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CONTENT

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THE FORMATION OF ANTI-CORROSIVE STRUCTURES AND THIN FILMS ON METAL SURFACES BY APPLYING EDM

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Abstract. The methods of formation anti-corrosive strata and thin films on metal surfaces by applying electric discharge machining (EDM) are presented in this chapter. It has been demonstrated the increase of anti-corrosion resistance of metal surfaces by the formation of palladium depositions, carbon films, oxide and hydroxide films. Corrosion and electrochemical behavior of titanium with palladium powder coatings were investigated in sulfuric acid solutions at temperatures of 80 and 100° C. In order to increase the diffusion of palladium in the base material and to increase the layer homogeneity, after coating, the samples were annealed in vacuum at 1150 °C for 1 hour. The proposed method allows to reduce the corrosion speed of titanium at least by 2 orders (from 18.7 down to 0.3 $g \cdot m^{-2} \cdot h^{-1}$), the corrosion potential is changed towards positive values (from -0.56 mV to +0.3 V). The research on surface electrical resistance and resistance to corrosion of oxide and hydroxide films formed on steel C45 surfaces by applying EDM have shown that the surface electrical resistance of the samples increased by 10^7 times, the potential of corrosion increased from -0.44 mV to +0.4 V, the resistance to corrosion has increased by about 2 times in 1% NaCl water solution, and by about 10 times in 30% H_2SO_4 water solution. The less pronounced increase of anti-corrosion properties is possessed by carbon films formed on the same steel C45 surface, instead they increase superficial microhardness, the functional durability and processing productivity of the active piece surfaces.

Keywords: *carbon, corrosion, electric discharge machining, microhardness, thin films.*

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FORMAREA STRUCTURILOR ANTI-CORROSIVE ȘI A STRATURILOR SUBȚIRI PE SUPRAFETE METALICE CU APLICAREA DESCĂRCĂRILOR ELECTRICE (EDM)

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Rezumat. În lucrare sunt prezentate metodele de formare a depunerilor anticorozive și a straturilor subțiri pe suprafețe metalice prin aplicarea mecanismelor de descărcare electrică (EDM). S-a demonstrat creșterea rezistenței la coroziune a suprafețelor metalice prin formarea depunerilor de paladiu, a filmelor de carbon și a filmelor de oxid și hidroxid. Coroziunea și comportamentul electrochimic al titanului cu depuneri de pulbere de paladiu au fost investigate în soluții de acid sulfuric la temperaturi de 80 și 100 °C. Pentru a crește difuzia de paladiu în materialul de bază și a omogenității stratului depus, după acoperire probele au fost tratate termic în vid la 1150 °C timp de 1 oră. Metoda propusă permite reducerea vitezei de coroziune a titanului cu cel puțin 2 ordine (de la 18,7 până la 0,3 $g.m^{-2} \cdot h^{-1}$). Potențialul de coroziune este deplasat spre valori pozitive (de la -0,56 mV la +0,3 V). Cercetările privind rezistența electrică la suprafață și rezistența la coroziune a filmelor oxidice și hidroxidice formate pe suprafețele din oțel C45 prin aplicarea EDM au arătat, că rezistența electrică la suprafață a probelor a crescut de 107 ori, potențialul de coroziune a crescut de la -0,44 mV la +0,4 V, iar rezistența la coroziune a crescut de aproximativ 2 ori în soluție apoasă de 1% NaCl și de aproximativ 10 ori în soluție de 30% H_2SO_4. O crestere mai putin pronuntata a proprietatilor anticorozive au manifestat filmele de carbon formate pe suprafata C45, in schimb s-a majorat microduritatea superficiala, durabilitatea functionala si productivitatea procesarii suprafetelor active ale pieselor.

Cuvinte cheie: *carbon, coroziune, descărcare electrică, microduritate, straturi subțiri.*

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THERMAL DEFORMATION WAVES IN HETEROGENEOUS MATERIALS

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Abstract. In the paper, a stress-strain detection method is used by correlation point interferometry, in which the resolution of the recording surface changes has been significantly (ten times) improved. This result was obtained by applying a different image-processing algorithm, which allows the recording of 3D surface changes in on-line mode. The deformation wave that occurs during heating propagates through the entire sample and interacts with the interfaces. The inhomogeneity and residual deformations of a material lead to a distortion of the front. The speckle electron interferometry (ESI) method allows the recording of this thermal deformation wave front and the estimation of the stress state of the studied material.

Keywords: *heterogeneous materials, stress strain, thermal deformation wave, speckle electron interferometry (ESI).*

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DEFORMAȚII TERMICE ÎN MATERIALE HETEROGENE

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Rezumat. În lucrare este analizată o metodă de detectare a stării de încordare la stres folosind interferometria cu punct de corespondență, în care a fost îmbunătățită semnificativ (de zece ori) rezoluția modificărilor suprafeței de înregistrare. Acest rezultat a fost obținut prin aplicarea unui algoritm diferit de procesare a imaginii, care oferă posibilitatea înregistrării modificărilor suprafeței 3D în modul on-line. Valul de deformare care apare în timpul încălzirii se propagă prin întregul eșantion și interacționează cu interfețele. Neomogenitatea și deformările reziduale ale unui material conduc la distorsionarea frontului. Metoda de interferometrie electronică cu speckle (ESI) permite înregistrarea acestei fronturi ale valurilor de deformare termică și estimarea stării de încordare la stres a materialului studiat.

Cuvinte cheie: *materiale heterogene, încordare la stres, val de deformare termică. interferometrie electronică cu speckle (ESI).*

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ALGORITHM OF PROCESSING MICROSPIRAL CT-SCAN RESULTS FOR CONSTRUCTING A THREE-DIMENSIONAL MODEL OF ORBIT THIN BONES

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Abstract. We developed the algorithm for preparation of DICOM images for the construction of a three-dimensional model of the bones of the facial skull. The DICOM image-processing algorithm reduced the data loss level about the thin bones of the orbit during building a three-dimensional model of the bones of the facial skull from 22–31% to 3–5%. The developed software automatically changes the color of the pixels of the thin bones of the orbit from gray to white. Thin bones of the orbit were expanded over one pixel using the DICOM image-processing algorithm. The analysis of the image processing results by the developed software was carried out using 3D Slicer software.

Keywords: *DICOM images processing algorithm, orbit bones, DICOM images, 3D model.*

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ALGORITMUL DE PROCESARE A REZULTATELOR CT-SCAN MICROSPIRALE PENTRU CONSTRUCTIA MODELULUI 3-D DE ORGANE

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Rezumat. În lucrare este analizat algoritmul de pregătire a imaginilor DICOM pentru construirea unui model tridimensional al oaselor craniului facial. Algoritmul de procesare a imaginii DICOM a redus nivelul de pierdere a datelor despre oasele subțiri ale orbitei în timpul construirii unui model tridimensional al oaselor craniului facial de la 22-31% la 3-5%. Software-ul dezvoltat modifică automat culoarea pixelilor oaselor subțiri ale orbitei de la gri la alb. Oasele subțiri ale orbitei au fost extinse peste un pixel utilizând algoritmul de procesare a imaginilor DICOM. Analiza rezultatelor procesării imaginilor prin software-ul dezvoltat a fost realizat folosind software-ul 3D Slicer.

Cuvinte cheie: *algoritm de procesare a imaginilor DICOM, orbitele oaselor, imagini DICOM, model 3D.*

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THE RISKS OF ARTIFICIAL INTELLIGENCE

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Abstract. The artificial intelligence (AI) revolution is the fastest of all revolutions that we have known. The AI is most often presented as a how to improve and refine existing processes in order to spectacular. Much more than a technology, AI represents a new way of interacting with our environment and doing business. While some welcome this innovation favourably, others call for a break to assess the potential risks to consumers. The paper examines the possible risks and benefits of AI for different areas of human activity.

Key words: *Risks of misuse, AI advantages, large-scale cybercrime, safety, reliability.*

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RISCURILE INTELIGENȚEI ARTIFICIALE

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Rezumat. Revoluția inteligenței artificiale (AI) este cea mai rapidă dintre toate revoluțiile pe care le-am cunoscut. AI este cel mai adesea prezentată ca o modalitate de îmbunătățire și rafinare a proceselor existente pentru a fi spectaculoase. Mult mai mult decât o tehnologie, AI reprezintă un nou mod de a interacționa cu mediul nostru și de a face afaceri. În timp ce unii apreciază favorabil această inovație, alții solicită o pauză pentru a evalua potențialele riscuri pentru consumatori. În lucrare sunt examinate posibilele riscuri și avantaje ale AI pentru difeite domenii ale activității umane.

Cuvinte cheie. *Riscuri de utilizare incorectă, avantaje AI, criminalitate informatică la scară largă, siguranță, fiabilitate.*

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THE CONSEQUENCES OF THE OMISSION OF THE PROPERTY RIGHTS STUDY IN THE REAL ESTATE ASSESSMENT PROCESS

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Abstract. The article focuses on property valuation. It examines the value, its qualitative and quantitative aspects through the static and dynamic prism; the essence of value and the factors of impact, behavioral aspects over time. The development of the evaluation in recent years has highlighted two directions: the financial and economic assessment centered on evaluation theory and the evaluation of financial investments, focused on evaluation theory. Property valuation takes place through the interference of economic, technical and legal sciences. In recent years, international valuation practice has changed its vision of the subject of evaluation; the focus has been shifted from "real estate" to "property rights". The value of the property depends directly on the real estate property rights, along with the existing tasks. In the process of estimating value, neglecting the survey or superficial examination of real estate has serious consequences for both the owner of the good and the user of the valuation report as well as directly for value. In the article, this situation is exemplified using the case study method.

Keywords: *real estate, property interests, valuation of rights, special value, market value for an alternative use.*

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CONSECINȚELE OMOLOGĂRII STUDIULUI DREPTURILOR DE PROPRIETATE ÎN PROCESUL DE EVALUARE IMOBILIARĂ

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Rezumat. Articolul se axează pe evaluarea proprietății. Este examinată valoarea, aspectele sale calitative și cantitative prin prisma statică și dinamică; esența valorii și factorii de impact, aspectele comportamentale în timp. Dezvoltarea evaluării în ultimii ani a subliniat două direcții: evaluarea financiară și economică centrată pe teoria evaluării și evaluarea investițiilor financiare, axată pe teoria evaluării. Evaluarea proprietății are loc prin interferența științelor economice, tehnice și juridice. În ultimii ani, practica internațională de evaluare și-a schimbat viziunea asupra subiectului evaluării; accentul a fost mutat de la "imobiliar" la "drepturi de proprietate". Valoarea bunului depinde în mod direct de drepturile de proprietate imobiliară, împreună cu sarcinile existente. În procesul de estimare a valorii, neglijarea studiului sau examinarea superficială a intereselor imobiliare are consecințe grave atât pentru proprietarul bunului cât și pentru utilizatorul raportului de evaluare, precum și, în mod direct, pentru valoare. In articol această situație este exemplificată folosind metoda studiului de caz.

Cuvinte cheie: *bunuri imobiliare, interese de proprietate, evaluarea drepturilor, valoare specială, valoarea de piață pentru utilizare alternativă*.

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CZU 004.42:699.8

APPLICATION OF MODERN SOFTWARE COMPLEXES FOR MODELING THE WORK OF DAMAGED STONE STRUCTURES

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Abstract. The article focuses on the estimation problem of the residual rolling capacity and the reliability of the stone structures elements of the buildings and structures in the historical part of the cities, which are approaching the normative term of service. To prevent the destruction of existing buildings and structures and to optimize solutions related to the reinforcement and reconstruction of damaged structures, information on their residual capacity is required. The paper proposes a method for assessing residual carrying capacity in the software complex. The analysis by applying the proposed algorithm (non-destructive method) allows a real prognosis, the difference between the calculation results and the experimental research of the stone structures being 5%.

Keywords: *reliability, reconstruction of stone structures, residual capacity, software modeling*.

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APLICAREA COMPLEXELOR MODERNE DE SOFTWARE PENTRU MODELAREA LUCRĂRILOR PE STRUCTURI DE PIATRĂ DETERIORATE

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Rezumat. Articolul se concentrează asupra problemei estimării capacității de rulare reziduale și a fiabilității elementelor structurilor de piatră ale clădirilor și structurilor din partea istorică a orașelor, care se apropie de termenul normativ de serviciu. Pentru a preveni distrugerea clădirilor și structurilor existente și pentru a optimiza soluțiile legate de consolidarea și reconstrucția structurilor deteriorate, sunt necesare informații privind capacitatea lor reziduală. Lucrarea propune o metodă de evaluare a capacității de rulare reziduale în complexul software. Analiza prin aplicarea algoritmului propus (metodă nedistructivă) permite o prognoză reală, diferența dintre rezultatele de calcul și cercetarea experimentală a structurilor de piatră fiind de doar 5%.

Cuvinte cheie: *fiabilitate, reconstrucția structurilor din piatră, capacitate reziduală, modelare software*.

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THE EVOLUTION OF FOOD PRODUCTS CONSUMPTION IN REPUBLIC OF MOLDOVA IN THE DEMOGRAPHIC TRANSITION PERIOD

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Abstract. Republic of Moldova has experienced economic changes in the past three decades. This has resulted in sustained increase in consumer income, which in turn has led to important changes in food consumption. This report examines the recent trends in Moldova's food consumption, with a focus on the period of 1990-2017. Data for Food intake recommendations of the World Health Organization (WHO) are used as a starting point to look into Moldova's likely future demand and possible import needs. The article analyzes the consumption of basic products by the population of Moldova from the point of view of ensuring the economic and physical accessibility of food, the trends in changes in the volume and structure of consumption are revealed; assessment of the degree of achievement of rational norms. To assess the quality of diets, their energy and nutritional values there have been investigated: the content of energy, proteins, including animal origin, fats and carbohydrates.

Keywords:*food consumption, production growth, nutrition, diet's quality, autochthon outlook.*

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EVOLUŢIA CONSUMULUI ALIMENTAR ÎN REPUBLICA MOLDOVA ÎN PERIOADA DE TRANZIŢIE DEMOGRAFICĂ

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Rezumat. Republica Moldova a cunoscut schimbări economice intense în ultimele trei decenii. Acest lucru a dus la o creștere continuă a veniturilor consumatorilor, ceea ce, la rândul său, a dus la schimbări importante în consumul de alimente. Acest raport analizează tendințele recente ale consumului alimentar în Republica Moldova, cu accent pe perioada anilor 1990-2017. Datele şi recomandările privind consumul alimentar ale Organizației pentru Alimentație și Agricultură (FAO) sunt utilizate ca punct de plecare pentru a examina cererea viitoare a Republicii Moldova în alimente și posibilele nevoi de import. Articolul analizează consumul de produse de bază de către populația Moldovei din punct de vedere al asigurării accesibilității economice și fizice a alimentelor, sunt evidențiate tendințele schimbării volumului și structurii consumului alimentar, evaluat gradul de satisfacere a normelor raționale. Pentru aprecierea calității alimentației, a valorii energetice și nutriționale au fost cercetate: aportul de energie, conținutul de proteine, inclusiv a celor animaliere, grăsimi și carbohidrați.

Cuvinte-cheie*: consum alimentar, creșterea producției, nutriție, calitatea alimentației, perspective autohtone*

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THE DETERMINATION OF OXIDATION BEHAVIOR OF WHITE WINES PRODUCED FROM LOCAL AND EUROPEAN GRAPE VARIETIES USING SPECTROPHOTOMETRIC METHOD

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Abstract: The article deals with the oxidation processes of experimental wines produced from indigenous grape varieties *Legenda*, *Viorica* and European grapes *Chardonnay*, *Sauvignon*. The browning processes in wine are corelated with oxidation of hydroxycinnamates (hydroxycinnamic acids and their tartaric esters, HCAs) – the most important group of phenolic compounds in white wines. The potential degree of wine colour changes have been appreciated using *Polyphenols Oxidative Medium test* (*POM-test*). The oxidative crocin bleaching (CBA – Crocin Bleaching Assay) has been studied using the method of competition kinetics. The comparative antioxidant capacity of wines has been determined with peroxy radicals 2,2'-Azobis (2-amidinopropane) dihydrochloride (AAPH).

Key words: *antioxidant capacity, crocin oxidative bleaching, flavonoids, hydroxycinnamates, phenolic compounds, POM-test, wine oxidation*.

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DETERMINAREA OXIDABILITĂȚII VINURILOR ALBE PRODUSE DIN SOIURI DE STRUGURI AUTOHTONE ȘI EUROPENE PRIN METODA SPECTROFOTOMETRICĂ

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Rezumat: În lucrare au fost examinate procesele de oxidare a vinurilor experimentale obținute din soiurile de struguri albe autohtone: Legenda, Viorica și soiuri de strugurii europene: Chardonnay, Sauvignon. Procesele de oxidare în vin sunt corelate cu oxidarea hidroxicinamatelor (acizii hidroxicarnic și a esterilor lor tartrici, HCA) - cel mai important grup de compuși fenolici din vinurile albe. Gradul potențial de modificare a culorii vinului a fost apreciat utilizând testul Polifenols Oxidative Medium (*POM-test*). Albirea oxidativă a crocinei (CBA - testul de albire a cristalelor) a fost analizată prin metoda cineticii concurențiale. Capacitatea antioxidantă comparativă a vinurilor a fost determinată cu radicali peroxidiclorhidrat de 2,2'-Azobis (2-amidinopropan) (AAPH).

Cuvinte cheie: *capacitate antioxidantă, albire oxidativă, crocină, flavonoide, hidroxicinamați, compuși fenolici, testul POM, oxidarea vinului*.

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IN VITRO BIOAVAILABILITY OF SUNFLOWER OIL FORTIFIED WITH IODINE

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Abstract. The use of iodized sunflower oil as an additive is an affordable and inexpensive method. In addition, iodine is a liposoluble element, which facilitates its incorporation into oil. But the incorporation of iodine in oil is a complex phenomenon, accompanied by a change in the physicochemical properties of the finished product, and therefore the evolution of the composition of triglycerides in iodinated oil has been investigated, depending on the amount of iodine administered. Free fatty acids (FFAs) are subjected to a different metabolic mechanism depending on the length of their chain (their molar mass). Thus, long chain fatty acids after re-esterification are deposited in the adipose tissue in the form of triglyceride-rich lipoproteins, while medium chain FFAs are usually oxidized in the liver. The structure of triglycerides (the distribution of fatty acids in the triglyceride molecule) can also influence the digestibility of this product. The purpose of the researches is to determine the influence of sunflower oil iodine on the digestibility of triglycerides and the evolution of the iodine content in the system during the enzymatic hydrolysis of the product. The kinetics of MGs, DGs and FFAs accumulation and the percentage of iodine recovered from the digestate were investigated during in vitro pancreatic digestion of iodinated sunflower oil.

Keywords: *iodine, triglycerides, oil, free fatty acids, pancreatic digestion in vitro.*

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BIODISPONIBILITATEA IN VITRO A ULEIULUI DE FLOAREA SOARELUI FORTIFICAT CU IOD

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Rezumat. Utilizarea uleiului de floarea-soarelui iodat ca aditiv reprezintă o metodă accesibilă şi necostisitoare. În plus, iodul este un element liposolubil, ceea ce facilitează încorporarea sa în ulei. Dar incorporarea iodului în ulei este un fenomen complex, însoţit de modificarea proprietăţilor fizico-chimice ale produsului finit, de aceea a fost cercetată evoluţia compoziţiei trigliceridelor din uleiul iodat, în funcţie de cantitatea de iod administrată. Acizii graşi liberi (AGL) sunt supuşi la un mecanism metabolic diferit în funcţie de lungimea catenei lor (de masa lor molară). Astfel, acizii graşi cu catenă lungă după reesterificare sunt depuşi în ţesutul adipos în formă de lipoproteine bogate în trigliceride, în timp ce AGL catenă medie sunt, de regulă, oxidaţi în ficat. Structura trigliceridelor (distribuţia AG în molecula de trigliceridă) poate, de asemenea influenţa digestibilitatea acestui produs. Scopul cercetărilor efectuate constă în stabilirea influenţei iodării uleiului de floarea soarelui asupra digestibilităţii trigliceridelor și evoluţia conţinutului de iod în sistem pe parcursul hidrolizei enzimatice a produsului. Cinetica acumulării MG, DG, AGL și procentul de iod recuperat în timpul digestiei pancreatice *in vitro* a uleiului de floarea soarelui au fost investigate.

Cuvinte chee: *iod, triglyceride, ulei, acizi grași liberi, digestie pancreatică in vitro.*

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ANTIMICROBIAL ACTIVITY OF ROSE HIP AND HAWTHORN POWDERS ON PATHOGENIC BACTERIA

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Abstract. In this present study, rose hip and hawthorn powders were investigated against three pathogenic bacteria strains: *Staphylococcus aureus*, *Escherichia coli* și *Klebsiella pneumoniae*. The chemical composition and antiradical activity of the plant extracts were investigated. The antiradical activity of the hydroalcoholic extracts of rose hip is 85.11 ± 0.02 and hawthorn - 80.27 ± 0.23% DPPH inhibited, which correlates with the high content of polyphenolic and flavonoid compounds. The content of β-carotene and lycopene in the liposoluble extracts of rose hip is 14.85 times and 28.83 times higher than in hawthorn extracts. The rose hip powders show an antimicrobial activity pronounced to *Staphylococcus aureus*. In the case of *Escherichia coli* and *Klebsiella pneumoniae* antimicrobial activity of hips is on average 1.3 times higher than that hawthorn powders. The rose hip powders showed the best inhibitory activity against *Staphylococcus aureus*, Gram-positive bacteria, followed by *Escherichia coli* and *Klebsiella pneumoniae* - Gram-negative bacteria. The investigated plant powders have shown promising antimicrobial potential against pathogenic microorganisms and can be used in the food industry to reduce the microbial contamination of raw materials and food.

Keywords: *rosehip, hawthorn, pathogenic bacteria, chemical composition, antimicrobial activity, food safety*.

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ACTIVITATEA ANTIMICROBIANĂ A PULBERILOR DE MĂCEȘ ȘI DE PĂDUCEL ASUPRA BACTERIILOR PATOGENE

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Rezumat. În lucrare au fost investigate pulberile de măceș și de păducel împotriva a trei tulpini de bacterii patogene: *Staphylococcus aureus*, *Escherichia coli* și *Klebsiella pneumoniae*. S-a investigat compoziția chimică și activitatea antiradicală a extractelor vegetale. Activitatea antiradicală a extractelor hidroalcoolice de măceș este de 85,11 ± 0,02 și de păducel - 80,27 ± 0,23% inhibat DPPH, care se corelează cu conținutul ridicat de compuși polifenolici și flavonoizi. Conținutul de ß-caroten și licopen în extractele liposolubile de măceș este de 14,85 ori și de 28,83 ori mai mare decât în extractele de păducel. Pulberile de măceș prezintă o activitate antimicrobiană pronunțată față de *Staphylococcus aureus*. În cazul *Escherichia coli* și *Klebsiella pneumoniae*, activitatea antimicrobiană a măcesului este în medie de 1,3 ori mai mare decât cea a pulberilor de păducel. Pulberile de măceș au prezentat cea mai bună activitate inhibitorie împotriva bacteriilor *Staphylococcus aureus,* fiind Gram-pozitive, urmate de bacteriile *Escherichia coli* și *Klebsiella pneumoniae* - Gram-negative. Pulberile vegetale investigate au arătat un potențial antimicrobian promițător împotriva microorganismelor patogene și pot fi utilizate în industria alimentară pentru a reduce contaminarea microbiană a materiilor prime și a alimentelor.

Cuvinte cheie: *măceș, păducel, bacterii patogene, compoziția chimică, activitatea antimicrobiană, siguranța alimentară.*

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THE FORMATION OF ANTI-CORROSIVE STRUCTURES AND THIN FILMS ON METAL SURFACES BY APPLYING EDM

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Abstract. The methods of formation anti-corrosive strata and thin films on metal surfaces by applying electric discharge machining (EDM) are presented in this chapter. It has been demonstrated the increase of anti-corrosion resistance of metal surfaces by the formation of palladium depositions, carbon films and oxide and hydroxide films. Corrosion and electrochemical behavior of titanium with palladium powder coatings were investigated in sulfuric acid solutions at temperatures of 80 and 100° C. In order to increase the diffusion of palladium in the base material and to increase the layer homogeneity, after coating, the samples were annealed in vacuum at 1150 °C for 1 hour. The proposed method allows to reduce the corrosion speed of titanium at least by 2 orders (from 18.7 down to 0.3 $g \cdot m^{-2} \cdot h^{-1}$), the corrosion potential is changed towards positive values (from -0.56 mV to +0.3 V). The research on surface electrical resistance and resistance to corrosion of oxide and hydroxide films formed on steel C45 surfaces by applying EDM have shown that the surface electrical resistance of the samples increased by 10^7 times, the potential of corrosion increased from -0.44 mV to +0.4 V, the resistance to corrosion has increased by about 2 times in 1% NaCl water solution, and by about 10 times in 30% H_2SO_4 water solution. The less pronounced increase of anti-corrosion properties is possessed by carbon films formed on the same steel C45 surface, instead they increase superficial microhardness, the functional durability and processing productivity of the active piece surfaces.

Keywords: *carbon, corrosion, electric discharge machining, microhardness, thin films*.

Introduction

Corrosion is a damaging process for the absolute majority of parts that work in active environments, from the chemical point of view, and becomes even more pronounced when they operate in energy fields of different types: of high temperatures, of light, of electrical action, etc. It consists in the destruction of metallic materials under the chemical or electrochemical action of the environment or the substances they come into contact with.

With the exception of noble metals, all other metals are unstable in contact with the atmospheric air and aggressive environments. The way this instability manifests itself, and the degree to which it occurs, depends on the nature of the metal and the environment in which it is placed.

Two types of corrosion can be highlighted considering the deployment mechanism: chemical corrosion [1] which refers to the processes of destruction of metals and alloys produced in dry gases, as well as, in liquids without electrical conductivity and in most organic substances, and electrochemical corrosion [1, 4-10] which causes processes of metal and alloy degradation in electrolyte solutions in the presence of humidity, accompanied by the flow of electric current through the metal.

In all cases, when talking about the functionality of the machines and apparatuses or the parts from which they are assembled and their durability, the process of component degradation of different constructions is a damaging one. Throughout the practical encountered corrosion problems, it is important to know the real speed the process is taking place. If the corrosion process is possible, but has a very low deployment speed, the material is considered corrosion resistant.

Taking into account that iron and its alloys are used in the contemporary construction of machinery and apparatus as basic materials, and, on the other hand, a material for present and future is considered to be titanium and its alloys, in the following, we will focus on the research of behaviour of these materials in different working environments.

In the case of iron, its corrosion takes place in stages by its oxidation in the atmosphere with the formation of iron oxides (rust).

During the first stage of iron oxidation, FeO is formed, ferrous oxide, which is stable only in the absence of oxygen. When atmospheric oxygen appears, iron oxide is converted into iron hydroxide ($Fe_2O_3 \cdot H_2O$) or FeO(OH), as of which 2 phases are known:

- Phase 1 that corresponds to a large excess of oxygen;
- Phase 2 characterized by an insufficient amount of oxygen, which is why oxidation evolves slowly.

Depending on their colour, there are three types of rust:

1. $Fe(OH)_2$ white rust, formed after the reaction:

$Fe+2H_2O \rightarrow Fe(OH)_2+H_2$

This type of rust quickly passes through oxidation to brown rust, which is why it is rarely seen.

2. Brown rust occurs as a result of the following reaction:

$4Fe(OH)_2+O_2 \rightarrow 4FeO(OH)+2H_2O$

3. The black rust is made of ferrous and ferric oxide; being also called magnetite because of its magnetic properties and it is considered to be the most stable form of iron oxide. It forms a protective layer on the surface of the metal, with a homogeneous and adherent structure. The reaction is as follows:

$2FeO(OH)+Fe(OH)_2 \rightarrow Fe_3O_4+2H_2O$.

Iron and its alloys are reacted with electrochemically active acids and salts of metals with the destruction of the workpiece surface in working environments:

$Fe+H_2SO_4 \rightarrow FeSO_4+H_2$

$Fe+2HCl \rightarrow FeCl_2+H_2$

$Fe+CuSO_4 \rightarrow FeSO_4+Cu$

$Fe+2NaCl \rightarrow FeCl_2+2Na$.

Titanium and its alloys are more resistant to corrosion, since, under normal conditions in the atmosphere, the TiO_2 oxide film is formed, which is stable in different environments, other than those alkaline, for instance:

$TiO_2+Na_2CO_3$ (K_2CO_3) $\rightarrow Na_2TiO_3$ (K_2TiO_3)$+CO_2$

Under certain conditions (high temperature, high concentration), titanium also reacts with some acids:

$Ti+H_2SO_4 \rightarrow TiSO_4+H_2$

$2Ti+3H_2SO_4 \rightarrow Ti_2(SO_4)_3+3H_2$

$Ti+8HNO_3 \rightarrow Ti(NO_3)_4+4NO_2+4H_2O$

$2Ti+6HCl \rightarrow 2TiCl_3+3H_2$

$2Ti+6HBr \rightarrow 2TiBr_3+3H_2$

$2Ti+6HI \rightarrow 2TiI_3+3H_2$, etc.

They destroy the base metal and cause further damage of the workpieces in those environments.

The methods and techniques of anticorrosive protection are various and numerous and they can be grouped into the following categories [2]:

- methods of preventing corrosion;
- use of metals and alloys resistant to corrosion;
- methods of influencing the corrosive medium [33, 34];
- methods of covering metal surfaces with protective layers [11, 19, 32];
- passivation of surfaces by depositing anticorrosive strata, etc.

The essence of preventing corrosion consists in [2]:

- choosing the correct option of materials used in building devices, industrial equipment from the point of view of resistance to corrosion;
- avoiding the contact of two metals, one of which is more electronegative than the other, e.g. aluminium and copper alloys or alloyed steel, bronze and steel, etc;
- avoiding the contact of cold-hardened metals with annealed or cast metals, for the reason that due to the difference of electrochemical potential between them, the last one corrodes in the presence of an electrolyte;
- choosing a more careful processing of the metal surface, since hollows and scratches favour and accelerate corrosion.

The group of metals and alloys resistant to corrosion contain noble metals in their alloys, but their use becomes difficult because of the high cost. Self-protective metals and alloys will be used instead. These are metals and alloys which, after an initial corrosion, are covered with an isolating pellicle or film as a result of the passivation phenomenon (e.g. the passivation of Ag in HCI by forming the AgCl film of Fe in HNO_3 concentrated through the formation of the $Fe(NO_3)_3$ pellicle, etc).

In most cases, metals are alloyed with an adequate component. Sometimes the relatively low concentration of the alloyed component considerably reduces the corrosion speed (e.g. the introduction of such elements as Cu, Cr or Ni of 0.2...0.3 % in steels, etc).

There are many cases when it is possible to influence the corrosive medium to lower the speed of corrosion. There are many possibilities.

The following can be mentioned [2]:

- modification of the pH, which means bringing it to a convenient value for the metal that is to be protected. This consists in the elimination from the medium of corrosion, by use of physical, chemical and mechanic methods (e.g. neutralization of waste water with chemical substances);

- removal of gases (O_2 and CO_2), which increase the speed of corrosion in corrosive media, particularly that of the water;

- use of inhibitory elements (organic or inorganic substances) [33, 34], which, being introduced in small quantities in the corrosive medium, lower or completely annihilate its corrosive capacity;

- cathode protection (electro-defence) means the use of galvanic methods of metal protection with the help of auxiliary metal anodes, which take over the corrosive capacity of the medium, thus protecting the material used for the workpiece.

The protection realized by applying anticorrosive layers [2, 11, 19, 32] means to cover the metal with a thin layer or self-protective material. The self-protective layer should meet the following requirements: it should be compact and adherent, it should be elastic and plastic enough, and its thickness should be uniform in addition to being as small as possible. The protective layer may be metallic or non-metallic. Metallic deposits may be realized through different methods: galvanic, thermal, through plating, laser radiation, bombarding with ions, alloying by means of electric discharge machining, etc. The formed surface layers, except those obtained through plating, usually present a certain porosity, which determines the appearance of local portions of corrosion with all the consequences. Non-metallic protective layers may be organic or inorganic, realized with the help of varnish, paints, enamels or plastic thin sheets.

The formation of inorganic thin films or pellicles (oxide or graphite) on the workpiece surface is a progressive method of anticorrosive protection of superficial layers. The oxide or the graphite, being much more passive than the proper metal, and, in the interaction with the work media lowers the corrosive potential of the whole piece. The key problem that should be solved is the one that deals with the formation of structurally stable deposits with a high mechanic and electric resistance, having a uniform continuity and thickness on the whole surface.

The choice of the method to be used for the production of the protective layer depends on [2]:

- the conditions and working surroundings of the piece;
- the shape and the dimensions of the protective item;
- the quality of the supportive material or of the protected item;
- the functional technological parameters of the device;
- the way the item to be protected is placed in the device;
- the technologies of application and executive possibilities for anticorrosive protection.

Methodology of experimental investigations

Experimental setup

The experimental setup for the formation of anticorrosive coatings on the metal surfaces of the parts by applying pulsed electric discharge machining (PEDM) comprises the following electric blocks: the power pulse generator, the priming block (intended for initiating the electrical discharge) and the control block, the role of which is to synchronize the power and the priming discharge pulses.

As a result of the specialty bibliographic analysis [11-19], it was concluded that, for the formation of these layers, RC-type generators, with parallel priming, can be successfully used. The deposition of layers of metallic powders with the use of electric fields is produced as a result of interaction of the powder particles with the plasma jet and the transport of the liquid and vapour phase on the surface of the piece-cathode [11, 19]. The powder particles,

having the dimensions of (20...200) μm, are inserted in the (0.3...1.5) mm gap at a capacitor voltage of Uc=(80...400) V.

Methodology of anticorrosive coatings formation

Research on the interactions of the plasma channel of PEDM with the surfaces of the electrodes have shown that for the phenomenon of electroerosion two types of effects are characteristic: type I - the appearance of the "cold" electrode spots on the electrode surfaces, which give rise to the asperities and impurities on their surface [11, 19] and cause both, the cleaning of the surfaces of impurities and their thermal interaction, producing structural changes in the superficial layers of small thicknesses (just about the size of micro- and Nano-meters); type II - on the electrode surfaces, after the "cold" electrode spots, the "warm" ones cause the essential melting of the electrode, accompanied by the vaporization phenomena and the dropping of the electrode material [19]. If type II interaction of the plasma channel with electrodes surfaces has found a rather wide application in dimensional processing [22-27] and the deposition layer formation (both of the compact materials [18] and the powders [11, 19]), then type I actions are described in the literature only as scientific findings, and for this reason, it is necessary to elucidate the conditions and the effects of surface thermal treatment and to reveal whether this type of interaction is purely thermal or is a thermo-chemical one.

Analyzing the results obtained by the author of the paper [19], it was established that, in order to obtain a type I interaction with the plasma channel (in the absence of surface melting) or type II interaction (when the liquid phase is attested) on the surfaces of the workpieces, it is necessary that the energy density emitted on the processed surface to be lower or higher than the specific heat of melting of the material, and the later can be appreciated by the relation [3, 13, 19]:

$$\frac{4W}{\pi d_c^2 \cdot S} < Q < \frac{4W}{\pi d_c^2 \cdot S}, \tag{1}$$

$$Q = q\rho$$

where q and ρ are the specific heat of melting and the density of the workpiece material respectively; W is the energy emitted in the gap, d_c is the diameter of the plasma channel and S is the gap value.

As it can be seen from the relation (1), at the time of the energetic processing regime, the size of the gap and the thermo-physical properties of the workpiece material are known, the diameter of the plasma channel can be determined, which coincides with the size of its trace on the processed surface. If a coefficient of overlapping of the traces (of type I or type II) k=0,5…1,0 and the frequency of the electrical impulses f are known, the productivity of the technological process can be determined by the relation:

$$\eta = \frac{k\pi d_c^2 f}{4} \tag{2}$$

In the paper [19], it has been demonstrated that when PEDM is applied for superficial processing, the erosion processes take place, accompanied by explosive melting and vaporization of the electrode material for the vast majority of studied metals and alloys, for

the current pulse duration contained in the limits 10^{-4}...10^{-9} s. It results that, in order to obtain the expected effects, it is necessary to provide a relatively low duration pulses of discharge.

Effects on electrode surfaces are a function depending on the way of the workpiece connection in the discharge circuit (as anode or as cathode) [13, 18, 19]. These desiderata have been studied in [19] and it has been established that for short-term discharge pulses they are "cathodic" and for the long-term ones they are "anodic", thus, in the case of superficial thermal treatments and deposition of materials, the workpiece will be included in the discharge circuit as cathode. In the case of thermal treatment of steel surfaces, their hardness increases by 2...3 times, and for titanium surfaces by 2...5 times, for the formed layers thicknesses from a few micrometres to several dozens of micrometres. The depth of these layers reaches a maximum at three passes of technological cycle for steels and at five passes for titanium and its alloys.

The interaction of the plasma channel with the surface of the electrode-workpiece is not always purely thermal, nonetheless the surface of the piece is often enriched with elements contained in the environment and with the contents of the tool-anode material. The penetration depth [19] of these elements in the superficial layer of the piece is a function of both the energy of the discharge pulse and the size of the gap, and can be expressed with the relation:

$$h = \frac{kW_S}{AS} \tag{3}$$

where $W_S = \int_o^\tau U(t)I(t)dt$ is the energy emitted in the gap during a singular discharge; *U* and *I* is the voltage and the current in the gap, respectively; τ is the pulse duration; *A* is the area of the workpiece surface processed at a singular discharge; *k* is a constant that depends on the thermo-physical properties of the workpiece material.

Technology of powder deposition formation

From the results of the experimental researches carried out by the authors [11, 19] it has been demonstrated that, in order to obtain the powder depositions, it is necessary to introduce the powder in the anode zone of the gap. From a technological point of view, a parameter that needs to be predicted is the thickness of the deposition layer. This parameter is quite important, because in some cases it is determinant in the technological application of the method. Analyzing the experimental results of the authors of this chapter and those of the works [15, 16, 19-21], in the case of the deposition layers of different materials, the following relationship was deduced for the deposition thickness:

$$H = \frac{P^c \cdot f^d \cdot W^k (a - bS^2) \cdot r^m}{\rho \cdot A} \cdot n \tag{4}$$

where *P* is the powder flow; *f* is the frequency of impulse discharges; *r* is the equivalent radius of powder particles; *W* is the energy released in the gap; *S* is the size of the gap; ρ is the density of the particles' material; *A* is the area of the processed surface; *n* is the number of passes of the tool-electrode on the workpiece surface; *a, b* are individual constants of the deposition materials; *c, d, k, m* are the power exponents that are experimentally established

and constitute the both functions, of the properties of the powder material and of the processing conditions.

Taking into account the experimental results obtained by the authors of the papers [18, 19] for the determination of the thickness of the deposition layer, the relation (2.4) can be written as:

$$H = \frac{\Delta m}{\rho \cdot A} \cdot n \tag{5}$$

Where $$\Delta m = P^c \cdot f^d \cdot W^k (a - bS^2) r^m \tag{6}$$

The uniformity of deposition of the layer is characterized by the thickness of the deposited layer (or by the dimension Δm on each surface unit). If the processing time is different during the manual processing on different surface portions, the surface is not continuous; the mechanization of the process ensures the formation of uniform deposition on the entire surface of the workpiece.

The compactness of the layers and the existence of recesses or asperities are visually appreciated or measured using the microscope analysis method.

Technology of oxide films formation

In order to achieve the experimental researches, the pulse current generator with priming from a high voltage block with 12 kV voltage and 0.3 μA current was used, the laboratory installation which ensures the positioning, fixing and rotation of the samples during the processing with an adjustable rotation frequency ranging from 0 to 150 rpm [3]. The used tool-electrode was made in the form of cylindrical bar, rounded at the working end in the shape of a hemisphere and made of stainless steel. The cathode piece was a cylindrical bar 13 mm in diameter. The piece was firmly fixed to the tool-machine frame and the tool-electrode into the tool-port. The workpiece was connected to the pulse generator as cathode, and the tool-electrode as anode, their axes forming an angle of 90°. In the case of flat surface processing, both, the piece and the tool-electrode were made in the form of cylinders with a diameter of 10 mm, they were firmly fixed to the tool-machine port with parallel active surfaces and the electric discharge scanning the workpiece surface by migration of the plasma channel on these surfaces at a processing cycle. As the material for the pairs of electrodes (workpiece/tool-electrode) were chosen: aluminum alloy AlCu4Mg1; steel C45; titanium alloy TiAl6Mo4, and copper alloys.

Technology of graphite deposition formation

Experimental research on graphite deposits was carried out under normal conditions in the air environment, under sub-excitation regime of PEDM. For the purpose of realizing the experiments, the power supply having the following parameters was used: the energy released in the gap W_S=0÷4.8 J, the energy accumulated on the capacitor battery W_c=0÷12 J, the voltage on the capacitor battery U_c=0÷200 V, the capacity C=100÷600 μF with step of 100 μF, the gap value S=0.05÷2.5 mm; discharge frequency f=0÷50 Hz, impulse duration τ=0÷250 μs. Due to these parameters, we can provide the PEDM operation under the regime of "hot" electrode spots (with the melting of the processed surfaces) and under the regime of the "cold" electrode spots (without melting the surfaces undergoing processing, although at Nano-meter scale it occurs).

Between the two electrodes - a graphite cathode and an anode made of the metal specimen, micro-electric discharge is applied. The micro-electric arc that is produced for a very short period of time - microseconds - has a very high temperature of about 10^4 °C. At this temperature the graphite erodes (in the form of separated carbon atoms or chemical compounds of the type CO and CO_2 which further decompose into carbon and oxygen, the first being ionized, is deposited in the form of film on the metal surface and the oxygen is released in the plasma [3]) and due to the fact that it is in an electric field, the graphite particles in the vapour state are transported to the opposite sign electrode (anode) made up of the metal specimen. Thus, on the metal surface of the anode, a graphite layer of the micrometer dimension is deposited.

Methodology for determining the corrosion potential and speed of the samples

In order to measure the potential and the speed of corrosion, a set-up was developed, the scheme of which is shown in Figure 1. In a vessel 1 with electrolyte 2 (3% NaCl water solution for samples made of construction steels and 40% H_2SO_4 water solution for titanium, copper and aluminium alloys samples), the sample and the cathode 6 are fixed. Cathode joins at the "-" pole, and the sample at the "+" pole of the DC source with smooth voltage regulation. A milliammeter is connected in serial with the source and a voltmeter, in parallel respectively. To measure the corrosion potential of the superficial oxide layer 4, the base metal 3 is placed in a rubber gasket 5 having a hole 7 so that only the oxidized surface of the sample is in contact with the electrolyte. The voltage is gradually increasing until the current appears which will be indicated by the voltmeter - the value of the corrosion potential, and the milliammeter - the corrosion current. In order to increase the measurement precision, several measurements are made for different parts of the sample surface. In order to perform the chemical corrosion resistance tests of the processed samples (with PEDM-coated oxide films on the active surface), electrolytes from distilled water and chemical agents with the respective concentration at room temperature were prepared or, in separate cases, the device was continuously fed with an electrolyte of a certain temperature via a thermostat.

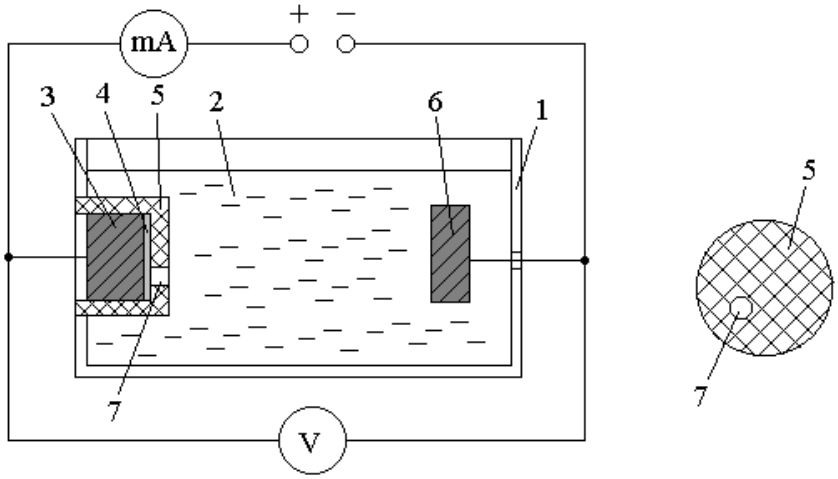

Figure 1. Potential and speed of corrosion measurement scheme: 1 – vessel; 2 – electrolyte; 3 – sample connected as anode; 4 – oxide layer; 5 – rubber gasket; 6 – cathode; 7 – hole for contacting the oxidized surface with the electrolyte in the water solution.

The samples were firmly fixed in the prepared device (Fig. 2) so that only a circle-shaped part of the processed surface was subjected to dissolution. This was included in the anode dissolution circuit as anode. The tests were carried out in the operating mode of the experimental DC installation and the 0.1 V step-by-step voltage change [3].

The corrosion speed is determined by weighing the samples before and after the test at the analytical electronic balance KERN ABS-N ABJ-NM with the accuracy of 10^{-5} g.

The corrosion speed index is determined with the relation [3]:

$$K = \frac{\Delta m}{S \cdot t} \tag{10}$$

where K is the speed of corrosion (mass indicator), $g \cdot m^{-2} \cdot h^{-1}$; S is the area of the workpiece surface, m^2; t is the test duration (work time), h; Δm is the mass lost (or the mass addition), g:

$$\Delta m = m_i - m_f \tag{11}$$

where m_i is the initial mass of the sample, g; m_f is the final mass of the sample, g.

Results

Determination of corrosion resistance of titanium and its alloys with deposited layers of metallic powder

In the process of deposition with electrodes made of compact materials by PEDM method, it is difficult to form layers with a full continuity, constant thickness, without pores, without impurities, etc., important elements for obtaining corrosion-resistant layers. The depositions obtained by the authors of the papers [13, 19-21] have shown good results in their corrosion resistance. When depositing metal powders, it is possible to form layers with highest thickness, but the problem of porosity remains unresolved.

Up to now, detailed research has been carried out on the corrosion resistance of titanium samples on which palladium (Pd), ruthenium (Ru) and nickel (Ni) depositions have been formed [20, 21]. The modification of the superficial titanium chemical composition with these metals was performed in order to obtain anodes on the base of titanium resistant to corrosion. The obtained results [20, 21] indicate that deposits formed by this method increase the corrosion resistance of titanium by about 5 times.

The corrosion and the electrochemical behaviour of titanium, with layers formed with the use of metal powders, were investigated by the authors [21] for the application of the 10% H_2SO_4 solution in distilled water at temperatures of 80 and 100 °C respectively. After the formation of the layers, some of the samples were subjected to annealing in vacuum at 1150 °C for 1 hour for the purpose of palladium diffusion in the sample material. The corrosion and the electrochemical tests for the annealed samples were carried out in 10% H_2SO_4 solution in distilled water at 80 and 100 °C and in 20, 30, 40% H_2SO_4 solution in distilled water at 100 °C. The palladium content was determined in the solution by the photo-calorimetric method. In the annealed samples, the palladium content was 5.6 $mg \cdot cm^{-2}$.

The corrosion speed of titanium with powder depositions in 10% H_2SO_4 solution in distilled water at 80 °C was 0.2 $g \cdot m^{-2} \cdot h^{-1}$), and at 100 °C the first 5 hours of testing was 0.78 $g \cdot m^{-2} \cdot h^{-1}$, and then, during the tests, the speed decreased and, in 50 hours of testing, has dropped to 0.3 $g \cdot m^{-2} \cdot h^{-1}$. This situation of diminishing the corrosion speed can be caused by the dissolution of the unstable phases in the first hours. The corrosion potential, under these conditions, is situated within the passivity limits and equals to +400 mV in 10% H_2SO_4

solutions at 80 °C (relative to the standard hydrogen electrode) and at 100 °C – equals to +300 mV compared to the titanium samples, without protecting depositions in the 10% H_2SO_4 solution in distilled water, which actively dissolves at potential of -0.56 mV with the speed of 18.72 $g \cdot m^{-2} \cdot h^{-1}$. Thus, we can state that, in the case of deposits application, the corrosion speed decreases up to 100 times.

After annealing, the corrosion speed has become even smaller.

For 10% H_2SO_4 solution in water at 80 °C, this was 0.056 $g \cdot m^{-2} \cdot h^{-1}$ and at 100 °C the corrosion process was completely absent.

With increasing the solution concentration to 20, 30 and 40% H_2SO_4, respectively, in water, the corrosion rate at 100 °C increased accordingly to: 0.5, 0.9 and 1.8 $g \cdot m^{-2} \cdot h^{-1}$. The corrosion potentials, under these conditions, is situated within the passivity limits and is equal to 10% H_2SO_4 solution in water at 80 °C and 100 °C after 5 hours of testing to +700 mV, in addition, corresponding to solutions containing 20, 30 and 40% H_2SO_4 in water, it ranged from +335 to +400 mV (Figure 2). For comparison, it can be mentioned that the corrosion speed of Pd layers in 10% H_2SO_4 solution in water at 100 °C, depending on the specific processing time and regime, varies from 0.1 to 0.8 $g \cdot m^{-2} \cdot h^{-1}$. With increasing acid concentration in water, the speed increases for 40% H_2SO_4 solution at 100 °C for different samples, ranging from 0.85 to 2.5 $g \cdot m^{-2} \cdot h^{-1}$.

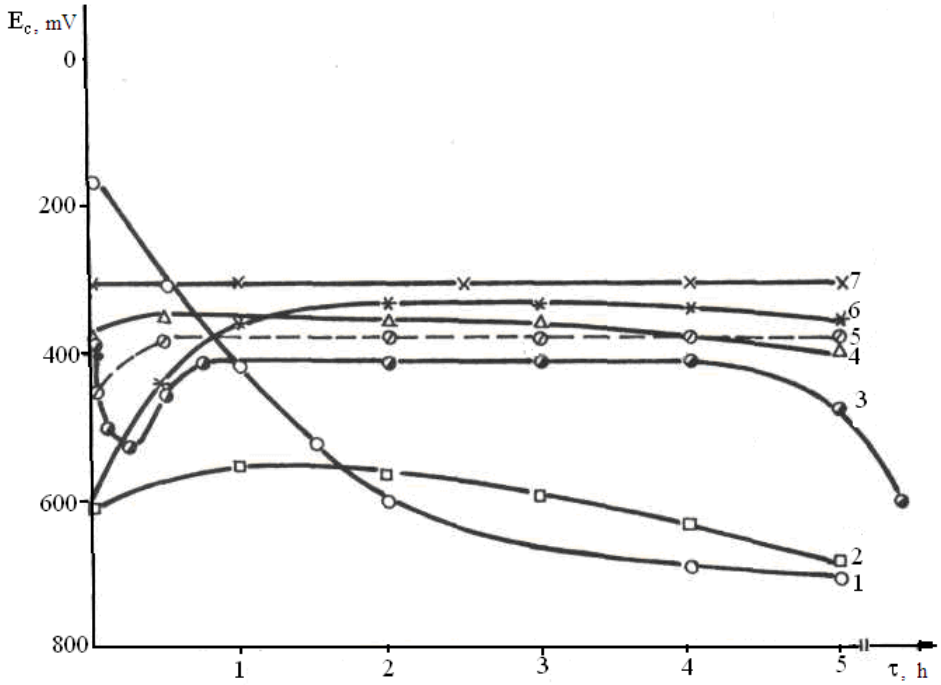

Figure 2. Changing in time the corrosion potential of palladium deposited samples (without annealing and after annealing) in water solutions of 10; 20; 30 and 40% H_2SO_4 at 80 °C and at 100 °C: 1 – 10% H_2SO_4, 80 °C without annealing; 2 – 10% H_2SO_4, 100 °C, with annealing, 3 – 10% H_2SO_4, 80 °C, without annealing; 4 – 40% H_2SO_4, 100 °C, with annealing;
5 – 30% H_2SO_4, 100 °C, with annealing; 6 – 20% H_2SO_4, 100 °C, with annealing;
7 – 10% H_2SO_4, 80 °C, without annealing.

The research made by authors, in order to determine the corrosion resistance of titanium and its alloys with the deposited metallic powders, has shown that their corrosion speed can be reduced by 100 times in water solution containing 10-40% H_2SO_4 at the temperature of 100 °C, and, in the case of additional subjecting, the annealing process and

the corrosion speed can be reduced by more than 100 times, with the intention of homogenizing the structure of the layer and developing the diffusion processes of the elements deposited in the material of the piece.

These layers allow to increase the corrosion potential up to +400 mV in 10% H_2SO_4 solution at 80 °C and up to +300 mV at 100 °C, while the titanium, in the absence of protective depositions, dissolves very actively at the potential of -0.56 mV.

Finally, we can conclude that the deposition of anticorrosive coatings on the surfaces of titanium and its alloys pieces can be applied in the construction of machines, ensuring a considerable duration of their functionality in aggressive environments.

The results of research on the corrosion properties of oxide films

In the researches carried out by the authors, the results of the experimental measurement of active electrical surface resistance for the samples made of C45 steel, processed by applying PEDM, under atmospheric conditions, at room temperature, are presented both for the surface of the anode electrode samples and for the surface of cathode workpiece (Table 1).

Table 1

Electrical surface resistance of oxide films for steel C45 samples

Sample	Electrical surface resistance, $\times 10^6$ Ω·mm^{-2}				
	Experimental data				Average value
Cathode	0.88	0.72	1.46	0.71	0.98
	0.97	1.52	0.68	0.72	
	0.73	1.09	0.76	0.83	
	1.33	1.10	1.04	0.73	
	1.07	0.88	1.21	0.78	
Anode	0.81	0.26	0.46	0.31	0.33
	0.11	0.14	0.56	0.34	
	0.29	0.11	0.62	0.38	
	0.87	0.38	0.11	0.15	
	0.12	0.13	0.27	0.17	

The electrical surface resistance of the unprocessed samples by PEDM plasma ranges from 0.05÷0.09 Ω·mm^{-2}. From the analysis of the experimental results presented in Table 1, we can state that, in all cases, there is a substantial increase in the surface of active resistance of the electrodes (both of anode and cathode) that participated in the PEDM process, but the active surface resistance of the anode-electrode sample is about 3 times smaller than that of the cathode-workpiece sample.

The last finding can be explained by the fact that at the surface of the anode, under the same conditions, a higher amount of energy is released and possibly more intense vaporization processes take place and, on the other hand, the oxygen ions are predominantly directed by the forces of the electric field from the gap to the cathode surface, which is why the intensity of the oxide film formation is less intense on the anode surface.

Further (Table 2), the measurements of the surface electrical resistance of the superficial layer for cathode samples made from titanium, aluminium and copper alloys were made.

Table 2

Electrical surface resistance of oxide films formed on the workpiece-cathode surfaces

Processed sample material	Average value of surface resistance, $\times 10^6$ $\Omega \cdot mm^{-2}$
Titanium alloy BT8 (TiAl6Mo4)	1.6
Duralumin Д16 (AlCu4Mg1)	0.25
Technically pure copper M0	0.15
Bronze БрА5 (Cu95Al5)	0.17
Brass Л63 (Cu63Zn37)	0.19

As can be seen from the results presented in Tables 1 and Table 2, the electrical surface resistance is a function of the material of the investigated samples and has higher values for the materials with increased oxygen avidity.

If we analyze the obtained results, we can see that, for the case of processed samples made of C45 steel, the corrosion speed in 3% NaCl water solution, at the applied voltage of 2 V, is, practically in all cases, twice lower than for the unprocessed samples by oxidation. The speed of corrosion of titanium samples with oxide films in 30% H_2SO_4 water solution at 80 ºC decreases by about 100 times comparatively with the unprocessed titanium surfaces.

If it is taken into account that the potential for natural corrosion is tens and hundreds of times less than in the case of the tests carried out, then the effectiveness of the application of oxides and hydroxides, in the amorphous state, will increase more significantly. Finally, we can admit that the application of amorphous oxides and hydroxides to metal surfaces by PEDM is beneficial for increasing their active corrosion resistance.

The corrosion resistance of the graphite film

When samples are placed in electrolyte, in the absence of external electric current, a stationary potential is established. In the case when both electrodes are made from the same type of steel, the stationary potential is almost zero and, in the case when the anode is covered with graphite, the stationary potential is 0.1 V. It is observed that, for the steel sample, with the increasing potential, an increase in current intensity occurs as well, up to the value of 2 V, followed by an area where a decrease of intensity occurs up to the value of 2.9 V. This effect may be due to the oxidation and hydroxylation chemical reactions that lead to the steel surface passivation, in the absence of the graphite film. After this value with increasing the potential difference the corrosion current decreases and the corrosion process takes place at low speed, i.e. passive film emerges, which does not allow anodic dissolution. The passive state is maintained until the potential of 2.8 V, then the current intensity increases considerably, accelerating the corrosion process.

From the analysis results, related to corrosion speed variation, depending on the duration of samples exposure in aggressive environment, we can outline essentially higher corrosion rates for the initiation stage of corrosive process, in the case of unprocessed Steel 45 without a graphite pellicle. Afterwards, with the passing of time, the process of corrosion is attenuated; the determined corrosion rate is smaller, when the time of immersion is longer. Similarly, with the passing of time, the nature of the corrosion product is modified, oxides are most likely formed, having a low oxygen content and being more stable (Fe_3O_4) ($FeO \cdot Fe_2O_3$).

In the case of steel coated with graphite film, lower corrosion rates are found;

afterwards, they begin to rise due to degradation of graphite film, as a result of its destruction.

It was experimentally established that in acid solution of 30% HNO_3, after 3 minutes, the amount of uncovered graphite steel electrochemically dissolved 1.4 times greater than graphite-coated steel - 1.3 times greater in 10 minutes. In salt solution of 1% NaCl, the amount of uncovered graphite steel electrochemically dissolved was 1.2-1.4 times greater than graphite-coated steel deposited by PEDM.

Instead of the less pronounced increase of anti-corrosion properties comparatively with the surface with oxide and hydroxide films, the graphite films formed on the same steel C45 surface increases the superficial microhardness, the functional durability and the processing productivity of the active piece surfaces.

Conclusions

Analyzing the results of the experimental researches, we can conclude the following:

- the thermal treatment, in the absence of liquid phase formation on the processed surface, can be performed only in the regime of maintenance of the electrical discharge in impulse on "cold" electrode spots;

- under superficial processing conditions, with the maintenance of electric spell released on "cold" electrode spots, the mass transfer in the solid phase can reach depths dozens of μm diameters, which will allow the working surfaces of the parts and cutting tools of the layers with prescribed physic-mechanical properties that will provide them with high performance features;

- the thermal and chemical-thermal processes that result in the surface layers of the parts under the action of the plasma channel of the electrical discharges in impulse cause not only the modification of their chemical composition, but also the modification of their physical and mechanical properties;

- the oxide films, formed as a result of the interaction with PEDM plasma, increase the resistance by 10^6-10^7 times, which, in turn, influences the corrosion resistance.

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THERMAL DEFORMATION WAVES IN HETEROGENEOUS MATERIALS

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Abstract. In the paper, a stress-strain detection method is used by correlation point interferometry, in which the resolution of the recording surface changes has been significantly (ten times) improved. This result was obtained by applying a different image-processing algorithm, which allows the recording of 3D surface changes in on-line mode. The deformation wave that occurs during heating propagates through the entire sample and interacts with the interfaces. The inhomogeneity and residual deformations of a material lead to a distortion of the front. The speckle electron interferometry (ESI) method allows the recording of this thermal deformation wave front and the estimation of the stress state of the studied material.

Keywords: *heterogeneous materials, stress strain, thermal deformation wave, speckle electron interferometry (ESI).*

Introduction

In earlier works [6-8], a method for studying the stress-strain state using correlation speckle interferometry was proposed. Recently, this method has been significantly improved by us, namely, the resolution of recording surface changes (about 10 nm) has been increased tenfold and the possibility of observing 3D surface changes in on-line mode has been implemented. Due to the use of a different image processing algorithm, this method should be called the method of electronic speckle interferometry (ESI) since here the measurement of movements on the surface is due to the measurement of the intensity of speckles, and not due to their correlation analysis as it was before [9]. The increase in the destructive ability of the ESI method allows us to reveal a number of new features of the deformation of stress-strain materials at a smaller scale level.

1. Hypothesis

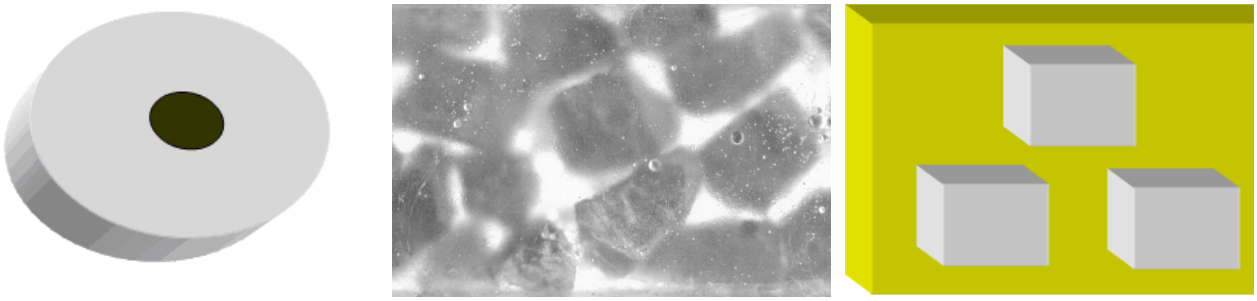
In works [1-5] it was assumed that when heterogeneous or defective materials are heated, inhomogeneous deformation occurs due to the distribution of areas with different coefficients of linear thermal expansion (CLTE). According to local inhomogeneity's of deformation during heating, structural heterogeneity in the material can be detected. In principle, this assumption is valid for a relatively high temperature and the stationary process. However, according to new data, the presence of areas with positive and negative CTE with

a small temperature increment ($\Delta T \approx 1^0 C$) requires a non-trivial explanation. The presence of deformation at the edges of the sample, which are not heated under small local temperature perturbations, requires an explanation.

In this paper, it is hypothesized that a deformation wave arises during heating, which is ahead of the temperature increase and propagates through the entire sample. The result of the interaction of a deformation wave with interfaces, inhomogeneity's, and residual deformations of a material leads to a distortion of its front. The ESI method makes it possible to register this front of a thermal deformation wave and estimate the stress-strain state of the material under study.

2. The methodology of the experiment

Samples of cement and epoxy resin-coated steel cylinders of rice were investigated. 1a, epoxy poured on clay expanded clay Figure 1b, epoxy poured on epoxy resin cubes Figure



a) *b)* *c)*

Figure 1. The investigated samples: a - steel cylinders filled in with cement and epoxy resin; b - clay filled with epoxy resin; c - epoxy poured dices of the eraser.

1b, marble aggregate poured with concrete.

Sample sizes 50 × 50 × 10 mm.

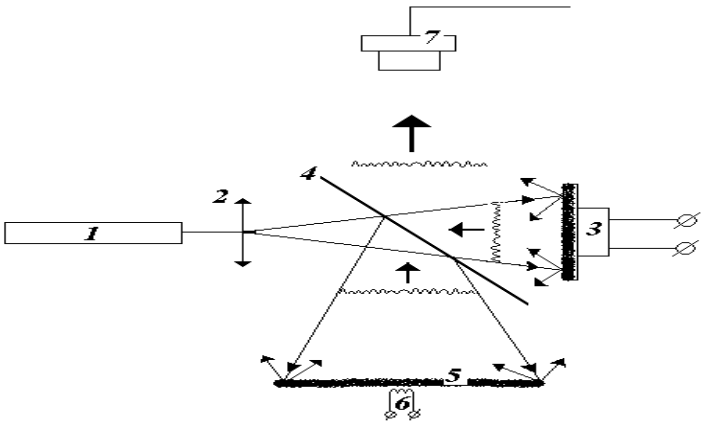


Figure 2. Scheme of the speckle interferometer.

1 - Helium neon laser, 2 - beam expander, 3 - diffuse scatterer mounted on piezoceramics, 4 - translucent mirror, 5 - sample, 6 - heater (tungsten helix 10 × 5 mm), 7 - camera.

The studies were conducted using a speckle interferometer, the circuit of which is shown in Figure 2.

Samples 5 in the center were heated by a heater 6 with a power of 2W until the surface temperature changed by 50°C. The temperature was controlled by a thermocouple with an accuracy of 0.5°C. With an interval of 5s, a change in the strain field of Figure 3 was recorded.

3. Discussion about the results of the experiment

The argument of the existence of a thermal deformation wave is the fact that the deformation of the surface of a bulk sample (thickness about 10 mm) begins literally from the first seconds after connecting the heater, when no change in temperature on the surface is observed. This can be explained by the fact that the expansion of a small volume that is in contact with a heater, caused by heating, is transmitted to the entire sample ahead of the heat wave up to its borders. The intensity of the transmitted strain essentially depends on the structural features and the stress state of the material under study. In fig. Figure 4 shows the deformation profile of clay filled with epoxy resin (Figure 1b).

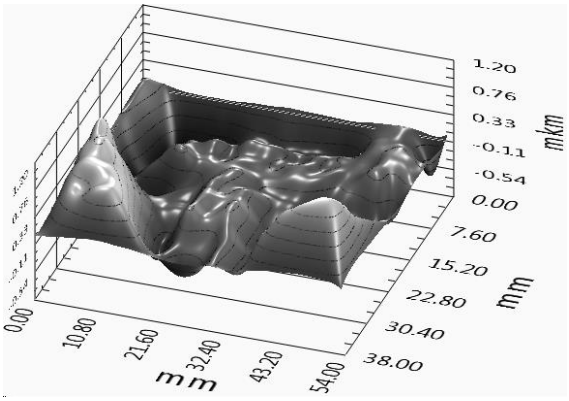


Figure 3. Deformation of a composite of erase cubes filled with epoxy resin (Fig. 1c) when heated in the center at 50°C.

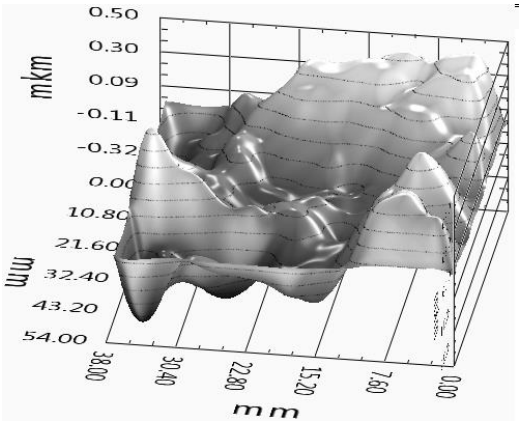
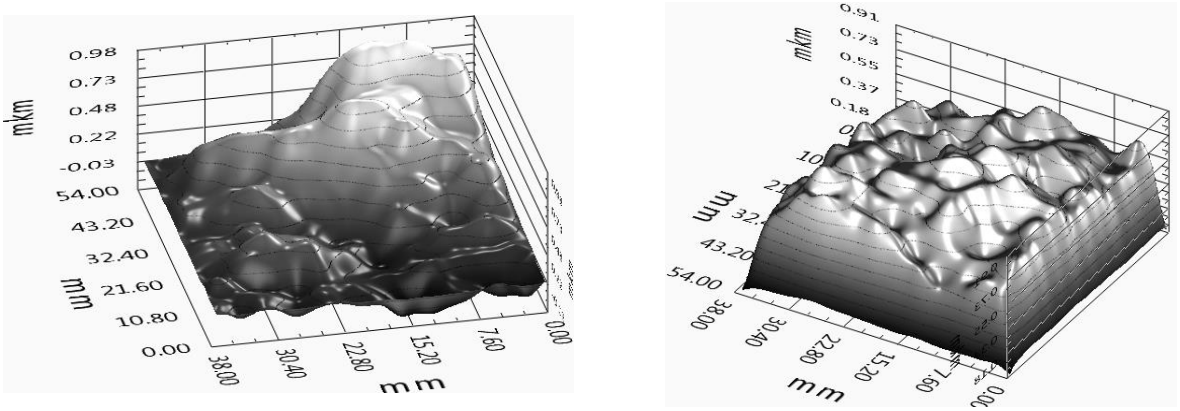


Figure 4. Deformation profile of epoxy poured clay.

It is obvious that the deformation profile of the sample (Figure 4) characterizes its structural inhomogeneity. An interesting fact is that the sample has alternating deformations that are most intense at the edges where the temperature has not changed much. The most interesting is the case of deformation of a concrete sample with small marble chips (Figure 5).

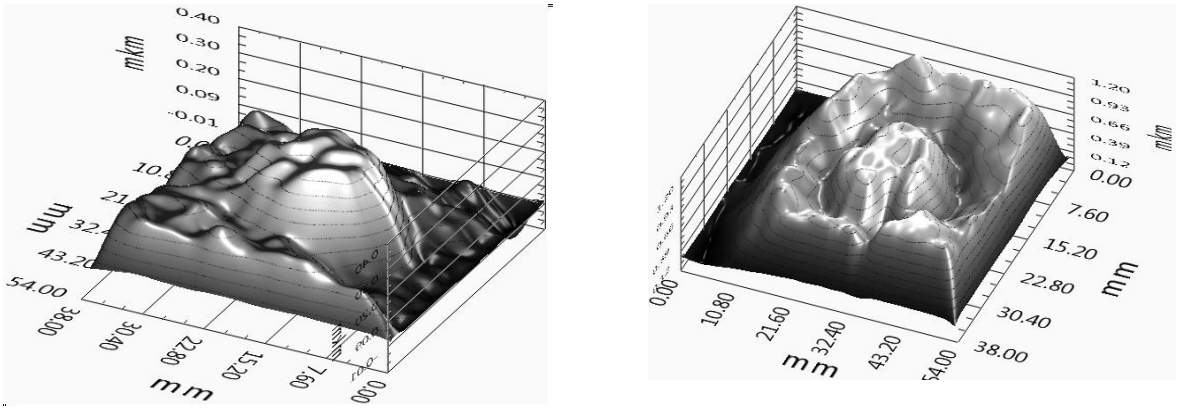


a) *b)*

Figure 5. Profiles of deformation of a concrete sample with small marble chips: a - initial sample; b - the same sample subjected to shock loads.

Comparing the concrete samples before the shock load and after (Figure 5a, Figure 5b), one can notice that under the same conditions, the deformation of the latter occurs more evenly. This is due to the fact that shock loads stimulated the formation of microcracks and

the relaxation of internal residual deformations (stresses). The conduct of a turn well demonstrated in Figure 6.



a) *b)*

Figure 6. Deformation profile of the composite filled with a - cement, b - epoxy resin of a metal cylinder (Figure 1a).

In figure 6a, the absence of matrix material in the right part is clearly visible. This indicates that in this part there is no adhesion between the metal and cement, and, accordingly, the general line of normal deformation is interrupted. A different picture is observed in figure 6b, where with good adhesion of metal with epoxy resin, but because of the differences in CLTE, the matrix material is squeezed out. In figure 3 shows the opposite pattern, when the matrix (epoxy resin), on the contrary, squeezes out less hard inclusions (eraser).

4. Conclusion

The use of the ESI method in the qualitative analysis of the stress-strain state of heterogeneous structures allows us to confidently turn to real materials that are beyond the limits of the applicability of the photoelasticity method. The question of quantitative analysis remains open. As shown in this paper, a series of cross-effects occur on a small scale level that require rethinking.

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ALGORITHM OF PROCESSING MICROSPIRAL CT-SCAN RESULTS FOR CONSTRUCTING A THREE-DIMENSIONAL MODEL OF ORBIT THIN BONES

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Abstract. We developed the algorithm for preparation of DICOM images for the construction of a three-dimensional model of the bones of the facial skull. The DICOM image-processing algorithm reduced the data loss level about the thin bones of the orbit during building a three-dimensional model of the bones of the facial skull from 22–31% to 3–5%. The developed software automatically changes the color of the pixels of the thin bones of the orbit from gray to white. Thin bones of the orbit were expanded over one pixel using the DICOM image-processing algorithm. The analysis of the image processing results by the developed software was carried out using 3D Slicer software.

Keywords: *DICOM images processing algorithm, orbit bones, DICOM images, 3D model.*

1. Introduction

Post-traumatic defects and deformities disrupt the habitual geometry of the face, lead to the development of functional disorders, the formation of cosmetic defects and, as a consequence, the violation of social adaptation of patients. The main place in the rehabilitation system for patients with posttraumatic changes in the bones of the facial skeleton is occupied by reconstructive and restorative operations, whose goal is to restore normal anatomy of the damaged area in order to achieve good functional and aesthetic results.

To eliminate posttraumatic defects of the bones of the skull, various materials of both biological and synthetic origin are used. However, the main problem with the use of the majority of existing materials is the need for intraoperative implant modeling that not only increases the duration of the intervention but, with extensive damage, does not allow the surgeon to accurately reconstruct the three-dimensional shape of the eye socket and achieve the desired cosmetic result when eliminating posttraumatic enophthalmos and hypophthalmia [1].

Currently, medical practice is introducing modern computer technologies for the production of personalized implants to remove defects in the bones of the skull [2, 3]. The

use of personalized implants in reconstructive and reconstructive surgery of the face has demonstrated their undeniable advantages, which, in high accuracy, reduce trauma, shorten the duration of the operation and ultimately achieve a predictable stable functional and cosmetic result [4].

To create such high-precision personalized implants, the quality of microspiral computed tomography (MSCT) is of decisive importance.

The analysis of the images obtained in the MSCT [5 – 7] in the DICOM [8] format and the three-dimensional reconstruction of the skull allows the surgeon to more reliably estimate the anatomical features of the individual patient, localization, boundaries and prevalence of the pathological process, and plan the scope of the surgery [9, 10].

However, among all bones of the facial skeleton, the lower and medial walls of the orbit are very thin structures (thickness ~ 0.1-0.3 mm), which is less than the resolving power of the existing apparatus (up to 0.625 mm). In this connection, the construction of a 3D model using the tomography software does not provide complete information about the state of the lower and medial walls of the orbit, they look like a cellular structure, have pores (Figure 1).

As a result of converting DICOM files to a 3D model, some of the information about the thin and small bones of the orbit is lost.

These losses lead to difficulties in determining the geometry of the damaged bones. It should also be noted that the software of existing MSCT does not allow you to edit the resulting 2D images, 3D models of the result of reconstruction, which leads to the use of additional software.

A software processing [11] and image analysis [12] get a great importance in medicine in general and in traumatology in particular.

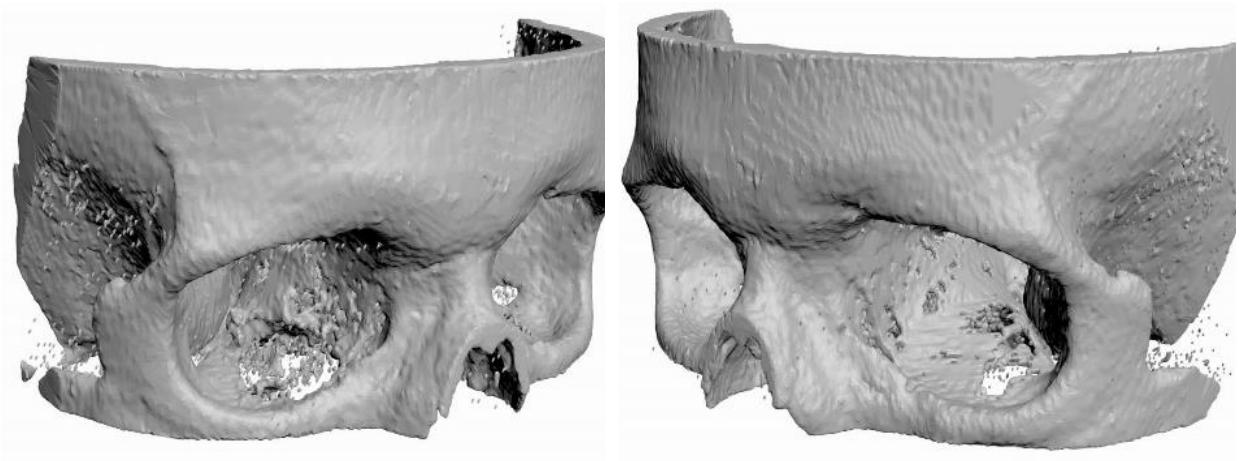

Figure 1. Type of three-dimensional model of bones of the facial skull: the result of the construction of a 3D editor.

The target of the work is to develop a technology for constructing a 3D model of the lower and medial bones of the facial skull while retaining complete information about their geometry based on the results of microspiral computed tomography (DICOM files).

2. Materials and Methods

During research, we analyzed DICOM images of several patients. The DICOM images contained data of MSCT scan of patients head including damaged eye socket bone. The DICOM images were received with device Siemens Emotion 6. We analyzed data of different patients of both genders aged between 20 and 40 with damage of eye socket bone.

DICOM images show slices of human head using density of body parts. The more the density the more intensive white color on the DICOM image. Soft parts colored as gray color, and voids colored as black color.

Analysis of the images of three projections using 3D Slicer software showed that in some places the thin eye socket bones absorbed X-ray beam less than the bones should absorb. As a result thin eye socket bones have a color that differs from white on the DICOM image. This is true for other slice orientations (Figure 2). Figure 2A shows axial slice of head where distance from MSCT starting point is -172.8 mm. Figure 2B shows sagittal slice of head where distance from MSCT starting point is -15.7 mm. Figure 2C shows coronal slice of head where distance from MSCT starting point is 213.2 mm. Figures 2B and 2C are the result of approximation built with 3D Slicer software.

The 3D Slicer software uses white pixels as input for building a 3D model of skull. As a result, 3D Slicer software loses a data about thin eye socket bones while generating the 3D model. We determined amount of data loss through the ratio between the area of eye socket bones and the area of defects.

a) b) c)

Figure 2. Images of the three projections of the patient's head: a – axial orientation; b – sagittal orientation; c – coronal orientation.

Therefore, it is necessary to make additions to the original DICOM images. We need to make thin bones visible to 3D Slicer software algorithms and do not distort the result of building a 3D model of the bones of the patient's head skull. The geometry of damage to the orbital bones should be preserved. Additions should only applied to the bones of a healthy orbit.

The analysis of three plane projections showed that the thin bones of the orbit border on the voids in the skull. At the same time, if the orbital bone is damaged, these voids are filled with biological cells, mostly fat cells. This leads to a change in the level of X-ray absorption and a change in the DICOM image of a healthy orbit bone. We need to note these circumstances while developing software that modifies the original DICOM files.

We propose the following technological chain to achieve the goal.

1) Process the original DICOM images with the developed special software. The flowchart of developed algorithm is presented in Figure 3. We implemented developed algorithm as software using C# programming language in the integrated development environment Visual Studio 2017 Community.

2) View the results of processing DICOM images in software 3D Slicer.

3) Set up 3D Slicer to build a 3D model of the bones of the facial skull by doing the following:

– Select the module "Volume Rendering". Select the DICOM image set in the "Volume" column.

– Select the display format "CT-AAA" in the "Preset" column. If the model is not displayed in the work area, center it with the function "Center the 3D view on the scene".

– Select the "Editor" module and confirm the model display properties.

– go to the "Edit Selected Label Map" tab and select the "ThresholdEffect" function; set the "Threshold Range" parameter to a filter value of 230 (this value can vary from 100 to 300); confirm the selected band with the "Apply" button.

4) Start the construction of the 3D model of the facial skull bones in the 3D Slicer software by selecting the "MakeModelEffect" function and pressing the "Apply" button.

The format of DICOM files pixel data is gray16 [13]. We analyzed color spectrum of the gray16 format to determine black, white and gray colors in RGB format in purpose of developing special software. The color spectrum of gray16 format is presented in Figure 4. We chose the average number of black pixels, white pixels and gray pixels as a basis of spectrum analysis, and were determining them visually. The black pixels match to voids, the white color pixels match to bone tissue, and gray pixels match to other body tissues and fluids. We checked results of analysis by processing DICOM images with the developed software. The size of an array of pixel data, which is [*n*; *n*], depends on the resolution of the source DICOM files: the height and width of the image.

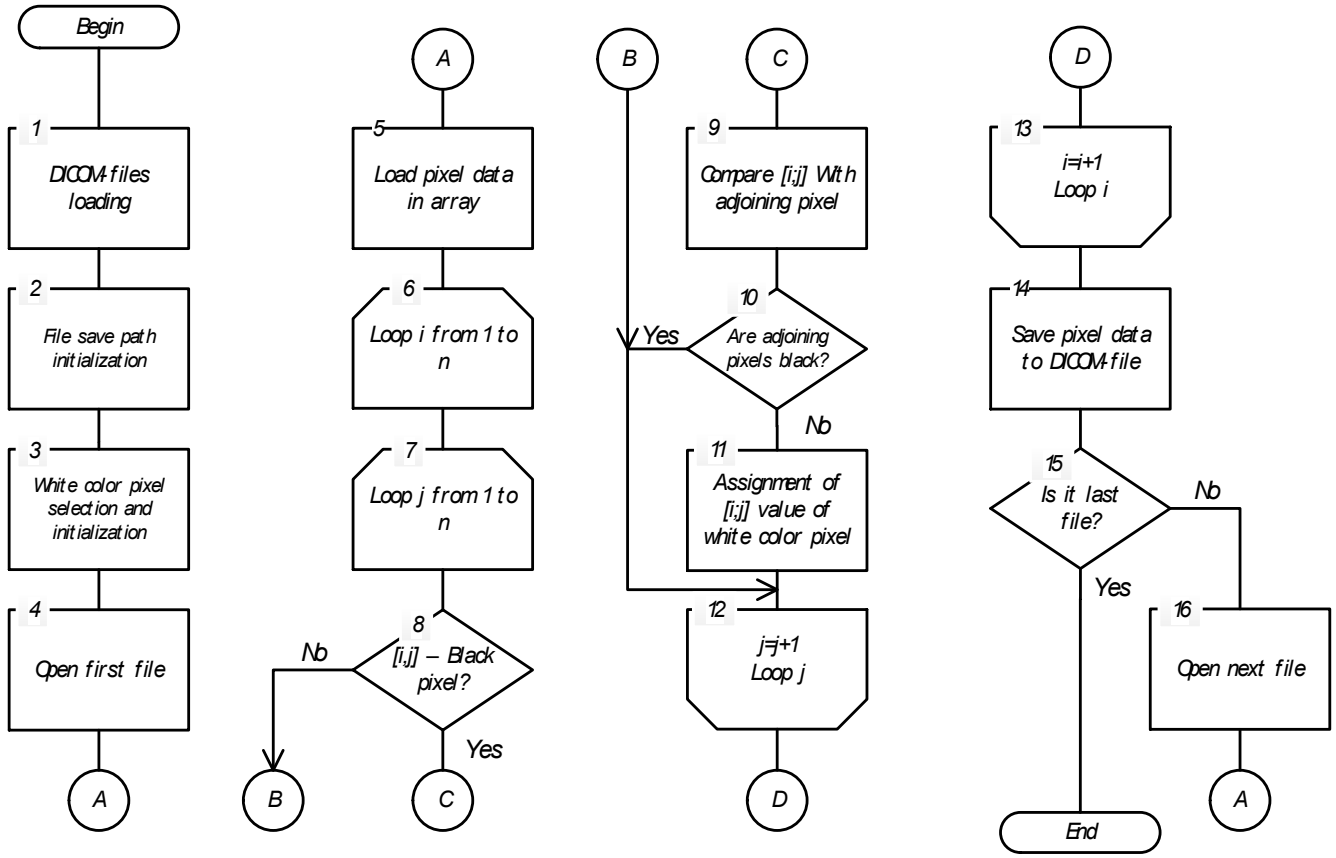

Figure 3. DICOM images processing flowchart.

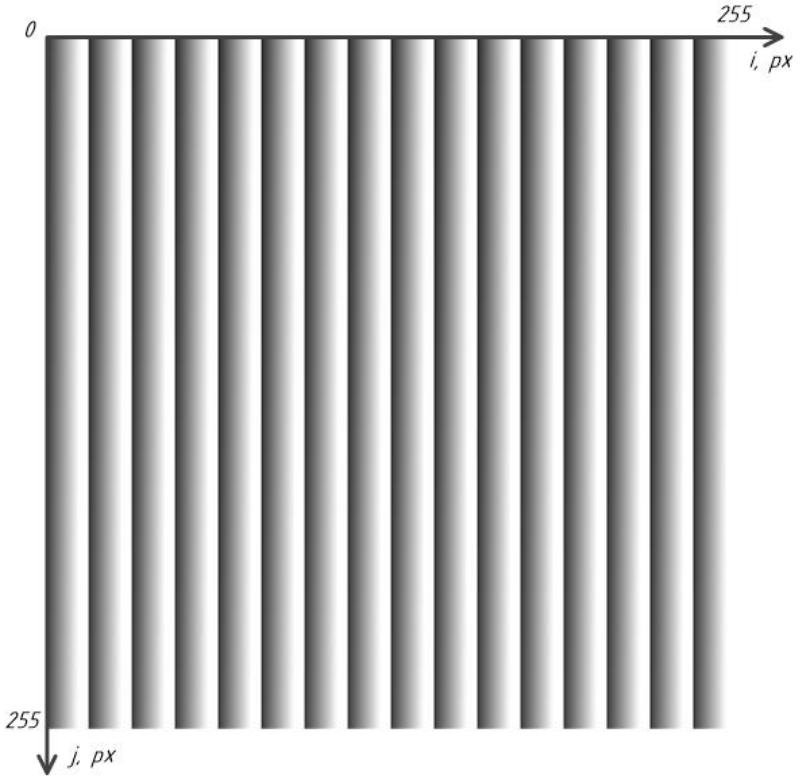

Figure 4. Color spectrum of DICOM images: i – the value low byte of the gray16 format pixel, $i = \overline{0, 255}$, j – the value of high byte of the gray16 format pixel, $j = \overline{0, 255}$.

The spectrum analysis of the DICOM file led to the next results. Black pixels of gray16 format have the following values of low byte and high byte:

$$i = 16 \cdot n,\ n = \overline{0, 15},$$
$$j = \overline{0, 255},$$

where n is an whole number.

White pixels of gray16 format have the following values of low byte and high byte:

$$i = 12 + 16 \cdot n,\ n = \overline{0, 15};$$
$$j = \overline{144, 255};$$
$$i = \overline{13, 15} + 16 \cdot n,\ n = \overline{0, 15};$$
$$j = \overline{0, 255}.$$

The remaining values of low byte and high byte correspond to gray pixels of gray16 format.

3. Results and its discussion

The result of processing DICOM images by special software is another set of DICOM images with expanded white color. Figure 5 contains three projections of resulting DICOM images. In comparison with Figure 2, we can see the next result. The marked places in Figure 2, fragments with an implicit bone, are transformed into an explicit white color, characterizing the presence of bone tissue. Figure 5A shows axial slice of head where distance from MSCT starting point is -172.8 mm. Figure 5B shows sagittal slice of head where distance from MSCT starting point is -15.7 mm. Figure 5C shows coronal slice of head where distance from MSCT starting point is 213.2 mm. Figures 2B and 2C are the result of approximation

built with 3D Slicer software. The thin orbit bone became visibly better on axial orientation (figure 5A).

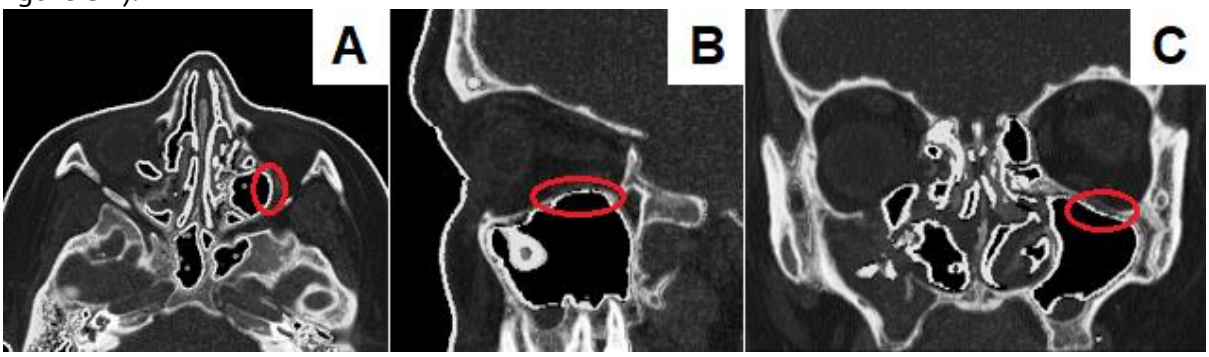

Figure 5. Three projections of the patient's head, constructed on the basis of the original DICOM images converted by special software: a – axial orientation; b – sagittal orientation; c – coronal orientation.

Results of approximation with 3D Slicer became visibly better too: sagittal orientation (figure 5B) and coronal orientation (figure 5C).

However, there is a significant weakness of algorithm of DICOM image processing within the developed software. The algorithm converts the skin on the patient's face into bone (Figure 5).

This complicates viewing and further work on the analysis and construction of the geometry of damage, for the manufacture of an individual implant. In order to eliminate this weakness, we modified the algorithm of processing the DICOM images: additional actions were added after block 13 of the algorithm (Figure 3) to correct the array of pixel data (Figure 6).

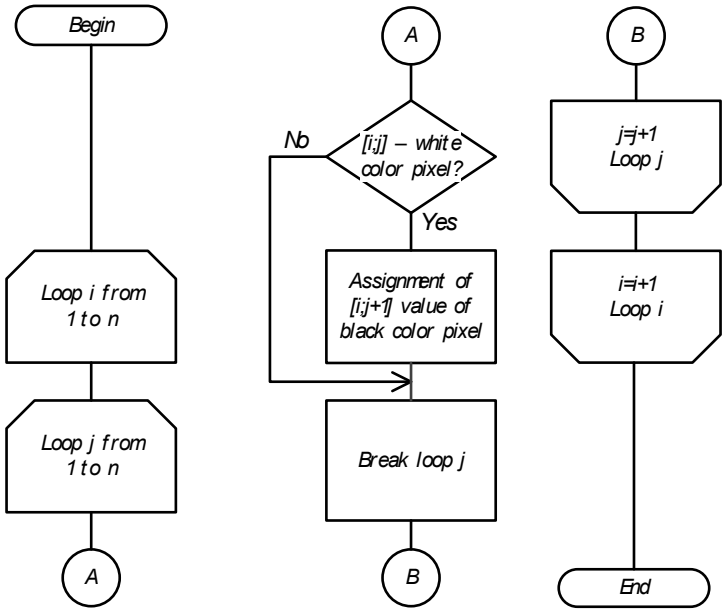

Figure 6. Modified flowchart for processing the source DICOM images.

Figure 7 contains three projections of resulting DICOM images using a modified algorithm. The distance of all projection planes from the MSCT starting point in Figure 7 is identical to those in Figures 2 and 5.

Figure 7. Three projections of the patient's head, constructed on the basis of the original DICOM images converted by modified special software: a – axial orientation; b – sagittal orientation; c – coronal orientation.

As a result of processing the original DICOM images with modified special software and performing operations 2 through 4 of the proposed technological chain, we built a three-dimensional model of the bones of the facial skull (Figure 8). When analyzing the image in Figure 8, we can see that the left eye socket of the three-dimensional model (the right part of the figure) has clear, without holes, the bones of the orbit. This allows you to uniquely identify the eye socket with damaged bones. Later, using 3D modeling editors, it is possible to build a three-dimensional model of the orbital bones.

Calculation of the loss of information on the bones of the eye sockets during the construction of a three-dimensional model of the bones of the facial skull showed that when using DICOM images without preliminary processing, the average loss value is 22 – 31 % at the scan step 0,63 mm, using DICOM images after processing the developed software – 3 – 5 %.

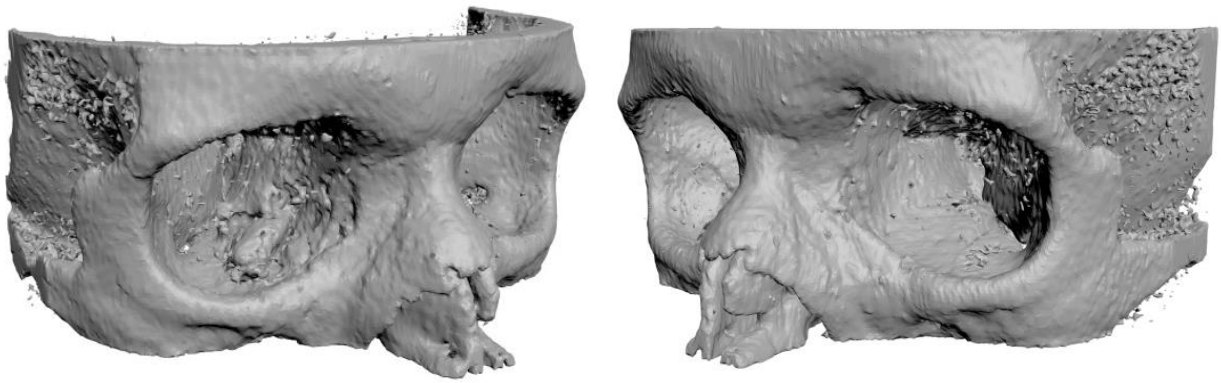

Figure 8. The appearance of the three-dimensional model of the bones of the facial skull after processing by special software: the result of construction by a 3D editor.

We built four versions of 3D-models based of DICOM images with expanding of white color by one, two, three and four pixels. Analysis of four versions of 3D-models showed that it is enough to expand white color by one pixel to achieve a level of data loss of 3-5%.

4. Conclusions

Expanding of bone tissue color over one pixel during preliminary processing by special software is the optimal amount for constructing a three-dimensional model with preservation of complete information about the structure of the orbital bones.

Processing of the original DICOM images with developed software decreases the loss data level about the orbital bones from 22-31% to 3-5% during constructing a three-

dimensional model of the bones of the facial skull. The DICOM image correction was performed automatically using developed software.

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THE RISKS OF ARTIFICIAL INTELLIGENCE

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Abstract. The artificial intelligence (AI) revolution is the fastest of all revolutions that we have known. The AI is most often presented as a how to improve and refine existing processes in order to spectacular. Much more than a technology, AI represents a new way of interacting with our environment and doing business. While some welcome this innovation favourably, others call for a break to assess the potential risks to consumers. The paper examines the possible risks and benefits of AI for different areas of human activity.

Key words: *Risks of misuse, AI advantages, large-scale cybercrime, safety, reliability.*

Introduction

Artificial intelligence (AI) is found in many devices that enrich our everyday life with modern comfort functions. The spectrum ranges from smartphones to intelligent thermostats. AI is also used to meet important social challenges. It is a branch of computer science in which machines capture, learn, conclude, act and adapt to the real world - and thus strengthen human abilities and automate tedious or dangerous tasks. Some experts believe that it has the potential for a real social revolution [1-14, 16-18].

Perhaps - before we try to define what artificial intelligence (AI) is - we should know what intelligence is. Unfortunately, defining intelligence is a particularly delicate problem, and dictionaries are not very helpful. It is true that most authors agree that intelligence is "the ability to understand" of the human spirit; when it comes to defining it, we are struggling with extremely varied definitions - such as "sensing meaning," "embracing thinking," "making a clear idea," "understanding through knowledge," etc. And when we want to know what knowledge is, we read that it is what we have learned, what I understand, that ideas are representations that form thought, and that the meaning of a word, for example, is the ensemble of the intelligible ideas it conveys. We enter into a loop from where we can no longer go out, for in order to define a word we need other words and so on. There is nothing left to do but to consider intelligence as a primitive word that we will not try to define. Why should we talk about artificial intelligence? This term designates a science that has gradually emerged since the emergence of the modern computers: it is the set of concepts and methods used to make computers behave intelligently, similar to that of people who exercise their intelligence. The domain is vast and is rapidly growing, among other things due to the fact that the power of the handlers is growing fast, so it can manipulate masses of information that are increasingly important with the help of increasingly elaborate algorithms.

What is AI?

Very simply, it's machines doing things that are considered to require intelligence when humans do them: understanding natural language, recognising faces in photos, driving a car, or guessing what other books we might like based on what we have previously enjoyed reading.

It's the difference between a mechanical arm on a factory production line programmed to repeat the same basic task over and over again, and an arm that learns through trial and error how to handle different tasks by itself.

AIs are at work wherever you look, in industries from finance to transportation, monitoring the share market for suspicious trading activity or assisting with ground and air traffic control. They even help to keep spam out of your inbox. And this is just the beginning for artificial intelligence. As the technology advances, so too does the number of applications.

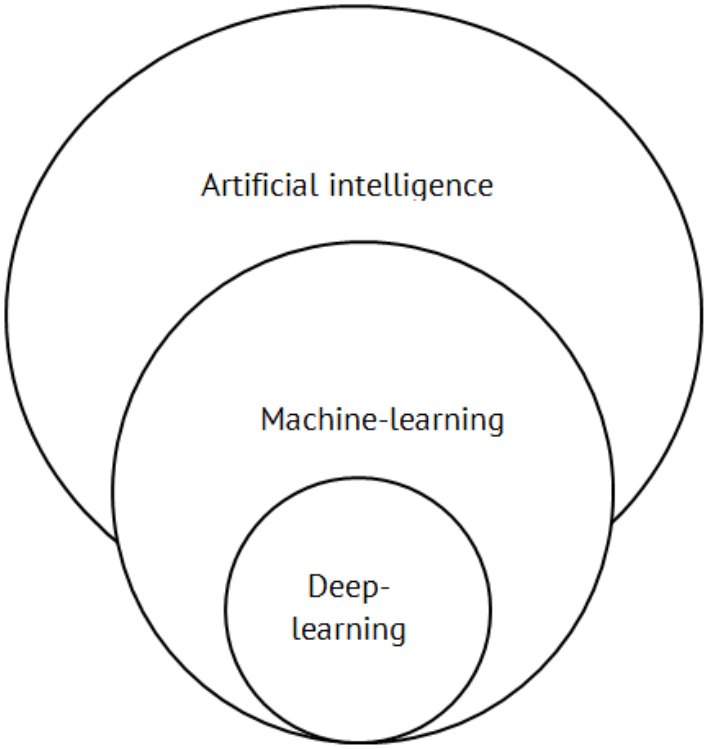

Figure 1. Relationships between AI, Machine-Learning and Deep-Learning.

As AIs are rolled out to assess everything, the risks that they will sometimes get it wrong – without us necessarily knowing – get worse. Since so much of the data that we feed AIs is imperfect, we should not expect perfect answers all the time. Recognising that is the first step in managing the risk. Decision-making processes built on top of AIs need to be made more open to scrutiny. Since we are building artificial intelligence in our own image, it is likely to be both as brilliant and as flawed as we are.

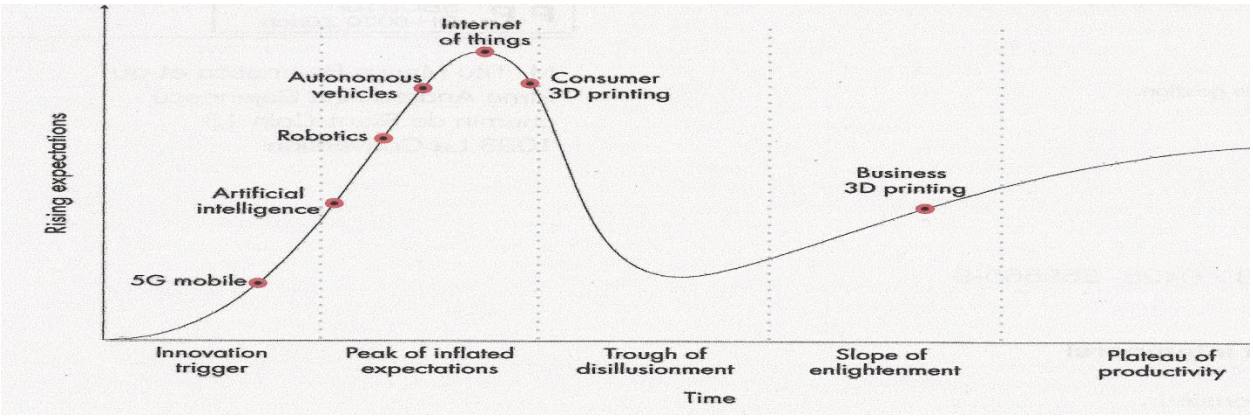

Figure 2. Gartner "hype" cycle applied to selected digital technologies.
Source: WDR 2016 team; adapted from Gartner 2015.

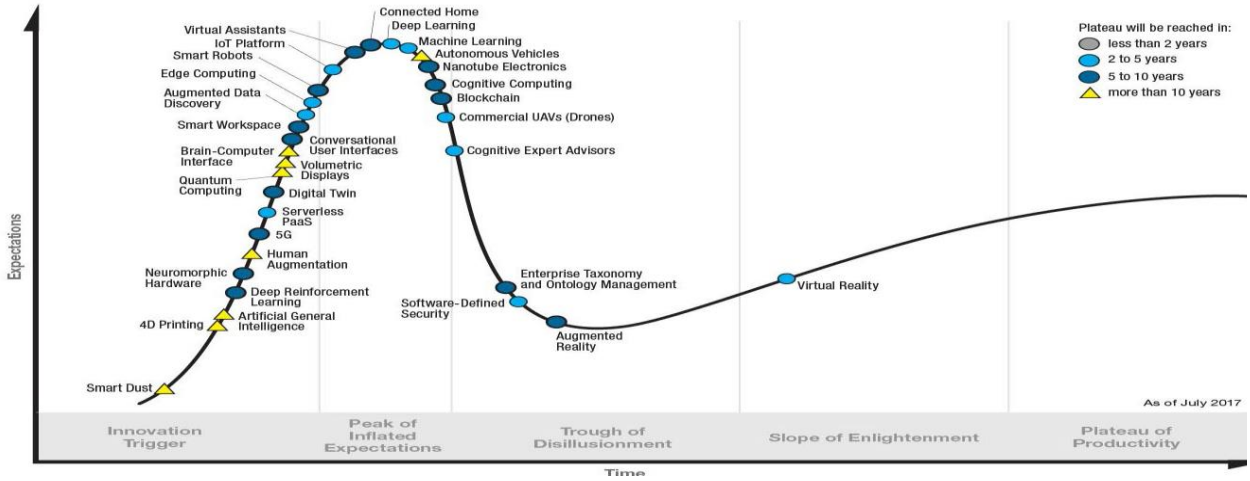

Figure 3. Overview of AI technologies (Source: Capgemini).

Machine-learning [2][12] is a very general and useful framework, but it is not "magic" and will not always work. In order to better understand when it will and when it will not work, it is useful to formalize the learning problem more. This will also help us develop debugging strategies for learning algorithms.

"Artificial intelligence will advance humanity," said Indian Prime Minister Narendra Modi in a speech in New Delhi with a view to a new *eGovernment initiativ*e using appropriate technologies to create paperless offices. "There will be arguments about whether jobs are left over or not. However, experts believe that there is a high probability that AI will create jobs," Modi said. And he added that AI is increasingly gaining influence and has the potential to transform economies (figure 4).

The question is which jobs are most at risk in which sectors. According to MIT economist David Autor, automation will substitute for more routinized occupations and complement high-skill, non-routine jobs. Whereas the effects on low-skill jobs will remain relatively unaffected, medium-skill jobs will gradually disappear, while demand for high-skill jobs will rise.

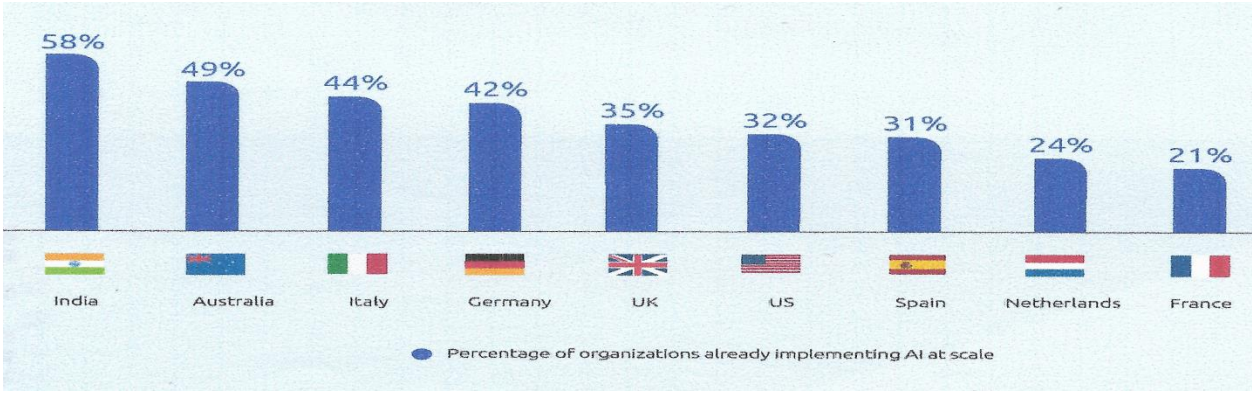

Figure 4. India leads in AI implementation at scale.
(Source: Capgemini Digital Transformation Institute, State of AI survey, June 2017).

Global risks

Many experts believe that alongside global opportunities, AI poses global risks, which will be greater than, say, the risks of nuclear technology - which in any case have historically been underestimated. Furthermore, scientific risk analysis suggests that high potential damages should be taken very seriously even if the probability of their occurrence were low.

While the risks from domain-specific AIs appear limited in the near future, there are long-term developments to take into consideration: in the not-so-distant future, artificial intelligence could in principle pose an existential threat, similar in scope to the pandemic risks associated with biotechnology [4, 6, 17].

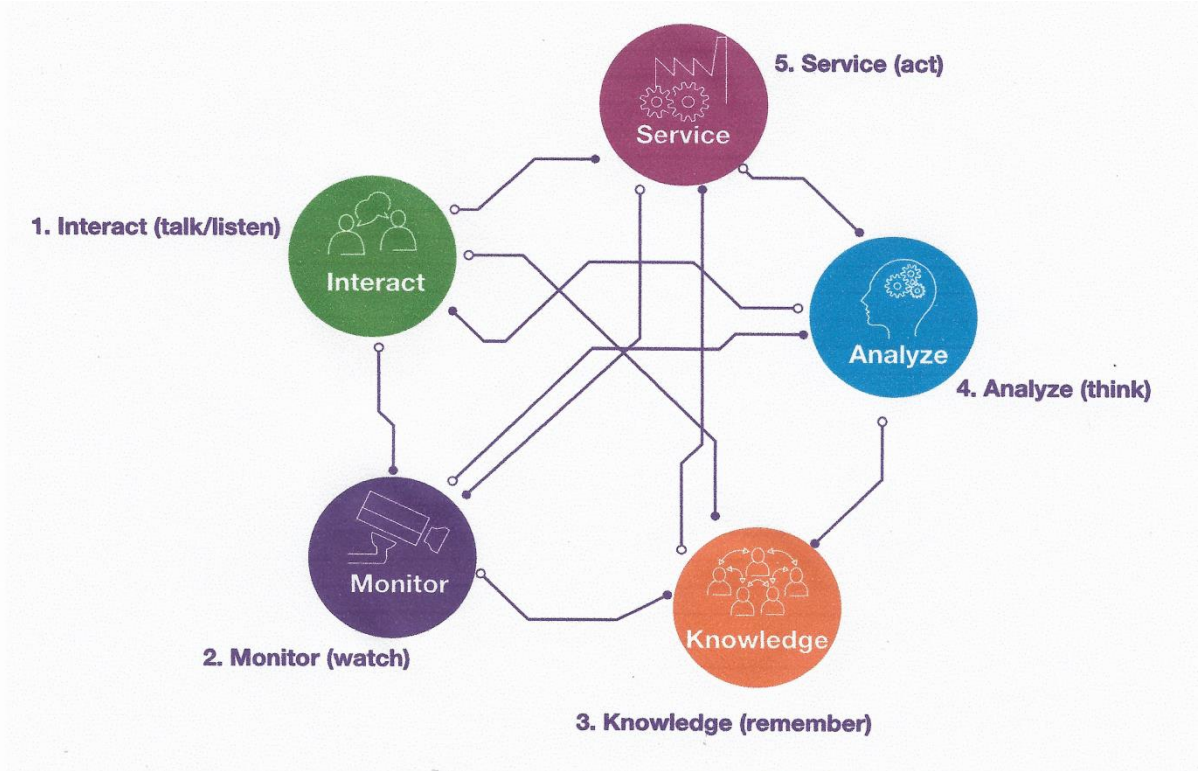

Figure 5. Five senses of artificial intelligence.
(Source: Capgemini, "The five senses of artificial intelligence: Christopher Stancombe", May 2017).

While the entertainment industry does offer significant opportunities for better education through personalized AI teaching and the gamification of learning material [66], it also increases the risk that a growing proportion of young people will have trouble completing their education due to a pathological addiction to video games and/or the internet [3].

On terrorism, crime, and other sources of risk:

The dangerous applications for AI would be criminals or large terrorist organizations using it to disrupt large processes or simply do pure harm. Terrorists could cause harm via digital warfare, or it could be a combination of robotics, drones, with AI and other things as well that could be really dangerous.

And, of course, other risks come from things like job losses. If we have massive numbers of people losing jobs and don't find a solution, it will be extremely dangerous. Things like lethal autonomous weapons systems should be properly governed - otherwise there's massive potential of misuse.

But this is the duality of this technology. Certainly, my conviction is that AI is not a weapon; AI is a tool. It is a powerful tool, and this powerful tool could be used for good or bad things. Our mission is to make sure that this is used for the good things, the most benefits are extracted from it, and most risks are understood and mitigated.

Some of the main risks associated with AI include:

Algorithmic bias: Machine-learning algorithms identify patterns in data and codify them in predictions, rules and decisions. If those patterns reflect some existing bias, the algorithms are likely to amplify that bias and may produce outcomes that reinforce existing patterns of discrimination.

Overestimating the capabilities of AI: Since AI systems do not understand the tasks they perform, and rely on their training data, they are far from infallible.

The reliability of their outcomes can be jeopardized if the input data is biased, incomplete or of poor quality.

Programmatic errors: Where errors exist, algorithms may not perform as expected and may deliver misleading results that have serious consequences.

Risk of cyber attacks: Hackers who want to steal personal data or confidential information about a company are increasingly likely to target AI systems.

*Legal risks and liabilities***:** At present, there is little legislation governing AI, but that is set to change. Systems that analyze large volumes of consumer data may not comply with existing and imminent data privacy regulations, especially the EU's General Data Protection Regulation.

Reputational risks: AI systems handle large amounts of sensitive data and make critical decisions about individuals in a range of areas including credit, education, employment and health care. So any system that is biased, error-prone, hacked or used for unethical purposes poses significant reputational risks to the organization that owns it.

In the example of autonomous cars, the blind use of deep neural nets (DNNs) coupled directly to vehicle action control systems would be very risky: it would be equivalent to asking a taxi driver who has lost more than 80% of his brain as a result of an accident (and only keeping this occipito-temporary lane) to drive a car. It is simply not possible to ask these systems to do more than what they were originally designed for, at the risk of producing dramatic accidents.

Artificial intelligence brings with it not only enormous potential, but also a number of challenges, fears and risks.

There are five types of major risks of AI: bugs, cybersecurity, the "Sorcerer's Apprentice" phenomenon, shared autonomy, and possible negative socio-economic effects. Bugs refer to programming errors in the AI software. Just as there are dangers from cyberattacks, this risk is not different from current IT systems. "Sorcerer's Apprentice" risks refer to AI systems that perform incorrect actions when unclear instructions are present from the user.

Not a few experts are of the opinion that, in addition to global opportunities, the AI also poses global risks, which have been historically underestimated for a long time, such as those of nuclear technology. In addition, a knowledge-based risk analysis suggests that high potential damage levels should be taken very seriously even if the probabilities of occurrence were low.

The risks of AI are real and important:

Misuse risks. The discussion of risk is *not* dependent on the view that AI is now on a successful path toward superintelligence - though it gains urgency if such "success" is a no negligible possibility in the coming decades. It also gains urgency if the stakes are set high, even up to human extinction. If the stakes are so high as to include extinction of humankind, even a fairly small possibility of a disastrous outcome (say, 3%) is entirely sufficient to

motivate the research. Consider that if there were a 3% possibility that a plane you are about to board will crash: that would be sufficient motivation for getting off.

The utility at stake in scientific or philosophical research is usually quite a bit lower. It appears that the outcome of superintelligence is more likely to be extreme: either extremely bad or extremely good for humanity. Therefore, there is the risk that "the machines take over" and this loss of control is a significant risk, perhaps an existential risk for humanity [14].

When Bostrom [5, 6] discuss about the transition to machine intelligence and existential risk, he is not referring to artificial intelligence systems as they exist in today's world.

He is thinking about the future and the advent of what might be called "artificial, global intelligence", the kind of global intelligence of reasoning and problem solving that allows us to dominate our environment as human species have done. We are not at that point at all at the moment and experts differ as to how long it will take us to achieve this. However, it is very likely to take more than a decade and even, according to some, several decades. However, if we do, the world will be so upset that it is difficult for us to imagine what it will look like.

By 2050 the probability of high-level machine intelligence (that surpasses human ability in nearly all respects) goes beyond the 50% mark, that is, it becomes more probable than not [10]. 2050 is also the year that "RoboCup" set itself for fielding a robot team that can beat the human football world champions (actually an aim that does not make much sense).

Like many people working in AI, Bishop [4] remains unimpressed by the discussion about risks of superintelligence because he thinks that there are principled reasons why machines will not reach these abilities: they will lack phenomenal consciousness, understanding, and insight.

International experts are sounding the alarm about the risks of the misuse of artificial intelligence (AI) by "rogue states, criminals, terrorists", in a report published recently. According to them, in the next ten years, the increasing effectiveness of AI is likely to increase cybercrime, but also to lead to the use of drones or robots for terrorist purposes. It is also likely to facilitate the manipulation of elections via social networks through automated accounts (bots).

This 100-page report entitled *The Malicious Use of Artificial Intelligence* was written by 26 experts in artificial intelligence, cybersecurity and robotics.

They work for universities (Cambridge, Oxford, Yale, Stanford) and non-governmental organizations (OpenAI, Center for a New American Security, Electronic Frontier Foundation). These experts call on governments and the various stakeholders to put in place measures to limit potential threats related to artificial intelligence.

One of the main ways in which AI could be transformative is by *enabling/accelerating the development of one or more enormously powerful technologies*. In the wrong hands, this could make for an enormously powerful tool of authoritarians, terrorists, or other power-seeking individuals or institutions.

The potential damage in such a scenario is nearly limitless (if transformative AI causes enough acceleration of a powerful enough technology), and could include long-lasting or even permanent effects on the world as a whole. It is worth asking whether there is anything we can do today to lay the groundwork for avoiding misuse risks in the future.

Accident risks. Tthere is a substantial class of potential “accident risks” that could rise (like misuse risks) to the level of *global catastrophic risks*.

We’ve seen substantial (though far from universal) concern that such risks could arise and no clear arguments for being confident that they will be easy to address. These risks are difficult to summarize.

The above risks could be amplified if AI capabilities improved relatively rapidly and unexpectedly, making it harder for society to anticipate, prepare for, and adapt to risks.

Some signs of interrogation arise:

What kinds of technical research are most important for reducing the risk of unexpected/undesirable outcomes from progress in artificial intelligence? Who are the best people to do this research?

What could be done - especially in terms of policy research or advocacy - to reduce risks from the weaponization/misuse of artificial intelligence?

What is the comparative size of the risk from intentional misuse of artificial intelligence (e.g. through weaponization) vs. loss of control of an advanced artificial intelligence agent with misaligned values?

Why the advantages of artificial intelligence outweigh the risks

The arguments against artificial intelligence (AI) are clearly anxiety-driven: fear of the unknown and fear of (information) intelligence. If Stephen

Hawking is believed, we have every reason to guard against the consequences of the further development of artificial intelligence, including the possibility of sealing the end of humanity.

However, the rise of the machines does not pose an immediate threat today, as artificial intelligence is still in a primitive stage. The most realistic scenario is probably the fear that artificial intelligence will destroy jobs.

AI and large-scale cybercrime

"We believe that the attacks that will be made possible by the increasing use of AI will be particularly effective, finely targeted and difficult to attribute," the report says.

To illustrate their fears, these specialists refer to several "hypothetical scenarios" of misguided use of AI. They point out that terrorists could modify commercially available AI systems (drones, autonomous vehicles) to cause crashes, collisions or explosions.

The authors imagine the case of a manipulated cleaning robot that surreptitiously slips among other robots in charge of cleaning in a Berlin ministry.

One day, the intruder would attack after visually recognizing the Minister of Finance. He would approach him and explode autonomously, killing his target.

In addition, "cybercrime, already on the rise, is likely to increase with the tools provided by AI," *Seán Ó hÉigeartaigh*, (or Sean O'Hegarty) director of the Centre for the Study of Existential Risk at Cambridge University, one of the report authors, told AFP. Spear phishing attacks could this become much easier to conduct on a large scale.

The most serious risk, although less likely, is political risk. We have already seen how people use technology to try to interfere in elections and democracy. If AI allows these threats to become stronger, more difficult to identify and attribute, this could pose major problems of political stability and perhaps contribute to outbreaks of war," says *Seán* Ó *hÉigeartaigh*.

With AI, it should be possible to make very realistic fake videos and this could be used to discredit politicians, the report warns. Authoritarian states will also be able to rely on AI to strengthen surveillance of their citizens, he added.

This is not the first time that concerns have been expressed about AI. As early as 2014, astrophysicist Stephen Hawking warned of the risks it could pose to humanity, surpassing human intelligence. Entrepreneur Elon Musk and others have also sounded the alarm.

Specific reports on the use of killer drones or how AI could affect US security have also been published. This new report provides "an overview of how AI creates new threats or changes the nature of existing threats in the areas of digital, physical and political security," explains Sean O'Hegarty.

Safety and reliability

The safety and reliability of software systems are a top priority in the areas of embedded systems, communication and application software.

Software technology must help ensure that data and communication channels are secure against unauthorized access and unintentional changes. In addition, the reliable and correct operation of components and services under normal operating conditions must be ensured.

The openness and flexibility of service-oriented architectures are a particular security challenge. Here, cross-instrument activities on ICT security for service-oriented architectures can form a decisive basis for the success of lead innovations.

Quality problems in large hardware and software systems limit the possibilities of functional innovation. Reliability must be increased here.

Google's banned AI applications

Technologies that could cause major harm: "When such a risk is identified, we will ensure that the benefits far outweigh the risks and that the integrated safety rules are sufficient".

Weaponing-related technologies: Google is committed to not developing technologies that can cause injuries to people (main objective or possible use of AI-based technology).

Surveillance technologies: mechanisms that collect information on individuals or use this information to monitor them, "in violation of globally accepted standards" will be banned. Google obviously does not want to be associated with the slogan "Big brother is watching you".

Technologies contrary to human rights: more generally, the Mountain View firm undertakes not to develop technologies that would contravene the principles of international law and human rights.

The European Economic and Social Committee *EESC* takes stock of its benefits and risks

Artificial intelligence will be a major upheaval for workers, explains the European Economic and Social Committee *EESC*. In a report, he unveils his recommendations on the subject, with an emphasis on the social side of course. Employment, ethics, influence on our decisions and education are all covered.

For several years, artificial intelligence - in the broadest sense of the term - has been growing rapidly in many areas. The latest example to date is Alpha Go's 3-0 clear victory (created by *DeepMind,* a Google subsidiary) over *Ke Jie,* which is considered the world's

number one in the game of Go. However, artificial intelligence also raises many ethical, technological and societal questions.

As is often the case in such situations, the report begins by looking at the benefits that artificial intelligence could bring to everyday life: "making agriculture more sustainable and production processes less polluting, improving transport and workplace safety, making the financial system more stable, providing better quality medical care" and so on. In its synthesis, the European Union's advisory body goes so far as to assume that artificial intelligence "could even contribute to the eradication of disease and poverty". A whole program....

However, before it comes to that, the road is long and full of obstacles. The ***EESC*** identifies eleven areas where a framework needs to be defined: ethics, security, privacy, transparency and accountability, work, education and skills, (in) equality and inclusion, legislation and regulation, governance and democracy, war, and finally *superintelligence*.

The delicate issue of autonomous weapons and cyberwarfare like many other organizations, the EESC supports the call to ban autonomous weapon s systems, but believes that issue should be raised more broadly in *cyberwarfare*.

The idea is attractive on paper, but unfortunately there is little chance that all governments and private arms companies will leave out AI for the development of their weapons, digital or not. It is already more or less too late with drones and the automatic interception of messages on the Internet.

According to this report, it is "necessary to prevent AI from reaching the hands of people or regimes likely to use it for terrorist purposes"... certainly easier said that did.

The report then raises several questions about machine safety. He would like specific requirements to be put in place to answer and anticipate the following questions: is the algorithm reliable and effective, even in an unknown or unpredictable situation? Can it stop working or be hacked? The answers should not be taken lightly.

As we regularly see in IT security, there is no such thing as zero risk. However, the consequences of a failure could be quite different between an AI in charge of filtering sites for parental control and that of an autonomous car.

There is also the question of the legal personality of robots. The EESC has a clear-cut opinion on the subject: recognising it would represent an "unacceptable moral risk".

Conclusion

To sum up, the EESC's assessment focuses mainly on the impact that artificial intelligence will have on people's lives, both at work and in their private lives. They will be more or less important, but everyone will a priori be concerned, so we must be prepared for them. In any case, the Committee advocates that humans maintain control of AI in all circumstances, and prepare for the arrival of strong artificial intelligence.

It also recommends that Europe place itself at the heart of the debates, but this will not be an easy fight given that the vast majority of societies at the forefront of this field are outside our borders. There are certainly many start-ups and research centres in France (with a good reputation in general), but those with massive access to and use of data are located outside Europe.

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THE CONSEQUENCES OF THE OMISSION OF THE PROPERTY RIGHTS STUDY IN THE REAL ESTATE ASSESSMENT PROCESS

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Abstract. The article focuses on property valuation. It examines the value, its qualitative and quantitative aspects through the static and dynamic prism; the essence of value and the factors of impact, behavioral aspects over time. The development of the evaluation in recent years has highlighted two directions: the financial and economic assessment centered on evaluation theory and the evaluation of financial investments, focused on evaluation theory. Property valuation takes place through the interference of economic, technical and legal sciences. In recent years, international valuation practice has changed its vision of the subject of evaluation; the focus has been shifted from "real estate" to "property rights". The value of the property depends directly on the real estate property rights, along with the existing tasks. In the process of estimating value, neglecting the survey or superficial examination of real estate has serious consequences for both the owner of the good and the user of the valuation report as well as directly for value. In the article, this situation is exemplified using the case study method.

Keywords: *real estate, property interests, valuation of rights, special value, market value for an alternative use.*

Introduction

One of the priorities of the modern society is the tendency towards sustainable social and economic development. Sustainable development is possible by keeping and using efficiently the values created by our ancestors, along with meeting the needs of the present, without compromising the ability of future generations to meet their own needs. The real estate appraisal activity is used in this sense by estimating the impact on properties. Any action on property, whether physical or legal, is justified only if the future value is not affected.

Appraisal is often perceived as a mathematical tool that allows determination of property value at a specific moment in time. Such a view represents just one side of appraisal – quantitative aspect of the moment.

The property valuation is the science (subject) whose object of study is *the value*, its qualitative and quantitative aspects examined from static and dynamic perspectives; the

essence of value and the impacting factors, the behavioural aspects over time. The valuation development in the last years outlined two directions: the financial and economic assessment centred on the appraisal theory and the financial-investment evaluation focused on the valuation theory. Property appraisal occurs through the interference of economic, technical and legal sciences [1].

Over the past years, international valuation practice has changed its vision of the subject of the valuation, the focus has been shifted from "real estate" to "property rights".

The eighth edition, International Valuation Standards 2007 [2], includes the Guidance Notes1 *Valuation of Real Property*, which specifies that "The term *property*, in a legal sense, may be defined as ownership rather than the physical entity of land, buildings and tangible personal items. In this context, IVSC identifies four general types of ownership: Real Property; Personal Property; Businesses; Financial Interests".[2, p. 165].

Real estate is defined as "Land and all things that are a natural part of the land, e.g., trees and minerals, as well as all things that are attached by people, e.g., buildings and site improvements. All permanent buildings attachments such as plumbing, heating cooling systems; electrical wiring; and built-in items like elevators, or lifts, are also part of the real estate. Real estate includes all attachments, both below and above the ground." [2, p. 168].

The undated 2017 edition of International Valuation Standards [3] includes the valuation standard IVS 400 Real Property Interests. According to it, the right to property is to be examined for the following reasons:

"A real property interest is a right of ownership, control, use or occupation of land and buildings. There are three basic types of interest:

(a) the superior interest in any defined area of land. The owner of this interest has an absolute right of possession and control of the land and any buildings upon it in perpetuity subject only to any subordinate interests and any statutory constraints;

(b) a subordinate interest that gives the holder rights of exclusive possession and control of a defined area of land or buildings for a defined period, e.g., under the terms of a lease contract;

(c) a right to use land or buildings but without a right of exclusive possession or control, e.g., a right to pass over land or to use it only for a specified activity." [3, p. 81].

To comply with the requirement to identify the asset to be valued in IVS 101 Scope of Work, para 2 (d) the following matters shall be included:

(a) a description of the real property interest to be valued,

(b) identification of any superior or subordinate interests that affect the interest to be valued." [3, 82]

Neglecting the study or the superficial examination of real property interests has serious consequences for both the beneficiary and / or the user of the appraisal report, as well as, directly, for the valuer. This statement is exemplified using a real situation.

1. Case study. The subject of the valuation.

The asset being valued is a plot of land for mining with an area of 9.2 ha, of an irregular shape, partially forested. At the time of inspection, there were signs of crumbling of riverbank of the adjacent pond.

The plot of land is located in the North of clay deposit "Pruncul" leased to SC "P". The useful mineral material of the clay deposit complies with the requirements of GOST 530-80 for the production of "100-125" brick.

From a physical and legal point of view, the plot of land cannot be entirely used for any other purpose than mining.

From the physical point of view if splitting the land in the sectors, it could be potentially used partly for agricultural purposes, partly for industrial purposes – such as land without construction (e.g. parking or open warehouse) or light industrial buildings.

From the legal point of view, using the plot of land for agricultural purposes requires to change its destination (zoning).

The right of ownership of land was registered in accordance with the Land Code in 2006 by the Local Public Administration, which in 2008 sold the property to a natural person. Subsequently, after 3 years, the natural person sold the land to a legal entity - "I" Ltd. A mortgage transferred the interest in the plot of land from the owner to the mortgage lender - the "Bank" SC. In 2012, the notice of the execution of the pledge right was submitted and subsequently the land was transferred to the bank. At the beginning of 2013, a court decision declared Ltd "I" insolvent, and an administrator of insolvency was appointed.

Consequently, on the valuation date (2014), the property interests on the real estate as land for mining is divided:

direct **ownership** of the ***land***	Ltd „I", in the process of insolvency
the **right of alienation** of the ***land***	SC „Banca"
complete **ownership** of the ***subsoil***	The Republic of Moldova (state)
the **right** of ***subsoil*** **use**	SC „P"

In such case the interests in real property is held jointly, this fact created a situation where potential buyers of land for mining are: SC "P" - as the owner of the layer and / or SC "Macon" – as the largest user of clay for bricks production in the Republic of Moldova.

Consequently, if asset being valued is used for its direct utilization (mining), it does not have market value[1] and according to the International Valuation Standards cannot pledge loans.[2]

CONSEQUENCE No.1. The bank has a non-performing loan.

2. Analysis of the best use

According to the International Valuation Standards 2011 edition, IVS Framework [4, 22]:

"The market value of an asset will reflect its highest and best use. The highest and best use is the use of an asset that maximises its productivity and that is possible, legally permissible and financially feasible. The highest and best use may be for continuation of an asset's existing use or for some alternative use. This is determined by the use that a market participant would have in mind for the asset when formulating the price that it would be willing to bid.

The highest and best use of an asset valued on a stand-alone basis may be different from its highest and best use as part of a group, when its contribution to the overall value of the group must be considered.

[1] Market Value is the estimated amount for which an asset or liability should exchange on the valuation date between a willing buyer and a willing seller in an arm's length transaction, after proper marketing and where the parties had each acted knowledgeably, prudently and without compulsion.

[2] The basis of value to be specified in accordance with IVS 101 para 2(e) will normally be market value. (according to IVS 310 Valuations of Real Property Interests for Secured Lending, paragraph 4).

The determination of the highest and best use involves consideration of the following:

(a) to establish whether a use is possible, regard will be had to what would be considered reasonable by market participants,

(b) to reflect the requirement to be legally permissible, any legal restrictions on the use of the asset, eg zoning designations, need to be taken into account,

(c) the requirement that the use be financially feasible takes into account whether an alternative use that is physically possible and legally permissible will generate sufficient return to a typical market participant, after taking into account the costs of conversion to that use, over and above the return on the existing use."

Based on the location, destination and physical state, we determine the possible use of the asset being valued (Table 1).

In view of the fact that the existing deposit in the perimeter of the plot of land under valuation is clay, and its extraction technically is on the surface of the soil, the following situation has been created:

• Ltd "I" has a direct ownership of the land, but cannot extract the clay because the right of subsoil use belongs to SC "P".

• SC "P" cannot extract the clay because it would violate the ownership of "I" Ltd on the land (by altering its shape and structure both vertically and horizontally).

In the context of the respective use (mining), the land has no market value but has a special value for SC "P" (as a holder of the right of subsoil use) and for Macon SC (as the main user of clay).

The special value[3] diverges considerably from market value, and in this case, the special value is different for SC "P" or SC "Macon".

Therefore, the asset being valued could have a *market value for an alternative use*. However, according to the Land Code [5]:

Article 52. *Land designated for industry, transportation, telecommunications, and land for other specific purposes* is the land allocated by the local public administration authorities to locate and use administrative and service providing structures, auxiliary and industrial buildings, mining transportation, and other enterprises, institutions, and organizations to build access roads, engineering infrastructure, manage industrial production, build highways, install telecommunication and electric lines… The allocation of land to enterprises, institutions, and organizations for use of underground resources shall be conducted subject to legalization of alienation of such land for mining purposes and reintegration into the agricultural cycle of land previously used for such purposes.

[3] **Special value** is an amount that reflects particular attributes of an asset that are only of value to a special purchaser. A special purchaser is a particular buyer for whom a particular asset has special value because of advantages arising from its ownership that would not be available to other buyers in the market.

Table 1

Potential use			
Possible use	Possibility of physical use	Legal Restrictions	Note [4]
mining (production of minerals)	possible	forbidden	the right to use the subsoil belongs to another economic agent
agricultural work	partly possible	forbidden	it is necessary to change the land destination
dwelling buildings	forbidden	forbidden	it is necessary to change the land destination
industrial buildings	possible	forbidden	only for the purpose of extracting the deposits

Article 75. *Change of Specific Land Zoning*. A change in zoning of land for industry, transport, telecommunication and for other similar purposes shall be approved by Government Decision. Such land shall be used in strict compliance with its zoning. Other activities may be conducted on such land, provided that these works do not interfere with the land main zoning. Executors of industrial, investment and other specific works shall undertake measures necessary to provide the improvement and levelling of land no longer used in their production works and which remained from raw material extraction (kaolin, clay,

[4] Subsoil Code [6] Article 6:
(1) The riches of any kind in the subsoil of the Republic of Moldova, including the useful mineral substances it contains, as well as its underground spaces are exclusively the object of the public property of the state, are inalienable, insensible and imprescriptible.
(2) The sub-sectors cannot be alienated, they can only be put into service. All legal acts or actions that, directly or indirectly, violate the public ownership of the state over the subsoil are affected by absolute nullity.
(3) The extracted mineral raw material belongs to the beneficial owner of the subsoil, unless the contract stipulates otherwise.
Article 13. The right to use the subsoil sector
(1) The right to use on the subsoil means the possibility of the beneficiary of the subsoil to realize the types of use of the underground sector stipulated in art.14.
(2) The right to use the subsoil shall be carried out within the limits of the sector assigned to the beneficiary of the subsoil in the form of a mining or geological perimeter, according to the clauses stipulated in the contract.
(3) The right to extraction of useful mineral substances, including groundwater and natural curative resources, gives the beneficiary of the subsoil, who has obtained a license in accordance with the provisions of the Law no. 451-XV of 30 July 2001 on the licensing regulation of the entrepreneurial activity, the possibility to carry out activities for a set period, with the obligatory observance of the licensing conditions for the use of the subsoil.
Article 14. Types of use of the subsoil
The base is assigned to use for:
a) geological research, including prospecting, assessment and exploration of mineral deposits and other geological research;
b) extraction of useful mineral substances, including groundwater and natural curative resources;
c) construction and operation of underground constructions not related to extraction of useful mineral substances;
d) burial (storage) of harmful substances and industrial wastes;
e) organization of protected geological objectives;
f) collection of mineralogical, paleontological, other geological collections.

gravel), and reinstate such land in the agricultural cycle, or, if this is not possible, in fish breeding or forestry use. If land users do not observe the provisions of paragraph 3 of this Article, they shall not be allocated any other land.

The following conclusions were drawn after analysing the best use:

- ✓ the utilization of the asset being valued for other purposes than mining is not possible, and the estimation of the value for another use is incorrect.
- ✓ the asset being valued used for the mining does not have market value.
- ✓ the asset being valued used for mining exploitation has a special value.

CONSEQUENCE no. 2: estimation of the market value for the asset being valued is treated as a falsification of the results of the evaluation, for which the valuator is responsible to administrative and criminal liability for the unlawful activity according to the legislation of the Republic of Moldova [7, art.24, para.2].

3. Value Estimation

Special value – an amount that reflects particular attributes of an asset that are only of value to a special purchaser. The only buyer for the asset being valued is SC "P" because it is the holder of the right to use the subsoil.

Another potentially interested buyer could be SC "Macon" as a final user of the clay deposit within the perimeter of the asset being valued. However, for SC "Macon" the special value is lower than for SC "P", because in the case it purchases the land, an extraction permission is to be obtained from SC "P".

According to the valuation principles only the special buyer - SC "P" is examined.

The value of the asset being valued, under existing legal conditions, is the value of the right to extract the clay from the perimeter of the asset being valued expressed by a fix amount payment[5].

The methodology of estimating the value of the license in the Republic of Moldova is explained in the Annex to the *Regulations on Evaluation of Intellectual Property Rights* [8], Methodological Guidelines on *Evaluation of Intellectual Property Rights*. Chapter X. *The calculation of the license value* stipulates that the value of the license can be calculated based on profit, based on royalties, as a fix amount or in a combined form.

Referring to the asset being valued, its special value for SC "P" is the license value expressed by a fix amount payment. As a basis for calculating royalties, the sales price of clay is applied. The potential volume of the clay deposit is determined as a proportion to the surface. As the plot of land is located at the periphery of the "Pruncul" clay deposit, a correction coefficient of 0.9 is included for estimating the size of the potential volume of the clay deposit. As a result, the clay reserves in the perimeter of the asset being valued are approx. 2 283.8 thousand m^3 or 3 654.1 thousand tonnes.

The price per tonne of clay was estimated based on the prices actually paid by SC "Macon" to SC "P" for "Pruncul" clay - 46 lei including transportation. Considering the cost of transport during the year 2007 (on average 400 lei per one car of 8 m^3), the clay price was 14.75 lei / t. At the time of the valuation, there were no offers of clay on the Moldovan market.

[5] **A fix amount payment** is the amount of the fixed payment in the form of a lump-sum payment for granting the right to use the intellectual property under the license agreement, regardless the actual volume of sales of the licensed products (services). It can be paid out as a single lump-sum or as periodic payments through a structured settlement.

If necessary, construction companies are paying the excavator 350 lei / hour and the transportation - 600 lei / car of 8 m^3, without a separate payment for the clay.

Table 2

Determination of the clay deposit volume

Criteria	„Pruncul"	Asset being valued	Note
area, ha	40,7	9.2	
reserves on 16.06.1983, thousand m^3	11 226.0	2 283.8	11 226 / 40.7 x 9.2 x 0.9
reserves on 01.01.2013, thousand m^3	10 536.1		
extracted volume, thousand m^3	689.9		11 226 - 10 536.1
average annual extraction volume, thousand m^3	23.79		689.9 / 29 years
dry density of clay, kg / dm^3		1.6	
reserves, thousands of tons		3 654.1	2 283.8 x 1.6

There are offers of clay from the Ukrainian mines. Prices, with and without transportation, range between 50 - 100 UAH / t in the Kiev region, 25 UAH / t in the Odessa region, 33 - 45 UAH / t in the Zaporozhye region. Due to market conditions, increased transportation costs and lack of special extracted material costs, we consider the potential price of clay for bricks of 13.5 lei / t. According to the "25% rule" used to determine the amount of royalties, the annual amount of the royalties is around 96.7 thousand lei, determined as 25% of the potential profit before taxes (Table 3 and 4). However, under that rule it is assumed that the right to use the subsoil is also subject to licensing. Since the subject of licensing is only the land ownership, the royalty size can not exceed half of the size determined under the "25% rule". Consequently, the maximum amount of considered fees is around 48,000 lei annually.

The potential sales revenue that can be obtained by SC "P", based on the average annual volume extracted in "Pruncul" mine, is 449 thousand lei / year (23.79 thousand m^3 x 1.6 x 13.5 lei / t = 513 857 lei / year). Royalties, according to international practice for similar situations, are ranging between 5-10% of sales, which for the asset being valued is approximately 6,64 - 13.27% of forecasted profit before taxes. Royalties based on of 5% rate are 25 693 euro / year. Royalties based 10% are 51 386 euro / year. Assuming the discount rate equals to the bank interest rate for deposits of legal entities of 7,98% (the alternative investment method in the minimum risk circumstances), we determine the discount coefficient (compounded interest) for 96 years (until the resource is exhausted: 2 283 800 m^3 / 23.79 thousand m^3 / year = 96 years).

Discount coefficient = $[(1+0.0798)^{96} - 1] / [(1+0.0798)^{96} \times 0.0798] = 12.523439$

Consequently, considering the basis of royalties the sales revenue is:

The minimum license value is 25 693 x 12.523439 = 321 763 lei or 322 thousand lei.

The maximum license value is 51 386 x 12.523439 = 643 525 lei or 644 thousand lei.

Based on the "25% rule"

The license value is 48 374 x 12.523439 = 605 804 lei or 606 thousand lei.

Table 3

Assessment of income and costs account of clay extraction activity[6]

Criteria	Value
Amount extracted on average per year, thousand t	38.06
The quantity transported on average by a truck type CAMAZ6520, t	12.8
Number of cars needed to transport the quantity extracted annually	2 973.71
The minimum number of cars	2
Average transportation distance: mine – Chisinau – mine, km	30
Cost of diesel, lei / l	17.45
Consumption, l / 100 km	45
The cost of the necessary diesel for a work shift ride, lei	235.58
Cost of diesel required annually, lei	700 531
The annual amortization of 2 trucks, lei	74 000
Payroll fund for 2 drivers, lei / year	96 000
Expenses for transportation, lei / year	**870 531**
Cost of transportation, lei / car	*293*
Bucket capacity a excavator, type Э 304A, m^3	0.4
Extraction volume, according to normative productivity, m^3/h	15
Time required to excavate annual volume, hours / year	1 585.98
Normative diesel consumption, l / h	9.6
Cost of diesel, lei / year	265 682
Excavator amortization , lei / year	74 000
Payroll Fund, lei / year	60 000
Expenses for excavation, lei / year	**399 683**
Cost of excavator, lei / hour	*252*
Cost of excavation and transportation, lei / car	***427.15***
Total excavation and transportation costs, lei / year	1 270 213
Overheads, %	10
Total with overheads, lei / year	1 397 235
Average market price, lei / car	600
The added value, lei / car	172.85
Added value, lei / t.	13.5
Sales revenue, lei / year (600 lei / car x nr. car / year)	**1 784 224**
Profit before taxes, lei	386 989
Profits tax, %	12
Net profit, lei / year	**340 550**

As a result, the value of the right (the right on land + the right on the deposit) to extract the clay deposit from the perimeter of the plot of land under evaluation is within the limits 644 thousand lei – 1 288 thousand lei.

[6] Calculations are aggregated, additional special costs supported by holder of the right of subsoil use are not included.

Table 4

Estimation of license value

Criteria	„Pruncul"	Asset being valued	Note
area, ha	40.7	9.2	
reserves on 16.06.1983, thousand m^3	11 226.0	2 283.8	11 226 / 40.7 x 9.2 x 0.9
reserves on 01.01.2013, thousands m^3	10 536.1		
extracted volume, thousand m^3	689.9		11 226 – 10 536.1
average annual extraction volume, thousand m^3	23.79		689.9 / 29 years
density of dry clay, kg / dm^3		1.6	
reserves, thousands of tons		3 248.1	2 283.8 x 1.6
clay price, lei / t		13.5	
Revenue from potential sales / year	513 857		
years		96	2 283.8 / 23.79
discount rate, %		7.98	NBM deposit, legal pers.
K act.		12.523439	$(1.0798^{96}- 1) / (0.0798*1.0798^{96})$
royalty rate, minimum		5%	
royalty rate, maximum		10%	
amount of royalties, minimum, lei		25 693	513 857 x 5%
amount of royalties, maximum, lei		51 386	513 857 x 10%
License value, minimum, lei		321 763	25 693 x 12.523439
License value, maximum, lei		643 525	51 386 x 12.523439
Royalty rate to profit before taxes for the amount of 25.7 thousand lei / year		6.64 %	for partial right
Royalty rate to profit before taxes for the amount of 51.3 thousand lei / year		13.27 %	for partial right
Minimum royalty rate for absolute right on extraction	13.28%		for absolute right
Maximum royalty rate for absolute right on extraction	26.54%		for absolute right
"25% rule" – royalty rate to profit before tax	25%		for absolute right
Amount of royalties according to "25% rule", lei / year	96 747		for absolute right
The value of absolute right on extraction according to "25% rule", lei	1 211 608		for absolute right

The value of the right on land or the special value for the special purchaser SA "P" is within the limits 322 thousand lei - 644 thousand lei (or ½ of the value of the absolute right of extraction). These figures represent the benchmark for direct negotiations with a potential special buyer.

In the case of omission of the study of property interests, and applying the valuation methodology, the estimated value by Discounted Cash Flow method would be approximately 4.3 million lei (340 550 x 12.523439).

CONSEQUENCE No. 3: The value of the asset being valued would be approx. 4.3 million lei in the case of omitting the study of the ownership rights compared to the zero market value and to the 644 thousand lei – special value in the case of considering the effects of the ownership rights.

Conclusions

Neglecting the study or the superficial examination of real property interests of asset being valued has serious consequences:

• for the beneficiary of the valuation report (the owner of the good) – the owner believes that the asset valuable, de facto the asset may be of no value or may have a net inferior value;

• for the user of the valuation report – the banking institution will offer a mortgage without a real collateral;

• for the valuator – the falsification of the valuation results is followed by administrative and criminal liability.

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APPLICATION OF MODERN SOFTWARE COMPLEXES FOR MODELING THE WORK OF DAMAGED STONE STRUCTURES

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Abstract. The article focuses on the estimation problem of the residual rolling capacity and the reliability of the stone structures elements of the buildings and structures in the historical part of the cities, which are approaching the normative term of service. To prevent the destruction of existing buildings and structures and to optimize solutions related to the reinforcement and reconstruction of damaged structures, information on their residual capacity is required. The paper proposes a method for assessing residual carrying capacity in the software complex. The analysis by applying the proposed algorithm (non-destructive method) allows a real prognosis, the difference between the calculation results and the experimental research of the stone structures being 5%.

Keywords: *reliability, reconstruction of stone structures, residual capacity, software modeling.*

Introduction

Stone materials from ancient times, as well as the wooden materials, form the basis of construction, so the existing monuments of history and architecture, in the vast majority of them, were made of solid red brick on limestone and complex solutions.

It is known that a large part of them is located in large cities. These are historical centers of not only Ukrainian, but also European cities and separate houses and churches.

Modern aggressive ecology, as well as other destructive factors, worsen seriously the physical and mechanical properties of brickwork of structures of historic buildings. This suggests that brick buildings and architectural heritage buildings today are in dire need of their protection and timely restoration.

Figure 1. Diocletian Palace, listed on the UNESCO list, Croatia.

Attempts to restore architectural monuments have been already known in antiquity, but until the XVIII-XIX centuries they usually were reduced to simple repair or to restore an object with actual changes in the current history of history. As an independent discipline, the restoration of monuments originates in the middle of the XIX century. in the framework of the

Christian worldview, in which "time is evaluated as a directed process with beginning and end, past and future. Therefore, the possibility of irreversible loss of those values that form the fundamentals of culture, and hence the requirements for their unconditional preservation "[1, p. 32]. By this time, mostly engaged in repair, adjustment, and it was this value that was put into the very term "restoration".

1. The purpose of the research

Nowadays for further reconstruction or re-equipment of existing facilities for the purpose of their further exploitation, in turn, requires the availability of a universal method for assessing the actual state of the structural elements of such buildings and structures.

2. Relevance of work

The problem of estimating the residual bearing capacity and reliability of stone structures elements has also recently intensively increased due to the fact that the age of a significant part of buildings and structures in the historical part of European cities and in Ukraine, which were built 50 and more years ago, are approaching normative term of service.

In order to prevent the destruction of existing buildings and structures, as well as to optimize solutions related to the reinforcement and reconstruction of damaged structures, it is necessary to have information about their level of residual bearing capacity.

3. Normative documents

Existing Ukrainian norms - DBN B. 2. 6 - 162: 2010 and European standards regulates the calculation of such elements, taking into account the nonlinearity of deformation.

The science of the strength and methods of calculating stone structures is based on extensive experimental and theoretical studies, was created for the first time in the USSR in 1932-39. Its founder was L. I. Onishchik [1]. Noncentral compression in the stone structures are the most common type of stress state. All walls and pillars of buildings, bridges, constructions, etc. Are prone to off-center compression. In this regard, the study of the centrifugal compression of the masonry was given much attention in the studies [7-15].

However, the complexity of the phenomenon, which had to meet during the solution of the problem, was so great that, to date, there is no strictly developed theory of off-center compression masonry, and the practical solution to the problem was reduced to the development of empirical calculation formulas [16, 22, 25]. The features of the masonry work from different types of stone and mortar, as well as factors influencing its strength, were studied.

It is established that in a stone masonry, consisting of separate layers alternating between stone and a solution, during the transfer of effort across the intersection there is a complex stressed state and separate stones (bricks) work not only on compression but also on the bend, on the stretching, cut and local compression. The reason for this is the inequality of the stone bed, the uneven thickness and density of the horizontal joints of the masonry, which depends on the

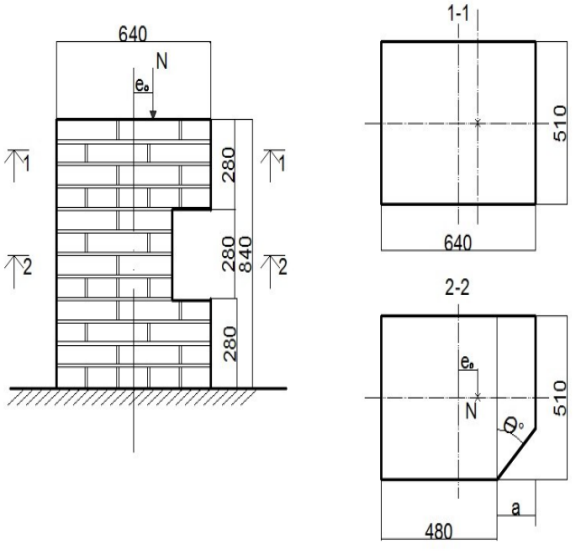

Figure 2. Diagram of simulation of damaged sample-pillar.

thoroughness of the mixing of the solution, the degree of alignment and compression at the laying of the stone, the conditions of hardening, etc. A stone masonry, made by a qualified mason, is stronger (by 20-30%) than that performed by the worker of secondary qualification. Another reason for the complex stressed state of the masonry - various elastic-plastic properties of the solution and stone. For example, the stiffer the solution, the worse the seams come out.On the strength of masonry can provide a great influence and shape of the bricks. If the surface in them is very distorted, the thickness of the seams turns out very uneven, and from this increases the bend of the brick in the masonry. Reducing the strength of masonry for that reason can reach 25%.
Belyov V. V. call a spurious analysis of the causes of defects (Table 1).

Table 1.

Quantitative assessment of the reasons for the refusal of construction sites

Causes of Avarities	Share in total
not uniform rainfall reasons	(65-75%)
overload designs	(10-15%)
temperature deformations	(10-15%)
humid deformations	(5-8%)
special load and action	(2-5%)

To prevent the destruction of structures and accidents it is needed to have information about their level of residual bearing capacity, reliability and residual resource.

The development of new numerical modeling methods allows the study of the residual duration of load bearing capacity by comparing the data obtained both with theoretical and practical studies. Establishing the most efficient and most modern method of assessing the bearing capacity of damaged structures can be done on the basis of their stress-strain analysis.

One of the main methods on the basis of which most of the applications (ANSYS, MatLab, SCAD, LIRA) are written is the finite element method used to calculate linear and nonlinear problems in various branches of science in the technical field.

One of the most popular software complexes used by most of our country's scientists and researchers who are studying and improving building constructions is the PC LIRA software package, which has gained popularity [5, 6, 8, 9]. That is why we decided to use PC LIRA 9.4 development of the Institute of Nuclear Physics, Kyiv. Based on the analysis of scientific and technical literature and preliminary studies [18-21, 23, 24], an experiment was planned on three the most significant factors influencing the residual bearing capacity of damaged stone pillars of a rectangular cross section, namely: depth of damage, angle of inclination of the front of the damage on one of the main axes of the intersections and eccentricity.

Before conducting modeling in the PC LIRA in the laboratory of OSACEA experiments [4] were conducted on the examination of the bearing capacity of damaged stone pillars.

4. Modeling in pc lira

According to the current norms, on the proposal of L. I. Onishchik diagram of "stress-deformation" for the masonry has the following form (Figure 3).

To construct the dependence curve "ε - σ" for this masonry, we use the preconditions for calculating from the textbook Vakhnenko P.F.

$$\varepsilon = \frac{\sigma_1}{E_0 \cdot \left(1 - \frac{\sigma_1}{1.1 \cdot R_u}\right)} \quad (1)$$

where:
E_0 - initial modulus of masonry deformation (modulus of elasticity at stressed, close to zero)
R_u - average compressive strength

The initial modulus E_0 of elasticity can be expressed through the ultimate strength:

$$E_0 = \alpha \cdot R_u \quad (2)$$

where:

α - elastic characteristics of the masonry, which depends on the type of masonry and brand of the solution.

The strength of a masonry, studied in this work is theoretically determined by the formula of L.I. Onishchik:

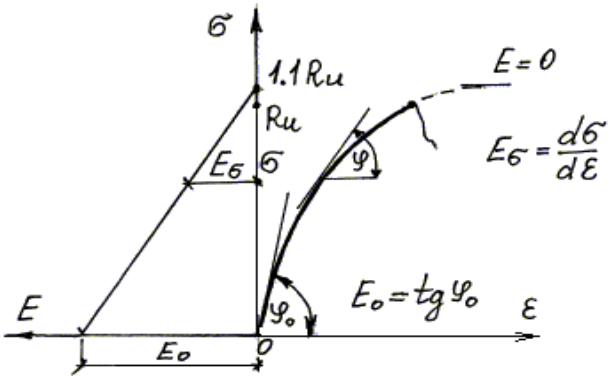

Figure 3. The deformation pattern of the masonry.

$$R_u = AR_1\left(1 - \frac{a}{b + {}^{R_2}/_{2R_1}}\right) \quad (3)$$

where:

R_1 - the compressive strength of the stone;

R_2 - strength of the solution (cubic strength);

A — coefficient that characterizes the maximum possible strength of the masonry and is determined by the formula:

$$A = \frac{100 + R_1}{100m + nR_1} \quad (4)$$

γ — coefficient that is used in determining the strength of masonry on different solutions of low grades (M25 and below)

In this case, the brand M25: = 11.1 MPa; = 5.52 MPa; a = 0.2;

b = 0.3; m = 1.25; n = 3 (Table 2 [75]); A = 0.46; γ = 1 substituting in the formula (3)

$$R_u = 0{,}46 \cdot 11{,}1 \cdot \left(1 - \frac{0{,}2}{0{,}3 + {}^{5{,}52}/_{2 \cdot 11{,}1}}\right) \cdot 1 = 3{,}24 \text{ МПа} \quad (5)$$

$$E_0 = \alpha \cdot R_u = 1200 \cdot 3{,}24 = 3800 \text{Мпа} \quad (6)$$

To solve the problem, it is necessary to construct a graph of the dependence of "ε - σ" by substituting the coordinates into formula 3 (Tab. 2). Using the Microsoft Excel software program, the resulting characteristic points are presented as a graph.

Table 2.

The dependence of "ε - σ" by substituting the coordinates into formula 3

R_u	E_0	σ	ε
3,24	3800	0	0
		0.5	0.000153
		1	0.000366
		1.5	0.000682
		2	0.001201
		2.5	0.00221
		3	0.005019
		3.24	0.009486

The resulting calculation results are presented in Figure 4

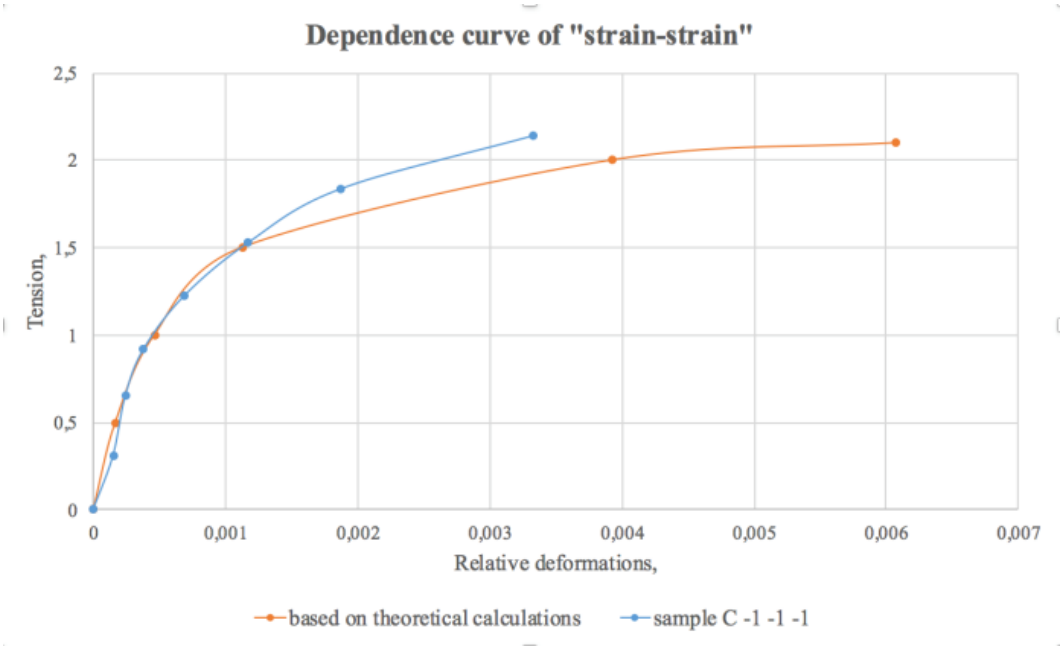

Figure 4. Graph of tension and deformation.

The method of evaluation of residual bearing capacity in the software complex, non-destructive method is proposed hereafter. At the first stage, we create points on coordinates, which later connect and set the boundary conditions to nodes in five degrees of freedom. At the second stage, we set the stiffness of the elements. Using the "Hardness → Hardness Elements" menu, we call the "Elemental Hardness" dialog. In this window, click on the "Add" button to display the list. Choose the third dialog "Plastic, Volume, Numerical", the type of section - "Volume Limit Elements", and then put a tick on the account of nonlinearity and press "parameters of the material", choose the "law of nonlinear deformation", in our case, it is 14 (piecewise -linear law of deformation), and then we introduce data on the characteristics of the material from the received graph of the dependence of "stress-deformation" (Figure 4)

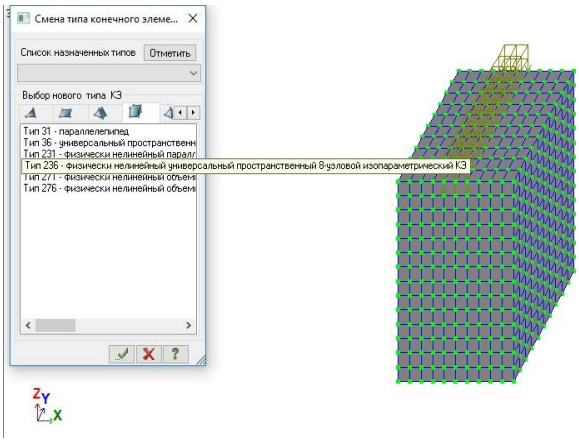

Figure 5. Selecting the type of the final element.

The pillar was divided into finite elements in the form of rectangular parallelepipeds with a face dimension of 1 to 2 cm, as well as octal and six-node endpoints in the form of triangular and quadrangular prisms in places where this required the geometry of the sample for modeling the slope of the shelves and the front of the damage.

The laying was given by physically nonlinear spatial eight-node and six-node isoparametric KEs of type 236 - "physically nonlinear universal spatial 8-node isoperimetric Limit Elements" (Figure 5) and a metal plate for the transfer of load 234, taking into account geometric and physical nonlinearity.

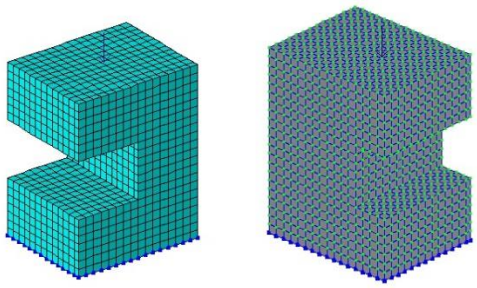

Figure 6. Finite Element Model of a Damaged Column.

The resulting model is close to a full-scale experiment (Figures 7, 8). We perform the calculation of the model, and the results are obtained in tabular form.

Figure 7. Isolation of normal voltages in t/m^2.

Figures 7, 8 show that in the case of small areas of damage, the protective layer of concrete is less, compressing stresses are approximately the same throughout the section under consideration. In the case when the rebars of concrete exposed the reinforcing bars, a redistribution of compressive stresses on the reinforcement is observed, which provides additional strength of the damaged columns during compression.

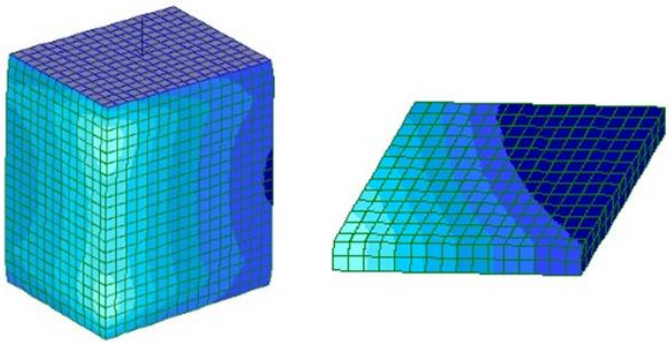

Figure 8. Isolation stresses in the C -1-1-1 column.

Figures 7, 8 show that in the case of small areas of damage, the protective layer of concrete is less, compressing stresses are approximately the same throughout the section under consideration. In the case when the rebars of concrete exposed the reinforcing bars, a redistribution of compressive stresses on the reinforcement is observed, which provides additional strength of the damaged columns during compression.

In all the specimens examined, the neutral line in the damaged section is beyond its limits and has the form close to the straight line. It is parallel to the damage front in the case of its parallelism of one of the main axes of the section. In the case of "skew" damage, the turn of the neutral line occurs relative to the main axes of the section and the front of the damage.

Conclusion

The analysis of the above method of calculating the damaged stone pillar allows us to conclude that this method completely takes into account the actual work of the material. The difference between the calculation results and the experimental research of stone structures is within 5%.

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THE EVOLUTION OF FOOD PRODUCTS CONSUMPTION IN REPUBLIC OF MOLDOVA IN THE DEMOGRAPHIC TRANSITION PERIOD

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Abstract. Republic of Moldova has experienced economic changes in the past three decades. This has resulted in sustained increase in consumer income, which in turn has led to important changes in food consumption. This report examines the recent trends in Moldova's food consumption, with a focus on the period of 1990-2017. Data for Food intake recommendations of the World Health Organization (WHO) are used as a starting point to look into Moldova's likely future demand and possible import needs. The article analyzes the consumption of basic products by the population of Moldova from the point of view of ensuring the economic and physical accessibility of food, the trends in changes in the volume and structure of consumption are revealed; assessment of the degree of achievement of rational norms. To assess the quality of diets, their energy and nutritional values there have been investigated: the content of energy, proteins, including animal origin, fats and carbohydrates.

Keywords:*food consumption, production growth, nutrition, diet's quality, autochthon outlook.*

Introduction

Changes in agricultural practice over the past 50 years have increased the world's capacity to provide food for its people through increases in productivity, greater diversity of foods and less seasonal dependence. Food availability has also increased because of rising income levels and falling food prices [1] Promoting healthy diets and lifestyles to reduce the global burden of noncommunicable diseases requires a multisectoral approach involving the various relevant sectors in societies [2]. The agriculture and food sector figures prominently in this enterprise and must be given due importance in any consideration of the promotion of healthy diets for individuals and population groups [3].

Such numbers can determine the role of food in the process of continuous renewal of the human body: it is estimated that in 70 years of life a person drinks 50 tons of water, eats 2.5 tons of protein, 2.3 tons of fat, over 10 tons of carbohydrates, almost 300 kilograms of salt. Proteins, fats, carbohydrates, mineral salts and vitamins - these are the components of food that are necessary for life. Scientific studies have revealed the required number of food products that fully satisfy the human need for the above elements. The duty of the state in

this case is to ensure food security [4].Food security means ensuring for the entire population, regardless of social and economic status, access to food stocks of sufficient quantity and quality [12]. Reliable food supplies meet the needs of consumers, without jeopardizing the production process in the short or long term. It ensures the sustainability of supply and, at the same time, takes due account of the safety of production methods and the food availability of products produced [5, 9]. In addition, food security means that everyone always has both physical and economic access to such a quantity of foodstuffs, which is enough for an active, healthy lifestyle. In this article, some quantitative comparisons and qualitative explanations are presented to know better food consumption in Republic of Moldova in different periods.

Materials and Methods

This paper sets as the object of study - the current situation in the field of nutrition of the population of the Republic of Moldova in the period 1990 - 2017. The statistics are obtained from official sources. - Anuarul Statistic al RM [6].

Research methods

As the research methods were used the method of studying statistical aggregates, the method of statistical observation - questioning, summary and grouping of materials of statistical observation, method of empirical research - comparison [3].

Food consumption per capita per day (Table 1) is a key variable used for measuring the evolution of the global and regional food situation [7]. Food production and consumption may be measured in a variety of ways, most commonly in terms of either expenditures or caloric content.

Further a comparative analysis is conducted between normative (by WHO data) and the factual consumption queries in Republic of Moldova.

Results and discussions

Availability and changes in consumption of animal products

Meat and meat products.

As can be seen from Table 1, consumption in the 1990s, the average of which reached the minimum in 1996-2000, constituted 35,96 % of the norms. This is due to the economic crisis of the 2000s and the decline in the general welfare of the population. Then, the rate of animal protein intake began to grow and reached a peak in 2016-2017, reaching 48,9 kg per capita per year, which is 69,76% of the WHO standard. FAO's research talks about meat starvation of the world's population [8]. There is also a version of FAO that these statistics are typical for developing countries, which include the Republic of Moldova.

Table 1.

Food consumption per capita, kg/year

Period	Product groups						
	Meat, meat products	*Milk, dairy products*	*Eggs*	*Potatoes*	*Vegetables*	*Fruits, berries, grapes*	*Bread, pastry, pasta, cereals and legumes.*
WHO recomm.	**70,1**	**404**	**243**	**96,7**	**140,3**	**80,3**	**120,5**
1990	58	303	203	69	112	79	171

Continuation *Table 1*

1991	56	259	194	68	113	79	174
1992	46	198	166	67	95	63	170
1993	35	174	130	95	94	80	170
1994	30	163	100	84	78	68	138
1995	24	165	107	68	86	30	135
Average kg/year 1990-1995	**41,50**	**210,33**	**150,00**	**75,17**	**96,33**	**66,50**	**159,67**
%WHO 1990-1995	***59,20***	***52,06***	***61,73***	***77,73***	***68,66***	***82,81***	***132,50***
1996	25	161	116	71	65	59	127
1997	25	155	121	69	69	78	135
1998	27	155	122	65	113	48	134
1999	25	145	132	62	109	27	133
2000	24	153	133	53	83	32	134
Average kg/year 1996-2000	**25,2**	**153,8**	**124,8**	**64**	**87,8**	**48,8**	**132,6**
%WHO 1996-2000	***35,95***	***38,07***	***51,36***	***66,18***	***62,58***	***60,77***	***110,04***
2001	24	155	139	65	104	33	139
2002	27	167	158	68	99	38	141
2003	27	164	158	69	107	43	133
2004	32	166	162	63	88	38	146
2005	40	174	177	75	101	37	142
Average kg/year 2001-2005	**30**	**165,2**	**158,8**	**68**	**99,8**	**37,8**	**140,2**
%WHO 2001-2005	***42,80***	***40,89***	***65,35***	***70,32***	***71,13***	***47,07***	***116,35***
2006	38	177	168	88	132	39	136
2007	36	175	177	59	76	28	119
2008	32	155	141	88	99	41	123
2009	30	169	162	59	106	35	119
2010	43	159	160	54	92	62	101
Average kg/year 2006-2010	**35,8**	**167**	**161,6**	**69,6**	**101**	**41**	**119,6**
%WHO 2006-2010	***51,07***	***41,34***	***66,50***	***71,98***	***71,99***	***51,06***	***99,25***
2011	38	170	190	60	115	43	116
2012	40	171	156	52	78	41	109
2013	46	166	165	53	86	42	106
2014	43	212	180	47	104	71	110
2015	43	159	160	54	92	62	101
Average kg/year 2010-2015	**42**	**175,6**	**170,2**	**53,2**	**95**	**51,8**	**108,4**
%WHO 2010-2015	***59,91***	***43,47***	***70,04***	***55,02***	***67,71***	***64,51***	***89,96***
2016	47,1	217,5	186	47,5	114,2	49,3	116,8
2017	50,7	227	197	46	117,8	51,8	121,7
Average kg/year 2016 - 2017	**48,9**	**222,25**	**191,5**	**46,75**	**116**	**50,55**	**119,25**
%WHO 2016-2017	***69,76***	***55,01***	***78,81***	***48,35***	***82,68***	***62,95***	***98,96***

Source: Biroul National de Statistica

Milk and dairy products

From Table 1 it can be seen that for a long period people do not receive enough milk and dairy products. The gap between the norm and the maximum consumption over the past 25 years in the Republic of Moldova is more than 2 times. Since the 1990s, the average annual consumption of dairy products has significantly decreased, reaching 159 kg/year in 2015, which is 39% of the WHO standard. The situation seems to have a positive trend in the last years, having an average consumption of dairy products of 222,5 kg/year for the 2016-2017 period. FAO data on the consumption of milk and dairy products also confirm a large gap with the norm and reflect disappointing forecasts, despite positive trends since the beginning of 2000.

Eggs.

The consumption of eggs in the Republic of Moldova varies from 100 to 200 pieces per person per year, given that WHO recommends using 243 eggs per year. In general, Moldova's indicators are not bad - on average they exceed 50% of the norm, having the same increasing trend as for dairy products. Since 1995, there has been a steady upward trend in the consumption of egg products, which has a positive effect on the health of society. The percentage of covering the WHO norms for 2016-2017 period reaches 78,81 %.

Availability and changes in consumption of plant origin products

Potatoes.

Potatoes are one of the most affordable products for all social groups and are the basis of the diet of most families. Accordingly, the level of consumption of potatoes by the people of the Republic of Moldova is high. The closest indicators to the norm were revealed in 1994, 2006 and 2008 (91% of the WHO norm). Potato consumption is then significantly reduced due to the availability of other carbohydrate products and the expansion of the range on the market. The lowest indicator was registered in 2016 - 46 kg/person/year, which is 47,7%.

Vegetables.

Recommended consumption rates are sustained only in 2006, when the consumption reached 132 kg/person/year. The remaining data vary from year to year, while there is no clear trend to increase or decrease the number of consumed vegetables. The Republic of Moldova is an agrarian country, we have a large variety of fruits and vegetables, but at the same time, the yield of a particular year depends on many factors. Accordingly, the affordability of vegetables is determined by the yield. The lowest consumption of vegetables, which are the main sources of fibers, was recorded in 1996, 2007 and 2012, accounting for about 50% of the norm. Analyzing the trends for the last three years, we can say that the vegetable consumption shows an increasing trend, covering 116% of the WHO norms. This values show the population concern for a healthier lifestyle.

Fruits, berries and grapes.

Nowadays, not only in the world, but also in our country, young people started to give preference to a healthy diet, to make a choice in favor of a healthy and nutritionally balanced diet. Compared with the beginning of the 2000s, when fruit consumption was about 50% of the norm, in 2014 fruit consumption was 71 kg/person/year, which is 89% of the WHO norm. However, this trend has not yet become fundamental, so that it can be allowed to drift. It is safe to say that without adequate support, it can come to naught. Therefore, widespread agitation of healthy eating with the involvement of the media is very important.

Bread and pastry, pasta, cereals and legumes.

Until 2010, the consumption of bread is much higher than the rational norm. Only in the last 7 years, a decline in the consumption of flour and pasta has been recorded, which is a positive trend in public health. In 2011, compliance with the WHO standard of 120 kg per person per year was achieved. In the last 5 years, there has been an insufficient intake of complex carbohydrates, which is not a favorable factor for the population.

Analysis of food consumption indicates that the key deviations from the recommendations were characteristic for the period 1990-2005. Since 2005, we have seen a stabilization of consumption across all product groups. It is clear from the diagram that food consumption meets the WHO recommended guidelines within the range of 60-80%. Less dairy products are consumed, and the 80-100% coverage is achieved only in the case of bread, cereals and vegetables in the period 2015-2017.

Figure 1 presents the food requirements coverage in Moldova according to WHO recommendations. As it can be seen from the figure 1, the only group of products that overpasses the WHO recommendation is bread and cereals, all the others showing an unstable trend (sometimes increasing, sometimes decreasing).

As a summary, in general, the consumption of some food products in Republic of Moldova has slightly decreased (potatoes, bread and pastry) while the consumption of other products has increased (fresh meat, eggs and vegetables). Altogether, food consumption in Moldova, in quantity terms is still under the recommendation of WHO.

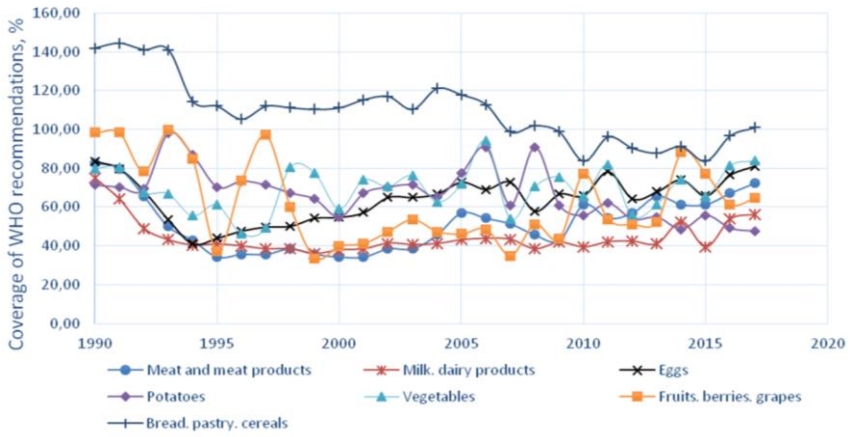

Figure 1. Food requirements coverage (%) in Moldova according to WHO recommendations.

Product consumption per capita analysis is not sufficient to assess the true consumption of products of rational standards recommended by the WHO. To assess the quality of diets, their energy and nutritional values there have been investigated: the content of energy, proteins, including animal origin, fats and carbohydrates. WHO developed norms of physiological needs for energy and food [10, 11]. However, these norms are established for different age and gender groups of the population (Table 2).

Compared to the nutritional intake values recommended by the World Health Organization (WHO), the composition of an average citizen's diet in the Republic of Moldova includes adequate proportions of carbohydrates and proteins but contains a certain excess of fat. In 2013, the average energy intake in the Republic of Moldova contained 54% of carbohydrates, 35% of fat and 11% of protein. For the other periods the values are shown below (Table 2, Figure 2).

Daily food consumption per capita, increased from 2413,4 calories in 2006 to 2529 calories in 2017. As the table shows, this slight increase is due to the increasing consumption of animal products. Starting with 2013 the daily energy intake has started to recover, although it has not yet reached the values recommended by the WHO until 2017.

Protein consumption increased during the analyzed period from 65,7 in 2006 to 72,7 g in 2017. This data are also confirmed and by the increasing meat consumption during this period.

Table 2.

Food consumption on Calories and Nutritional Factors

Year	Calories	Calories from animal sources	Proteins, g	Lipids, g	Sugars, g
WHO recommendation	**2520**	-	**78**	**70**	**395**
2006	2 413,4	502,2	65,7	86,4	345,1
2007	2 273,1	504,5	62,2	82,5	321,3
2008	2 203,7	440,8	58,1	80,3	314,7
2009	2 240,3	473,3	60,7	83,0	317,5
2010	2 210,7	477,5	60,0	82,6	311,4
Average kg/year 2006-2010	**2310,20**	**479,66**	**64,12**	**80,80**	**334,17**
%WHO 2006-2010	***91,67***		***82,20***	***115,43***	***84,60***
2011	2 258,3	516,1	61,6	87,4	310,9
2012	2 291,8	548,0	63,3	89,8	313,8
2013	2 320,1	553,1	65,2	91,2	316,5
2014	2 329,4	549,2	66,0	92,0	316,7
2015	2 372,3	570,8	67,7	92,6	323,7
Average kg/year 2011-2015	**2314,38**	**547,44**	**64,76**	**90,60**	**316,32**
%WHO 2011-2015	***91,84***		***83,03***	***129,43***	***80,08***
2016	2 441,7	583,3	69,3	95,2	333,2
2017	2 529,3	615,5	72,7	98,4	345,2
Average kg/year 2016-2017	**2485,50**	**599,40**	**71,00**	**96,80**	**339,20**
%WHO 2016-2017	***98,63***		***91,03***	***138,29***	***85,87***

Source: Biroul National de Statistica

Lipid consumption has increased and this fact is also closely related to the increase of the consumption of meat, milk and dairy products.

According to WHO data, the highest level of fat consumption in the European region is found in the Baltic countries and Western Europe - 41% and 38% of the daily energy requirements [12, 13]. In Republic of Moldova the level of fat consumption in daily energy intake represents 35%, which is specific to these countries.

For sugars, consumption was relatively constant (around 316,0 g) until 2014, after which it started to increase reaching 345,2 g in 2017. It has to be mentioned that the increase in carbohydrate intake occurred due to the increase in consumption of vegetables, fruits and berries, but not from the cereals, especially bread account - the consumption of which has diminished. Compared to the nutritional intake values recommended by the World Health Organization (WHO), the composition of an average citizen's diet in the Republic of Moldova

includes adequate proportions of carbohydrates and proteins but contains a certain excess of fat.

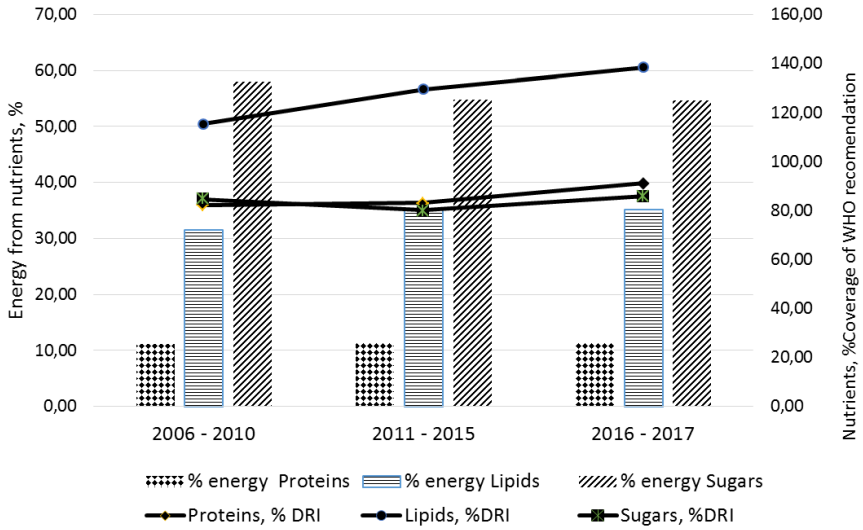

Figure 2. Average nutritional intake in the Republic of Moldova contained %.

Conclusion.

A comparative analysis of actual consumption and recommended rational norms of food consumption in the Republic of Moldova illustrates the insufficient provision of the inhabitants of the region with basic foodstuffs (vegetables and fruits, meat, dairy products). The main problem in the country is associated with inadequate consumption of dairy products - about 40%, vegetables - 60%, fruits - 50%, eggs - 70% compared with recommended amounts of food consumption. It was found that the consumption of food by the population is directly related to the food security of the country. Therefore, the state authorities of the Republic of Moldova should take into account the following areas of food security:

- Increasing the availability of all food products for all groups of the population;
- Improving product quality;
- Attracting additional investment in agriculture;
- Livestock development;
- Use of unused arable land.

Concerning the energy and nutritional compounds intake, compared to the nutritional intake values recommended by the World Health Organization (WHO), the composition of an average citizen's diet in the Republic of Moldova includes adequate proportions of carbohydrates and proteins but contains a certain excess of fat. Compared to the nutritional intake values recommended by the World Health Organization (WHO), the composition of an average citizen's diet in the Republic of Moldova includes adequate proportions of carbohydrates and proteins but contains a certain excess of fat. In 2013, the average nutritional intake in the Republic of Moldova contained 54% of carbohydrates, 35% of fats and 11% of protein.

In general, the average diet does not appear to have undergone any significant changes after 2006. In terms of food composition, Moldovan families have gradually reduced basic food consumption, maintained the level of meat and fish consumption and gradually increased product consumption dairy, fruit and vegetables, fats and oils.

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THE DETERMINATION OF OXIDATION BEHAVIOR OF WHITE WINES PRODUCED FROM LOCAL AND EUROPEAN GRAPE VARIETIES USING SPECTROPHOTOMETRIC METHOD

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Abstract: The article deals with the oxidation processes of experimental wines produced from indigenous grape varieties *Legenda*, *Viorica* and European grapes *Chardonnay*, *Sauvignon*. The browning processes in wine are corelated with oxidation of hydroxycinnamates (hydroxycinnamic acids and their tartaric esters, HCAs) – the most important group of phenolic compounds in white wines. The potential degree of wine colour changes has been appreciated using *Polyphenols Oxidative Medium test* (*POM-test*). The oxidative crocin bleaching (CBA – Crocin Bleaching Assay) has been studied using the method of competition kinetics. The comparative antioxidant capacity of wines has been determined with peroxy radicals 2,2'-Azobis (2-amidinopropane) dihydrochloride (AAPH).

Key words: *antioxidant capacity, crocin oxidative bleaching, flavonoids, hydroxycinnamates, phenolic compounds, POM-test, wine oxidation*.

Introduction

The biggest part of Moldovan wines are produced from European grape varieties, that are adapted to local growing conditions. These grape varieties are: *Chardonnay*, *Sauvignon*, *Cabernet-Sauvignon*, *Merlot* etc. At the same time, recently, in Republic of Moldova, much attention has been given to the goal of using the potential of old local grape varieties (*Feteasca Alba*, *Feteasca Regala*, *Feteasca Neagra*, *Rara Neagra*) and new grape varieties (*Viorica*, *Legenda, Riton)*. This kind of grape varieties are used by winemakers for producing high quality wines, single grape variety or blended. In this context, it is necessary to study the physico-chemical and organoleptic properties of them, polyphenol metabolism during processing of grapes, winemaking and wine storage.

The importance of phenolic compounds is well known [1]: these chemical substances are responsible for oxidative browning, process that are catalysed by enzyme polyphenol oxidase (PFO) or by ions and transition metals (preponderant Fe and Cu). Phenolic compounds are oxidized by the polyphenol oxidase (PPO) during the alcoholic fermentation, while the oxidation of phenolic compounds by ions and transition metals occurs after alcoholic fermentation, or under certain conditions, after wine bottling.

In addition, hydroxycinnamic acids can be the chemical precursors of 4-vinylphenol, that is further reduced to 4-ethylphenol by the enzyme vinyl phenol reductase of spoilage yeast *Brettanomyces*. This volatile substance, 4-ethylphenol, is responsible for such wine fault like smell of barnyards, fecal and gamey horse aromas.

The (HCAs) determines largely the colour of white wines, the antioxidant properties and some aromas after the alcoholic fermentation. In this regard, it is important to evaluate the phenolic profile and antioxidant capacity of the wine, the oxidation behaviour of phenolic compounds.

According to many scientific studies, (HCAs) and their derivatives have unique biological features. Hydroxycinnamic acids have antioxidant and anti-inflammatory properties, the ability to prevent renal failure, cardiovascular diseases, oxidative stress, insulin resistance, weight gain, dyslipidemia, improve liver functions [2]. Recent data support their beneficial application as preventive and/or therapeutic agents in several oxidative stress related diseases, such as atherosclerosis and cancer [3].

Thus, it's very important to provide conditions for producing high quality and healthy white wines. In this context, the determination of oxidation behaviour of (HCAs), in order to preserve them in wine, is the important task of enology. The development of effective and reliable methods for rapid testing the selective oxidation of (HCAs) is relevant. The currently techniques for appreciation the white wines oxidation are based on the qualitative and quantitative monitoring of chemical composition – liquid chromatography (HLPC), gas chromatography/mass spectrometry (GS/MS), based on colour change characteristics, that reflect the total oxidative reactions – UV-VIS spectrophotometry [4]. It is known that the levels of specific antioxidants, like polyphenols and redox mechanisms may be evaluated by electrochemical methods [5, 6], for example cyclic voltammetry [7]. The lack of a simple and accessible method for studying the oxidation of (HCAs) was the motivation for the research.

Materials and methods

The wines produced from 2 European grape varieties *Chardonnay* (Ch), *Sauvignon Blanc* (S) and 2 local grape varieties *Viorica* (V), *Legenda* (L) have been selected for research. The wines have been produced in 2017 at micro-winery of Enology department, Technical University of Moldova using general technologies of white winemaking. The sulphur dioxide (SO_2) has been added in grape crusher (50 – 75 mg /kg). The grapes have been destemmed and crushed at roller crusher. The grape must has been macerated for 2 hours at 12 – 14°C. In the grape must during maceration there have been added enzymes Ultrazym® 100G (Novozymes A/S, Denmark) (0,5 – 1 g/dl). From the grape variety Legenda, the samples also have been taken directly from the grape press without maceration (L1), after 4 hours of maceration (L2) and after 2 hours of maceration (L3). For all wines the post-fermentation period lasted for 40 days (14 – 16°C).

The wine samples have been filtered through the filter of 0,45 μ for spectrophotometric investigations (absorption spectra, total polyphenol index – IPT, phenolic compounds, the test of oxidation behaviour – POM-test, antioxidant capacity of wines etc.). The spectrophotometric analyses have been done at single beam spectrophotometer PG T70 (PG Instruments, UK) and double beam spectrophotometer Specord 250 Plus (Analytik Jena, Germania). These spectrophotometres have in their software application the function for calculating of derivatives.

The preparation of test samples and analysis of the basic parameters of wine has been done using automatic distiller Gibertini DEE and hydrostatic scale Densimat CE with module Alcomat-2 (Gibertini Elettronica, Italy), (the volumetric content determination of ethyl alcohol and dry residue), distillers GlassChem VA-1 (the determination of volatile acidity), and GlassChem SO_2 (GlassChem, South African Republic) (the determination of all SO_2 forms),

electronic titrators Titrette (Brand, Germany). The measurements of the pH values have been performed on pH Meter WTW Inolab 7110 (WTW, Germany). The used reagents (H_2O_2, AAPH) were produced by Sigma-Aldrich.

For the deposition of phenolic substances there have been used bentonite Bento Zero (Dal Cin, Italy), as well as polyvinylpolypyrrolidone (PVPP Vason Enologica, Italy). All necessary solutions have been prepared on distilled water (GFL 2004, Germany).

The deposition of sediment has been done using the centrifuge Universal 320 R (Hettich, Germany). The IPT has been determined by measurement of wine absorption at 280 nm in quartz cuvette (0,1 cm), with recalculation for the cuvette 1 cm.

The POM-test, proposed by Muller-Spath [8] for the oxidation behaviour determination of white wines, consists in the artificial oxidation of wine in the presence of certain concentrations of H_2O_2 within 60 minutes at 60°C. Herewith, there is optical absorption changes of samples at 420 nm in cuvette 1cm. Calculations are made according to the formula:

$$POM\ test\ (\%) = 100 * \frac{A_{420}(wine + H_2O_2) - A_{420}(wine)}{A_{420}\ (wine)}$$

The comparative antioxidant capacity of wines has been determined using the method Crocin Bleaching Assay (CBA) [9, 10]. The absorbance capacity of crocin (water-soluble carotenoid) has been measured at 443 nm. The generation of the radicals and its reaction with substrates have been performed in cuvettes held in thermostat at 40°C. Crocin has been extracted from commercial saffron (*Crocus Sativus L.*) (Aromatica SRL, Italia) and it has been purified according to Ordoudi and Tsimidou [11]. The concentration of the extract has been determined using spectrophotometric analysis. In reactant solutions with added wine it is ensured the crocin concentration of 10^{-6} M. The concentration of total phenolic compounds, flavonoids and cinnamic compounds has been performed at the spectrophotometer according to Somers and Verette [12].

Results and discussion

The absorption spectra of the studied wines in UV-vis region are measured at 260 – 280 nm. This value is based on the characteristic absorption of the benzene cycles of the majority phenols at 280 nm. Hydroxycinnamates (C6 – C3 phenolic compounds) have the maximum absorption with bathochromic shift at wavelength 300 – 350 nm.

The (HCAs) are the major non-flavonoid phenolic compounds in white grape and wine and thus their absorption spectra differ from the absorption spectra of red wine to balance of the maximum absorption at wavelengths at 260 – 280 and 300 – 350 nm. The visual analysis offers a first information about (HCAs) content in the complex of total phenols. However, original spectra do not show the fine differences between studied samples, oxidized wine and unoxidized wine. This is possible if we study the second order derivative spectra. The minimum interdependences $d^2A/d\lambda^2$ show the exact positions of the obvious and latent maximum. The final spectra, the algebraic sum of individual spectra, can distinguish them and have no coincidence of maximum values with the values presented in the specialty literature. The second order derivative spectra are more sensitive at quantitative and quality changes of wines and allow to find out the differences using spectrophotometry, a method more accesible than chromatography.

The absorption spectra UV-vis of experimental wines *Legenda* without preliminary treatment (L1, L2, L3) and their second order derivative spectra are shown in the "Figure 1". The second order derivative spectra in original forms are similar and highlight the essential differences in different spectral ranges. The major differences have been revealed at wavelength 260 – 280 nm, 300 – 315 nm and to a lesser extent at 330 – 345 nm. The sample with the less level of browning (L1-0) had a minimum of second derivative spectra at 269 nm and it had nearby the inflection point (281 nm), while the most oxidized wine (L2-0) has the minumum value at wavelength of inflection point (L1-0), where the (L1-0) has the minumum.

The wine (L3-0) with intermediate browning have 2 minimum values in these positions (270 and 279 nm). This fact allow us to consider wavelength 269 – 270 nm suitable to maximum of unoxidized polyphenols, while the products of its oxidation correspond to wavelength with bathochromic shift 279 – 281 nm. The differences in the range 300 – 315 are less expressed where the second order derivative spectra (L1-0) have extreme points.

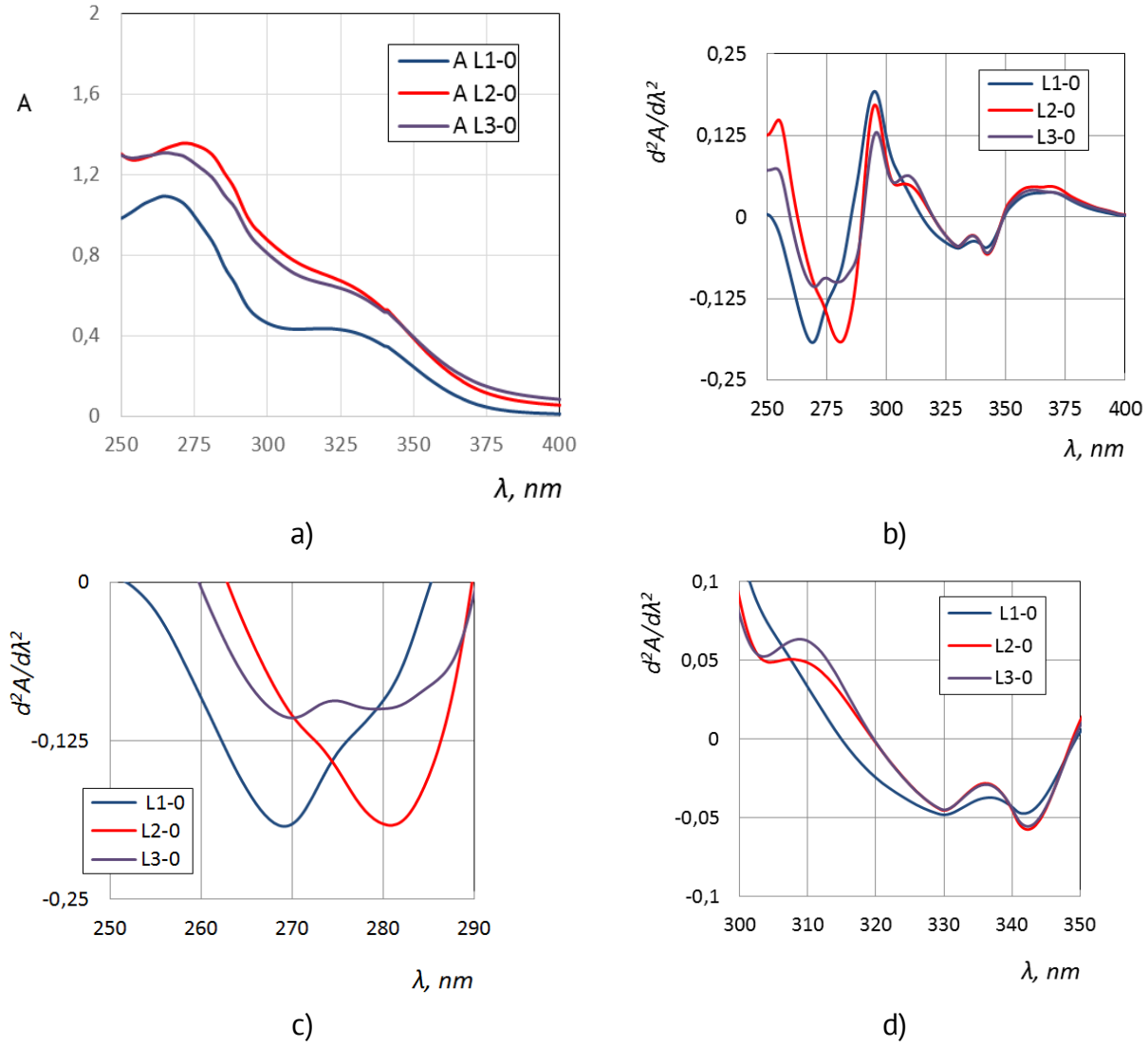

Figure 1. The absorption spectra of experimental raw wines Legenda with different level of oxidation (L1-0, L2-0 and L3-0 – a), and its second order derivative spectra (b, c, d). The wines are undiluted, the cuvettes path length – 0,1 cm.

The more oxidized samples (L2-0, L3-0) are characterized by minimum – maximum wavelength at 304 and 309 nm respectively. The samples (L2-0 and L3-0) have more

expressed minimum values than (L1-0) at 342 nm, because they have a higher content of oxidized polyphenols. These differences can be used for monitoring the oxidative processes in wines produced from *Legenda* grape variety.

The significant differences according to level of oxidation have been observed and in the visible region. These differences generally are quantitative, not qualitative. *Legenda* wines have no obvious or latent maximum values in the visible region. The absorbance at 420 nm for oxidized samples (L2-0, L3-0) is 0,538 and 0,567 (the layer thickness = 1cm) and 0,164 for unoxidized sample (L1-0). *Viorica*, *Chardonnay* and *Sauvignon* wines in UV-vis region have absorption spectra with 2 distinct regions 250 – 300 nm and 300 – 350 nm "Figure 2".

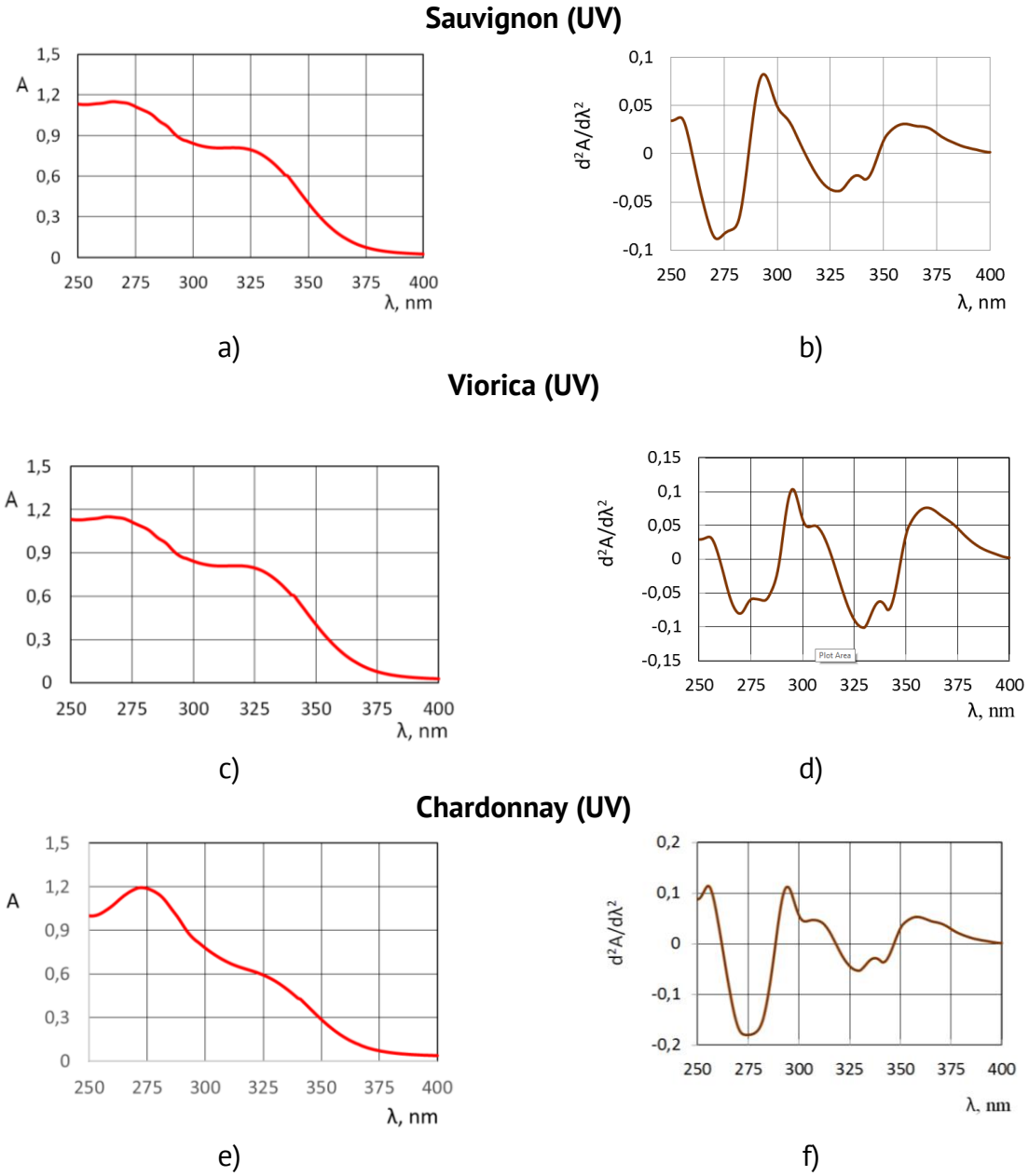

Figure 2. The absorption spectra of experimental raw wines Sauvignon (a), Viorica (c), Chardonnay (e) and its second order derivative spectra (b, d, f). The wines are undiluted, the cuvettes path length – 0,1 cm.

They are similar to *Legenda* wine spectra. In the case of *Sauvignon* wine it prevails the first minimum value (272 nm), the second minimum is masked and is presented by an inflection point. Absorption spectra show an increased (HCAs) content in *Viorica* wine. The quantitative differences are more evident in second order derivative spectra. The same groups of minimum values in 300 – 350 nm region have been observed. In the interval between 250 – 300 nm, 2 minimum values 270 nm and 281 nm are evident for *Viorica* wine. At Chardonnay wine the both minimum have the very close values and its superposition gives a single band with λ_{min} = 274 nm.

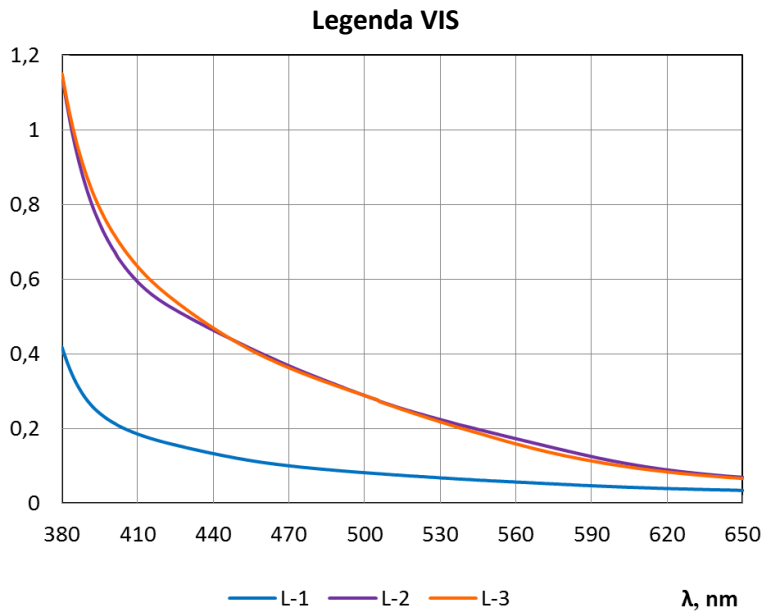

Figure 3. The absorption spectra of Legenda wine samples in the visible region, (undiluted wines, cuvettes path length 1 cm).

In the visible region, the absorption spectra of samples *Legenda* are quantitatively different. So, according to "Figure 3", oxidized samples (L-2 and L-3) are characterized by significantly large absorption (about 3 times) than non-oxidized sample.

The spectrum of non-oxidized sample of *Legenda* wine (L-1) are quantitatively similar to the spectra of non-oxidized samples wines *Viorica*, *Chardonnay* and *Sauvignon* "Figure 4". In the visible region of spectrum, the using of second derivatives spectra of the studied wines unnecessarily due to their low information content (the gentle course of the spectra, lack of characteristic points clear highs on them and / or inflection points).

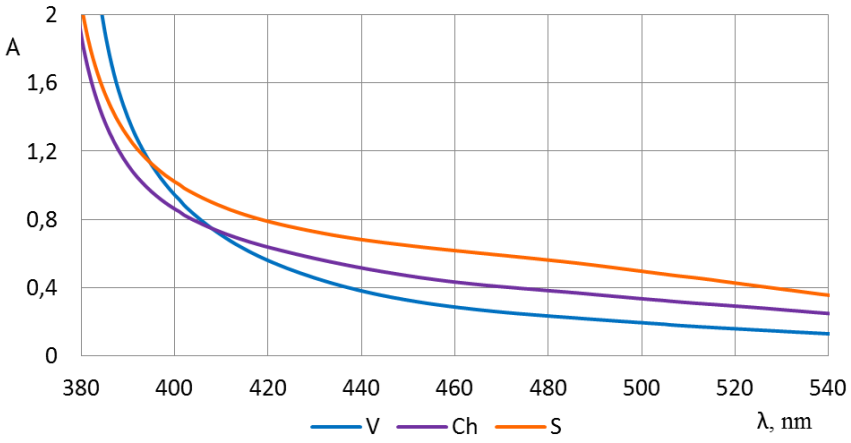

Figure 4. The absorption spectra of Viorica (V), Chardonnay (Ch) and Sauvignon (S) wine samples in the visible region, (undiluted wine, cuvettes path length 5 cm).

The concentration of total phenolic compounds – SFT (Galic Acid Equivalents, mg/l), phenolic cinnamic compounds – SFC (Caffeic Acid Equivalents, mg/l) and phenolic flavonoid compounds – SFF (Catechin Equivalents, mg/l) are presented in "Table 1".

Table 1

The concentrations of main phenolic compounds, the index of oxidation behavior (POM-test) and the parameter of relative antioxidant capacity (K).

Parameter	Wine					
	L1-0	L2-0	L3-0	V	Ch	S
Total phenolic compounds, SFT (Galic Acid Eq., mg/l)	145,1	269,4	236,1	199,3	220,4	68,8
Hydroxycinnamic acids and their derivatives, SFC (Caffeic Acid Eq., mg/l)	29,6	56,2	51,7	67,0	48,1	25,7
Flavonoid compounds, SFF (Catechin Eq., mg/l)	206,2	377,0	319,1	160,1	298,7	43,6
IPT	8,95	12,98	11,94	10,76	11,47	6,59
POM-test (%)	81,8	74,2	42,1	24,0	10,1	67,7
K ($K_o/K_v \div f$ (wine volume)	1,34	5,46	9,14	1,.9	2,07	1,06
R^2	0,8964	0,9960	0,9759	0,9409	0,9793	0,9359

The maceration of (L2-0) and (L3-0) wines have been ensured the better extraction of hydroxycinnamic acids and their derivatives (SFC), total phenolic compounds (SFT) and flavonoid compounds (SFF) than in (L1-0) wine.

The POM-test shows the increased oxidation behavior in (L1-0) wine. This fact can be explained by the presence in the respective samples of unoxidized forms of hydroxycinnamic acids and their derivatives. The smallest value of POM-test have been identified in *Chardonnay* wine samples.

The value of oxidation index (67,7%) for Sauvignon wine can be the consequence of decreased content of phenolic compounds extracted during processing. Our experiments show that wine treatment with bentonite and polyvinylpolypyrrolidone (PVPP) can reduce efficiently the content of oxidized polyphenols with brown tones in the studied wines.

The deposition of part of the phenol complex have been carried out by using bentonite in the concentration range 0.5 ÷ 2 g/l. As a result of wine analysis before and after treatment by bentonite, there has been found out that the sorbent works differently on different groups of phenolic compounds. This is clearly seen in "Figure 5".

As in the case of *Legenda* wine, as well as in the case of *Viorica*, *Chardonnay* and *Sauvignon* wines "Figure 6", bentonites exhibit large sorption properties in relation to flavonoid phenolic compounds of wine, which being bigger molecules than (HCAs), easier precipitate them. With this type of bentonite hydroxycinnamic acids and their derivatives are practically not removed from the wine.

In this way, the use of bentonites to reduce the concentration of phenolic substances in order to provide increased resistance of white wines to oxidative processes, should be

argumented by experimental treatments with quantitative determination of the main groups of phenolic compounds.

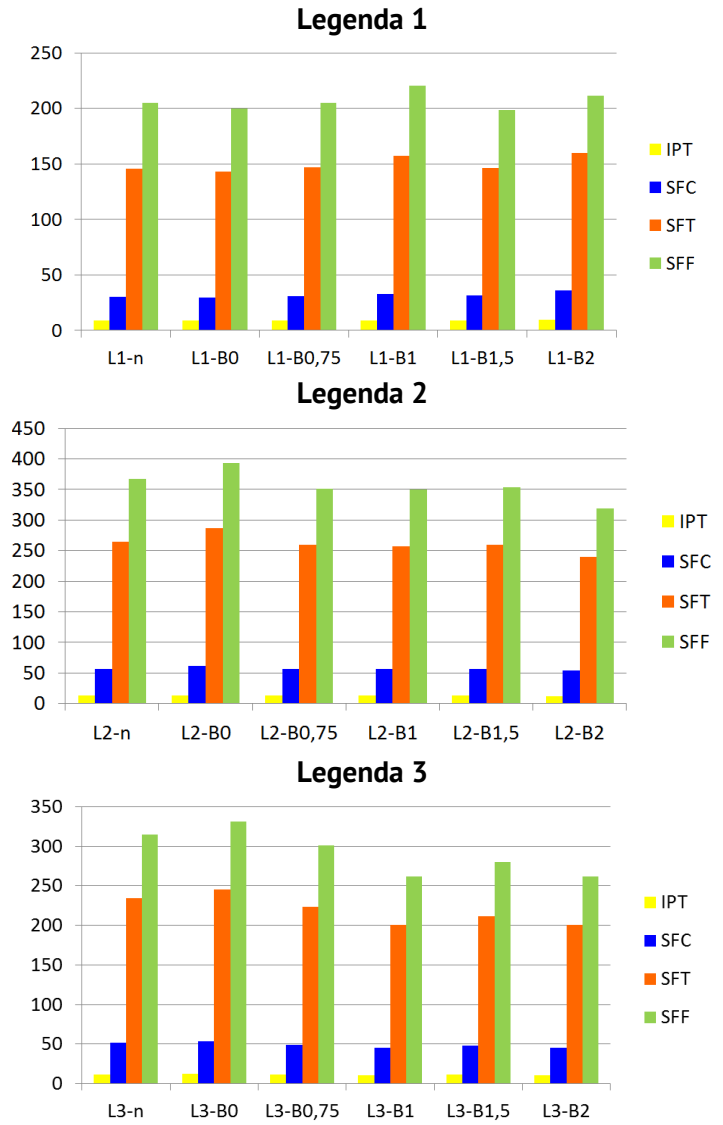

Figure 5. The impact of increasing doses of bentonite on total polyphenol index (IPT) and main groups of phenolic compounds in Legenda wines.

The involvement of wine components in redox reactions with various active forms of oxygen influences the wine capacity to withstand the oxidation during formation, ageing and after bottling. Of course, winemakers can add sulfur dioxide (SO_2) for better wine preservation. Sulfur dioxide is the most preservative used in the wine industry and has been widely applied, as antioxidant and antibacterial agent. However, in recent times, it has been shown that the intake of (SO_2) implicates a wide range of adverse health consequences, such as allergic reactions and cumulative harmful effects. For this reason, reducing the amount of SO_2 in wines is a decisive strategy for the wine industry and one of the current topics on the oenological science. This is also highly recommended by The World Health Organization (WHO).

The total antioxidant capacity of experimental wine samples have been determined by watching the competitive kinetics of crocin bleaching. The antioxidant capacity has been expressed by the interdependance between constant of colour fading speed in absence of

wine addition (Ko) and in the presence of wine addition in different volumes (v), in the reactant mixture (5 ml), in the spectrophotometer cuvettes (Kv). The monitoring of process has been done at 443 nm.

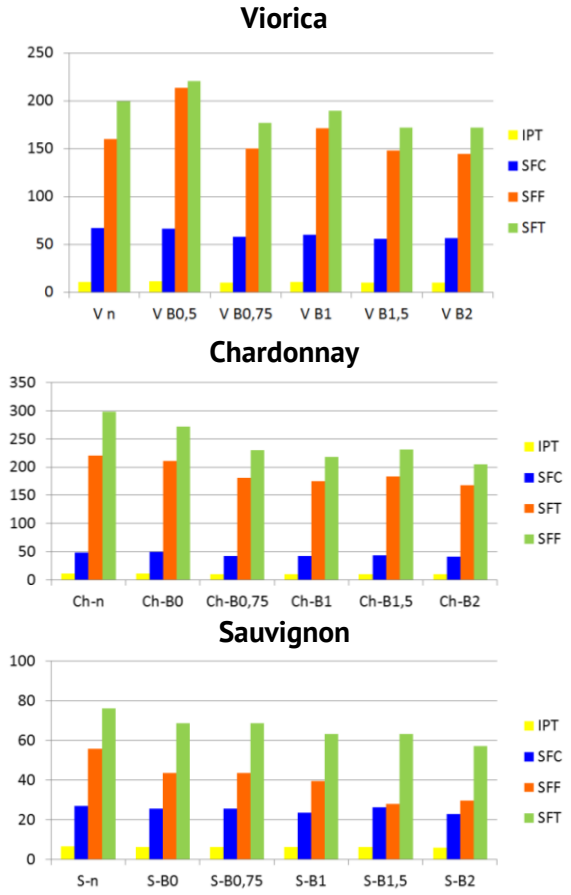

Figure 6. The effect of increasing doses of bentonite on total polyphenol index (IPT) and on the main groups of phenolic compounds in the Viorica, Chardonnay and Sauvignon wines.

The scheme of the reactions is the following:

(1) $R\text{-}N{=}N\text{-}R \rightarrow 2R^{\cdot} + N_2$

(2) $R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$

(3) $ROO^{\cdot} + CH \rightarrow ROOH + C^{\cdot}$

(4) $ROO^{\cdot} + AH \rightarrow ROOH + A^{\cdot}$

(5) $CH + A^{\cdot} \rightarrow C^{\cdot} + AH$

where:

R-N=N-R – radical initiator, AAPH;
$R^{\cdot}$ – primary radicals;
$ROO^{\cdot}$ – peroxy radicals;
CH – crocin (orange);
$C^{\cdot}$ – crocin radical (oxidation product, colorless);
AH – wine antioxidants (phenolic compounds);
$A^{\cdot}$ – antioxidant radicals of wine $ROO^{\cdot}$.

Since the concentrations of A· is significantly lower than concentrations of ROO·, the reaction (5) in the crocin bleaching may be neglected. The ROO· radicals, in the presence of wine antioxidants, have been spent not only in the crocin oxidation (reaction 3), but also in the interaction with wine antioxidants (reaction 4).

As a result, their concentration decrease and the reaction speed (3) decreases proportionally to the concentration of AN. Under the same addition of wine, in the same conditions, the higher total antioxidant activity of the wine, the higher will be the inhibition of crocin oxidation. In the "Figure 7" there are presented the results of the kinetic curves of crocin oxidation in the reaction mixture of various amounts of *Chardonnay* wine. There is also shown the linearization of the kinetic curves A443 ÷ t in coordinates ln (1 / At) ÷ t with high values of correlation coefficients "Figure 8".

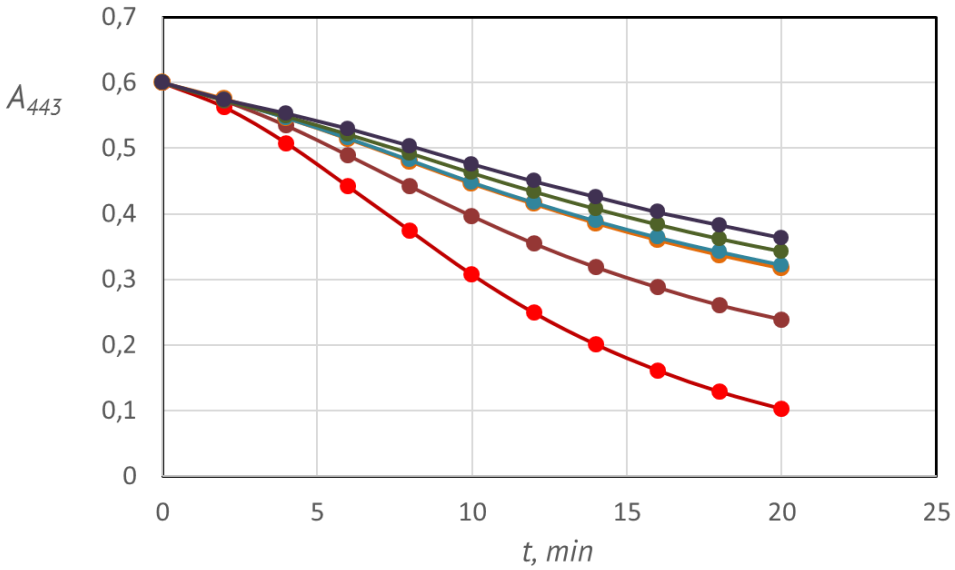

Figure 7. The kinetic curves of crocin oxidation (443 nm) in the absence (Ch-0) and in the presence in the reaction mixture of various amounts of Chardonnay wine: 0,15; 0,30; 0,45; 0,60 and 0,90 ml / 4 ml of the reaction mixture.Thermal initiation of peroxy radicals using (AAPH) in thermostated (at 40° C) cuvettes path lenght (1 cm).

From the slopes of the straight lines, the kinetic rate constants of the reaction between the wine antioxidants and peroxy radicals have been calculated. The higher capacity of wine antioxidants to react with the generated peroxy radicals, the more inhibited is crocin bleaching due to the competition of the crocin and the wine for ROO·. The phenolic radicals that are formed from reaction with ROO· are stable and inert compounds by the delocalization

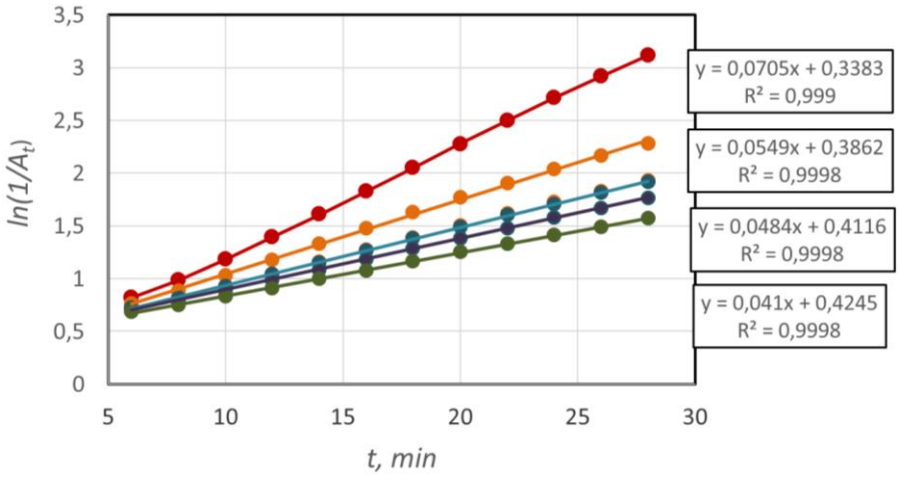

Figure 8. The linearization of the kinetic curves for the crocin bleaching with various Chardonnay wine supplements in the coordinates ln (1 / At) ÷ t.

of the electron density of the unpaired electron. The efficiency of inhibition depends on the nature of the phenolic antioxidants and their content.

The interdependencies Ko/Kv for all studied wines show more expressed antioxidant capacity at *Sauvignon*, *Viorica*, *Legenda* (L1-0) wines and unexpected expressed antioxidant capacity at *Legenda* (L2-0) and (L3-0) wines "Figure 9".

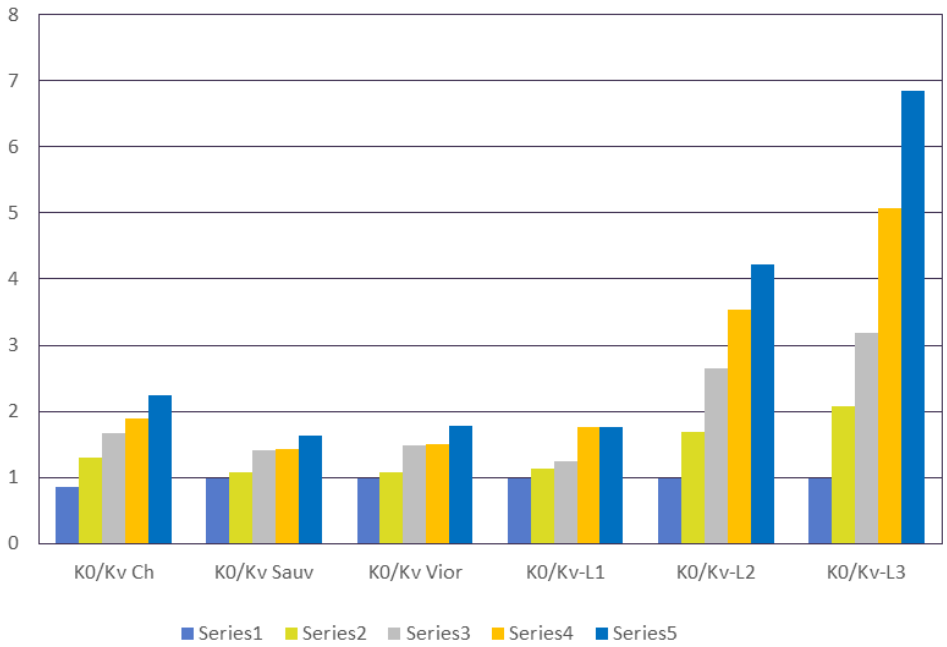

Figure 9. The comparative total antioxidant properties of Chardonnay, Sauvignon, Viorica, Legenda 1, Legenda 2 and Legenda 3 wines depending on their concentration in the reaction mixture, by reaction with crocin in the presence of radicals initiator AAPH.

Series 1 – without wine supplements; Series 2-0.15 ml / 4 ml of reaction mixture; Series 3-0.30 ml / 4 ml of reaction mixture, Series 4-0.45 ml / 4 ml of reaction mixture, Series 5-0,60 ml / 4 ml of the reaction mixture.

The close correlation between antioxidant capacity and content of SFT, SFC and SFF have not been found, although the trend has been barely observed. The oxidation behavior of browning (L2-0) and (L3-0) wines can be explained due to high content of compounds mentioned before and possible antioxidant capacity of some products of browning, although there has not been identified direct connection between the antioxidant capacity and browning degree of Maillard products in hydrophilic medium.

The strict elucidation of these interdependencies requires the complex investigations to determine the influence of different wine antioxidant compounds, to reveal the possible effect of endogenous antioxidants of wine, the redox transformations that are catalized by transition metals, enzymes.

The constants of linear dependencies Ko/Kv on the wine concentration in the reactant mixture have been determined with high values of correlation coefficient R^2 "Table 1".

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We would like to express our sincere gratitude to the partners of the Project WINE SECTOR RESTRUCTURING PROGRAM and for their invaluable contribution to re-equipment of Oenology Department laboratories.

Conclusions

1. The oxidation of hydroxycinnamic acids and their derivatives in experimental white wines *Legenda*, produced by using different technologies, are correlated by quantitative spectral changes in UV region, that are visible in second order derivative spectra.
2. The POM-test offers the possibility to predict the risk of white wine browning.
3. The using of bentonite as sorbent of phenolic compounds in order to reduce the risk of wine oxidation at storage requires preliminary study of the removal level of various wine phenolic fractions.
4. The total antioxidant capacity of white wines *Legenda*, *Viorica*, *Chardonnay*, *Sauvignon* can be determined from dependencies of the oxidation rate of crocin bleaching by peroxy radicals that are formed at thermal decomposition of AAPH at 40°C.

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IN VITRO BIOAVAILABILITY OF SUNFLOWER OIL FORTIFIED WITH IODINE

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Abstract. The use of iodized sunflower oil as an additive is an affordable and inexpensive method. In addition, iodine is a liposoluble element, which facilitates its incorporation into oil. But the incorporation of iodine in oil is a complex phenomenon, accompanied by a change in the physicochemical properties of the finished product, and therefore the evolution of the composition of triglycerides in iodinated oil has been investigated, depending on the amount of iodine administered. Free fatty acids (FFAs) are subjected to a different metabolic mechanism depending on the length of their chain (their molar mass). Thus, long chain fatty acids after re-esterification are deposited in the adipose tissue in the form of triglyceride-rich lipoproteins, while medium chain FFAs are usually oxidized in the liver. The structure of triglycerides (the distribution of fatty acids in the triglyceride molecule) can also influence the digestibility of this product. The purpose of the researches is to determine the influence of sunflower oil iodine on the digestibility of triglycerides and the evolution of the iodine content in the system during the enzymatic hydrolysis of the product. The kinetics of MGs, DGs and FFAs accumulation and the percentage of iodine recovered from the digestate were investigated during in vitro pancreatic digestion of iodinated sunflower oil.

Keywords: *iodine, triglycerides, oil, free fatty acids, pancreatic digestion in vitro.*

Introduction

The problem of food iodine deficiency is one of the most common cases of nutritional diseases on the earth [1, 2]. In the last 10 years in Moldova the incidence of endemic diseases of the thyroid gland increased by 8-10 times. The percentage of children and adolescents with endemic hyperplasia of the thyroid gland is 33-47%; 2.8-5.7% of the population has a goiter, which is often expressed by the appearance of nodules, while 1.5-4.2% of people suffer from hypothyroidism [3, 4].

Iodine is a mineral essential to the body, being essential for the synthesis of thyroid hormones. As a liposoluble element, its use in products of lipid origin is of particular interest. Firstly, it allows easy incorporation of iodine into food. Secondly, because the daily intake of fat is limited, the iodine intake can be easily adjusted. The advantage of this method of regulating iodine intake is that the absorption of iodine from foods of lipid origin occurs gradually, depending on the needs of the organism [5, 6].

Sunflower oil is a current consumer product for the Republic of Moldova, so that the manufacture of iodine fortified oil would constitute a considerable iodine supplement (40-50μg / day) which, associated with the iodine intake of kitchen salt, would contribute to the eradication of iodine deficiency [7,8]. Of particular interest is the incorporation of iodine oil into different food groups in order to broaden the spectrum of products with adequate iodine content [9].

The objective of this paper is to develop the process of fortification of sunflower oil and to evaluate the quality index (of the physicochemical properties) of the iodine oil.

Materials and methods

The advantage of this research lies in usage of inland products for fortification, products that are characteristic to this area.

Vegetable oils in the commercial, nutritional and medicinal planes are of particular importance, since a number of methods for analyzing the digestibility of triglycerides have been developed. Some of these studies are performed using pancreatic lipase, but most involve enzymes of industrial products of microbial origin [10, 11]. All currently known methods can be classified into two categories: in vivo methods and in vitro methods.

In vivo methods are the most reliable, but due to the many uncontrollable factors present in real systems that can directly influence processes, the study of triglyceride hydrolysis is technically impossible. Verifiable results can only be obtained with the use of radioactive labeling (isotope analysis). In addition, the duration of in vivo testing is, in these cases, quite long.

The advantage of in vitro methods is the possibility of isolation of the studied parameter - free fatty acids (FFAs), mono-, bi- and triglycerides [12,13]. This is an important quality parameter in fat and oil processing. However, the practical way to trigger hydrolysis of triglycerides essentially influences the results, which can not be reproduced in the physiological environment. Thus, in vitro investigations are performed with pancreatic lipases in an aqueous medium, in the presence of a buffer solution, an emulsifier and cofactors. The need to provide a stable interface complicates the in vitro research of the kinetics of triglyceride hydrolysis. Since enzyme activity is optimal only in organic media, the nature of the solvents used also influences the results obtained.

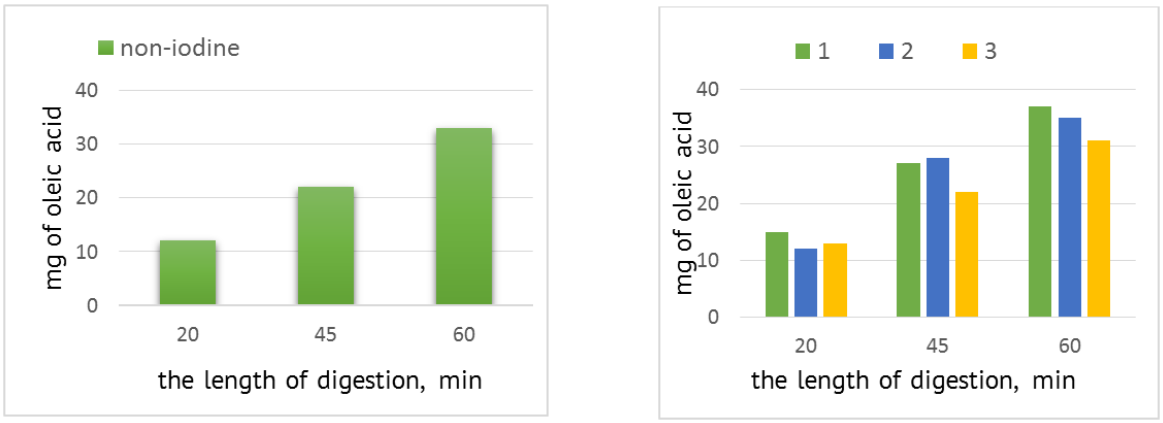
Results and discussions

The investigations carried out aimed to determine the influence of sunflower oil iodine on the digestibility of triglycerides. Also, the evolution of iodine content in the system during the enzymatic hydrolysis of the product was analyzed [14, 15].

FFAs dosing after pancreatic digestion was performed at 20, 45 and 60 minute intervals. The results obtained for the control sample (unedged oil) are shown in Figure 1a.

It is observed that hydrolysis of triglycerides in sunflower oil occurs during in vitro pancreatic digestion, which confirms the correctness of the experiment. Testing of the FFAs content in the iodine oil samples containing 1, 10 and 100 μg iodine/ml of oil was then performed. The results obtained are shown in Figure 1b.

It is noted that at low concentrations of iodine the content of FFAs, expressed in mg of oleic acid, does not vary significantly from the control sample. Only at the concentration of 100 μg iodine/ml of oil is a decrease of up to 10%, the rate of enzymatic hydrolysis reaction of triglycerides and the accumulation of FFAs in the digestate.



a) b)

Figure 1. Evolution of the FFAs content, expressed in mg of oleic acid, during the in vitro pancreatic digestion of sunflower oil: a) non-iodine (control sample); b) iodate: 1 – 1 μg iodine/ml oil; 2-10 μg iodine/ml oil; 3 – 100 μg iodine/ml oil.

In the digestate samples taken at the same time intervals, the total iodine content was analyzed after extraction in chloroform. The results obtained are shown in Figure 2.

It is found that the percentage of iodine recovered from the digestate (in relation to the administered content) varies between 57 and 92%, being lower for the maximum iodine content (100 μg iodine/ml of oil).

This is due to the more significant iodine losses during digestion when such a large amount of iodine is administered. However, such a recovery rate demonstrates that iodine from the iodine sunflower oil could serve as an important source of this deficient micronutrient for the organism because it is mostly preserved in the digestive medium.

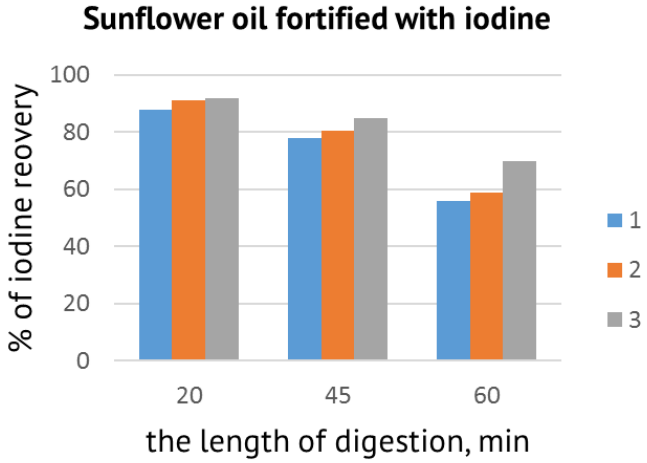


Figure 2. Percentage of iodine recovered during pancreatic digestion of iodized sunflower oil with an iodine content of: 1 – 1 μg iodine/ml oil; 2-10 μg iodine/mL oil; 3 - 100 μg iodine ml of oil. Duration of digestion: 20, 45 and 60 minute.

Analysis of lipid digestion products. To determine the kinetics of hydrolysis of triglycerides in sunflower oil, a pre-test with pure glycerides was performed.

The purpose of this experiment was to determine the yield of enzyme dosing of glycerin from standard solutions. The results obtained are shown in Table 1.

Hydrolysis of glycerides does not occur completely, even in the case of the maximum duration of pancreatic digestion (6 hours). The recovery percentage is in the average at 80%. This was taken into account in the analysis of the data obtained for the iodine sunflower oil.

Table 1.

Yield of enzyme dosing of glycerol from standard solutions of triolein, diolein and monoolein *

Glyceride	% recovery of glycerol **		
	0,5 g/l	1,0 g/l	1,5 g/l
TGs	92,7 ± 6,8***	77,1 ± 4,2	76,7 ± 7,8
DGs	78,4 ± 5,7	79,8 ± 5,9	81,7 ± 7,2
MGs	81,6 ± 7,2	80,9 ± 5,2	83,1 ± 4,5

* solvent - absolute ethanol; ** - duration of pancreatic digestion - 6 hours.
*** - average and dispersion of results from 3 parallel trials.

Figure 3 shows the kinetics of triglyceride hydrolysis in iodine sunflower oil during 6 hours of pancreatic digestion. In all cases, the residual amount of triglycerides is very low and does not exceed 15% of the initial amount. Thus, it is evident that administration of iodine in sunflower oil does not influence the degree of pancreatic digestion of triglycerides, demonstrating that the biological value of the product is not impaired.

Of particular interest is the analysis of the structure of products of pancreatic digestion of triglycerides (TGs) from iodine sunflower oil [16,17]. In the paper, the kinetics of the accumulation of monoglycerides (MGs), diglycerides (DGs) and FFAs during the in vitro pancreatic digestion of the iodine sunflower oil and the control sample were investigated. It is noted that the maximum level of MGs and DGs is already reached after 2 hours of pancreatic digestion (Figure 4). For DGs, the maximum obtained corresponds to only 14,7% of the total glyceride, while the MGs peak corresponds to about 37% of the total glyceride content. Over the next 4 hours an insignificant decrease in MGs and DGs content occurs, and a significant increase in FFAs content. There was not a significant difference between kinetics of in vitro pancreatic hydrolysis and the structure of products obtained during iodine oil hydrolysis as compared to the control sample.

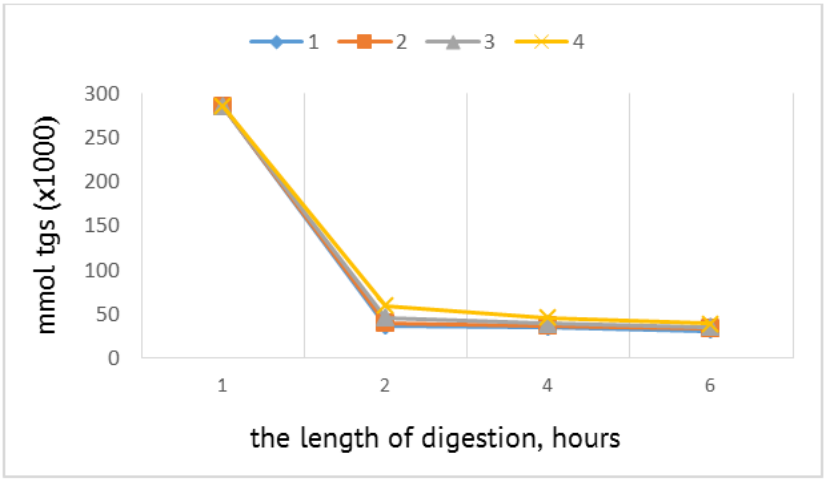
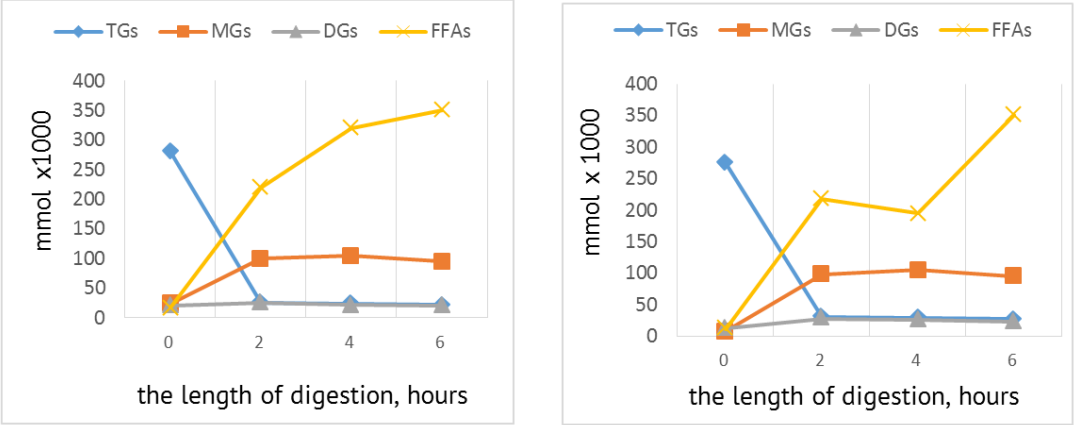


Figure 3. Kinetics of pancreatic hydrolysis of TGs from iodine sunflower oil: 1 - control sample (unrendered oil); 2 – 1 μg iodine ml oil; 3 - 10 μg iodine/ml oil; 4 – 100 μg iodine/ml of oil.

The disappearance of TGs during hydrolysis is a global indicator of the digestibility of a lipid source. DGs shows an intermediate substrate because they generate MGs after release of an FFAs molecule under the influence of pancreatic lipase. Analyzing the distribution of digestive products of a lipid source resulting from hydrolysis allows to highlight the difference between the biological value of these sources. In the examined case no significant

difference was found between the distribution of the iodine sunflower oil hydrolysis products compared to the control sample. This is due, first of all, to the advanced degree of hydrolysis of the substrate in the first two hours.



a) b)

Figure 4. Kinetics of the appearance of pancreatic digestion products (in vitro) of sunflower oil (a) and iodized sunflower oil (b) with an iodine content of 10 μg iodine/ml of oil.

When taking into account that the final products of hydrolysis are glycerine and FFAs, hydrolysis reactions may be described schematically as follows:

$$TGs \rightarrow DGs_1 + FFAs_1$$

$$DGs_2 \rightarrow MGs_2 + FFAs_2$$

$$MGs_3 \rightarrow glycerine + FFAs_3$$

DGs1 is the amount of diglycerides formed by hydrolysis of triglycerides, and DGs2 is the amount of diglycerides remaining after the formation of monoglycerides (MGs2) and FFAs2. Hydrolysis of a triglyceride generates a DGs and releases an FFAs, etc. If the content of TGs, glycerine and FFAs is known in the given environment, the FFAs content formed at DGs hydrolysis can be calculated:

$$FFAs_2 = FFAs_{total} - FFAs_1 - FFAs_3$$

Subsequently, the amounts of DGs and MGs remaining in the reaction medium can be calculated:

$$DGs_2 = FFAs_1 - FFAs_2; \quad MGs_3 = FFAs_2 - FFAs_3$$

These calculations can be carried out without necessity of determining the rate of hydrolysis of the intermediate reactions involved, only by final testing of the glycerin content and FFAs, which reduces the number of experiments to be performed [18,19]. Obviously, the presence of other substances in the reaction medium, which could affect to some extent the digestibility of lipids, was not taken into account. In particular, it is about Ca^{2+} proteins and ions, which, according to bibliographic sources, can significantly alter the rate of lipid hydrolysis.

Conclusions

Research on pancreatic (in vitro) digestion of iodinated sunflower oil and control sample showed that at low concentrations of iodine the content of FFAs, expressed in mg of oleic acid, did not vary significantly from the control sample. Only at the concentration of 100 μg iodine/ml of oil is a decrease of up to 10% of the rate of enzymatic hydrolysis reaction

of triglycerides and accumulation of FFAs in the digestate. The percentage of iodine recovered from the digestate (in relation to the administered content) varies between 57 and 92%, which shows that iodine from the iodine sunflower oil could serve as an important source of this deficient micronutrient for the body.

The kinetics of triglyceride hydrolysis of iodine sunflower oil were investigated during 6 hours of in vitro pancreatic digestion. In all examined cases (iodine content ranges from 1-100 μg iodine/ml of oil, the remaining amount of triglycerides is very low and does not exceed 15% of the initial amount). Iodine administration in sunflower oil does not influence the degree of pancreatic digestion of triglycerides. The kinetics of MGs, DGs and FFAs accumulation were investigated during in vitro pancreatic digestion of iodinated sunflower oil (10 μg iodine/ml of oil) and in the control sample. It has been established that the maximum level of MGs and DGs is already reached after 2 hours of pancreatic digestion. For DGs, the maximum obtained corresponds to only 14,7% of the total glyceride, while the MGs peak corresponds to about 37% of the total glyceride content. There was no significant difference between the kinetics of in vitro pancreatic hydrolysis and the structure of the products obtained during the iodine oil hydrolysis as compared to the control sample, which demonstrates that the biological value of sunflower oil is not affected by iodine administration.

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ANTIMICROBIAL ACTIVITY OF ROSE HIP AND HAWTHORN POWDERS ON PATHOGENIC BACTERIA

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Abstract. In this present study, rose hip and hawthorn powders were investigated against three pathogenic bacteria strains: *Staphylococcus aureus*, *Escherichia coli* și *Klebsiella pneumoniae*. The chemical composition and antiradical activity of the plant extracts were investigated. The antiradical activity of the hydroalcoholic extracts of rose hip is 85.11 ± 0.02 and hawthorn - 80.27 ± 0.23% DPPH inhibited, which correlates with the high content of polyphenolic and flavonoid compounds. The content of β-carotene and lycopene in the liposoluble extracts of rose hip is 14.85 times and 28.83 times higher than in hawthorn extracts. The rose hip powders show an antimicrobial activity pronounced to *Staphylococcus aureus*. In the case of *Escherichia coli* and *Klebsiella pneumoniae* antimicrobial activity of hips is on average 1.3 times higher than that hawthorn powders. The rose hip powders showed the best inhibitory activity against *Staphylococcus aureus*, Gram-positive bacteria, followed by *Escherichia coli* and *Klebsiella pneumoniae* - Gram-negative bacteria. The investigated plant powders have shown promising antimicrobial potential against pathogenic microorganisms and can be used in the food industry to reduce the microbial contamination of raw materials and food.

Keywords: *rosehip, hawthorn, pathogenic bacteria, chemical composition, antimicrobial activity, food safety.*

Introduction

At present, an important concern for public health is food poisoning, which results from the consumption of food contaminated with pathogenic bacteria. The Food and Agriculture Organization of the United Nations (FAO) has reported that diseases due to contaminated food are the most widespread health problem in the world and an important cause of economic productivity decline [1]. *Staphylococcus aureus* and *Escherichia coli* present the most frequent causes of the mass diseases of the population caused by contaminated food [2]. *Klebsiella pneumoniae* belongs to the *Enterobacteriaceae* family is a pathogen, which is responsible for nosocomial, urinary, respiratory tract and blood infections. Following manipulations, raw material and food can be contaminated with this type of pathogenic bacteria [3]. In this context, worldwide researchers are concerned with identifying and

evaluating antimicrobial agents to inhibit the development of these pathogenic bacteria in food, in order to ensure consumers with safe and healthy food.

With the increase in bacterial resistance to antibiotics, there is a particular interest in investigating the antimicrobial effects of natural bioactive compounds from plant, such as essential oils and extracts, against pathogenic bacteria, for the preservation of food by harmless methods to the health of the consumer [4]. The essential oils and plant extracts have an antimicrobial effect with low toxicity and can be recommended as potential natural preservatives. The possibilities of using plant extracts as natural antibiotics in food have been studied to extend their shelf life [5].

The analysis of bibliographic sources has shown that the antimicrobial effect of plants is due to their chemical composition, namely the presence of polyphenolic compounds, carotenoids, flavonoids, vitamins, etc. [6]. It is known that polyphenolic compounds, being in optimal combination, have a stronger impact on pathogenic microorganisms than on their own [4].

The aim of this study was to investigate antimicrobial activity, minimal inhibitory and bactericidal concentrations of rose hip and hawthorn powders on pathogenic microorganisms.

Materials and methods

The autochthonous fruits of rose hip (*Rosa Canina*) and hawthorn (*Crataegus monogyna*) were used for research. The hips and hawthorn were washed and dried at 65±1°C to a humidity of 8.0±0.25%, were ground to the powder and sieved. The granulation of the powder after sieving was 140±10μm.

The obtained powders were subjected to hydroalcoholic extraction using 50% vol. ethanol. The extraction was carried out in a solid-liquid ratio of 1:15 in the case of the fruits of the rose hip and 1:20 in the case of hawthorn fruits in the water bath at 45±1°C for 1 hour under stirring of 60 min^{-1}. The obtained extract was filtered and stored in dark-coloured containers at 5.0±1.0°C [7]. In the hydroalcoholic extracts of rose hip and hawthorn powders were determined the content of tannins [8], the content of polyphenolic compounds [8] and antiradical activity [9].

The extraction of the liposoluble fraction was carried out in a solid-liquid ratio of 1:15 in the case of fruit and in the ratio of 1:20 in the case of hawthorn fruits in a water bath at 45.0 ± 0.1°C for 1.5 h under stirring of 60 min^{-1}. As an organic solvent was used refined and deodorized sunflower oil „Floris". The obtained extract was filtered and stored in dark-coloured containers at 5.0±1.0°C [10]. The content of β-carotene and lycopene [11], antiradical activity [9] were determined in liposoluble extracts.

The antimicrobial activity of the plant powders was determined by the agar diffusion test [12].

Antibacterial action was determined by minimal inhibitory concentration (MIC) and minimal bactericidal concentration (MBC) [13]. By the ratio MBC/MIC, antibacterial activity was assessed. If the ratio MBC/MIC=1 or 2, the effect is bactericidal. If the ratio MBC/MIC=4 or 16, the effect is bacteriostatic [14].

The variance analysis of the results was carried out by least square method with application of Student test and Microsoft Office Excel program version 2010. The differences were considered statistically significant if probability was greater than 95% (p-value <0.05).

All assays were performed in triplicate at room temperature 20±1°C. The experimental results are expressed as average ± SD (standard deviation).

Results and discussions

It is known that there is a correlation between the chemical composition of the bioactive compounds and the antimicrobial activity of the plant matter [15]. Table 1 shows the content of biologically active compounds and antiradical activity in hydroalcoholic extracts from rose hip and hawthorn fruits.

The antiradical activity of the hydroalcoholic extracts of hips constitutes 85.11 ± 0.02% DPPH inhibited and hawthorn extracts - 80.27 ± 0.23% DPPH inhibited. In the case of hip extracts, the antiradical action correlates with the high content of polyphenolic and flavonoid compounds [16], since vitamin C-free extracts can still show considerable antioxidant activity [17].

This action has a protective effect against oxidative stress, increasing the activity of antioxidant enzymes such as superoxide-dismutase and catalase [18]. In the case of hawthorn extracts, the antioxidant activity is due to the presence of several groups of phenolic compounds such as epicatechin, aglycons, glycosides such as B-type oligomeric procyanidins, flavonols, phenolic acids, C-glycosyl flavones [19].

Table 1

The content of biologically active compounds and antiradical activity in hydroalcoholic extracts from rose hip and hawthorn fruits [7, 20].

Plant powders	Tannins (mg TAE·g^{-1} DW)	Total phenols (mg GAE·g^{-1} DW)	Antiradical activity (% of inhibition of DPPH)
Rose hip	106.41±1.34	26.98±0.36	85.11±0.02
Hawthorn	13.67±0.02	3.83±0.01	80.27±0.23

Note. The results are presented as means ± standard deviations of three experiments.

The results in Table 1 show that the tannin content and polyphenol content in the hip extracts are 7.78 times and 7.04 times higher than in hawthorn extracts. These can be explained by the fact that plant's genotype and development stages have a strong impact on the chemical composition of the studied fruits [21].

The content of liposoluble bioactive compounds and antiradical activity in extracts of rose hip and hawthorn fruits is shown in Table 2.

Table 2

The content of ß-carotene, lycopene, zeaxanthin and antiradical activity in liposoluble extracts of rose hip and hawthorn fruits [20]

Plant powders	Content of ß-carotene (mg·L^{-1} extract)	Content of lycopene (mg·L^{-1} extract)	Content of zeaxanthin (mg·L^{-1} extract)	Antiradical activity (% of inhibition of DPPH)
Rose hip	17.08±0.05	18.45±0.15	19.12±0.07	62.98±2.43
Hawthorn	1.15±0.02	0.64±0.01	nd	51.98±3.39

Note. The results are presented as means ± standard deviations of three experiments; nd - no detected

The results in Table 2 indicate that the rose is rich in carotenoids relative to the hawthorn, which has a low content. Thus, the content of β-carotene and lycopene in the rose hip extracts is 14.85 times and 28.83 times higher than in hawthorn extracts. Zeaxanthin in hawthorn extracts was not detected. Carotenoids have a property to protect the human body against free radicals and reduce the risk of cancer and cardiovascular disease [22]. The antiradical activity of the examined liposoluble extracts is on average 1.44 times lower than that of hydroalcoholic extracts. This phenomenon can be explained by the diversification of water-soluble bioactive compounds, which have antioxidant properties.

In this present study, three bacteria strains (Gram-negative and Gram-positive bacteria) were used. Table 3 shows the antimicrobial activity of rose hip and hawthorn powders on pathogenic microorganisms: *Staphylococcus aureus, Escherichia coli* și *Klebsiella pneumoniae*.

The results in Table 3 show that the hip powders have an antimicrobial activity more pronounced on *Staphylococcus aureus*, the diameter of the inhibition zone being 16 ± 1 mm. In the case of *Escherichia coli* and *Klebsiella pneumoniae* microorganisms, the antimicrobial activity of rose hip powders is on average 1.3 times higher than that of hawthorn powders.

Table 3

Inhibition zone diameters (mm) recorder in agar diffusion test using Rose hip and Hawthorn powders

Plant powders	***Staphylococcus aureus* ATCC *25923***	***Escherichia coli* ATCC *25922***	***Klebsiella pneumoniae* ATCC 13883**
Rose hip	16±1	10±1	9±1
Hawthorn	10±1	8±1	7±1

Note. The results are presented as means ± standard deviations of three experiments.

Minimum inhibitory concentrations (MIC) and minimum bactericidal concentrations (MBC) of the plant powders analyzed on pathogenic microorganisms capable of causing food contamination are shown in Table 4.

Table 4

Minimum inhibitory concentration (MIC), minimum bactericidal concentration (MBC) and bactericidal effect of plant powders

Bacteria	MIC ($mg \cdot mL^{-1}$)	MBC ($mg \cdot mL^{-1}$)	MIC / MBC	Bactericidal effect
Rose hip powder				
Staphylococcus aureus ATCC 25923	3.91±0.15	7.81±0.21	2	+
Escherichia coli ATCC 25922	31.25±0.98	62.5±1.8	2	+
Klebsiella pneumoniae ATCC 13883	62.5+2.1	125±5	2	+

Continuation Table 4

Hawthorn powder				
Staphylococcus aureus ATCC 25923	41.66±1.35	83.33±2.47	2	+
Escherichia coli ATCC 25922	62.5±2.2	125±5	2	+
Klebsiella pneumoniae ATCC 13883	nd	nd	nd	nd

Note. The results are presented as means ± standard deviations of three experiments.
nd: no detected activity; "+": bactericidal effect.

The results in Table 4 demonstrate that the rose hip powders have the smallest inhibitory and bactericidal concentrations on all pathogenic microorganisms investigated. The rose hip and hawthorn powders showed the bactericidal effect on all pathogenic microorganisms investigated except *Klebsiella pneumoniae* to which hawthorn powders not exhibited the bactericidal effect.

Plants are the largest source of natural antimicrobial agents. They produce very bioactive molecules that can interact with other organisms in their environment. Many of these compounds act against pathogenic bacteria [23].

Analysis of bibliographic data indicates that bioactive compounds, such as polyphenols, are responsible for antimicrobial activity, inhibiting several types of microorganisms [6]. It is well known that phenol is a strong chemical antiseptic [24]. In bibliographic sources, the antimicrobial activities of phenolic compounds are well documented [25].

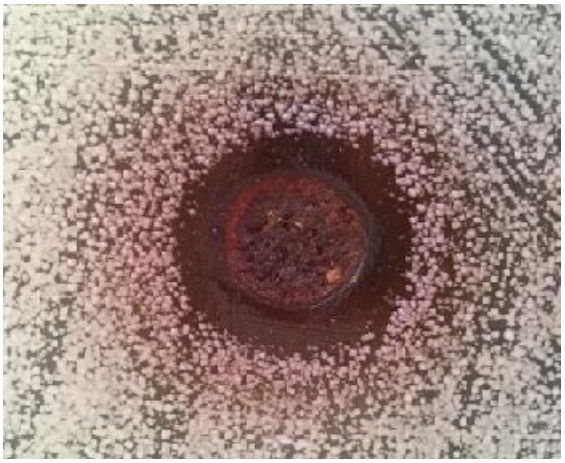
Figures 1 and 2 show the antimicrobial action of rose hip and hawthorn powders on pathogenic bacteria strains.

Polyphenols, such as flavonoids and tannins, show significant antibacterial activity [26]. The antimicrobial activity of flavonoids is due to their ability to form complexes with the extracellular and soluble proteins of the cell walls of the bacteria. In the case of tannins, antimicrobial activity may be related to their ability to inactivate microbial enzymes and proteins inside the cells of microorganisms [27].

It has been observed that rose hip powders have the best inhibitory activity against *Staphylococcus aureus*, being Gram-positive bacteria, followed by *Escherichia coli* and *Klebsiella pneumoniae* - Gram-negative bacteria. The sensitivity of Staphylococcus aureus microorganisms may be due to the cell wall structure and outer membrane [28].

Gram-positive bacteria are more sensitive to the action of plant powders than Gram-negative bacteria [29]. This phenomenon can be explained by important differences in the outer layers of Gram-positive bacteria. The high level of phospholipids reduces the cell wall permeability of Gram-negative microorganisms compared to gram-positive bacteria.

At the same time, Gram-negative bacteria have an outer membrane and a periplasmic space, not found in Gram-positive bacteria [30]. The hydrophilic surface of the outer membrane of the bacteria, which consists of lipopolysaccharide molecules, forms a resistance of Gram-negative bacteria to antibacterial substances.



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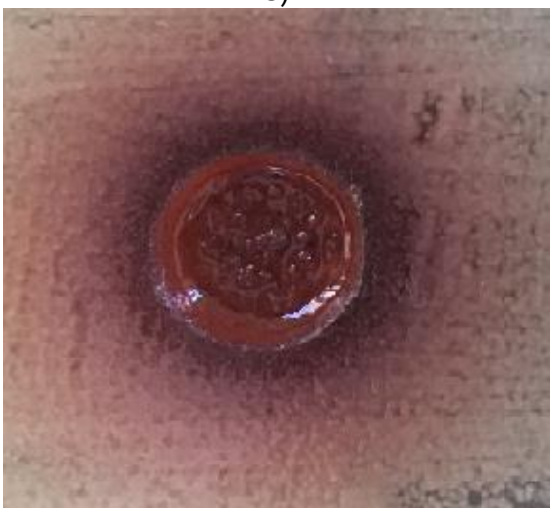

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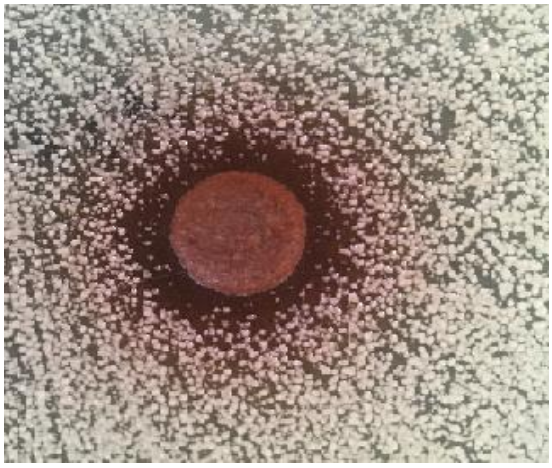
Figure 1. The antimicrobial action of rose hip powders on: a) *Staphylococcus aureus*; b) *Escherichia coli*; c) *Klebsiella pneumonia.*



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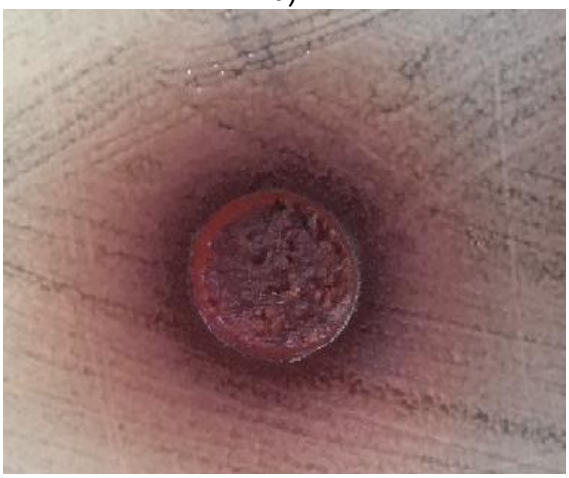

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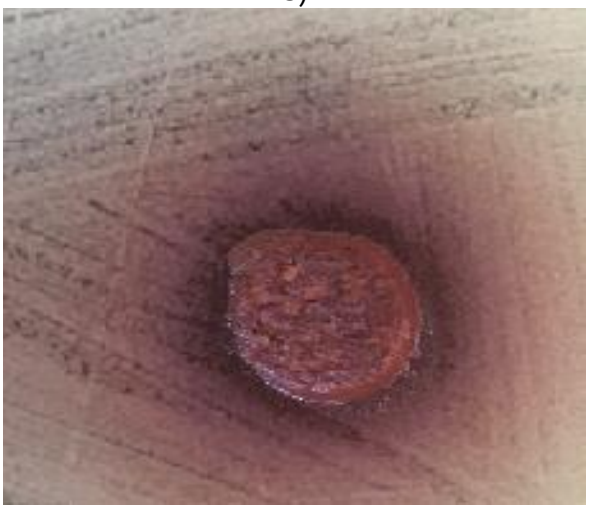

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Figure 2. The antimicrobial action of hawthorn powders on: a) *Staphylococcus aureus*; b) *Escherichia coli*; c) *Klebsiella pneumonia.*

Lipopolysaccharide molecules present a barrier to the penetration of numerous antibacterial molecules and are associated with enzymes from periplasmic space that are capable of breaking the molecules introduced from the outside [31]. Thus, rose hip and

hawthorn powders, having an antimicrobial potential against pathogenic microorganisms, can reduce the degree of microbial contamination of raw materials and food.

Conclusions

To decreasing the contamination of raw and food products with pathogenic microorganisms that cause food poisoning, the rose hip and hawthorn powders were investigated.

The antiradical activity of the hydroalcoholic extracts of rose hip is 85.11 ± 0.02 and hawthorn - 80.27 ± 0.23% DPPH inhibited, which correlates with the high content of polyphenolic and flavonoid compounds. The content of β-carotene and lycopene in the liposoluble extracts of rose hip is 14.85 times and 28.83 times higher than in hawthorn extracts. The antiradical activity of the liposoluble extracts of the examined fruits is on average 1.44 times lower than the hydroalcoholic extracts.

The rose hip powders show a pronounced antimicrobial activity against *Staphylococcus aureus*. In the case of *Escherichia coli* and *Klebsiella pneumoniae* antimicrobial activity of hips is on average 1.3 times higher than that hawthorn powders. The rose hip powders have the smallest inhibitory and bactericidal concentrations on all pathogenic microorganisms investigated. The plant powders showed the bactericidal effect on all pathogenic microorganisms investigated except *Klebsiella pneumoniae* to which hawthorn powders not exhibited the bactericidal effect. The rose hip powders showed the best inhibitory activity against *Staphylococcus aureus*, Gram-positive bacteria, followed by *Escherichia coli* and *Klebsiella pneumoniae* - Gram-negative bacteria. The sensitivity of Gram-positive microorganisms is due to the structure of the cell wall and the absence of an outer membrane.

The investigated plant powders have shown promising antimicrobial potential against pathogenic microorganisms and can be used in the food industry to reduce the microbial contamination of raw materials and food.

Acknowledgments

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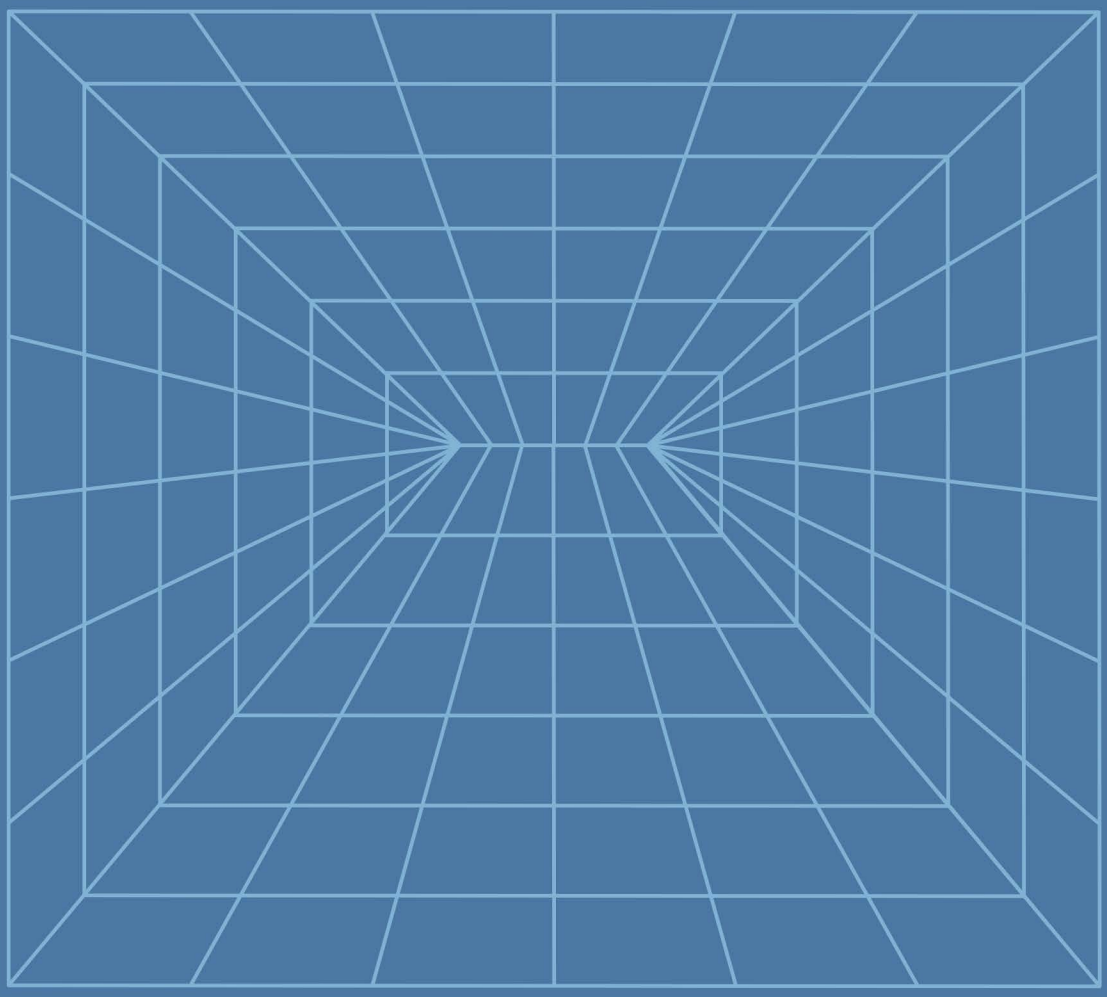

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