentist staff and the patients' care for oral hygiene allow to minimise its side effects. There is an ongoing search for new filling materials which would be an alternative for amalgams [27–31].

Several different groups of dental cavity fillings have been created, which do not cause such side effects as amalgams, are aesthetic and together with the development of biotechnology and nanomaterials, amalgams should not be the material of choice.

Low price of the amalgam fillings, quickness of their application and no added costs for the dental surgery (e.g. expensive binding systems for light–cured composite fillings) causes that it is the amalgam that is the only material refunded by social insurance to fill side teeth.

A patient who has amalgam fillings, should be aware of the effect the filling has on their bodily system and what side effects can occur after some time from applying the amalgam [29–32].

History of amalgam fillings

Although discovered about 600 years B.C., the amalgam fillings were adopted in treatment in the second half of the 19th century [1–3].

Silver amalgam was first used for a tooth filling (so–called Bell's putty) in 1819 by Joseph Bell in England. In 1833 mercury amalgam was brought to the United States from Europe by the Crawcour brothers. The advertising campaign for fillings that painlessly remove cavities, which was run by the brothers on a wide scale, was very successful. The Crawcours, regarded by many dentists as not obeying the ethical principles, removed gold fillings and replaced them with mercury amalgam, without the prior cleaning of the tooth cavities of the remains of decay. The variation of views on the methods of filling teeth has become known in history as "amalgam war". The amalgam war was the fight between craftsmen and medicine people [1]. The imprecise recipe of the amalgams and their random preparation supported many discussions raising doubts. It was not until Witzel and Black worked on the material that the advisability of applying this material to fill teeth cavities was scientifically proved [1]. A breakthrough date in the history of using amalgams was 1899 in Germany, when the work by Adolph Witzel (1847–1906) was published, entitled Amalgam teeth fillings. The author had performed thousands of experiments during which he and his team assessed the practical usability of various materials to fill tooth cavities. This way, at the turn of centuries, amalgams became a commonly used material in conservative dentistry, especially for patients of modest means. For many years amalgam would remain the standard reconstructing material in children's dentistry. Information on the possible harmful effect of amalgam to the health resulted in a decreased use of it, also in children. Since 1995 in Sweden amalgam has almost ceased to be used, while in Finland, Denmark, Norway, Canada and Germany this material was not recommended for use in children aged below 6.

In Polish public healthcare there has been no restriction on using amalgam in children under 18, as free–of–charge tooth fillings are provided with materials such as: capsule non–gamma 2 amalgam, glass ionomer cement, complex light–cured materials in the upper and lower front teeth [1].

Summary

Amalgams find their application on occlusal and proximal surfaces in the molars and premolars, in which the cosmetic aspect is not a major issue. In spite of a wide range of tooth fillings, such as composites, compomers, glass ionomer cement or ceramic and zirconium (overlay, inlay, onlay) low price and refunding by social insurance cause that the unaesthetic amalgam fillings are most often applied in adult patients in their premolars and molars.

Apart from many advantageous properties, such as high hardness and durability, good plasticity and a small change in shape and volume, amalgam fillings have many unfavourable properties. For a proper filling of the tooth with amalgam material, it is necessary to remove not only the decayed parts of the tooth, but also a part of the healthy tooth tissues in order to give the cavity a proper retention shape. In spite of following the principles of the cavity preparation, amalgam placing and condensing in the cavity and its perfect polishing, an amalgam filling will never retain the margin tightness. All modern dental materials show so–called adhesion to the tooth tissue by means of the chemical structure of the filling itself (e.g. glass ionomer cement, compomers) or by means of

adhesive systems ("dental glues", so–called Bond). Excellent marginal tightness prevents micro leaks of saliva with cariogenic bacteria into the interior of the cavity and secondary caries formation under the applied filling. Unfortunately leaking is unavoidable in amalgam, hence huge percentage of teeth with secondary caries after the lapse of 5 (ca. 75 %). The dark colour of the filling additionally masks the developing caries, therefore often patients come to the dental chair with pain and the need for endodontic treatment for vital teeth or with tooth crown breakage and the need to crown or extract dead teeth. Another disadvantageous property of amalgams is the fact that the metal oxides coming from amalgam fillings – when penetrating the dental tubules, permanently colour the whole tooth bluish–grey [6]. This makes it more difficult to diagnose possible secondary caries and an provide aesthetic reconstruction after replacement of the amalgam with composite materials.

The research on the release of mercury from amalgam fillings and its impact on patients' health is ongoing. Amalgam is toxic while preparation and application of the material, when damaged and during removal. In 2017 the European Parliament adopted so–called Minamata Convention on reduction of use of mercury.

In accordance with the Decision of the EU Council, it is advisable to, among others, gradually stop using the amalgam fillings, and by 2030 they should be completely withdrawn from use in dentistry in the European Union [32].

Conclusions

1. Modern dentistry aims at the best aesthetics possible with simultaneous preserving of teeth functionality, therefore amalgam fillings, in spite of unfavourable features, are used in the dental surgeries and are the fillings of choice for adult patients, thanks to the social insurance coverage.
2. Toxicity of the mercury compounds has caused that in line with the Decision of the EU Council, amalgams will disappear from dentistry in Europe.

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CHILDREN'S DENTAL CARIES AND THE KNOWLEDGE OF PARENTS ABOUT THE PROPHYLAXIS

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Abstract:

Dental caries is a communicable disease caused by Streptococcus mutans. It is noted – next to the ischemic heart disease, cancer, type 2 diabetes and allergies – as the contemporary disease of affluence, mainly caused by the environmental conditions.
The aim of the paper is to assess the health conscious behaviour in children and their parents as well as their knowledge on the prophylaxis preventing caries in children.
The study group covered 510 children aged 3–18 and their parents.
The authors' original, anonymous questionnaire was used in the survey, filled–in by the patient's parent. Establishing the CFE index was conducted based on the patient records.
Results: The level of parents' knowledge depends significantly on the age group of children. Slightly more than a half of the respondents (54.5 %) presented average knowledge on the causes of caries.
Conclusions: An effective method to improve health can be to raise the level of health education, in particular in the field of caries.

Keywords:

dental caries, caries prevention

Introduction

Dental caries is one of the ailments that is most frequently present in human mouth. It is a communicable disease caused by microorganisms – carious streptococci called *Streptococcus mutans* – which ferment carbohydrates to lactic acid. It is mentioned – next to the ischemic heart disease, cancer, type 2 diabetes and allergies – as the contemporary diseases of affluence, mainly caused by the environmental conditions (social, economic, natural ones), as well as the lifestyle itself. The significance of the existing healthcare system is also emphasised. Many of those elements can be influenced by shaping the health conscious behaviour of people and promoting direct oral care [1, 2].

Dental caries is a disease that is spread worldwide. The World Health Organisation has placed it on fourth place of the particularly costly ailments. Poland is one of the few countries in Europe, which have failed to reduce the incidence of tooth decay in children. Epidemiological studies of the oral health, which have been conducted in our country since 1987 show that dental caries and periodontitis are a serious problem in our society [3, 4, 5].

In developing countries, especially in the countries of the former Eastern bloc, undergoing economic and market transformations, including Poland, tooth decay is still a significant health problem. The development of urbanization, lifestyle changes and adopting "western" dietary patterns – based, among others, on consuming refined sugary products – is not accompanied with an adequately fast development in the health awareness of the population: resulting in inappropriate hygienic and dietary habits. In cooperation with WHO, since 1997 a program has been implemented in Poland of monitoring the oral health and its conditions \coordinator – Prof. Maria Wierzbicka. The epidemiological and sociomedical studies have been conducted in 16 voivodeships. The study results from 2005 showed that in Poland, a child aged 6 has an average of six untreated teeth with cavities, which affect their overall health. 8.2 % of the examined children in this age group already have newly erupted permanent teeth \1st molar\ with cavities. The dental caries frequency among the 12–year–olds is 83.6 %, and the average value of the caries indicator CFE – the sum of the teeth with active caries, extracted and filled per one child in a given population is 3.3. Juxtaposition of the results obtained in 2005 and the results from several years ago indicates a very slow decreasing trend in the dental caries of the schoolkids in Poland. The CFE index in 12–y.o. in 1995 – 4.3, in 2000 – 3.8, in 2005 – 3.3. Nevertheless this decline is too slow and does not keep up with the pace of the objectives and targets as specified by WHO with regard to the oral health [6].

Caries is an infectious communicable disease, which according to estimates affects 60 to 90 % of all children and the majority of adults. As the existing epidemiological studies show (2013) dental caries occurs in Poland in: 56.2 % 3–year–olds, 86.9 % 6–year–olds and 87.9 % 12–year–olds. In spite of a significant improvement in mouth health condition observed in children, dental carries remains one of the most frequently occurring diseases. Health education, health promotion, and comprehensive prevention are the only appropriate ways to make an improvement possible of the critically bad condition of dental health in children and youth, and thus the entire Polish population in the future.

In 2003 studies were carried out among Polish 12–year–olds. The studies showed that half of the children aged 12 have cavities in at least four teeth. Dental caries is present in 99.8 % patients aged 35–45; even as much as 100 % of the examined population [6]. 96 % of Polish population suffers from dental caries [6]. The problem, however, decreases over the years, which is certainly influenced by the promotion of oral cavity hygiene products and the growing awareness of the public. Due to the high frequency of occurrence, tooth decay is described as a social disease. Hardwick claims that nowadays we can talk about an increase in the dental caries incidence compared to previous centuries [6, 7]

Hygienic negligence, inappropriate hygiene or lack of it and omission of dental check–ups can cause serious health damage for the whole human organism [6, 7] . Failure to treat dental decay causes diseases of the pulp tissue, jaw bone, as well as periodontium. The above may result in the following ailments [6, 7]:

- rheumatoid arthritis,
- endocarditis and myocarditis,
- thromboangiitis obliterans,
- glomerulitis,
- eye diseases,
- suppurative dermatitis or allergic reactions.

In addition, numerous studies show that it is impossible to control caries and periodontal diseases only by treatment activities themselves. What is needed is education and prophylaxis [7–9]. The patients' awareness of the dental caries and its prevention is an important aspect. "An ounce of prevention is worth a pound of cure" is a common saying that also relates to tooth decay.

Aim of the paper

The aim of the paper is to assess the pro–health behaviour in children and their parents/carers as well as the their knowledge on the prophylaxis preventing caries in children, in relation to the guidelines of the National Health Program.

Material

The survey covered 510 children aged 3 – 18, of which 255 were girls and 255 boys and their parents/carers. The examined children were divided into age groups. The groups (1–3) were formed basing on the National Health Program guidelines. The largest group was of the age 7–12 (215 children, with 103 boys and 112 girls).

Method

The research method used in the work was the author's, anonymous questionnaire completed by the child's parent or carer. The questionnaire was composed of 20 questions concerning mouth hygiene, awareness of the caries disease and its consequences for the whole body, caries prophylaxis as well as educating and preventing programs in kindergartens or schools. The questionnaire survey was conducted from January 2015 to March 2016. Moreover, data was obtained from the medical records of the examined children and analysed retrospectively. The analysis covered data on the condition of teeth, hygiene and frequency of occurrence of dental caries (CFE).

The survey questionnaire has been tested in a pilot study. The test aimed at obtaining information whether the respondents properly understand all the questions asked and provide clear and reliable answers, whether the instructions attached to the questionnaire are clear for the surveyed people and whether any answers are missing from the questionnaire (additional notes from the respondents).

The pilot study covered an examined group of parents/carers (n = 30) of children aged 3–18 who were the patients of the *Stomatologia Brynów* dentist surgery.

The survey obtained a consent from the Bioethical Commission of the Medical University of Silesia in Katowice no. KNW/002/KB/102/15.

Statistical analysis

The data collated from the medical records and questionnaires was gathered in an MS Excel 2010 spreadsheet and then imported into the Statistica 12 software. Normality of distribution of quantitative variables was checked by the Shapiro–Wilk test. Mean average and standard deviations were calculated for the CFE index. The mean average values were compared basing on ANOVA/MANOVA analysis of variance. Chi–squared test with Yates correction was applied to assess the dependency between the qualitative features. The $p<0.05$ level was assumed as statistically significant.

Results

Most parents (60 %) assess their child's teeth condition as good, with almost 85 % claiming their child cleans their teeth in the morning and in the evening. Most often children use a medium–hard manual toothbrush. Parents most often use the dentist's recommendation when selecting the toothpaste.

Figure 1 presents the assessment of knowledge of parents/carers of the children, with regard to the preventive actions against occurrence of tooth decay in children.

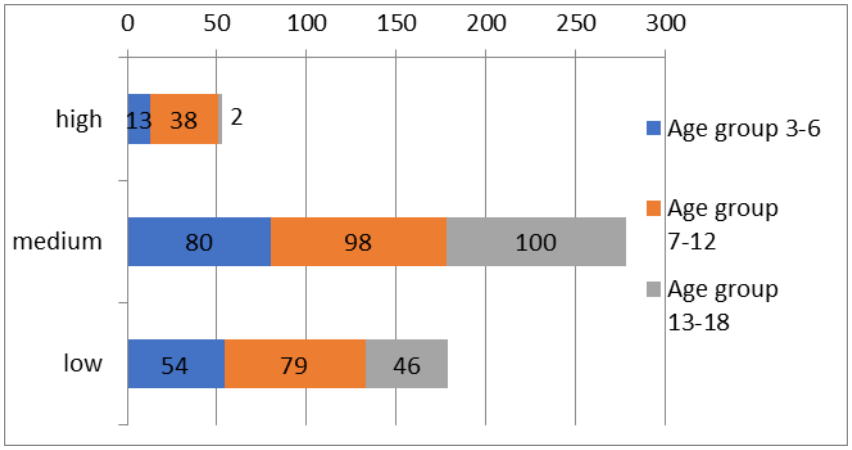

Figure 1. Level of knowledge of parents/carers of the examined children on dental caries.

The basis for the assessment of knowledge of parents/carers of the children, with regard to the preventive actions against occurrence of tooth decay in children was the analysis of their answers to the questions 8–11 as well as 16 and 18. In question 8 concerning the dental cavity symptoms, the correct answer of "b" (visible stains on teeth) was assigned mark 1.

Table 1. Level of knowledge of parents/carers of the examined children on dental caries prevention

Level of knowledge	Age group 3–6	Age group 7–12	Age group 13–18	Total
0	75	62	124	261
1	71	151	24	246

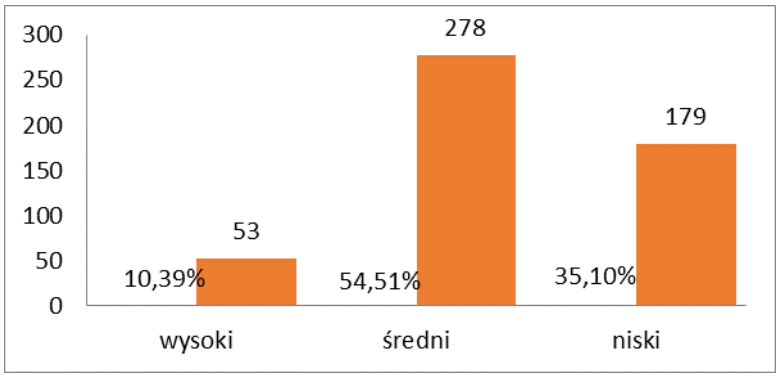

Figure 2. Level of knowledge of parents/carers of the examined children on causes of dental caries.

Table 2. CFE in groups of examined children

		N valid	Average	Median	Min	Max	Lower quartile	Upper quartile	Variance	Std. dev.	Variable ind.
All observations		510	6.139	6.000	0.00	20.00	2.00	9.00	18.87	4.34	70.76
Children's age group	3–6 yo	147	5.83	6.00	0.00	17.00	2.00	10.00	20.24	4.50	77.16
	7–12 yo	215	6.03	6.00	0.00	20.00	2.00	9.00	18.84	4.34	71.96
	13–18 yo	148	6.60	7.00	0.00	17.00	3.00	10.00	17.49	4.18	63.36

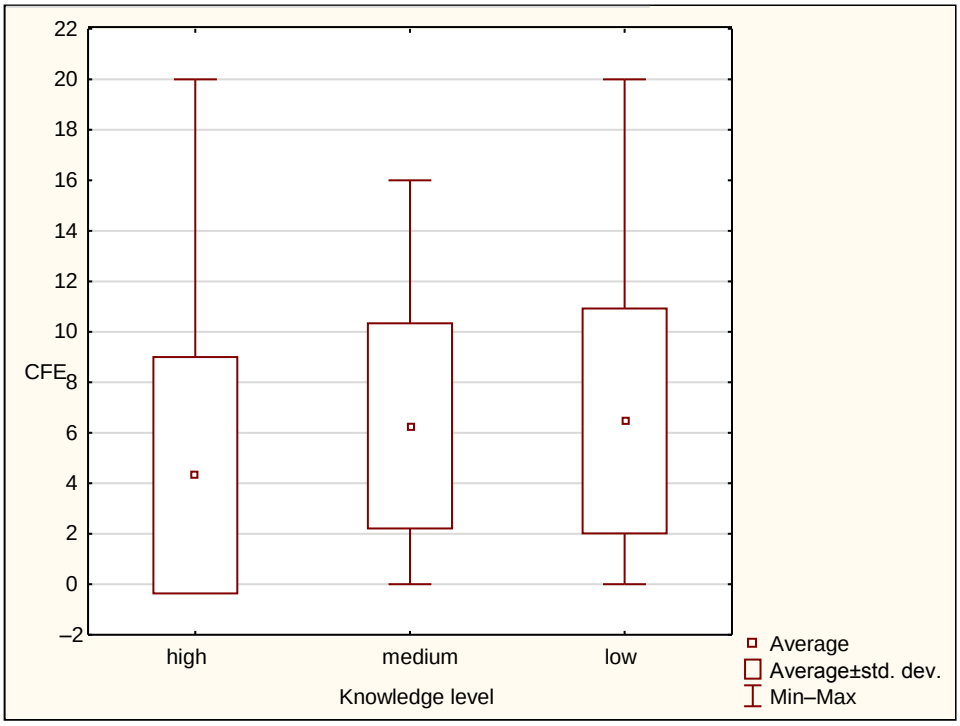

Figure 3. CFE index in the group of the examined children taking into account level of knowledge of parents/carers on causes of dental caries

Spearman's rank correlation coefficient confirmed the relation between the level of knowledge of the surveyed parents/carers and the condition of the oral health of their children as determined by the CFE index. As the parents' knowledge level increased, the CFE index fell (r_3= –0.40888, p=0.0000). The CFE index is at the level of 5.40 in the entire examined group. The children's age was of significant influence on the CFE index value. The worst condition of teeth was with the children aged 7 to 12.

Discussion

Dental caries is one of the most common communicable diseases that occur in the oral cavity. It is often described as a disease of affluence, mainly caused by environmental conditions and lifestyle [6]. Many of those elements can be influenced by shaping the health conscious behaviour of population and promoting direct dental care.

Dental caries is a disease that is spread worldwide. The World Health Organisation has placed it on fourth place of the particularly costly ailments. In its subsequent editions, the National Health Program incorporated actions serving health promotion, intensification of the caries prevention in children and youth.

Tooth decay is a major health problem in Poland as it concerns as much as 90 % of the population, with the largest group composed of children and youth. When untreated, the disease contributes to many serious systemic conditions.

As noted by Turska–Szybka et al. [7], regular visits with the dentist can reduce the dental caries incidence rate. Health education of the children and youth, as well as their parents/carers, health promotion, and comprehensive prevention are the only appropriate ways to make an improvement possible of the critically bad condition of mouth cavity health in children and youth, and thus the entire Polish population in the future [8–10].

High incidence rate, combined with the omnipresent advertisements of agents preventing and fighting cavities, should imply some knowledge in this field in the society, acquired in a way "alongside". Own research has been carried out on a group of 510 children (255 girls and 255 boys) aged 3–18, and their parents. The questionnaire survey documents that the level of knowledge of the parents/carers of children from group 1 (3–6 years old) with regard to dental caries was slightly over 37 % and proved low, with the high level of knowledge was presented by less than 9 % of the examined group. The level of knowledge of the remaining parents – more than half of the group (55 %) – was specified as average, which certainly does not boost fervent hope for the condition of the milk teeth which require exceptional care.

According to own studies the parents in the second age group of children (7–12 years) constituted the largest of the examined groups, and at the same time the best educated one with regard to the oral hygiene and dental caries. The studies also show that more than one–third of the parents/carers of children up to 12 years old have insufficient knowledge about tooth cavities, which undoubtedly affects the condition of teeth in children.

Hygienic negligence, lack or omission of dental check–ups can cause serious health damage for the whole human organism. Failure to treat teeth decay causes diseases of the pulp tissue, jaw bone, as well as of periodontium. The consequence may also be serious systemic diseases such as:

rheumatoid arthritis, endocarditis and myocarditis, thromboangiitis obliterans, glomerulitis, eye diseases or suppurative dermatitis or allergic reactions.

Under own study carried out among the parents of the children from the third age group (aged 13–18) only 1.35 % of the examined population possesses a high level of knowledge. The knowledge level of 31 % is low, while more than two–thirds (67.6 %) is at medium level.

Dental caries is a serious social issue – it concerns as much as 90 % of Poles. Fighting the disease is exceptionally expensive: the World Health Organisation has placed it on fourth place of the particularly costly ailments.

When untreated, the disease contributes to many serious systemic conditions. As noted by Turska–Szybka et al. [7], regular check–ups at a dentist can reduce the tooth decay incidence. Nevertheless, nothing can replace health education of children and youth as well as their parents and carers. It is health promotion, and comprehensive prevention that are the only appropriate way to make an improvement possible of the critically bad condition of oral health in children and youth, and thus the entire future Polish population [9]. In its subsequent editions, the National Health Program presented actions serving health promotion, intensification of the caries prevention in children and youth.

Conclusions

1. The level of parents' knowledge depends significantly on the age group of children.

2. A high level of knowledge on the cavity prevention was shown by the parents of children aged 7–12, with the low level of knowledge demonstrated by the oldest children's parents (13–18 years).

3. An effective method to improve health can be to raise the level of health consciousness, in particular in the field of caries.

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PROMOVENDI

Oferujemy:
– skład i łamanie tekstu,
– wydruk książek abstraktów i monografii z numerem ISBN,
– oprawę graficzną wydruków,
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