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DEEP ULTRAVIOLET LIGHT EMITTING DIODES (DUV LEDS)

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Abstract. There are a variety of applications for devices that extend into the deep-UV, including biological agent detection and optical storage. The nitride material system is a set of semiconducting compounds that have wavelengths that span a broad range, from yellow to deep-UV. AlGa_N has a direct bandgap that extends into the deep-UV range; the device-quality material, is deposited epitaxially using metalorganic chemical vapor deposition on sapphire substrates.

Keywords: *Duv Leds, deep-UV, ultraviolet leds, AlGa_N/AlGa_N Duv Leds*

1. Introduction to leds

An LED is what's called a "solid-state lighting" technology, or SSL. Stated very simply, an LED is a semiconductor device that emits light as the electricity flows through it.

The primary cause of LED lumen depreciation is heat generated by the LED, so the heat must be removed from the light by conduction or convection.

Without adequate heat sinking or ventilation, the device temperature will rise, resulting in lower light output.

There are a variety of applications for devices that extend into the deep-UV, including biological agent detection and optical storage.

The nitride material system is a set of semiconducting compounds that have wavelengths that span a broad range, from yellow to deep-UV. AlGa_N has a direct bandgap that extends into the deep-UV range; the device-quality material, is deposited epitaxially using metalorganic chemical vapor deposition on sapphire substrates.

The most obvious manifestation of its degradation is the gradual decrease in power output when the device is operated at a constant current (i. e. the spontaneous efficiency decreases with time).

The main cause of degradation - a consequence of forward biasing - is the inherent crystal defects; non-radiative recombination centers are formed at these defect sites, thereby impairing the quantum efficiency of the devices.

LED failure is a gradual process; the power output decreases with time, although not necessarily in any well behaved manner. Although the failure of light emitting devices has become considerably less erratic over the past years, there is a variation in reliability between LEDs within a specific batch.

A common approach is to consider the lifetest data as a statistical distribution, and to use its characteristic parameters to describe the device population as a whole.

2. Short leds history

1907: H. J. Round of Marconi Labs discovered that some inorganic substances glow if a electric voltage is impress on them.

1927: The Russian Oleg Vladimirovich Losev independently reported on the creation of an LED, but no practical use was made of the discovery.

1961: Bob Biard and Gary Pittman (*Texas Instruments*) find out that gallium arsenide (GaAs) give off infrared radiation when electric current is applied. They receive a patent for this diode.

1962: First visible red GaAsP-LEDs was developed by Nick Holonyak ("father of the light-emitting diode") at *General Electric Company*.

1971: The first blue LEDs (GaN) were made by Jacques Pankove at *RCA Laboratories*. Too little light output to be of much practical use.

1993: Shuji Nakamura (*Nichia Corporation*) demonstrates the first high-brightness blue LED based on InGaN.

A light-emitting diode (LED) (Figure 1) is a semiconductor-based p-n junction. When a forward bias is applied, the diode emits light in a very narrow range of wavelengths.

As in other diodes, current flows easily from the p-side (anode) to the n-side (cathode), but not in the reverse direction.

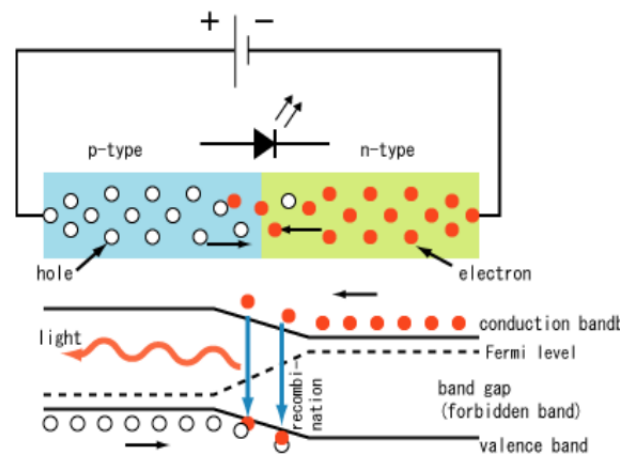


Figure 1. LED principle

3. Led principle

At the barrier layer electrons and holes recombine and energy in the form of a photon is emitting. The wavelength of the light depends on the band gap energy (Table 1).

New materials such as GaN and SiC which have good material properties, attracts increasing attention for use in power devices. Especially, GaN is expected as a material for power devices used in ~700 V from high electrical critical field (~3.3 MV/cm) and realizing high electron mobility (~2000 cm²/Vs) by using AlGaN/GaN heterostructure.

The attention of researchers focused on reducing contact resistance of AlGaN/GaN HEMT and improving surface morphology by using carbide¹ electrodes even in some problems. The high contact resistance cause higher electrical power loss, and 40% of the electrical

Table 1

Color	Wavelength (nm)	Semiconductor material
Infrared	>760	GaAs, AlGaAs
Red	610-760	AlGaAs, AlGaInP
Orange	590-610	GaAsP, GaP
Yellow	570-590	GaAsP, GaP
Green	500-570	InGaN, GaN
Blue	450-500	ZnSe, InGaN
UV	<400	GaN, AlN, AlGaN, AlGaInN

¹ The motivation for selecting carbide electrodes is that carbon has high melting point to endure being annealed at high temperature and high chemical resistance. TiC/TiN electrodes was deposited by RF sputtering as stacked electrodes on AlGaN/GaN substrate with changing Ti/C ratio to optimize the ratio, the passivation layer on AlGaN/GaN was SiO₂ deposited by tetraethylorthosilane (TEOS), and the contact resistance was measured by TLM patterning. The interface

power loss in breakdown voltages under 1000 V could be reduced if the specific contact resistance (Ωcm^2) decreases from $10^{-5}\Omega\text{cm}^2$ to $10^{-6}\Omega\text{cm}^2$. Also conventional ohmic contact electrodes have rough surface morphology which causes the misalignment and reduces reliability.

4. Examples of led assembly

An LED lamp contains power conversion electronics (AC/DC), driver IC for the LEDs, a heat sink for thermal management and optics to optimize light quality. Since LED bulbs are intended to be form factor-compatible with current incandescent and compact fluorescent lamps (CFL) bulbs, they will have an AC/DC power supply circuit so they can operate from standard bulb “sockets.” (Figure 2.)

For other applications, Figures 3 and 4 represent two other types of LED assemblies.

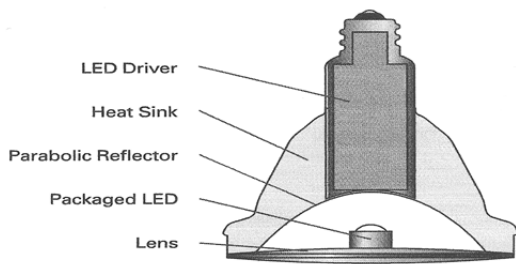


Figure 2. Typical residential LED lamp construction

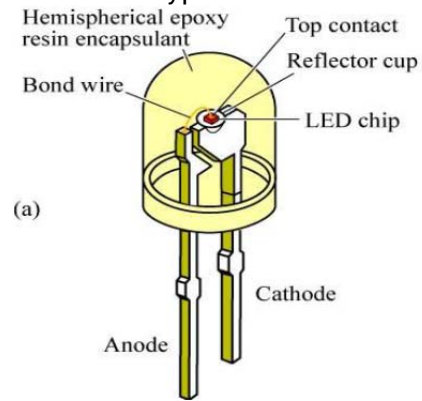


Figure 3. One of the LED types (after [1])

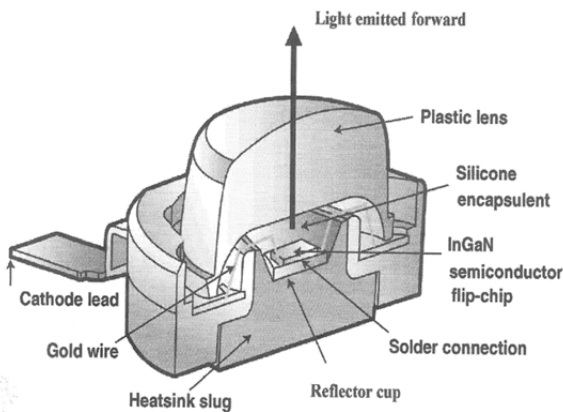


Figure 4. Another LED type with plastic lens (after [1a])

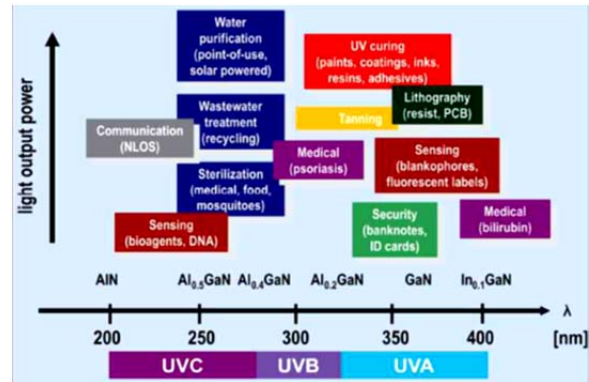


Figure 5. Potential applications for UV LEDs [3]

layer was observed by TEM, and the surface morphology was measured by AFM and SEM. If the ohmic contact resistance is lower than conventional ohmic contacts, by some treatment to substrates or different methods in more elaborate study, carbide electrodes could have good morphology and low contact resistance without gold and contamination to other substrates including Si substrate.

5. Applications

- Illuminations with high brightness
- Visual signal application
- Automotive lighting
- Flashlights
- Optical measurement systems
- LCD backlit screens
- Grow lights

6. Disadvantages

- High initial price
- Temperature dependence
- Shock resistance
- Parallel ray emission
- No mercury needed

8. Ultraviolet leds

Researchers today are under increasing pressure to quickly develop innovative technologies and new materials that meet the rapidly changing needs of society. The R&D mission is to contribute to the healthy development of society by delivering such innovative technologies and new materials through continuous inquiry and ceaseless effort.

Constituting a part of the solar spectrum, ultraviolet (UV) light has a shorter wavelength than blue light and is well known as being the cause of sunburn and other skin problems.

Since DNA has an absorption peak in the 260 nm range, devices generating light in this range are the best suited for sterilization applications² [2].

Benefits of UV LEDs: (i) Compactness; (ii) Robustness; (iii) Low cost of ownership (system level); (iv) Environmental-friendly composition.

The development of gallium nitride (GaN) has led to the main breakthroughs in LED technology due to its wide electronic band-gap, making it suitable for high-power, high frequency, and high temperature applications [4-6]. Continual improvement in the fabrication of high-quality bulk III-nitride crystals and their epitaxial layers has led to the recent advancements of GaN based light emitting diodes (LEDs) [7]. While much of the focus has been placed on visible light emitting diode technology for display and solid state lighting, scientific focus has turned towards the shorter-wavelength ultraviolet (UV) devices due to their technological importance.

Aluminum Gallium Nitride (AlGaIn)/Gallium Nitride (GaN) based deep ultraviolet (DUV) light emitting diodes (LEDs) with emission wavelengths between 200-280 nm enable

- Color rendering
- Current-regulated power supplies

7. Advantages

- Efficiency
- Direct colour generation
- Small size
- Fast switch time
- Frequent on-off cycling
- Easy dimming
- Cool light without IR
- Lon lifetime

² Conventionally, mercury lamps have been used for such applications, especially in the fields of medical care, water purification and food sanitation, due to their ability to emit DUV light in the 254 nm range. However, the use of mercury lamps poses several problems in terms of environmental impact, not the least of which is that they contain mercury, an environmental load substance. They also have a short life of approximately 2,000 hours, and require a high operating voltage. In recent years, on the back of the growing trend toward mercury-free products and heightening energy-conservation requirements, the possibility of DUV-LEDs has prompted their development as a substitute for mercury lamps.

key emerging technologies such as water/air purification and sterilization, covert communications and portable bio-agent detection/identification systems for homeland security, and surface and medical device sterilization. These devices produce a large amount of undesired heat due to low quantum efficiencies in converting electrical input to optical output. These low efficiencies are attributed to difficulties in the growth and doping of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($x \sim 0.7-1$) materials and UV absorbing substrates leading to excessive joule heating, which leads to device degradation and a spectral shift in the emission wavelength. With this regard, effective thermal management in these devices.

Depends on the removal of this heat and reduction of the junction temperature. This is achieved by decreasing the package thermal resistance from junction-to-air with cost-effective solutions. The use of heat sinks, thermal interface materials, and high conductivity heat spreaders is instrumental in the reduction of the overall junction-to-air thermal resistance.

9. Deep uv leds

Within the past ten years, a wide variety of group III-Nitride-based photonic and electronic devices have opened a new era in the field of semiconductor research. Fueled by their great potential which extends beyond the capabilities of Si technology, they have become of great commercial importance. The direct and large bandgap nature, intrinsic high carrier mobility, and the capability of forming heterostructures allow them to dominate photonic and electronic device market such as light emitters, photodiodes, or high-speed/high-power electronic devices.

High mobility III-V or Ge channel materials are one of the promising directions for performance improvement as well as reducing power consumption. Even though there are many challenges to the 10 nm technology node or beyond, the improvement of gate stack/channel interface properties and introduction of heterogeneous process integration for new channel materials with higher electron and hole mobility should enable aggressive V_{DD} scaling, thereby reducing power consumption.

There are plentiful ongoing endeavors to push emission wavelength into the deep UV regime for numerous applications including bio-aerosols sensing, air and water purification, and high density data storage. One of the most defining features of the nitride material system is the lack of high-quality bulk GaN or AlN substrates. To date, all commercially available III-nitride LEDs are grown heteroepitaxially on foreign substrates such as sapphire and SiC. Si has also received some attention as the substrate for low-power LEDs due to its clear advantages of low cost and high quality. Many efforts have been devoted to developing high-quality buffer layers to accommodate the mismatch in lattice constant and thermal expansion coefficient between the epilayers and substrates. The presence of a high density of threading dislocations and large residual strain in the heteroepitaxial structures, along with strong piezoelectricity and large compositional fluctuation of the nitride alloys, give rise to some unique electrical and optical characteristics of current III-nitride LEDs [8].

Nitride-based semiconductor materials InN, GaN, AlN and their alloys attract great attention due to their promising applications in optoelectronic devices such as light emitting devices (LEDs) and laser diodes (LDs) [9]. Depending on the alloy composition, these systems could in principle cover a wide wavelength range from red through yellow and green to blue [10].

III-Nitride based DUV LEDs are prospective candidates to replace the conventional bulky, expensive and environmentally harmful mercury lamp as new UV light sources, used in the applications of water and air purification, germicidal and biomedical instrumentation systems, etc. Due to the lack of native substrates and poor carrier injection, AlGaN-based deep UV LED is suffering from low optical power and low overall efficiency, which prevents the availability of low cost, high efficiency deep UV LED on the market.

The dissertation [11] is focused on improving the efficiency of deep UV LEDs, by improving the base template epilayers, specifically silicon doped n-type AlGaN electron cladding layer on which the subsequent quantum well and other device layers are grown. Approaches such as short period superlattice (SPSL) nAlGaN and silicon modulation doping nAlGaN are shown to effectively decrease the threading dislocation density (TDD) from $1.2 \times 10^9 \text{ cm}^{-2}$ to $3 \times 10^8 \text{ cm}^{-2}$, followed by the improvement of sheet resistance to $53 \Omega/\square$. The improvement of crystal defect density is believed to contribute to the increase of internal quantum efficiency (IQE) and thus the overall device efficiency. Deep UV LED on a wafer device employing proposed silicon doping modulation technique shows light emission peak at 281 nm and yields 25% improvement of the optical power due to the dramatic reduction of the dislocation density as well as the overall efficiency.

There are some other issues that cause the degradation of the recombination efficiency. Currently, most of the Nitride-based LED devices with crystal structures grown along c-orientation exhibit spontaneous and strain-induced piezoelectric fields which can cause degradation in device performance, especially the combination efficiency, due to the reduced recombination probability of the electrons cloud and holes cloud in the active region, which is also known as quantum confine stark effect (QCSE). H.-C. Chen has demonstrated that the use of semipolar or nonpolar sapphire substrate is effective in reducing the QCSE phenomenon; however, the device optical power was low, due to the existence of high threading dislocation in the active layer. To further reduce the defects density, a high quality AlN template is prerequisite for the development of the high power DUV LED on semipolar or nonpolar sapphire substrate.

Sapphire will likely be the substrate of choice for deep-UV LEDs due in part to its transparency. Milliwatt UV LEDs with emission wavelengths as short as 250 nm have emerged in the past several years. Further improvement in LED performance is expected in the near future as the heteroepitaxy of AlGaN materials on sapphire is refined. AlN is a much closer lattice and thermal match for High-Al content AlGaN heterostructures. If bulk AlN or AlGaN becomes commercially available, these materials would be the best choice as the substrate for deep UV LEDs.

The lack of low-cost, large-size, and flawless GaN wafers remains an obstacle. This obstacle must be overcome before III-nitride LEDs grown on GaN substrates have an impact on the development of high-brightness and cost-efficient solid-state lighting sources.

By alloying and forming heterostructures with AlN or InN, GaN has wide wavelength coverage ranging from entire visible spectral range in addition to the infrared and deep ultraviolet (1771 nm ~ 200 nm, 0.7 eV ~ 6.2 eV) ranges. The high thermal and chemical stability of GaN give those devices the advantage of operating in hostile environments. Like most wide bandgap semiconductors, the nitrides exhibit superior radiation hardness compared to the other smaller bandgap counterparts such as Si or GaAs, allowing them to be incorporated into demanding space applications. For these reasons, the research on

group III-Nitride semiconductor materials has attracted much attention in both the consumer and defense industries.

A wide variety of group III-Nitrides materials system has opened a new era in the field of semiconductor research for the past decade. They have become of great commercial importance fueled by their potentials that extend beyond the capability of Si technology. The direct and large bandgap nature, intrinsic high carrier mobility, and the capability of forming heterostructures allow them to dominate the photonic and electronic device markets such as light emitters, photodiodes, or high-speed/high-power electronic devices. MOCVD has become the dominant technology for epitaxial growth of epitaxial III-nitrides due to its versatility.

III-Nitride compounds exhibit superior electronic properties with direct band gaps of 0.7 eV (InN), 3.4 eV (GaN), and 6.2 eV (AlN), which cover the entire energy range of solar spectrum as well as visible lights. Besides, III-nitride compounds are formed with a special polar wurtzite lattice structure, which lacks a center of inversion symmetry and produces a large spin splitting by intrinsic spin-orbital interaction. By engineering the band structure of III-nitride compounds, one can fabricate III-nitride nanostructures for the applications of high-efficient lighting sources, sustainable solar cells, and high-speed spintronic³ devices.

III-Nitride semiconductor-based DUV LEDs are emerging as an enabling technology for diverse military, homeland security, industrial and commercial markets, and space exploration. Current technology allows to fabricate AlGaIn-based DUV LEDs with wall-plug efficiency (WPE) between 1-2%, which is substantially lower than WPE for visible and near UV LEDs. Significant R&D efforts are under way, including DARPA's "Compact Mid-Ultraviolet Technology" (CMUVT) program, to improve materials quality, device fabrication and light extraction to increase WPE of DUV LEDs by more than order of magnitude. The paper [12] presents an overview of the latest news in the development of DUV LED technology with the main focus on novel device designs to increase quantum efficiency and improve UV light extraction and reliability of devices emitting in the range of 230 nm - 340 nm. Novel QW design has been implemented to suppress polarization effects and phonon engineering approach to increase electron trapping in the active layer of the devices. Very narrow (< 3 nm) and deep (total energy band offset > 0.4 eV) quantum wells were used to suppress Stark effect and increase radiative recombination. Active region of DUV LEDs was embedded inside a deep potential well (larger than the energy of optical phonon) to increase electron-LO (longitudinal-optical) phonon scattering and accelerate cooling of hot injected electrons. This allowed increasing electron capture into the active region without using conventional electron "blocking layer" commonly used in visible LEDs. It was developed and incorporated UV-transparent p-type cladding layers to reduce optical losses due to strong absorption in the top p-AlGaIn cladding layer and p⁺-AlGaIn or p⁺-GaN contact layers. Combination with new type of ohmic contact reflecting in DUV spectral range allowed to significantly improve light extraction and increase output power of DUV LEDs by 2 times in the range of 275 nm -- 300 nm, and 2.5 times in the range from 310 nm to 340 nm. Improved quality of epitaxial layers and device fabrication technology enabled to increase reliability of DUV LEDs and fabricate devices with peak emission wavelength in the range of 270 to 280 nm with lifetime exceeding 10,000 hours for continuous wave (CW)

³ Spintronics, or spin electronics, involves the study of active control and manipulation of spin degrees of freedom in solid-state systems.

operation. Reliability data for DUV LEDs operating under high current (up to 400 mA) in the pulsed operation mode are presented. A new device fabrication technology was developed, primarily to reduce ohmic contact resistance for very high Al-content DUV LEDs with peak emission wavelengths shorter than 250 nm. This resulted in the reduction of the forward bias from > 20 V to less makes these devices suitable for CW operation. We will also present recent results of space qualification of 250–260 nm DUV LEDs for space applications, which include reliability testing up to 26,000 hours (CW mode), shake and bake, and radiation hardness.

Focusing on three growth fields, namely, “information and electronics,” “environment and energy” and “life and healthcare”, the researchers are proceeding now with the development of a high-performance deep ultraviolet light emitting diode (DUV-LED).

Deep ultraviolet (DUV) light has an even shorter wavelength and is not contained in the solar spectrum. DUV light also exerts strong sterilization ability, destroying the nucleic acids - DNA and RNA - of germs and viruses (Figure 5).

In order to realize DUV LEDs almost all research groups employ AlGaN or AlInGaN multiple quantum wells (MQWs)-based pn-junctions over sapphire substrates. However, with the recent availability of improved AlN substrates, Crystal IS and Hexatech reported DUV LEDs over bulk AlN. The use of sapphire was primarily dictated by the substrate transparency requirements for the emitted light.

Researchers from Japan and the USA have reported [13] the first fabrication on hydride vapour phase epitaxy (HVPE) aluminium nitride (AlN) substrates of aluminium gallium nitride (AlGaN) light-emitting diodes (LEDs) that emit at the deep ultraviolet (DUV) wavelength of 268 nm.

There is much interest in shrinking the wavelength of AlGaN LED emissions to the DUV range around 265 nm for air and water purification. This range is an absorption maximum for DNA, and hence 265 nm DUV can be used to disrupt biological agents such as bacteria. Most work on AlGaN LEDs for this wavelength range is carried out on sapphire substrates. However, large lattice mismatches lead to dislocations in the active material region that emits the light, reducing energy efficiency to a couple of percent.

HVPE was used to grow thick 250 nm AlN layers on c-plane physical vapor transport (PVT) AlN substrates. Chemical mechanical polishing (CMP) was used to prepare the HVPE AlN surface for the subsequent epitaxy of the LED structure. After CMP, the root-mean-square surface roughness was less than 0.2 nm. The device layers were grown using metal-organic chemical vapor deposition (MOCVD) in an Aixtron AIX200/4RF-S reactor (Figure 6).

The active region consisted of a three-period multi-quantum well (MQW). The p-type layers were an AlN electron-block layer, an AlGaN cladding layer, and a GaN contact layer. Although GaN absorbs DUV, the researchers felt that it was needed to provide a suitable ohmic contact with the nickel/gold p-electrode. Unfortunately, p-type doping becomes even more difficult as the aluminium content of AlGaN is increased.

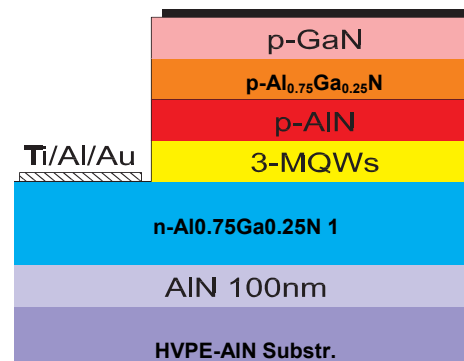


Figure 6. Schematic structure of a 268 nm DUV-LED

X-ray analysis showed that the layers of the device were strained pseudomorphically to the underlying AlN, except for the final p-GaN, which was almost completely relaxed due to the large lattice mismatch. The $400\mu\text{m} \times 600\mu\text{m}$ LED devices were produced using photolithography, dry etching, and metal evaporation.

The PVT-AlN was removed using mechanical polishing to reduce the amount of DUV absorption. Some of the HVPE-AlN was also removed, and the researchers estimate that the thickness of this layer after polishing was $170\ \mu\text{m}$. Fortunately, the HVPE-AlN absorbed far less of the 265 nm-wavelength radiation than does the PVT-AlN substrate. Below 300 nm wavelengths, the transmittance of the PVT-AlN substrate was effectively zero.

By contrast, the HVPE-AlN allowed as much as 62% of the 265 nm radiation through. "This value is close to the ideal value when surface reflection is taken into account," the researchers comment. The intrinsic absorption of HVPE-AlN was measured at 10/cm for 265 nm UV. Without removal of the PVT-AlN, LEDs produced little external radiation and none detectable below 300 nm.

10. Some recent studies

Paper [14] discusses physics, design, fabrication, performance, and selected applications of DUV LEDs. The analysis reveals the relative contributions of electrical injection, internal quantum efficiency, and light extraction efficiency to the overall DUV LED performance. The calculations show that the reduction of the dislocation density at least below value of $2 \times 10^8\ 1/\text{cm}^3$ is necessary for reaching high DUV LED efficiency. Better light extraction has been achieved using an innovative p-type transparent sub-contact layer and reflecting ohmic p-type contact resulting in nearly tripling DUV LED power. At high power dissipation, temperature rise might be significant, and data showing the power degradation with temperature increase and the results of the detailed 1D and 3D analysis of thermal impedance of DUV LEDs. As an example of DUV LED application, the paper reports on microbial disinfection using 19 watt 275 nanometer DUV LED.

Recently, the development of high efficiency 230-350 nm-band DUV LEDs or laser diodes (LDs) has been attracting considerable attention, because of their wide range of potential applications. AlGaIn and InAlGaIn alloys are very attractive for realizing high-efficiency DUV LEDs and LDs [15, 16]. Several groups have reported Al-GaN-, InAlGaIn-, or AlN-based DUV LEDs, such as 333–350 nm AlGaIn LEDs [17 - 19], 240–280 nm AlGaIn multi-quantum-wells (MQWs) LEDs [20-22], quaternary InAlGaIn MQW LEDs [23, 24] and a 210 nm AlN LED [25].

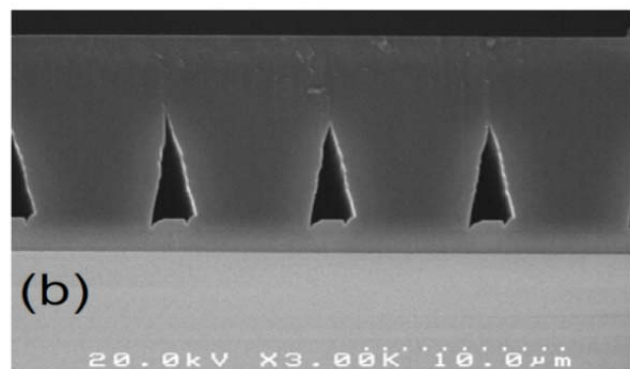
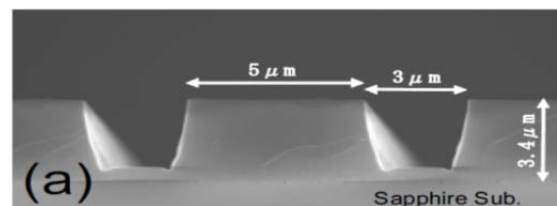


Figure 7. Cross-sectional high-resolution scanning electron microscope (HR-SEM) images of (a) an AlN stripe structure and (b) an ELO-AlN template [26]

However, the efficiency of AlGaN-based DUV-LEDs with wavelength below 360 nm is much lower than that of InGaN-based blue LEDs. In order to realize high efficiency AlGaN-based DUV-LEDs, the development of low threading dislocation density (TDD) AlN template is quite important.

The maximum output power of Al-GaN-MQW DUV-LED of the 273 nm LED was 2.7 mW under room temperature (RT) continuous wave (CW) operation. The external quantum efficiency (EQE) may be significantly improved by eliminating the abnormal AlN nucleation on the epitaxial lateral overgrowth (ELO)-AlN template. Figure 7 shows cross-sectional high-resolution scanning electron microscope (HR-SEM) images of (a) an AlN stripe structure and (b) an ELO-AlN template. DUV LEDs based on group III-Nitrides have numerous potential applications in water and air purification, food sterilization, ultraviolet curing, chemical and biological sensors, and medical instrumentation. However, DUV LEDs, with peak emission wavelength between 250 and 320 nm, are prone to self-heating. This rise in temperature during normal operation leads to early saturation of the light output power of these devices at relatively low injection currents and degrades their external quantum efficiency. Furthermore, this high heat dissipation also decreases the reliability of these devices and shorten their life span. Consequently, thermal management of high power LEDs is a crucial area of research and development. Thermal impedance quantifies the rise in the junction temperature of a device per unit of power dissipated. Lower thermal impedance of a device will result in higher dissipation of the heat energy and lower junction temperatures. In thesis [26], the junction temperature and thermal impedance of square-geometry and micro-pixel AlGaIn/AlGaIn DUV LEDs are measured using the electroluminescence (EL) peak position shift and forward voltage shift methods.

The EL peak-shift method was found to be more reliable than voltage-shift method to predict the thermal impedance for unpackaged devices. On the other hand, for packaged devices, the measurements using voltage-shift method were found to be more accurate than those from peak-shift method. Figure 8 shows (a) a bird's-eye view and (b) a cross-sectional image of the abnormal AlN cores generated on ELO-AlN layer observed by HR-SEM.

11. Raman spectroscopy

Raman spectroscopy is an optical method that reveals the molecular structure by measuring the inelastic scattering of light. The development of Raman spectrometry has often depended on a series of newly generated optical techniques. Over the last decade, the laser technology has been developed rapidly. Progress in semiconductor technology has

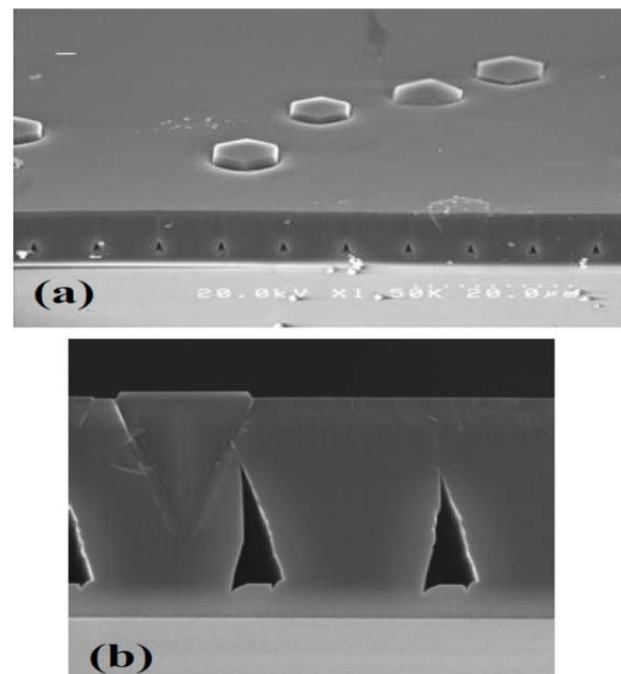


Figure 8. (a) A bird's-eye view and (b) a cross-sectional image of the abnormal AlN cores generated on ELO-AlN layer observed by HR-SEM [26]

occurred and various ultraviolet solid-state and gas lasers have appeared, and lasers with different properties, such as pulsed or continuous wave, working in single or multi mode have appeared in the commercial market. Different lasers could be suitable only for one particular application. A dedicated spectrometer and special optical components may be required, so in order to implement a DUV Raman system in practice, one has to deal with much optical knowledge.

The temperature rise in LEDs is an important parameter that must be determined for both thermal management and device lifetime/reliability assessment. Commonly used indirect methods of measuring the device temperature either estimate the multiple quantum well (MQW) temperature based on measuring temperature dependent device characteristics (e.g., forward voltage and electroluminescence methods), or they measure the average temperature across the device structure using optical methods such as infrared (IR) thermography and thermo-reflectance. However, none give true insight into the vertical distribution of temperature in these structures. Raman spectroscopy was applied to operating UV LEDs to give the temperature rise in discrete layers within the LED device structure, going from the growth substrate to layers adjacent to the MQWs [27].

A successful application of Raman spectrometry to food analysis generally requires that one has a resonance Raman effect to be active for the target compound. This is so because otherwise Raman is a quite weak effect that is against the possibility to realize high sensitivity detection [28].

12. Failure modes

The most important failure modes detected are [29]: (i) the modification of the optical properties of the encapsulation, due to the high temperatures involved, (ii) the detachment of the encapsulation layer in low flux white LEDs, that induced a thermal resistance increase and the total failure of the device, (iii) the generation of non-radiative recombination centers in UV LEDs, (iv) the generation of parasitic path that short the junction.

In [29] a study on DUV LEDs performance and reliability has been reported. The relation between the different radiative emission processes, by evaluating the relative electroluminescence intensity of the three main emission bands of the LEDs has been analyzed in detail. It was also presented an analysis of the mechanisms that limit the reliability of these devices during dc stress: it has been shown that (i) Optical power degradation can be ascribed to the increase of the non-radiative recombination rate, and (ii) the degradation rate is related to the molar fraction of Al inside the quantum wells (QWs). Capacitance versus voltage (C-V) analysis provided further information on the degradation process, indicating that as a consequence of stress, the charge distribution in the active layer is modified, possibly due to the generation of defective states. Together with reported degradation mechanisms, a failure mode responsible for sudden death of device was found and it has been ascribed to a poor morphology of the LED structure.

Work defects were observed in both the green and UV LEDs that could potentially reduce the lifetimes of the devices [30]. In the green LEDs, dark defect signals observed using the laser-based localization techniques were used to pinpoint large contact metallization defects. Defects in the contact metallization and at the metal/p-type semiconductor interface may create strong spatial non-uniformities in current injection. This type of defect could create hotspots and non-uniform light emission. Dark defect

signals observed in the UV LEDs were determined to be shorting paths. Part of the contact metallization had diffused along dislocation cores to create leakage currents through the quantum wells. It is theorized that failure occurred in the UV LEDs when enough of these leakage paths dominated current injection through the QWs.

For the UV LED it is clear that a dislocation is present at the failure site and that Au has diffused through the QW. However it is still unclear what materials properties the dislocation possessed to segregate itself from surrounding dislocations (size, presence of a micropit). Plan-view TEM can reveal another dimension of structure that is required for this type of failure to take place. One theory might be a cluster of dislocations. A quantitative correlation between increases in leakage current under laser stimulation and time to failure would be beneficial to monitor degradation of the devices. The TIVA / LIVA characterization technique can be a successful tool for III-nitride LED characterization of defects and degradation. This technique can be a powerful tool to predict early failure in commercial devices as well as support the development of in-house semiconductor devices. Further studies characterizing the multiple different defects observed in the UV LEDs and further laser-spotting characterization are expected to fully establish the TIVA / LIVA technique as a viable screening method and reliability technique for III-nitride optoelectronics [30].

13. Reliability

The reliability and output power of AlGaIn-based DUV-LEDs fabricated on AlN substrates prepared by hydride vapor phase epitaxy are reported in paper [31]. TEM analysis revealed that dislocation density in LED layers, except the p-GaN layer, was below 10^6 cm^{-2} . DUV-LEDs emitting at 261 nm exhibited an output power of 10.8 mw at 150 mA. The lifetime of these LEDs was estimated to be over 10,000 h for CW operation at 50 mA. No significant acceleration of output power decay at higher operation currents was observed. The estimated lifetime at the operation current of 150 mA was over 5,000 h.

14. Package-related failures, lifetime, and future possible solutions

To dissipate the amount of heat that is generated during operation, the LED die needs to be bonded to a heat sink or substrate, often with a solder attach. If voids in the solder attach create an insufficient thermal path, the resulting hot spots will eventually lead to thermal runaway and failure. Whisker growth caused by electromigration, which can come from internal strain, temperature, humidity, and material properties, usually happens near the bonded surface between the solder and the heat sink and can lead to electrical short circuits. In choosing a die attach material, the following should be considered: (1) stress relaxation at the interface; (2) excellent adhesion between the bonded surfaces; (3) effective heat dissipation as well as high thermal conductivity; and (4) CTE matching materials between the bonded surfaces.

Package-related failures can occur in the encapsulant, wire, and phosphor. Wire-bond breakage or detachment and die-attach strength loss are due to overheated epoxy encapsulant. These problems, in turn, cause a delamination between the chip and epoxy. Mechanical stress from lead wires is another failure mechanism, because it can generate open circuits inside the device. Inappropriate pressure, position, and direction applied to a lead wire soldering can accumulate the stress at normal operating temperature, bending the leads toward the body of the LED.

Most of white LEDs use yellow or red/green phosphors, which are susceptible to thermal degradation. When two or different phosphors are mixed, each constituent should

have compatible lifetime and degradation behavior to keep the status of color. The color temperature and purity level of phosphors also degrade over time.

New encapsulant materials for future high-power and high efficiency LED packaging should have the following properties: high refractive index, high thermal and UV resistance, low CTE, low modulus, good adhesion, and low moisture permeability. High refractive index is needed to achieve high light extraction. However, this need can be alleviated by using efficient packaging design, such as the multiple small chip mounting and lens/cup design. To take advantages of both epoxy resins and silicone, developing new epoxidized silicone materials is a possible solution for the packaging of high power LEDs [32].

15. Conclusions

The recent results on high efficiency devices clearly indicate a maturation of the technology to the point where the development of systems for air- and water-purification and bio-medical applications is very feasible. Several companies in the US, Japan, Korea, China and Europe are scaling up their production lines. This will certainly lead to large volume LEDs sales and a reduction of their unit price.

There is very little understanding of how the coupled response leads to the heat distribution within the active portion of the LED. Dissertation [33] gives device growth engineers and designers more insight into the impact that doping and the formation of p and n contacts has on the performance of the device. It is not clear at this time how much additional thermal control can be gained by coupling thermal design into the chip architecture as opposed to simply managing the heat loads via the packaging materials. Additional work needs to be done to couple the thermal packaging design along with the optical design for UV LED systems.

With improved performance, the transformative and enabling nature of DUV LED technology has the potential for reducing and, in many cases, eliminating the practice of using antibiotics for preventing infections and developing new testing procedures based on UV fluorescence. Once this expected performance is achieved, the market for DUV LEDs could explode [34].

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OXIDE NANOMETRIC PELLICLES FORMATION BY APPLYING ELECTRICAL DICHARGES IN INPULSE

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Abstract. The paper presents the results of theoretical and experimental investigations of phenomena that accompany the formation of nanometer oxide and hydroxide pellicles by applying electrical discharges in impulse (EDI). The chemical content of processed surface analysis (EDX – Energy Dispersive X-ray analysis) attests the presence of oxygen that reaches up to 60% at. for steel surfaces, 30-35% at. for those made of titanium alloys, up to 20% at. for those made of aluminum alloys, and up to 50% at. for those made of copper alloys. The presence of considerable amounts of nitrogen is found only in titanium and iron alloys (and constitutes about 15% at), while in aluminum and copper alloys its presence is not significant. The superficial phase analysis (XPS - X-ray Photoelectron Spectroscopy) of the oxygen allowed us to state that the oxygen in pellicle forms three base structures: $-O^{-2}$ (oxide), $-OH^{-}$ (hydroxide), and structures of the type O-C and O-C=O. The chemical analysis showed that the concentration of each of the three components is 0.89:1.00:0.50.

Keywords: *electrical discharges in impulse, oxide pellicle, "cold" electrode spot, micro-hardness, surface roughness*

Introduction

Oxidation of metal surfaces has found applications in various fields of technology for corrosion protection [9] and to change the electrical properties of surfaces in electrical and radio engineering [6, 7]. For this purpose, the method of electrolytic deposition of thermodynamically stable pellicles on some metal surfaces is applied [4], which can be obtained only at the so-called fed metals, which include aluminum, titanium, tantalum, niobium, etc. The spark-anodic electrolysis, also known as micro-plasma or micro-arc oxidation, has been developed [2, 3]. Depositions formed by this method are a large range of structural, technological and operational requirements: micro-hardness, wear resistance, low coefficient of friction, and ability of electro-isolation, erosion resistance, and high adhesive properties. An important advantage of such depositions is that their properties are of complex operational character.

Low-alkaline and acidic electrolytes and metal salt solutions are used to realize this process. Deposition properties depend on the chemical composition of the alloy, concentration, composition and temperature of the electrolyte, electrical regimes of the

process and its duration, etc. Coverings mainly consist of solid crystalline phases in the matrix of softer oxide phase of metals that form part of the alloy and the electrolyte. This structure provides a high micro-hardness, wear-proof and corrosion resistance, heat protection and electro-isolation properties of the covering. The application of this technology implies the use of special devices for electrolytic processes and the adoption of measures required to ensure safe working conditions for staff.

From the moment of application the electrical discharges in impulse (EDI) for technological purposes in dimensional processing [11], in deposit formation of compact and powder materials [1, 5], the micro-metallurgical processes that occur in the surface layer of the work-piece in both liquid and solid phases were studied. It has been established that the formation of new alloys in the processed surface is accompanied by convective mixing of the components in the liquid phase and the diffusion of elements in the substrate from the liquid phase of the deposition. In the work [1] it has been shown that for the interstice greater than 0.03 mm, the interaction of EDI plasma channel with the processed surface is manifested by the appearance of an indent consists of a central zone that represents a crater with liquid phase and a heat-affected zone of freshly etched metal color. For certain sizes of the interstice, the central zone disappears, and the processed surface represents only a heat-affected zone where phenomena of quenching and enriching piece material with elements from the work media occurs.

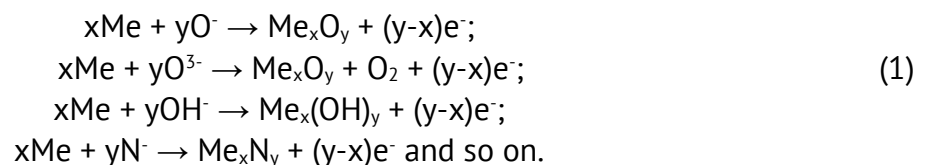
Recently, a number of works [6-10] has been published where the results on the electro-discharge oxidation of metal surfaces under ordinary conditions are presented. Coverings obtained by this method have usually a dual structure. It consists of an inner base layer on the edge of the metal-coating and external outer layer (coat).

The base layer is fine-porous, has a crystalline structure and constitutes 60...90% of the covering thickness. The outer layer coating is less hard, more porous, has an amorphous structure and takes on the 40...10% of the thickness.

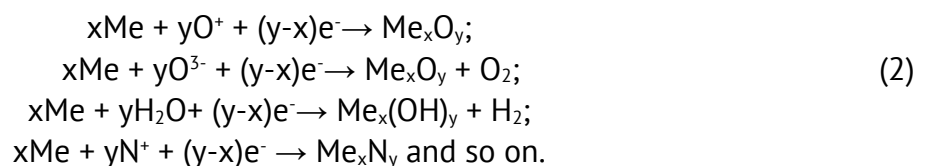
The coating under the oxidation process is able to germinate in metals in about 10 to 60% of the total thickness of the coating in the depth and consists mainly of oxides of the elements contained in the machined alloy and elements from the interstice.

The following chemical reactions are produced on the surface of the electrodes [10, 12]:

- on the anode:



- on the cathode:



EDI method allows to form coverings on pieces of complex shapes and of any configuration, including the internal surface of pipes [9].

The process operates at room temperature, which positively affects the constancy of the base metal physical properties.

The main characteristics of coverings formed by applying the EDI method are the following: layer thickness – up to 240 nm, micro-hardness – up to 2000 HV, approaches the hardness of corundum; surface roughness of coatings after oxidation – $R_a = 0.05...0.10 \mu\text{m}$.

The analysis of the operational properties of coatings obtained by EDI oxidation shows that these properties are closely related. Total thickness of covering, taking into account the number of electricity spent on it, demonstrates the high performance and efficiency of the process. The boundary between the main piece material and covering relative to its original size is essential both for the adoption of constructive decisions on the use of pieces with EDI coverings and for the design of technological process of manufacturing such pieces.

The purpose of this paper is the analysis of results of theoretical and experimental investigations of phenomena that accompany the formation of nanometer oxide and hydroxide pellicles by applying electrical discharges in impulse and their possible application in practice.

Methodology of experimental investigations

The main challenge for the stage of preliminary research of EDI coatings was to search for a technological regime of the oxidation that contributes to the formation of oxide pellicles with high operational properties on the pieces made of metallic materials and their alloys. The chemical content of machined pieces materials were taken into account during the EDI (Table 1).

Table 1

Chemical content of machined pieces materials

Alloy	Chemical content
Iron alloy	
Steel C45	0.42-0.50 % C; 0.17-0.37 % Si; 0.5-0.8 Mn; ≤ 0.25 % Cr; ≤ 0.04 % S; ≤ 0.035 % P; ≤ 0.25 % Cu; ≤ 0.25 % Ni; ≤ 0.08 % As; the rest (basis) – Fe
Titanium alloy	
TiAl6Mo4	5.8-7.0 % Al; 2.8-3.8 % Mo; ≤ 0.5 % Zr; 0.2-0.4 % Si; ≤ 0.30 % Fe; the rest (basis) – Ti
Aluminum alloy	
AlCu4Mg1	3.8-4.9 % Cu; 1.2-1.8 % Mg; 0.3-0.9 Mn; ≤ 0.5 % Fe; ≤ 0.5 % Si; ≤ 0.1 % Ni; ≤ 0.30 % Zn; ≤ 0.1 % Ti; the rest (basis) – Al
Copper alloys	
Technically pure copper M0	Basis – 99.95 % Cu, impurity - ≤ 0.05 %
Brass Cu63Zn37	Basis – 62.0-65.0 % Cu; 34.5-37.5 % Zn; impurity - ≤ 0.5 %
Bronze Cu95Al5	3.5-6 % Al; impurity - ≤ 0.5 %; the rest (basis) – Cu

To realize the EDI process the piece surface was processed in a sub-excitation regime, in which the processing occurs by “cold” electrode spots without surface layer melting of the processed material. The condition of the energy balance, in this case, takes the form [12]:

$$Q = \frac{4W_S}{\pi d_c^2 S} < Q_{melt}, \quad (3)$$

where Q is the heat emitted on the surface of electrodes per volume unit, J/m^3 ; $W_S = \int_0^\tau u(t)i(t)dt$ is the energy emitted in the interstice, J; $u(t)$ is the voltage on the interstice at the discharge, V; $i(t)$ is the instantaneous value of the current in the interstice, A; τ is the duration of the discharge impulse, s; d_c is the diameter of the plasma canal, m; S is the distance between the electrodes (the gap value), m; $Q_{melt} = q_{melt} \cdot \rho_{melt}$ is the volumetric melting heat of the processed piece, J/m^3 ; q_{melt} is the specific melting heat of the processed piece, $J \cdot kg^{-1}$; ρ_{melt} is the material density at the temperature of melting, $kg \cdot m^{-3}$. So, for the EDI of construction steel, the energy emitted in the interstice of 1-2 mm will not exceed 6-10 J.

The impulse current generator [8, 9] with voltage block for interstice pre-ionization was used as a source of energy. The discharge energy emitted in the interstice constitutes 1-6 J. And, thus, establishing the generator energy regime, the superficial piece oxidation for indicated materials without melting of the processed surface can be produced.

The thickness of the oxide pellicle subjected to the condition of the energy balance and according to Palatnik's criterion [11], is directly proportional, respectively, to the quantity of heat and the energy emitted on the electrode surfaces:

$$\begin{aligned} \delta &\sim Q; \\ \delta &\sim W_S. \end{aligned} \quad (4)$$

The power of electrical discharge:

$$P = \frac{dW_S}{dt} = \frac{W_S}{\tau} \quad (5)$$

where τ is duration of electrical discharge.

From the other point of view, the thickness of the oxide pellicle depends on the physical properties of processed surface material [5]:

$$\delta \sim \sqrt{\rho \cdot c \cdot \lambda}, \quad (6)$$

where ρ is material density, kg/m^3 ; c is specific thermal conductivity, $W/(m \cdot K)$; λ is specific melting heat, J/kg .

Thus, the thickness of the oxide pellicle is directly proportional to the power of electrical discharge emitted in the interstice and depends on the physical properties of processed surface material.

Technological schemes used in the formation of the oxide pellicles by applying EDI are shown in Figure 1. The work-piece was connected in the discharge circuit as a cathode, and the tool-electrode – as an anode.

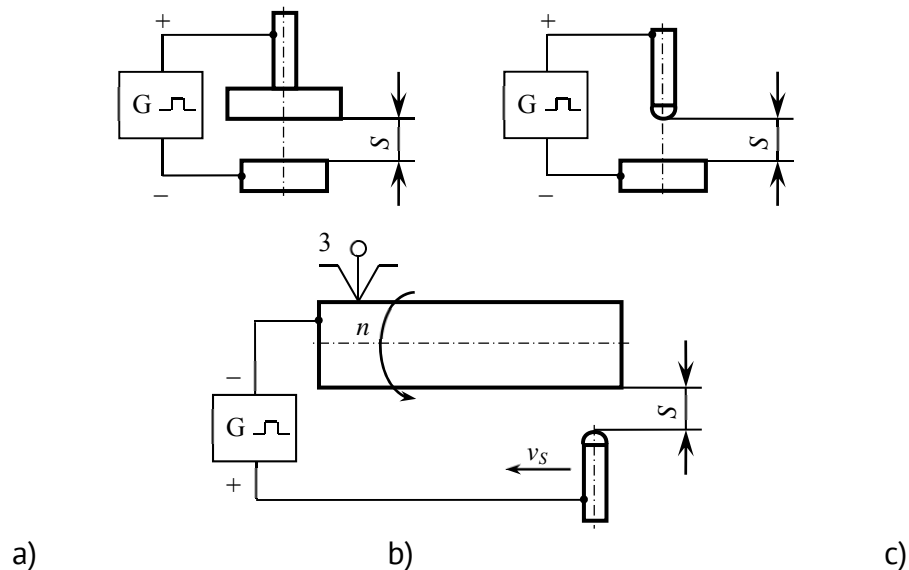


Figure 1. Technological schemes of the oxide pellicle formation by applying EDI: a) on the plane surface with plane tool-electrode; b) on the plane surface with a semi-circular tool-electrode; c) on the external cylindrical surfaces

The direct determination of operating properties that affect the functionality of pieces has required intensive investigations. Therefore, this task has been allocated for the performance that best suits the peculiarity of the work and does not require the use of lengthy and expensive techniques and equipment.

For evaluating and determining the operating properties of oxide coverings that characterize corrosion resistance, active surface resistance and other properties, the results of measuring the following characteristics of the coverings are presented: surface morphology (SEM), chemical (EDX) and phase (XPS) composition of coverings, the total pellicle thickness (Nanoscale Profilometer).

Results of experimental investigations and their analysis

The results of SEM and EDX analysis of investigated sample surfaces are represented in Figures 2 - 7 and in Table 2.

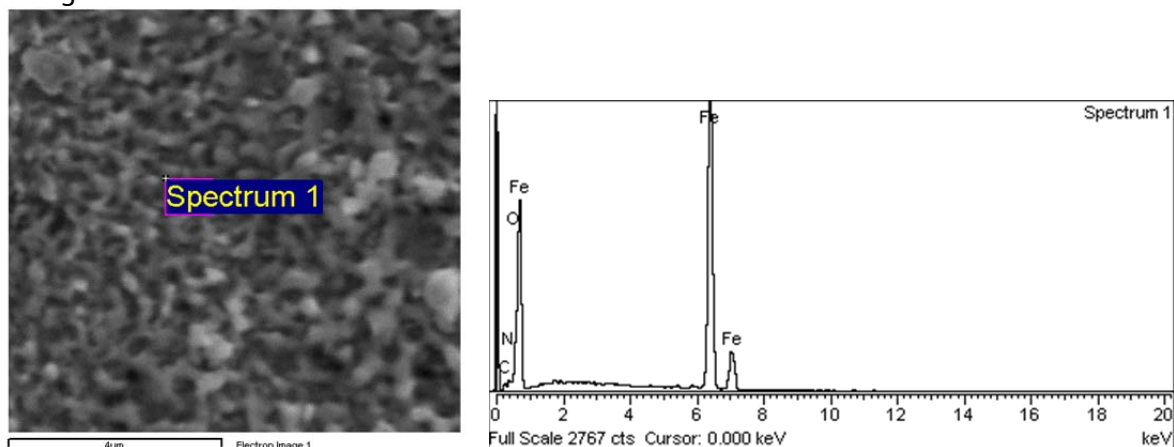


Figure 2. SEM and EDX analysis of steel C45 sample surface [6, 7]

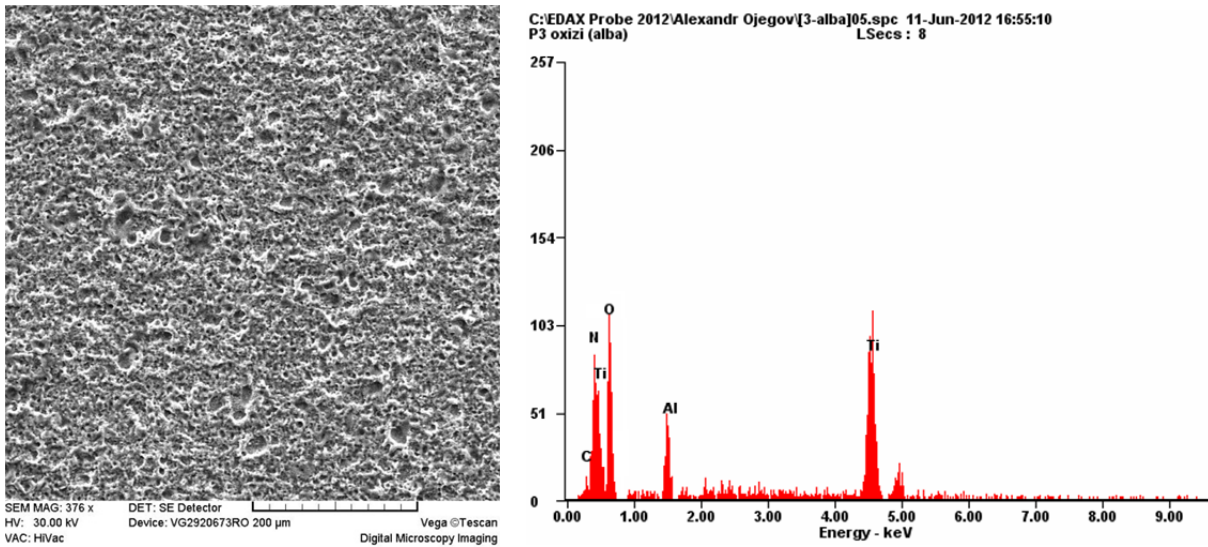


Figure 3. SEM and EDX analysis of TiAl6Mo4 titanium alloy sample surface

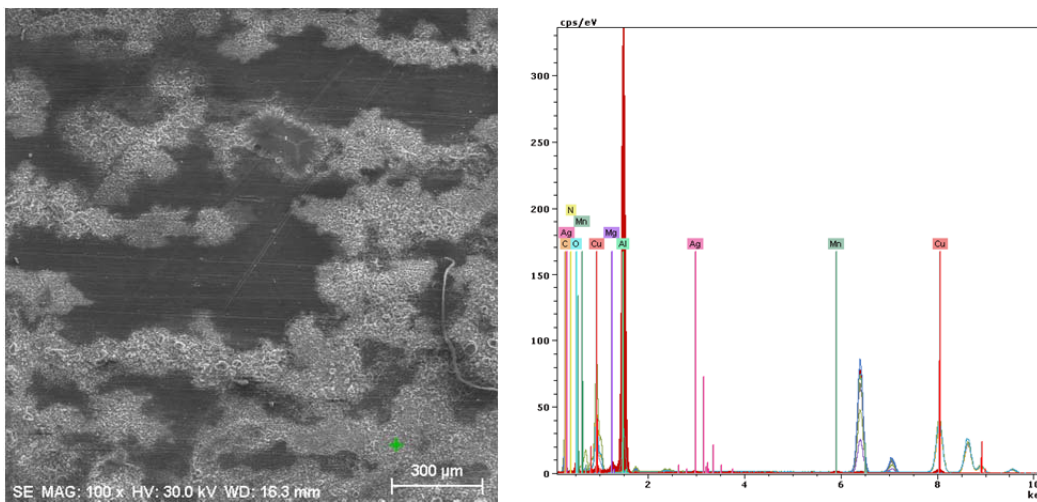


Figure 4. SEM and EDX analysis of AlCu4Mg1 aluminum alloy sample surface

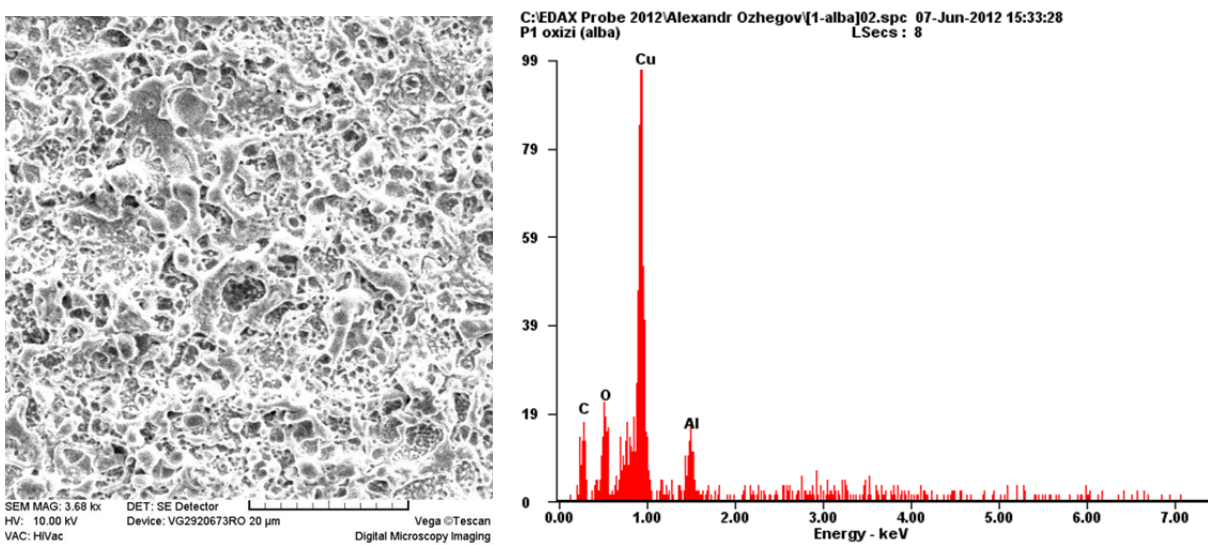


Figure 5. SEM and EDX analysis of M0 copper alloy sample surface

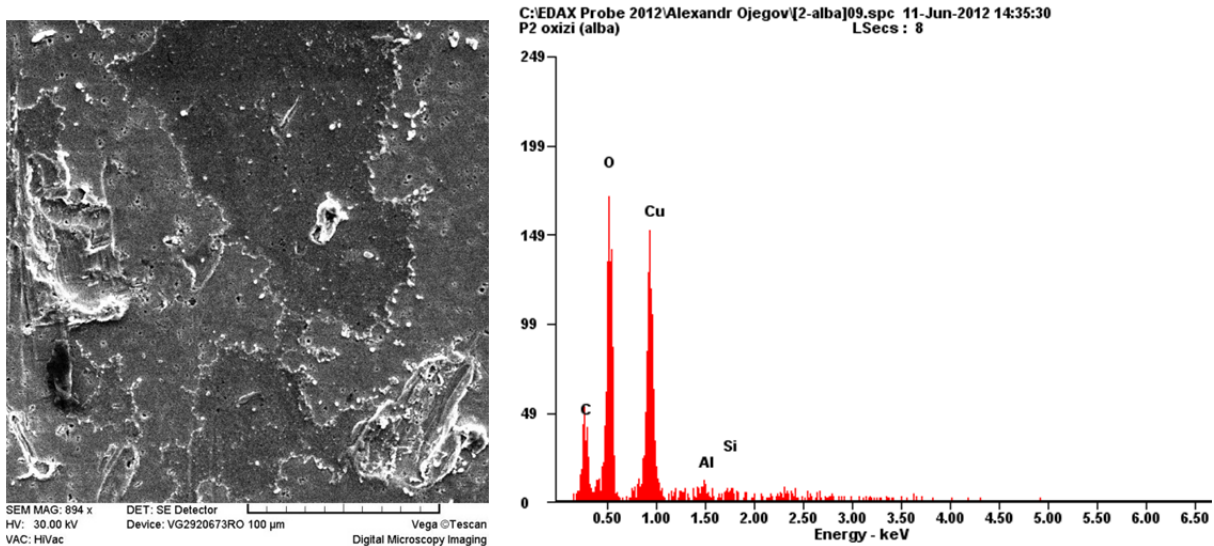


Figure 6. SEM and EDX analysis brass Cu63Zn37 sample surface

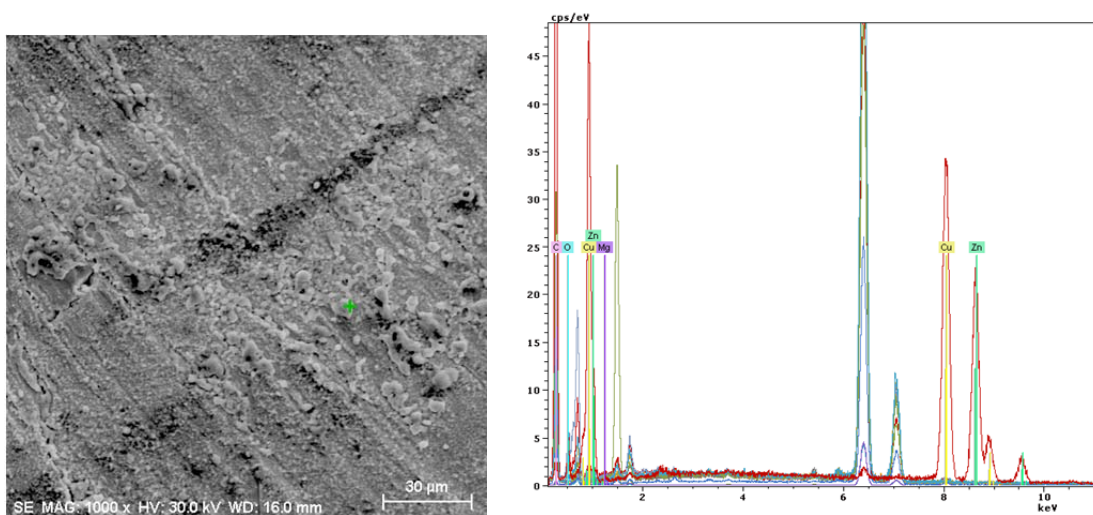


Figure 7. SEM and EDX analysis bronze Cu95Al5 sample surface

As we can see out of these results, the abnormal dissolving oxygen in metals is observed when processing metal surfaces by this method [6]. It is demonstrated that the desolation of the oxygen when processing the samples made of construction steel reaches 60% at, those made of titanium alloys – 30-35% at, the ones made of aluminum alloys – up to 20% at and those made of copper alloys – 50% at. The superficial layer of steel and titanium alloy surfaces includes, beside the oxygen, the nitrogen too.

Table 2

The EDX analysis of sample element content			
Basis material of the sample	EDX element content of processed surface		
	Element	[norm. wt.%]	[norm. at.%]
Steel C45	Carbon	1.89	4.32
	Nitrogen	7.82	12.43
	Oxygen	29.77	58.74
	Iron	60.52	24.51

Table 2 Continuation

Titanium alloy TiAl6Mo4	Carbon	00.41	01.38
	Oxygen	30.33	33.27
	Nitrogen	03.38	09.56
	Aluminum	05.84	08.57
	Titanium	60.04	47.22
Aluminum alloy AlCu4Mg1	Aluminum	66.84	55.68
	Oxygen	13.95	19.60
	Magnesium	2.49	2.30
	Carbon	1.82	3.40
	Copper	2.42	0.86
	Manganese	0.55	0.23
	Silver	0.86	0.18
Technically pure copper M0	Copper	59.5	25.55
	Oxygen	29.53	50.50
	Carbon	10.22	23.20
	Aluminum	0.75	0.76
Bronze Cu95Al5	Copper	52.97	21.18
	Oxygen	26.66	42.34
	Carbon	14.83	31.38
	Aluminum	02.66	02.50
	Silicate	02.87	02.60
Brass Cu63Zn37	Copper	42.30	23.25
	Zinc	32.89	17.57
	Oxygen	16.72	36.50
	Carbon	7.52	21.86
	Magnesium	0.57	0.82

Signal XPS analysis (Figure 8) revealed the presence of oxygen O-1s in three types of chemical bonds (collectively called components). These are: component O⁻² (which contains oxygen atoms of the metal oxides, in the sample is labeled number 3 in Figure 8, with the specific energy 529.6 eV); component OH⁻ with the specific energy 531.5 eV (indicated by the numeral 2 in Figure 8); the relationship of O-C and O-C=O type (with the specific energy 533.4 eV, the curve no. 4 in Figure 8).

The chemical analysis showed the concentration of each of the three components (C) (a): (C) (b): C (c) = 0.89: 1.00: 0.50. Additional studies have shown the possibility of the existence of the fourth component of oxygen within the context of type O-H₂, however, the relative concentration of the component value is assumed to be not greater than 0.15.

Studies have proven that when applying the EDI method for the formation of oxide pellicles there is no change in the geometry of the original surface. This makes it possible for us to recommend this method for surface processing of completed parts. The thickness of films is between 10-240 nm [10], which allows us to include it at the level of nanotechnology.

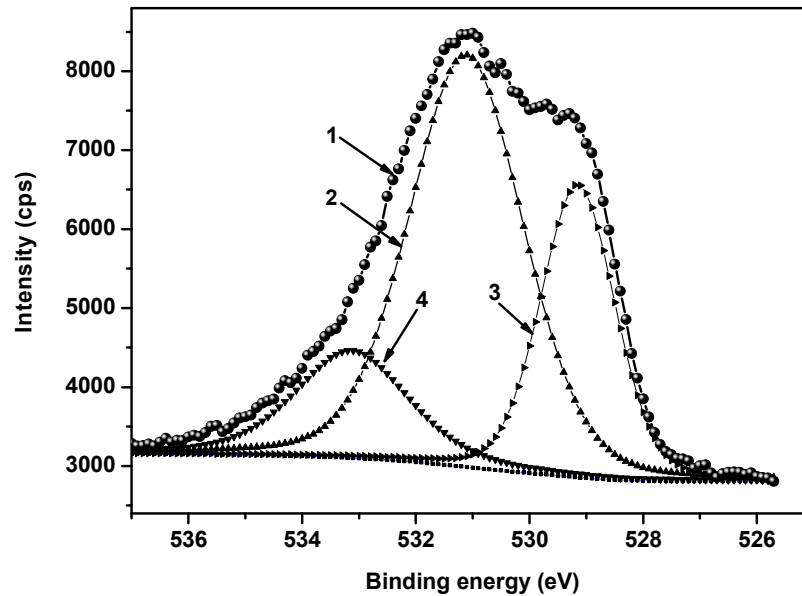


Figure 8. The phase composition (by XPS analysis) of oxide pellicles on samples of steel 45 (spectrum of oxygen on the surface) [12]: 1 – total spectrum; 2 – OH^- component; 3 – O^{2-} component; 4 – components of O-C and O-C=O types

Oxides of metals in the pellicle are in amorphous state. This probably explains why the surface electrical resistance for steel pieces increases up to $10^6 \Omega/\text{mm}$ [7], the potential to corrosion increases by 10 or more times, and the corrosion speed is reduced by 2...4 times [6, 7].

Conclusions

- the obtained results allow to recommend the ESO method for processing the internal and external surfaces of pieces made of iron, aluminum, copper and titanium alloys and to indicate the possibility of applying the method in anticorrosive protection of machine pieces, in surface passivation of pieces in the chemical industry;
- when processing the samples made of construction steel the desolation of the oxygen reaches 60% at, those made of titanium alloys constitutes 30-35% at, the ones made of aluminum alloys – up to 20% at and those made of copper alloys – 50% at.;
- XPS analysis of steel 45 samples' surfaces shows the presence of three types of oxygen components: OH^- component; O^{2-} component and the components of O-C and O-C=O types. The concentration of each of the three components is (C) (a): (C) (b): C (c) = 1.00: 0.89: 0.50;
- the superficial layer of steel and titanium alloy surfaces includes the nitrogen beside the oxygen;
- each compound formed while processing by electrical discharges in impulse is in amorphous non-stoichiometric state;
- maximal depth of oxide pellicles reaches up to 250 nm depending on energy regime and material of samples.

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DETERMINATION OF THERMOREOLOGICAL CHARACTERISTICS AT MICROSCOPIC SCALE FROM EXPERIENCES ON THIN WALL TUBES

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Abstract. The relationships between the module of stress and strain tensor deviator, in the case of thermorheological processes, are modeled by using the structural model. It is shown that sub-element properties can be determined from some experiences on thin walls tubes loaded with axial forces and interior pressure. Because the constants and material functions for this material are unknown the loaded conditions with constant state parameters are required. If the stretching process is produced with a constant speed of axial strain for each material there is one constant report among axial and circumstantial stresses which ensures in isothermal processes state constant parameters.

Keywords: *Stress, strain, structure, rheology, thermo-mechanic, crystals, polycrystal*

Introduction

It is well-known that the disordered environment characteristic of most of the materials used in the technique is considered statistically homogeneous at macroscopic level. The minimal volume, which satisfies this requirement we will note with ΔV_0 , but the surface which delimits it through ΔS_0 . The volume element ΔV_0 is considered compound from an infinite number of structural sub-elements, which in their turn, contain the sufficient number of atoms, that the conception of the continuous environment also remains valid at sub-element level. The subelements are cinematically linked to each other and have simple, but different, thermorheological properties. Due to subelements that are endowed with simple thermorheological properties, they are determined on the basis of restricted number of experiences. Complex properties which building materials possess at macroscopical level are due to extremely complex interactions among the subelements. Thus the advantage of the structural model in comparison with theories and phenomenological models, proposed by different authors, consists in possibility of description under unit form of broad spectrum of thermomechanical phenomena, on the basis of small amount of experiences.

1. The methodology of transition from micro-stresses and strains to macro-stresses and strains

The thermomechanical magnitudes, which describe the behavior of materials depending on their structure and historical exterior action, are defined at two levels: macroscopic (conglomerate/system of subelements) and microscopic (subelement). Thus, we will use the following parameters at macroscopical level: t_{ij} - stress tensor; d_{ij} - strain

tensor; $\sigma_{ij} = t_{ij} - \frac{1}{3}t_{nn}\delta_{ij}$ - stress tensor deviator; $\varepsilon_{ij} = d_{ij} - \frac{1}{3}d_{nn}\delta_{ij}$ - strain tensor deviator; σ - module of stress tensor deviator defined by the relationship $\sigma = \sqrt{\sigma_{ij}\sigma_{ij}}$, ε - module of strain tensor deviator, $\varepsilon = \sqrt{\varepsilon_{ij}\varepsilon_{ij}}$. At macroscopic level all magnitudes are noted with bars over them: $\bar{t}_{ij}, \bar{d}_{ij}, \bar{\sigma}_{ij}$.

If on the conglomerate's surface of subelements are homogeneous, then on the basis of equilibrium and Cauchy's geometrical equations in [1] R. Hill established the following fundamental relationships:

$$t_{ij} = \langle \bar{t}_{ij} \rangle = \frac{1}{\Delta V_0} \int_{\Delta V_0} \bar{t}_{ij} dV, \tag{1}$$

$$d_{ij} = \langle \bar{d}_{ij} \rangle = \frac{1}{\Delta V_0} \int_{\Delta V_0} \bar{d}_{ij} dV, \tag{2}$$

$$\langle \bar{t}_{ij} \bar{d}_{ij} \rangle = \langle \bar{t}_{nm} \rangle \langle \bar{d}_{nm} \rangle. \tag{3}$$

From „Eq.(1)” it results that macroscopic stresses are equal with average of microscopic stress and therefore by using „Eq.(2)” we obtain that macroscopic strains are equal with average of microscopic strains.

„Eq.(1) - (3)” are necessary, but not sufficient for construction of governing equations at conglomerate level on the basis of physic equations at subelement level. To achieve a complete system of equations new relationships are needed. From R.Hill relationships we can conclude, that volume means of stresses, strains and their scalar product (see „Eq.(1)”) depends univocally on data surface ΔS . But not all microscopic variables have this specific property. In [2, 3] it has been proven, that for spherical tensors and deviators (see „Eq.(1)”) the following relations may fail to hold:

$$\langle \sigma_{ij} \varepsilon_{ij} \rangle - \langle \sigma_{ij} \rangle \langle \varepsilon_{ij} \rangle \neq 0, \tag{4}$$

$$\langle \sigma_0 \varepsilon_0 \rangle - \langle \sigma_0 \rangle \langle \varepsilon_0 \rangle \neq 0. \tag{5}$$

In [3] the relations of type „Eq.(1), (6)” were named discordance. The discordance among macroscopic suitable values is carrier of information's about one string of structural subelements of composite material. In [2] it was postulated principle: *in all real interactions the discordances of microscopic values with their suitable macroscopic analogs the extreme values are obtained:*

$$\langle \bar{\sigma}_{ij} \bar{\varepsilon}_{ij} \rangle - \langle \bar{\sigma}_{ij} \rangle \langle \bar{\varepsilon}_{ij} \rangle \neq extr., \tag{6}$$

$$\langle \bar{\sigma}_0 \bar{\varepsilon}_0 \rangle - \langle \bar{\sigma}_0 \rangle \langle \bar{\varepsilon}_0 \rangle \neq extr. \tag{7}$$

The second principle was obtained starting from the mechanisms of crystals deformation in polycrystalline conglomerate. The experimental researches demonstrate

that there exists auto coordination of deformation processes among material particles from conglomerate.

In [3, 4] it was formulated the principle of medium ties, according to which, the interactions among sub-elements are formed only under medium ties influence. Starting with this principle and presentation of mentioned three R. Hill relationships under one single expression:

$$\langle \Delta \bar{t}_{ij} \Delta \bar{d}_{ij} \rangle = 0, \quad (8)$$

where $\Delta \bar{t}_{ij} = \bar{t}_{ij} - t_{ij}$, $\Delta \bar{d}_{ij} = \bar{d}_{ij} - d_{ij}$,
was postulated the principle

$$\Delta \bar{t}_{ij} \Delta \bar{d}_{ij} = 0. \quad (9)$$

According to „Eq.(9)”: *the scalar product (interior) among fluctuations of stress and strain tensors are canceled in each subelement of conglomerate.*

If in „Eq.(9)” we decompose the stress and strain tensors in deviators and spherical tensors, we establish an additional fundamental relationship [4]:

$$(\bar{\sigma}_{ij} - \sigma_{ij})(\bar{\varepsilon}_{ij} - \varepsilon_{ij}) = 3(\bar{\sigma}_0 - \sigma_0)(\varepsilon_0 - \bar{\varepsilon}_0). \quad (10)$$

From „Eq.(10)” it results, that in polycrystalline conglomerate, at sub-element level, any variation of stress/strain tensors deviators provokes spherical tensors variations. Due to these properties, we succeed to describe one string of thermomechanical properties, known from the experience, but can't be explained in another theories or models.

In order to obtain one complete system of equations in [3] it was postulated an additional principle: *for any thermomechanical processes the fluctuations of stress deviators are univocal functions of fluctuations of strain deviators.* In linear approximation we have:

$$\bar{\sigma}_{ij} - \sigma_{ij} = B_{ijnm}(\varepsilon_{ij} - \bar{\varepsilon}_{ij}), \quad (11)$$

in which fourth order tensor B_{ijnm} depends on structural factors at microscopical level and reflects the cinematic interaction among sub-elements in conglomerate.

On the basis of complete system of equations „Eq.(1) – (3), (6) or (7)”, „Eq.(10) and (11)” there can be established the governing equations at macroscopical level, in the case when physical relationships at microscopical level are known.

2. The thermorheological properties of subelements

Hereinafter we will admit that the subelements are isotropic. In this case the equation of composition „Eq.(11)” is simplified and gets the form:

$$\bar{\sigma}_{ij} - \sigma_{ij} = 2Gb(\varepsilon_{ij} - \bar{\varepsilon}_{ij}), \quad (12)$$

where through G is noted shearing module at macroscopic level, but through b - intern parameter, which reflects the inhomogeneities of stress and strain states in the inner of

conglomerate. If strain deviators in subelements and at macroscopic level are decomposed in deviators of strain reversible tensors - e_{ij} and irreversible - p_{ij} , namely:

$$\bar{\varepsilon}_{ij} = \bar{e}_{ij} + \bar{p}_{ij}, \quad \varepsilon_{ij} = e_{ij} + p_{ij}, \quad (13)$$

than „Eq.(12)” can be written under more convenient shape

$$\bar{e}_{ij} - e_{ij} = m(p_{ij} - \bar{p}_{ij}), \quad m = \frac{b}{b+1}. \quad (14)$$

In „Eq.(14)” only dimensionless values figurate and thus describing nonlinear processes, π - theorem is verified in automatic mode. On the basis of these values there can be obtained the direct relationship among reversible and irreversible strains.

Physical relationships for system with infinite number of sub-elements can be described by a single expression (proportional processes):

$$\bar{e}_{ij} = \frac{(\tau(\psi, \nu, \gamma) + a\bar{p})p_{ij}}{p}, \quad p = \sqrt{p_{ij}p_{ij}}, \quad (15)$$

where through τ is noted the elasticity limit of considered sub-element, ψ - the parameter of identification of subelements ($0 \leq \psi \leq 1$), ν - the thermal strain, a - the work-hardening coefficient, γ - the parameter, which is equal to average value of speed of irreversible strain in subsystem of strained subelements after the elasticity limit:

$$\gamma = \frac{\sqrt{\dot{p}_{ij}\dot{p}_{ij}}}{\psi^*} = \frac{\dot{p}}{\psi^*}. \quad (16)$$

In „Eq.(16)”, through ψ^* it was noted the actual weight of subelements loaded after the elasticity limit (subelements for which $0 \leq \psi \leq \psi^*$ are loaded after the elasticity limit, but subelements with values $\psi^* \leq \psi \leq 1$, continue to be required in the reversible field).

In the case of some proportional solicitations, „Eq.(14)” and „Eq.(15)” can be written as follow:

$$\bar{e} - e = m(p - \bar{p}), \quad (17)$$

$$\bar{e}(\psi) = \begin{cases} \tau(\psi, \nu, \gamma) + a\bar{p}, & \psi < \psi^* \\ \tau(\psi^*, \nu, \gamma), & \psi \geq \psi^* \end{cases}. \quad (18)$$

From „Eq.(17)” and „Eq.(18)” we obtain the relationships for sub-element characteristics:

$$\tau(\psi, \nu, \gamma) = e + mp(\psi, \nu, \gamma), \quad (19)$$

$$\psi = \frac{(a+m)p_{,e}}{1+mp_{,e}}, \quad p_{,e} = \frac{\partial p}{\partial e}. \quad (20)$$

Taking into account „Eq.(20)” in „Eq.(16)” we find the relation for state parameter γ :

$$\gamma = \frac{\dot{e} + m\dot{p}}{a+m} = \frac{1-\chi}{b+\chi} \left(\frac{\dot{\sigma}}{2G} + b\dot{\varepsilon} \right), \quad \chi = \frac{a}{1+a}. \quad (21)$$

3. Solicitation conditions with constant state parameters: $\gamma = const., \nu = const.$

Since we operate with tensorial values in experience we will pass in „Eq.(21)”, from speed of stress and strain tensors deviators modules to respective tensorial components. In the examined case we have

$$\frac{\sigma_{ij}}{\sigma} = \frac{\varepsilon_{ij}}{\varepsilon} = r_{ij} = const. \quad (22)$$

If in „Eq.(21), (22)” we use the tensorial values, than we obtain:

$$\gamma = \frac{1-\chi}{b+\chi} \left(\frac{\dot{t}_{ij} - \dot{\sigma}_0 \delta_{ij}}{2G} - b \frac{\dot{\sigma}_0}{K} \delta_{ij} + b \dot{d}_{ij} \right) \frac{1}{r_{ij}}, \quad \langle i, j = 1, 2, 3 \rangle, \quad (23)$$

where K is compression module.

Let's examine experiences on tubes with thin walls, solicited for stretching and internal pressure. Axial stresses and strains we denote respectively by - t_{11}, d_{11} , and circumferential stresses and strains denote by - t_{33}, d_{33} . In this case γ parameters are determined from one of three formulas:

$$\gamma = \frac{1-\chi}{b+\chi} \left\{ \left[\frac{\dot{t}_{11}}{2G} \left(1 - \frac{1+c_3}{3} \left(1 + b \frac{2G}{K} \right) \right) \right] + b \dot{d}_{11} \right\} \frac{1}{r_{11}}, \quad (24)$$

$$\gamma = \frac{1-\chi}{b+\chi} \left\{ \left[\frac{\dot{t}_{11}}{2G} \left(1 - \frac{1}{3} \left(1 + \frac{1}{c_3} \right) \left(1 + b \frac{2G}{K} \right) \right) \right] + b \dot{d}_{33} \right\} \frac{1}{r_{33}}, \quad (25)$$

$$\gamma = \frac{1-\chi}{b+\chi} \left\{ \left[- \frac{\dot{\sigma}_0}{2G} \left(1 + b \frac{2G}{K} \right) \right] + b \dot{d}_{22} \right\} \frac{1}{r_{22}}, \quad (26)$$

where

$$c_3 = \frac{t_{33}}{t_{11}}, \quad (27)$$

$$\sigma_0 = \frac{t_{11} + t_{33}}{3} = \frac{1 + c_3}{3} t_{11} \tag{28}$$

Form the required conditions we obtain the following values for r_{ij} :

$$r_{11} = \frac{t_{11} - \sigma_0}{\sqrt{(t_{11} - \sigma_0)^2 + (t_{33} - \sigma_0)^2 + \sigma_0^2}} = \frac{2 - c_3}{\sqrt{6(1 + c_3^2 - c_3)}}, \tag{29}$$

$$r_{11} = \frac{2c_3 - 1}{\sqrt{6(1 + c_3^2 - c_3)}}, \tag{30}$$

$$r_{22} = \frac{1 + c_3}{\sqrt{6(1 + c_3^2 - c_3)}}. \tag{31}$$

Analyzing relationships „Eq.(24) - (26)” we are convinced, that the signs and values of the expressions included in square brackets [] in the first two formulas, depend on the value of the parameter c_3 . This is the situation we can use during the solicitation with $\gamma = const$.

Under laboratory conditions, experiments are easier to accomplish when $\dot{d}_{11} = const$. The condition can be accomplished if in „Eq.(24)” we will admit

$$1 - \frac{1 + c_3}{3} \left(1 + b \frac{2G}{K} \right) = 0.$$

$$\gamma = b \frac{1 - \chi}{b + \chi} \frac{\sqrt{6(1 + c_3^2 - c_3)}}{2 - c_3} d_{11} \tag{33}$$

Thus, under the conditions of the relationship „Eq.(32)”, external stress indicator for $\gamma = const$. is strain with $\dot{d}_{11} = const$. Solving „Eq.(32)” to c_3 , we find the position of the trajectory in the space t_{11}, t_{33} , which will correspond to intern parameter b given:

$$c_3 = \frac{2 - b \frac{2G}{K}}{1 + b \frac{2G}{K}}. \tag{34}$$

Knowing the variation limits of the parameter $0 \leq b \leq \infty$, from „Eq.(34)” we set the size limits of the magnitudes of c_3 .

If $b=0$ (the homogeneous stress state), than from „Eq.(34)” result that $c_3 = 2$, but for $b = \infty$ (the homogeneous strain state), $c_3 = -1$. Therefore magnitude c_3 , based on which the

report among stress circumferential and axial values of tensors is established, varies in the following range:

$$-1 \leq c_3 \leq 2. \tag{35}$$

In this interval there can be realized sollicitations under thin walls pipes if $\gamma = const.$ for any possible scheme of cinematic interactions among subelements.

Expressing in „Eq.(34)” b through m , but the report $\frac{2G}{K}$ - through Poisson coefficient, we will find:

$$c_3 = \frac{2(1+\nu)-3m}{1+\nu-3m\nu}. \tag{36}$$

The laws of variations of report among stresses $\frac{t_{33}}{t_{11}} = c_3$, for different cinematic interactions schemes in subelements system, in function of Poisson coefficient values $0 \leq \nu \leq 0,5$, are presented in “Figure 1”.

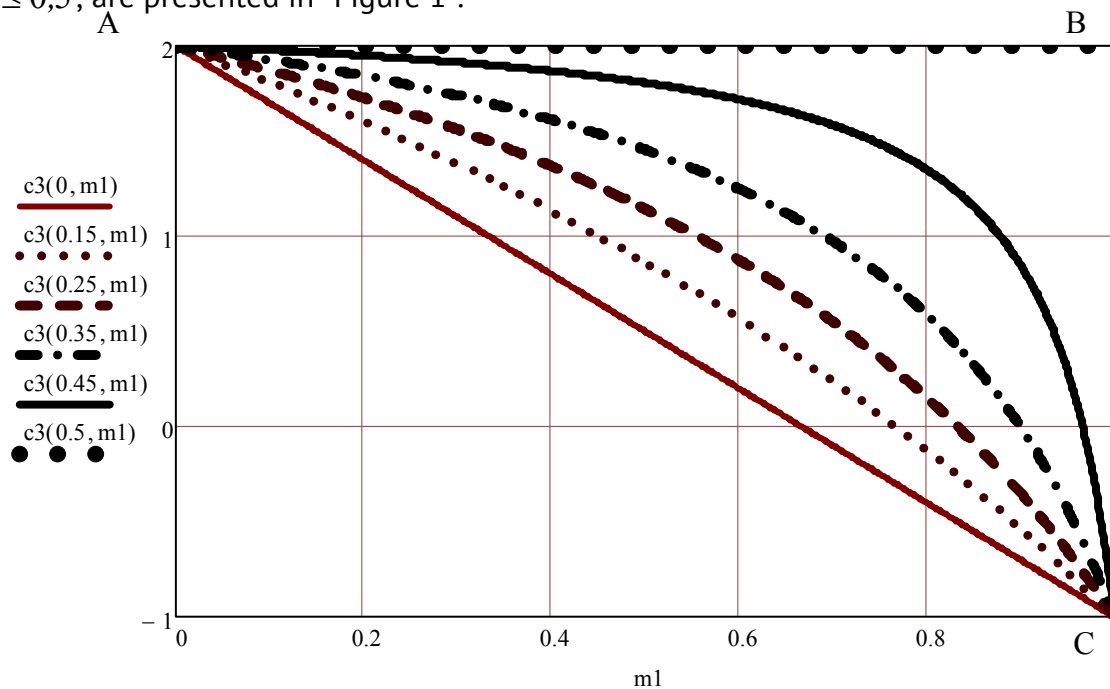


Figure 1. The laws of variations of report among stresses for different cinematic interactions schemes in function of Poisson coefficient values

From “Figure 1” we observe that c_3 curves for all possible values of ν coefficient are located inside of ABC triangle.

Results and discussion

Once the loading conditions with constant state parameters are established, we mention the material function:

$$\varepsilon = f\left(\frac{\sigma}{2G}, \gamma, \nu\right) = f(e, \gamma, \nu), \tag{37}$$

which can be presented as follows:

$$p(e, \gamma, \nu) = f(e, \gamma, \nu) - e. \quad (38)$$

By introducing „Eq.(38)” in „Eq.(19)” and „Eq.(20)”, we find the relationships of subelements characteristics in the following parametric form:

$$\psi = \frac{(a+m)(f(e, \gamma, \nu)_{,e} - 1)}{1+m(f(e, \gamma, \nu)_{,e} - 1)}, \quad (39)$$

$$\tau(\psi, \gamma, \nu) = e(1-m) + mf(e, \gamma, \nu). \quad (40)$$

Conclusions

The rheological state parameter γ in subelements of tube with thin walls, subject to action of some stretching force and interior pressure, doesn't change during the experience,

if the condition $\dot{d}_{11} = const.$ is satisfied in the action period and ratio $\frac{t_{33}}{t_{11}} = c_3$ is in

concordance with „Eq.(36)”. From the set of interaction schemes in the subelements, which concomitant reflects the no homogeneities of stress and strain state we obtain a special

case for $m = \frac{2}{3}(1+\nu)$.

The experience with $\gamma = const.$ for this value of m , according to the „Eq.(36)”, corresponds to an axial load ($c_3 = 0, t_{33} = 0$), with strain axial constant speed.

We also mention that from the „Eq.(21)” results, that for any type of loading, in the moment of reaching the threshold of material passing from reversible to irreversible domain the state parameter γ is proportional with speed of strain tensor deviator module. So, through this effect in any loading conditions at macroscopic level the continuum passing from reversible to irreversible material state is assured.

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TEMPERATURE DEPENDENT GAS SENSING PROPERTIES OF TIN-DOPED ZINC OXIDE FILMS

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Abstract. In this work, the temperature dependent gas sensing properties of tin-doped zinc oxide (ZnO:Sn) nanostructured films are investigated in detail. The two different contents of Sn in ZnO:Sn samples (0.1 and 0.4 at% Sn) and rapid thermal annealing (RTA) at 725 °C were used, in order to find out the optimal conditions for the highest gas sensing properties, i.e. higher gas response, selectivity and lowest operating temperature. Generally, the Sn-doped ZnO nanostructured films showed high selectivity to volatile organic compounds (VOCs) vapors, such as ethanol, acetone, 2-propanol and *n*-butanol, compared to different reducing gases such as H₂, NH₃ and CH₄. The optimal operating temperature for all films is 250 – 300 °C and the optimal content of Sn is 0.4 at%. The as-grown films showed higher gas response compared to RTA treated ones. The gas sensing mechanism was proposed and discussed in detail.

Keywords: *gas sensor, volatile organic compounds, zinc oxide, nanostructured films*

Introduction

VOCs are organic chemicals that have a high vapor pressure at room temperature. The detection of VOCs is one of the main tasks for indoor air quality control due to regulations in many countries of the world [1, 2]. Nowadays, many of people spend most of their day indoors. Therefore, the poor air quality is a serious risk which may cause short-term health problems. It has been demonstrated that the real-time monitoring with low-cost and robust sensors can be performed using micro- and nanostructured of metal oxides such as ZnO, SnO₂, etc. [3, 4]. These materials can efficiently detect a wide range of VOCs relevant to environmental monitoring such as ethanol, acetone, 2-propanol, methanol, *n*-butanol, hexane, benzene, xylene, etc. at relative low concentrations (ppb – sub-ppm level) [4 - 7]. Another important advantage of these oxide materials is the possibility to fabricate compact size and portable devices with low power consumption [7, 8].

Another application for VOCs sensors is the noninvasive breath analysis for diagnostic of metabolic diseases, which has attracted a considerable amount of scientific and clinical interest during the last decade due to rapid progress of nanotechnologies [9, 10]. Many studies demonstrated that different types of exhaled VOCs vapors have correlations with different diseases [11-13]. Recently, 17 diseases were diagnosed and classified from 1404 subjects via pattern analysis of exhaled molecules based on artificial intelligent nanoarray with an accuracy of 86% [11]. As an example, acetone in the human

breath is an important marker for noninvasive diagnosis of diabetes [12]. Therefore, the development of high performance portable VOCs sensors is very important for many fields. In this work, the VOCs sensing properties of Sn-doped ZnO nanostructured films is reported in detail, and demonstrated high sensitivity and selectivity to a series of low concentrations of VOCs vapors (ethanol, acetone, 2-propanol, *n*-butanol, methanol) at 250 – 300 °C operating temperature.

Experimental part

The Sn-doped ZnO nanostructured films were growth on glass substrates via a SCS approach from aqueous baths. The experimental conditions for growth of ZnO:Sn samples is described in previous work [14]. To achieve the concentration of 0.1 and 0.4 at% Sn, 2.5 and 11.5 mM of tin(II) sulfate [$SnSO_4$] was added in the complex solution [14]. The morphological, structural, chemical, electrical and UV sensing properties are reported in detail in our previous work [14]. In this work, only temperature dependent gas sensing properties of the ZnO:Sn nanosensor will be investigated. The thickness of films used in this study is $1.5 \pm 0.15 \mu\text{m}$. The as-grown films were exposed to rapid thermal annealing (RTA) treatment at 725 °C for 60 s. The gas sensing investigations were performed as described previously [15 - 17].

Results and discussions

First of all, we will investigate the influence of Sn content on gas response of ZnO:Sn films. Figure 1a and 1b shows the gas response versus operating temperature for as-grown samples with 0.1 and 0.4 at% Sn, respectively. The gas response is calculated as the ratio of current under gas exposure (I_{gas}) and under exposure to ambient air (I_{air}). The concentration

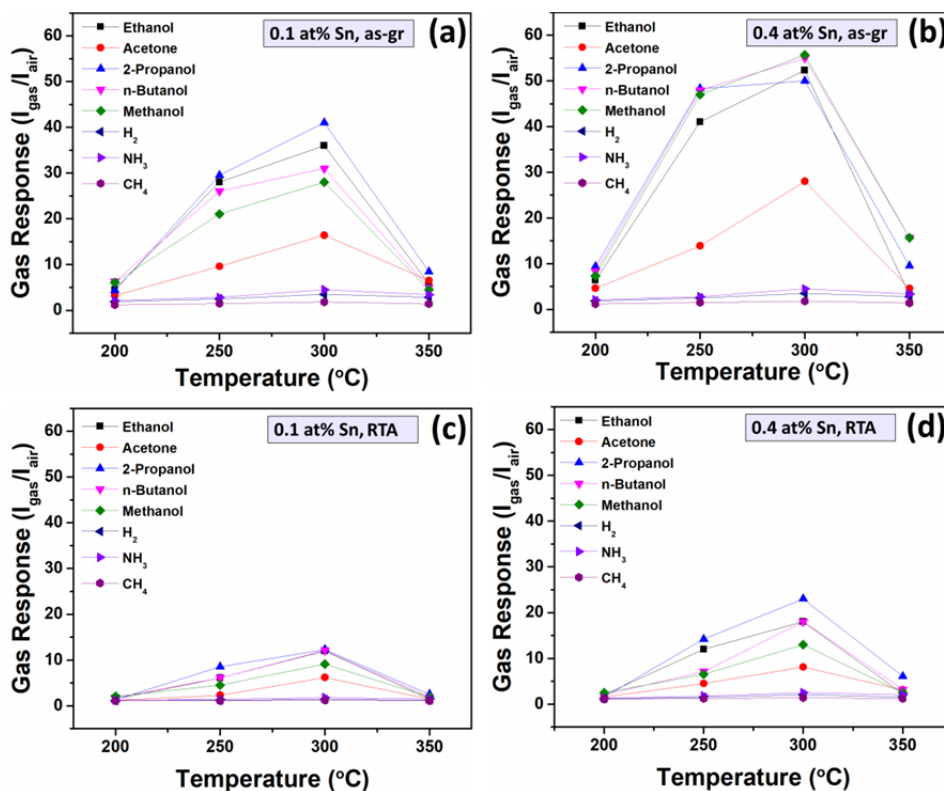


Figure 1. The gas response versus operating temperature for ZnO:Sn nanostructured films: (a) 0.1 at% Sn, as-grown; (b) 0.4 at% Sn, as-grown; (c) 0.1 at% Sn, RTA at 725 °C; (d) 0.4 at% Sn, RTA at 725 °C

of VOCs vapors (ethanol, acetone, 2-propanol, *n*-butanol and methanol) are 100 ppm, while concentrations of H₂, NH₃ and CH₄ are 1000 ppm. It can be seen, that the optimal operating temperature for both samples is 250 – 300 °C. The highest gas response is observed for samples with higher content of Sn, i.e. 0.4 at% (see Figure 1b). However, for H₂, NH₃ and CH₄ no response higher than 5 is observed, which demonstrates high selectivity of ZnO:Sn nanostructured films to VOCs vapors. The values of gas response are also presented in Table 1.

Next, the influence of RTA treatment at 725 °C for 60 s is investigated. Figure 1c and 1d show the gas response versus operating temperature for RTA treated samples with 0.1 and 0.4 at% Sn, respectively. For both cases, the considerable decrease in response is observed. The obtained results are also presented in Table 1.

Table 1

The gas response of ZnO:Sn samples to 100 ppm of VOCs vapors and 1000 ppm of H₂, NH₃ and CH₄ gas

ZnO:Sn sample	Temperature (°C)	Gas Response							
		Ethanol	Acetone	2-Propanol	<i>n</i> -Butanol	Methanol	H ₂	NH ₃	CH ₄
0.1 at% Sn, as-grown	200	4.5	3.2	4.3	6.3	6.1	1.9	2.1	1.2
	250	28	9.6	29.5	26	21	2.5	2.8	1.5
	300	36	16.4	4.1	31	28	3.5	4.5	1.8
	350	5.8	6.5	8.4	4.9	4.5	2.8	3.4	1.4
0.1 at% Sn, RTA at 725 °C	200	1.5	1.2	1.35	1.8	2.1	1.1	1.2	1.1
	250	6.1	2.3	8.5	6.1	4.5	1.2	1.4	1.1
	300	12	6.2	12.3	12.1	9.1	1.4	1.8	1.2
	350	1.5	1.5	2.5	1.9	1.95	1.2	1.5	1.1
0.4 at% Sn, as-grown	200	6.4	4.6	9.4	8.3	7.3	1.9	2.1	1.2
	250	41	13.9	48.3	47.9	47	2.5	2.8	1.5
	300	52.2	28	50	55	55.7	3.5	4.5	1.8
	350	3.1	4.6	9.5	15.7	15.7	2.8	3.4	1.4
0.4 at% Sn, RTA at 725 °C	200	2.1	1.6	1.6	2.1	2.5	1.2	1.3	1.1
	250	12	4.5	14.2	7.1	6.5	1.5	1.8	1.2
	300	18	8.1	23	18	13	2.1	2.5	1.4
	350	2.3	3.1	6.1	3.2	2.5	1.6	2.1	1.2

The dynamic response to 100 ppm of VOCs for ZnO:Sn nanostructured films with 0.4 at% Sn at 250 °C and 300 °C has been investigated. As can be observed, at both temperatures, which is the optimal regime for higher response to VOCs (see Figure 2), the recovery of signal is relatively fast and completely drops to the initial baseline, which is very important for practical applications. The response and recovery times are usually defined as the time to reach or to recover 90% of the total response, respectively. The response time is varying in a range of 100 – 150 s at 250 °C and 50 – 120 s at 300 °C, while the recovery times for all samples are 15 – 25 s at 250 °C and 5 – 15 s at 300 °C, respectively.

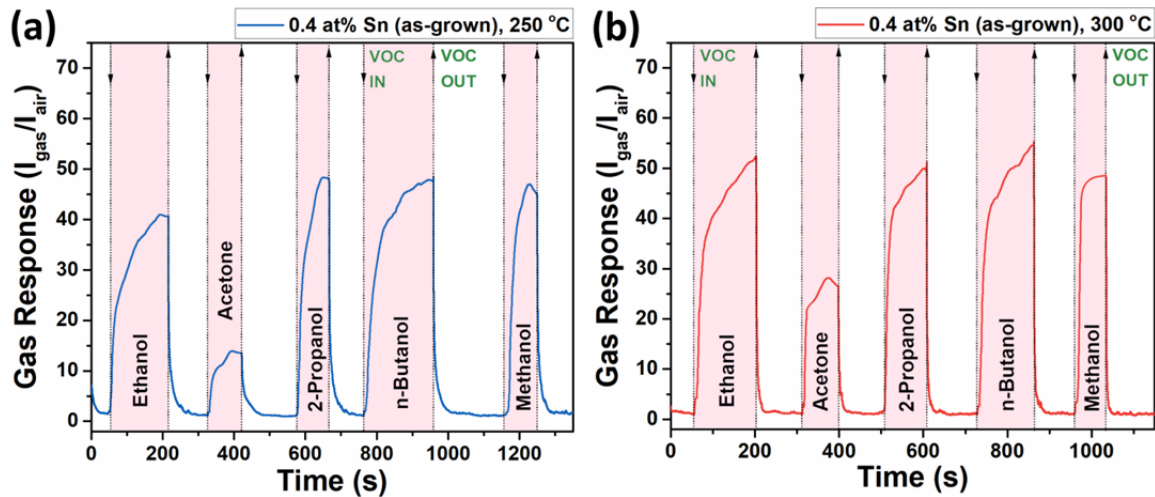


Figure 2. The dynamic gas response to 100 ppm of VOCs vapors for samples with 0.4 at% Sn: (a) at 250 °C and (b) at 300 °C

Based on gas sensing investigations of ZnO:Sn nanostructured films the following conclusions can be made: (i) doping of ZnO with Sn leads to high selectivity to VOCs vapors; (ii) the higher content of Sn, i.e. 0.4 at% for this study is more favorable for higher gas response to VOCs vapors; (iii) RTA treatment leads to decrease in gas response.

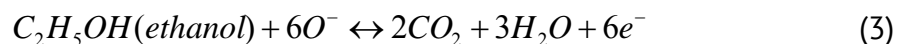
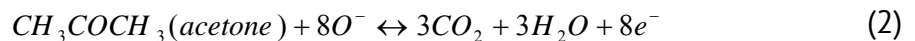
The gas response of ZnO nanostructured films composed of partially interconnected grains was already illustrated and discussed in detail in our previous work [18], and was based on the modulation of potential barriers height ($q\Delta V_s$) formed between grains due to the adsorption of oxygen species at the surface of ZnO grains [19]:



In this case, the gas response of sensors can be expressed as follow:

$$S = \frac{I_{gas}}{I_{air}} \approx \exp\left(-\frac{q\Delta V_s}{2kT}\right) \quad (2)$$

where k is the Boltzmann constant and T is the absolute temperature. During exposure of the sensor to VOCs vapors, the VOC molecules are oxidized by the following reactions [20]:



In our case, the increase in gas response for samples with higher content of Sn can be explained as follow. Previous optical investigations, namely photoluminescence of ZnO:Sn nanostructured films demonstrated that increase in Sn content leads to a higher amount of defects such as oxygen vacancies (V_o), interstitial oxygen (O_i) and interstitial zinc (Zn_i) [14]. It is well known and experimentally demonstrated that V_o -related defects can significantly enhance the gas sensitivity due to more adsorbed oxygen species [21]. This, will lead to a higher coverage with oxygen species and higher modulation of potential barriers height, i.e. higher gas response (see Eq. (2)) [22, 23]. This also explains very well the decrease in gas response for RTA treated samples, independent on Sn content. The RTA treatment is known to reduce the surface defects of ZnO micro- and nanostructures [24], which was also demonstrated for these ZnO:Sn nanostructured films in previous work [14], and therefore reduces the gas response of these samples. Another reason for decrease in response is the increase in grains size. Figure 3 shows the distribution of ZnO:Sn grains diameter for as-grown and RTA treated samples with 0.4 at% Sn. As can be observed, the as-grown films have the grains diameter in range of 200 – 400 nm, while RTA treatment increases the diameter of grains to 250 – 600 nm.

The grains size is also an important parameter for gas sensing properties of nanostructured films [25]. It is demonstrated that the smaller the grain size, the higher its gas response will be [25, 26]. Decrease in grains size leads to an increased surface activity of ZnO and the formation of more potential barriers between grains, which as was discussed, are very important factor for the increase in the performances of gas sensors based on micro- and nanostructures of metal oxides [25, 26].

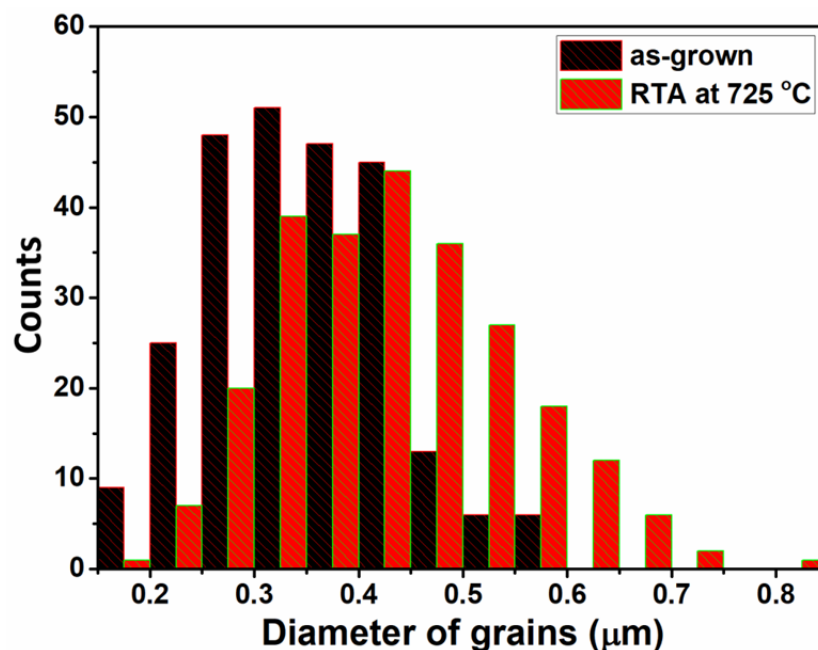


Figure 3. The grain diameter distribution for as-grown and RTA treated ZnO:Sn nanostructured films

Conclusions

The gas sensing properties of Sn-doped ZnO nanostructured films synthesized via an SCS approach are investigated in detail. The two relatively low contents of Sn in samples are used, namely the 0.1 and 0.4 at% Sn. It is found that the ZnO:Sn samples are highly selective to VOCs vapors as compared to other gases such as H_2 , CH_4 and NH_3 , which makes

them very attractive as VOCs sensors for the indoor air quality monitoring. The higher content of Sn is found to be more favorable for high gas response. The optimal operating temperature is 250 – 300 °C. The grains diameter and defects density is found to be crucial for determination of gas sensitivity. The obtained results demonstrate that smaller grains and higher density of V_o defect, as in the case of ZnO:Sn as-grown films, are more favorable for fabrication of high-performance VOCs sensors.

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EXTENDED RSA-M ALGORITHM AS A WAY OF INCREASE COMPUTATIONAL COMPLEXITY OF CRYPTOSYSTEMS

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Abstract. Applications of extended and combined formant analysis of modern number theory are considered to protect binary information from hacking and deliberate distortion in various IT systems based on a modified RSA-m cryptosystem with fast key changes and encryption algorithms with independent transformation keys with guaranteed small or medium short-term secrecy. Such an approach can serve as one of the ways to increase the computational complexity of modern information security systems, increasing their crypto resilience and making them capable of overcoming the possible crisis of modern cryptography in the post-quantum period. Outlines the results of the development of high-speed ciphers based on controlled combinations of transformations.

Keywords. *crypto systems, RSA-m, formant analysis, modernization, expansion, fusion of algorithms - product cipher, crypto resistance, computational complexity, quantum and post quantum cryptography*

Introduction

The relatively low operation speed, but the high resistant crypto of the RSA make the cryptographs-developers search for different ways of refining this system for its use in the normal flow of information or for protection of information with short-term secrecy, in real time mode (from few minutes to months). As an example we can name mobile conversations or voice communication. We have explored the possibility of using the standard RSA algorithm modified, conversed into new one, and so named RSA-m, with several modifications. The essence of changes is in the idea of sending not encrypted information through open or even secured channels, but only some information (data) about its encryption. There are offered several options of modernization, which require additional research. The purpose of this approach is to increase the operation speed of the algorithm, similar to RSA system, for use of its abilities while real-time information transmission.

The following approach to improving the cryptographic strength of a modernized crypto system being designed is aimed at increasing the speed of a classical RSA for its use in real-time data protection. It is based on a combination of transformations performed on data encrypted by formant analysis algorithms and classical RSA in the form of a predetermined and / or randomly changing their sequence of application and is a complete encryption algorithm [1-3]. Many algorithms are known, for example, symmetric encryption [4], obtained by repeatedly repeating other encryption algorithms in some way. The

simplest example is the Triple DES algorithm, which is a threefold encryption using the usual DES algorithm and has been known since 1978. There are both Double DES (double) and Quadruple DES (fourfold), the first of which is practically no stronger than the usual DES, and the second is extremely slow. For the same DES, more complex combination options are invented, for example, the Ladder-DES algorithm, so named because of its relatively complex “ladder” structure, the “steps” of which are ordinary DES. Another option for obtaining composite ciphers is the sequential use of several different encryption algorithms with independent keys. Such a composite encryption algorithm when using truly independent keys and strong applied algorithms is very strong, but has many drawbacks, in particular, a low encryption speed, therefore sequential encryption using various algorithms has not found wide application (see, for example, [4, 7, 8]).

In this article we consider one of the several procedures, based not on the transmission of the information itself, but based on sending of some indirect data about this information in real time. The volume (of the length for bits) of this data is much less than the original information and, therefore, these data can be transmitted in encrypted form with required crypto resistant through the channels with limited speed and bandwidth (ex. 64 KB/s) based on the use of cryptosystem RSA, for example, but without significant delays in time. For this we can significantly reduce the amount of transmitted information, for example, presenting it in formant form, what will allow to reduce its encryption (decryption) time, commensurable with the bandwidth of mobile communication. Another feature or direction of the modernization of encryption algorithms of mobile communication is based in this case on the use of short keys, but with the provision of the high speed of their change (replaceability.). The author intends to consider this idea in another publication.

1.1 Some definitions, properties, and axiomatics of formant analysis

Note that the possibilities of the formant analysis noted in [1], described in detail in [2, 3] and selectively presented in this section, noted below, are purely demonstrative in nature and for an interested reader can only serve as a convincing argument for the need to carefully study this a new direction in number theory.

The key notion (concept) of formant analysis [1 – 3] is the definition of formant on the base by $p - F_p(M)$ – for the number M (or unknown x , algebraic expression or polynomial M), which means it (them) *linear representation in the form of a three-term (or three-dimensional) mathematical construction: $F_p(M) = pk + q$*

where p is the base of the formant, k is the kernel or the integer part after dividing M by the base of p , and q is a non-negative integer remainder (integer).

For example let's consider the notation of the formant of mathematical expression, and namely of the binomial $M = X^2 + 5Y$. It's formant appears as follows: $F_p(X^2 + 5Y)$, which means: *formant of the algebraic binomial of the form $X^2 + 5Y$ by base p .*

If $p = 5$, than the formant of the aforesaid binomial appears as follows: $F_5(X^2 + 5Y) = 5k + (1,4)$.

The mathematical meaning of the formant in this case means the following: *if X^2 is not divisible by 5, then with any whole X and Y , the remainder of this binomial by 5 will be equal to 1 or 4.*

A non-negative remainder (it can be zero) is called formant parenthesis (or just parenthesis), containing one or more numbers. Amount of numbers in the parenthesis defines formant dimensionality.

In the formant structure there is so-called core (k) of the formant, i.e. the integer part from the division of this number or algebraic expression on by base p .

Thus, the formant is completely defined by three values p , k and q .

Any number is uniquely defined by the formant on the given base. There are several types of the format. For more information, see [1].

1.2 Basic rules of formant arithmetic

It is known from theory [2], that when summing (subtracting) formant parenthesis of the different bases p (n - parenthesis and m - parenthesis) in resulting parenthesis will contain a elements of type $(n \times m)$, where many of elements are repeated. One can use the apparatus of string arithmetic to reduce the amount of computation. Let's remind its basics and essence.

Rule 1. If in the sum of two parentheses we will add any number to one parenthesis, and subtract the same number from another parenthesis, the sum of the parenthesis will not change.

Rule 2. If we increase or decrease all numbers in difference between 2 parentheses, the result will not change.

Rule 3. Any parenthesis can be represented as the sum of two 0- parentheses. 0- parentheses – is the parentheses, which contains zeros.

Rule 4. Base p can be added or subtracted from any number in parentheses, and it doesn't change the value of the parentheses. Parentheses are considered to be comparable if at least one number (remainder), equal to another.

The brackets are considered comparable if they have at least one number (remainder) equal to another, for example, the brackets $[1 - 3, 5] = [2-4]$ are comparable, since the numbers 2 and 3 are common, and the brackets $[1, 3, 5]$ and $[2, 4]$ are incomparable, since they have no common remainders.

The rules of string arithmetic are used in transformations of formant equations when calculating the sum of two identical incomparable formants a prime base p .

An interesting question is the comparison of the formants in terms of their equality or inequality to each other. If two different formants are compared, this leads to a linear Diophantine equation with two unknowns. If three or more formants are compared, then, respectively, the number of unknowns increases.

Let us give an example of solving a linear equation by converting the formants a unknowns variables X and Y to two identical and comparable formants

Example 1. Find a solution to the linear equation:

$$55X = 73Y + 11 \quad (1)$$

Let's assume X and Y as their formants of base 5 on:

$$X = 5k + A, \quad Y = 5p + B \quad (2)$$

It is clear, that A and B are less than 5^4 . After substituting of the formant into the initial equation (2), we get two following equations:

$$55k - 73p = C \quad \text{and} \quad (3, a)$$

$$73B - 55A + 11 = 5C \quad (3, b)$$

The last equation (3,b) will be written in the following way:

$$73B + 11 = 5(C + 11A) \quad (4)$$

Since the left part of this equation should be divisible by 5, then the minimum solution $B = 3$, and $73 \cdot 3 + 11 = 230$, which means:

$$C + 11A = 46 \quad \text{or} \quad 11A = 46 - C.$$

It is not difficult to see that, that five possible values of A are possible: $A: 0, 1, 2, 3, 4$, which have 5 corresponding values C , and namely: 46, 35, 24, 13, 2. Next, from the original equation (2) it follows, that Y is divisible by 11, therefore

$$Y = 5p + B = 5p + 3 = 11D \quad \text{or} \quad p = 6 + 11z.$$

But since $p < 11$ (Y should be less than 55), the only value p - is 6, i.e. $p = 6$. Then $Y = 33$, and from the initial equation (1) follows that $X = 44$.

Thus the general solution of the original equation will be the following:

$$X = 4 + 73m, \quad Y = 3 + 55m \quad (5)$$

Note. Linear equations solution, as we can see, can be found even not using well known methods (ex. Euler algorithm). But the peculiarities of the formant approach are purely methodical ones, and it is not an option to count on their great efficiency. Another case is if formant analysis is used for nonlinear equations solution. Let's show the possibilities of the formant analysis in working with nonlinear Diophantine equations.

Ex. 2. Find the equation minimum of solution

$$X^2 = 19Y + 7 \quad (6)$$

Since the formant X^2 can be represented⁵ as $5p + (1,4)$, we have:

$$F_5[X^2] = 5p + (1,4) = 19Y + 7 = F_5[?] \quad (7)$$

Reducing the formants of the left and right parts of the equation to a common base

⁴ Because they are formant remainders by base 5.

⁵ The formant of the square of any number on the basis of 5 always has 1 and 4 in remainder.

$p = 95$, we obtain the bracket of remainders for the formant of the left part of the equation:

(1,4; 6,9: 11,14: 16,19: 21,24: **26**, 29: 31,34: 36,39: 41,44: 46,49: 51,54:
56,59: 61, **64**: 66,69: 71,74: 76,79: 81,84: 86,89: 91,94)

and for bracket of right part of formant: (7, **26**, 45, **64**, 83).

Thus we can see, that the formant remainders of the left and right parts of equation have only two equal numbers 26 and 64, but only 64 is a square, that is why $X = 8$, from which follows that $Y = 3$; these are the smallest solution of the original equation (6).

2 Information protection according to the RSA-mab algorithm

The idea of the proposed approach is to use the numerical formants introduced in [1] and explained in detail in [2] and [3]. As shown above, numerical formants allow you to represent any number as the simplest linear structure. In this case, time spent on the operations on the calculation of formant and the encryption/decryption will be significantly lower than time of direct use of the algorithms of classical RSA cryptosystem.

It is known [1], that linear formants, regardless of the bit longue of the number and, with the use of only 3 parameters *can significantly reduce the informational length of the digital message*. The advantage of such approach is in the fact, that so-called the base or (module, the divisor) of formant can be any composite or simple number of significantly smaller, than it is required for the number encryption in classic RSA cryptosystem, but with a high frequency of its replacement

Below will be described several algorithms for the use of linear formants for the transmission of information having short-term secrecy. The advantage of these algorithms is a significant reduction in the total encryption and decryption time, even taking into account the use of additional code operations necessary to transmit a message.

2.1 AB1 Algorithm

Let us recall [2, 3], that any integer N number in the formant analysis can be represented in the form of binomial construction: $N = pk + q$, where p is the base of formant, k – formant's core, and q - integer remainder. Knowing these three parameters allows us very easy to restore the original number. Types, properties and characteristics of the formant algebra are described in [1].

Using of formant representation of integers, now it will be necessary to encrypt not the number N itself, but three small numbers. The difference is that N is a large number of the order of $10^{20} \dots 10^{500}$ and higher, while p , k and q are any integers, simple or composite, the length of which is determined only by the requirement of the desired transmission rate in the open channel. It is recommended to choose the formant base p as some integer number, approximately equal to the RSA key width, or similarly to the secret keys that correspond to the block cipher, but do not reduce the transmission speed. This requirement makes it possible to use RSA keys of medium length, and the presence in the system of a high-speed generator of primes [5] will allow you to quickly change secret keys, creating additional difficulties for cyber saboteur.

For the implementation of the RSA-m algorithm in ROM a dynamic database is created. It can be for example in the form of P matrix, the indexed cells which store preliminary generated information. These indexed cells are used for matrix construction. For example matrix 100×100 , can contain such information for 10 000 different formants.

And what is especially important is there that will also be enough short secret keys used to encrypt formant messages.

After each single use of all values p_{ij} of \mathbf{P} matrix, algorithm provides automatic update of all matrix cells, located both on the transmission side and on the receiving side.

Depending on the temporal requirements to degree crypto resistibility of the algorithm encryption, matrixes in ROM of microprocessor can be built with fixed or flexible updating program, with automatic or manual transmission of one matrix data array to another. In one of the cases it can be one and the same matrix, where cell names are changed on the base of indexes. In this case values of the formant remainders q and cores k are encrypted by the RSA-m algorithm, crypto resistibility of which is guaranteed by the real-time change with a large frequency of secret keys for each discrete value (binary d -bit number) of the analogue signal or system (number, byte, block) in the open digital code message. On the receiving side the encrypted message is decrypted by a special procedure, which recognizes transmitted addresses of cells and decrypts other parameters of each formant. After that the true value of the “number message” as a formants sequence is restored. The message itself can be a text in any language, as image of any class or type, as speech or musical track, etc.

Figure 1 show the block diagram of AB1 algorithm.

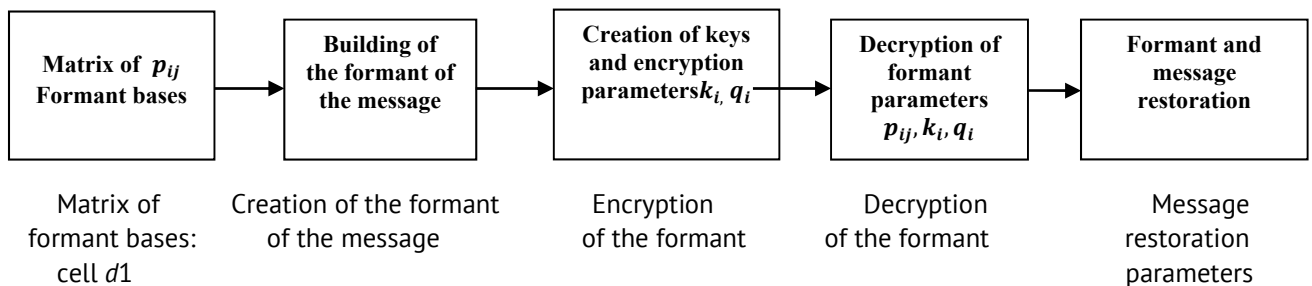


Figure 1. AB1 algorithm blockdiagram

1. Transmitted analogue signal, after ADC, forms the block: binary message in 32 (64) bit;
2. From the basic matrix block in ROM of the MPC formant the base p_{ij} is randomly selected and written $d1$ cell;
3. The digital block 64 bit according to p.1 is represented further in the form of formant and its core $k_i = d2$ and remainder $q_i = d3$ are defined;
4. Crypto keys for encryption of numbers $k_i = d2$ and $q_i = d3$ are chosen;
5. The $d1d2d3$ message about the formant is formed;
6. The $d1d2d3$ message about formant is encrypted;
7. Encrypted data are transmitted through an open communication channel;
8. Block 64... bit is received;
9. From the received block 64... bit the formant base p_{ij} is derived;
10. The numbers $k_i = d2$ and $q_i = d3$ are derived from the block.
11. Formant-message: $F = p_{ij} \cdot k_i + q_i = p_i \cdot d2 + d3$ is restored.

Let's consider a simple example that illustrates the use of RSA-m algorithm.

Ex.3. Let's encrypt the message “COIN”. For simplicity we will use small numbers (in practice much larger (on several orders) numbers are used).

Let's choose two simple numbers $p = 3$ and $q = 11$. Their product $N = 3 \cdot 11 = 33$.

We will find $(p - 1)(q - 1) = 2 \cdot 10 = 20$. Therefore, as a private key d , we can choose smaller and mutually simple with 20, for example, $d=3$ (or another: 7, 11, 13, 17, 19,...).

Now we select the public key – the some number e . There can be chosen any number, for which the following relation satisfied: $(e \cdot d) = 1(mod 20)$, for example, if $d = 3$; then it should be implemented $(e \cdot 3)(mod 20) = 1$; this condition is satisfied, for example, $e = 7$. Is real, $7 \cdot 3 = 21$; $21(mod 20) = 1$.

Let's present the encrypted message as a sequence of whole numbers, applying as an example the following (random) correspondence: $O \rightarrow 1, I \rightarrow 2, C \rightarrow 3, N = 4$. In this case, the code message takes the form «COIN» = (3,1,2,4) = S1. Let's encrypt this message with the help of public key $\{e, N\} = \{7, 33\}$.

CryptoT1 = $(P^7)(mod N) = (3^7)(mod 33) = \mathbf{2187(mod 33) = 9}$; first we raise to a power 7 encrypted number, then divide the result by the module N. The remainder of the division gives the result of encryption.

1. CryptoT2 = $(A^7)(mod N) = (1^7)(mod 33) = \mathbf{1(mod 33) = 1}$,
2. CryptoT3 = $(E^7)(mod N) = (2^7)(mod 33) = \mathbf{128(mod 33) = 29}$.
3. CryptoT4 = $(H^7)(mod N) = (4^7)(mod 33) = \mathbf{16384(mod 33) = 16}$.

Thus, public message S1 = COIN = (3,1,2,4) can be described (represented) in the form of encrypted SE1 message, i.e. numerical sequence of numbers, as SE1 = (9, 1, 29, 16), which, for example, corresponds to the text «TORY» if while alphabet encoding was preliminary et, that $T = 9, R = 29, Y = 16$.

5. Now let's create, as an example, a methodically possible encrypted message for transmission over an open channel, taking into account insertions of service information, which can be of any sequence and content, for example, of the following kind:

$$\underbrace{003}_{\text{for 3 ranks}} \quad \underbrace{023}_{\text{cell address}} \quad \underbrace{009}_T \quad \underbrace{001}_O \quad \underbrace{029}_R \quad \underbrace{016}_Y \quad \dots \quad \underbrace{[0? 101\&]}_{\text{operation information}}$$

- The first three decimal digits - the number of digits of the number to process part of the code; it determines the length of the machine word - that is, every three decimal digits.

- The second group of three decimal digits is the number of the matrix cell in the ROM MC or PLC, which must be selected from the memory by the controller on the receiving side.

- The third group of decimal digits is a sequence encoded by RSA-m algorithms (it can contain any number of "triples" depending on the length of the transmitted bits -16, 32, 64, etc.). The last 6 (or more) digits - information about the working protocol: the end of the sent message, parity check, etc. Thus, sending 32, 64 ... -bits, the first 6 and the last 6 single-digit digits should be selected, which contain all the information about the "structure" of the message, necessary for subsequent decryption.

As a result, was created an encrypted message {9, 1, 29, 16} which is the result of cryptography with a public key {7,33}. On the receiving side in the cell $p_i = p_{23}$ there are corresponding numbers: «private key d » and crypto key module: $d=3$; $N=33$. That is why private message «912916» is easily decrypted.

Let's decode the received encrypted message (9,1,29,16) = **TORY** on the basis of private key $\{d, N\} = \{3, 33\}$. We get

Initial T1 = $(9^3)(\text{mod } 33) = 729(\text{mod } 33) = 3$,

Initial T2 = $(1^3)(\text{mod } 33) = 1(\text{mod } 33) = 1$,

Initial T3 = $(29^3)(\text{mod } 33) = 24389(\text{mod } 33) = 2$.

Initial T4 = $(16^3)(\text{mod } 33) = 4096(\text{mod } 33) = 4$; (3,1,2,4) → «**COIN**» QED.

2.2 AB2 Algorithm

Variant 1. Indexing memory cells

There are 10 000 of cells (100 lines × 100 columns in a matrix. The cells are numerated in a natural order and can be represented also in the form of two-index variable p_{ij} , where $ij = 00,01, \dots, 99$. For example the cell №457 has the index p_{0457} , and the cell №4057 will have the number or address-index p_{4057} .

1. Each cell $P_{ij}(e, d, n)$ of P matrix will contain now the index number, encrypted by RSA-m system. For example, the cell №0009 will contain the digit 3; cell №0001 will contain digit 1; cell №0029 – digit 2; and cell №0016 – digit 4, which correspond to the decryption with the key $d = 3$; $N = 33$; and encryption with the key $e = 7$. In the same way all other cells of this array will be filled.

2. Controlled mixing algorithm of cells of the variant 1 does not change the contents of the cell. They only changes its' index address.

In order to increase crypto resistibility degree of RSA-mAB algorithm it is recommended to change randomly the length of encrypted blocks, with corresponding change of Crypto keys length. The number of such arrays and their volume depends on the long-termness of secret information and on the volume of ROM controller, where RSA-mAB will be implemented.

Variant 2. The use of the Formant analysis

The block-message with the length of 32 (64)... bit is created.

1. From the matrix of the bases \mathbf{P} there are randomly selected the base p_{ij} of formant. Formant address is recorded as message $d1$ (the base p_{ij} of formant, which is being created will be stored in cell $d1$).
2. The numeric view of the information block is formed as the formant - all the parameters of it (the core $k_i = d2$ and remainder = $d3$) are defined by the selected base p_{ij} and written in the messages $d2$ and $d3$.
3. A message $d1d2d3$ is being generated for transmission.
4. Keys for encryption of cores k_i and remainders q_i are generated.
5. The message about the $d1d2d3$ formant is encrypted.
6. Encrypted message is transmitted into the public communication channel.
7. The block of 64... bit is received.
8. Coordinate-address p_{ij} is extracted from the received block.
9. The value of the formant base is restored.
10. k_i and q_i are extracted from the corresponding block.
11. The formant is restored on the base of encrypted message on standard formula.

As a similar example let's consider the encryption of the message «EDA" or its' digital code 651. Let's present the digit 651 code as a formant, i.e. as a sum of

multiplication and remainder, and as a basis choice, for example, random simple numbers 237, 54, 119 etc. Matrix of key in RSA-m system from variant 1 is replaced by the matrix of formant bases and forms the set of randomly selected bases of different lengths and properties (simple and composite). So, our message is: $S2 = 651$.

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- Decryption of this block gives: $\underbrace{54}_{\text{base}} \underbrace{12}_{\text{core}} \underbrace{3}_{\text{remainder}}$
- Restore the formant: $S2=54 \times 12 + 3 = 651 \rightarrow EDA$.

3. Analysis of the robustness of RSA-m algorithms depending on the variable parameters of the algorithm

These examples show that voice encryption occurs without the direct participation of subscribers in the key exchange process. The communication channel does not explicitly include formant parameters or RSA algorithm. In the author's patent [2] different algorithms are claimed, requiring the transfer of either all the parameters of the formants or separately, eventually forming the so-called. hybrid or composite cipher. [3 - 9].

If only cell indices are transmitted, where the information for recovering the formant is located, then breaking into such a cipher will require a continuous search of n samples (where n is the sampling frequency), which is estimated by a huge time value:

Indeed, with a sampling frequency of a voice signal of 8 kHz, an attacker to recover even a second conversation, which gives scant information about the essence of the calls and subscribers!, Will need to be completed $(8 \cdot [10]^3)!$ operations matching the sequence of a discrete sequence for 1 sec, well, let it be in 10 sec (then declassifying a mobile conversation will go with a significant delay and go beyond the guaranteed secrecy period!). And this is only for one period, for 1 sec. And in order to recognize the voice, to make out the meaning of what has been said, it is necessary to process at least 10 periods (10 seconds of low-frequency periods of oscillations, that is, the envelope of the carrier frequency!). We consider that in order to do this with a continuous search (guessing or selecting speech by voice or by meaning are different time tasks!), You need to do the previous assessment at least 10 times, i.e. even at 1000! This is a very large number:

$$10 \cdot ((8 \cdot 10^3)!) \gg 1000! = 4,02387260077093773543702433923E + 2567 \text{ sec} = \\ = 1,2759616313961623970817555616534E + 2551 \approx 10^{2551} \text{ billion years}$$

a huge number that is difficult to estimate immediately and goes beyond common sense in estimating real-time hacking, Considering that today's modern computers are capable of performing up to $[10]^6$ multiplication operations per second, then performing so many comparisons of permutations will require even more low sampling rate of 1 kHz already $[10]^6$ billion years! Long have to wait. And with increasing n , Hz this time

exponentially grows. With an increase in the sampling rate of the voice signal from 8 to 12 kHz, the number of years for breaking will grow more than even with $n = 1$ kHz

$$1000! = 1,2759616313961623970817555616534E + 2560 \text{ years}$$

Or

$$= 1.2759616313961623970817555616534E + 2551 \text{ billion years}$$

When $n = 12$ kHz, this number will grow tens of thousands of times.

Such estimates we get about the robustness of the algorithms of FA, if we increase the sampling rate. But the FA allows introducing uncertainty when encrypting and decrypting if in the RSA crypto lock equation you enter an additional 2 parameters k and a .

As is known, the asymmetric RSA system uses the properties of one-sided functions for an integer argument that satisfy the conditions for the existence of a solution of one of the types of Diophantine equations with a parameter $a = 1$, see, for example, [1]. The advanced RSA algorithm (modernized "crypto lock" or RSA-m algorithm) is understood as the following diophantine equation linking open (e, n) and closed (p, q, d) RSA keys:

$$e \cdot d = k\varphi(n) + a = k \cdot \varphi(p) \cdot \varphi(q) + 1 = k(p-1)(q-1) + a; \text{ where } a > 1, (1)$$

When expression (1) is a crypto lock of the usual, classic RSA.

If a potential adversary (at least for a while) does not know about the use in (1) of the parameter $a \neq 1$, i.e. the use of the advanced RSA-m algorithm, such an upgrade will ensure high RSA reliability even with a small key length.

If the transferred information blocks are small (short), and it is necessary to ensure high cryptographic strength (for which the long key is chosen), then in this case, instead of adding text to the empty bits, you can perform an exponentiation operation. The cryptographic stability of such a system will not be lower than that of the classical RSA with the same key length, and the a parameter, which is undefined for the enemy, will make decryption difficult. It should be noted that in the case of placing meaningful information in the M-blocks, finding a will not be easy, especially if the values of a vary from block to block!

The use of the advanced RSA algorithm introduces an additional indefinite parameter a to be determined, which potentially increases the "hacking" time and, in the case of encryption of short-term (secrecy) information, can serve as a means of improving the system's cryptographic strength (for example, during operational negotiations). The introduction of an additional indefinite parameter is possible and would increase the robustness if it were large, i.e. not "susceptible to" "Attack by brute force", i.e. elementary selection, but since the proposed approach imposes certain restrictions on its size, it only provides a significant increase in durability with frequent changes of keys.

4 Advantages of the systems using RSA-m algorithm with quick key change

1. Encryption and decryption keys are constantly changing, and are randomly generated (or chosen from key matrix), what eliminates the possibility to predict the next pair of keys. For the period of time, required for the open key factorization, crypto-keys as well as the definition of the floating code will be changed many times. Moreover, in order to open the system cracker must know the module N and public key. He cannot determine

even the length (number of digits) of the number N . Which means that he doesn't know what number to factorize. That is why crypto resistibility of such system is almost absolute!

2. Main RSA system disadvantage - insufficient performance - eliminated by our algorithms. Considered system doesn't require providing the crypto resistibility for a very long time. It's enough to guarantee, that the key will not be decrypted for some time period, sufficient for the codes to be changed. In this case we can be satisfied with quite short keys, the generation of which will not take a long time.

3. The suggested system can be implemented in access control systems, based on different physical principles of "key" and "crypto-lock" interaction. It can be both contact systems and Off-contact systems, based on the exchange of radio signals, infra-red and optical interaction, etc.

4. One of the current trends in cryptography today is the development of new methods that will provide security, even if quantum computers (still fantastic) succeed in breaking down (cracking) traditional methods and crypto systems, such as RSA. The formant analysis (FA - a new direction in number theory) are an evolutionary way of developing the means of cryptographic information protection based on the modified RSA-m algorithm. This is explained by the fact that they allow the use of existing approaches to the protection of information against the background of the exponential growth of the computing power of rapidly developing so-called. quantum computers. Today, there is already a problem with the RSA algorithm – after some time, solving the problem of decomposing a prime number to factors will cease to be an unsolvable problem for the current level of computing power of computers. And it will happen in the near future (approximately in 15 years). Today, an increase in the computational complexity of the problem can already be solved, for example, by changing one and/or introducing new, additional, parameters into the proposed implementation of formant analysis algorithms for data encryption/decryption. The proposed implementation of our method is considered in relation to voice protection, where there are significant time constraints on the process of encrypting / decrypting data, on the one hand, and there is a requirement to achieve guaranteed cryptographic resistance, on the other hand.

5. Quantum computers will destroy (hack) the most popular public-key cryptographic systems, including RSA, DSA and ECDSA. But the next generation of cryptographic algorithms and systems that will resist attacks using quantum computers are already being developed: in particular, post-quantum encryption systems and public-key signature systems. The modified RSA-m answers these tasks, since its algorithms provide for the possibilities of unlimited growth of the computational complexity of the problem by changing the existing and introducing new parameters, which makes RSA-m more computationally complex compared to the RSA algorithm, which does not have such capabilities. At the same time, all mutable parameters are achievable and easily implemented within the existing hardware and do not lead to critical time delays of the parameters, namely, the encryption / decryption rate.

6. Inclusion in the process of encrypting additional cryptographic parameters associated with the use of formants, as well as the introduction of an additional parameter "a" in the crypto lock equation, complicates the task of hacking, requiring additional time for these operations, which is very long. With voice sampling rates from 4 to 12 kHz, this time exceeds all imaginable values of common sense! Therefore, such a crypto system with a combined and modernized RSA-m algorithm is not afraid of the impending crisis of

modern cryptography associated with the advent of fantastically high-speed quantum computers.

Conclusion

All the above examples highlight the ability to send encrypted voice messages in real time at a transfer rate of about 64 Kbps, for example, using any communication channel, or social networks like Telegram or Messenger

It is clear, that other variant of the formant use for message transmission can also exist, Ex., [3], where 10 different approaches are described. We considered the most obvious ones. For example, matrix M1 12x12 contains $64 \times 64 = 4096$ decimal numbers (digits), which will be encrypted with 64 (and more) different keys.

AB2 algorithm uses one and the same matrix, cell content of which remains unchanged, but changes their address. The redistribution of cells content of matrix M can be done in different ways, for example, randomly or according to some algorithms, which will be applied to each matrix cell. It can be for example the ratio of $p_{ij} = p_{i+k,j+l}$, changing k and j in a such way, so that the algorithm would affect all the cells, or just some of them.

In our library of algorithms there is an advanced AB-univ algorithm, that allows using message will be more difficult to decrypt in a really reasonable time. Even after writing a message on hard media, it could not be decrypted in a relatively short time, because diversant will require tens of years, because he doesn't know key length (range), block length, not to speak of the rule of transition from one pair of keys to another. Besides, he doesn't know keys at all. This is *internal information of security system*. Each external communication can be of one and the same type, but its' content will differ in the meaning of the current information in each session on communication and the same phonemes will be presented in messages by different codes.

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PROGRESS OF ARTIFICIAL INTELLIGENCE (AI)

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Abstract: In the past few years, systems like Siri and Google Now opened our minds to the idea that we don't have to be tethered to a laptop to have seamless interaction with information. In this model, AIs will move from speech recognition to natural language interaction, to natural language generation, and eventually to an ability to write as well as receive information. Machine learning is about man assisting computers. Deep learning is about systems beginning to progress and learn on their own. Historically, systems have always been trained, they've been programmed. And, over time, the programming languages changed. As we move into the area of AI and cognitive computing, we're exploring the ability of computers to do more unaided / unassisted learning.

AI definition: The theory and development of computer systems able to perform tasks normally requiring human intelligence, such as visual perception, speech recognition, decision-making, and translation between languages. In other words, artificial intelligence is the ability of a computer to understand what you're asking and then infer the best possible answer from all the available evidence. Soon AI will become the most important human collaboration tool ever created, amplifying our abilities and providing a simple user interface to all exponential technologies. Ultimately, it's helping us speed toward a world of abundance. It's only been in the last few years that we've seen a fundamental transformation in this technology.

Keywords: *Deep learning, automatic learning, robot, DeepStack, technology*

1. Introduction

Below (figure 1) is a brief description of the achievements and their circumstances. Some milestones represent significant progress towards human performance and others represent super-human performance achievements.

Skin Cancer Classification

In a 2017 *Nature* article, Esteva et al. [5] describe an AI system trained on a data set of 129,450 clinical images of 2,032 different diseases and compare its diagnostic performance against 21 board-certified dermatologists. They find the AI system capable of classifying skin cancer at a level of competence comparable to the dermatologists.

Speech Recognition on Switchboard

In 2017, Microsoft and IBM both achieved performance within close range of "human-parity" speech recognition in the limited Switchboard domain.

Poker

In January 2017, a program from CMU called Libratus defeated four top human players in a tournament of 120,000 games of two-player, heads up, no-limit Texas Hold'em. In February 2017, a program from the University of Alberta called DeepStack played a group of 11 professional players more than 3,000 games each. DeepStack won enough poker games to prove the statistical significance of its skill over the professionals.



Figure 1 Milestones of artificial intelligence (after [14])

Pac-Man

Maluuba, a deep learning team acquired by Microsoft, created an AI system that learned how to reach the game's maximum point value of 999,900 on Atari 2600.

2. Reliability and accuracy of the sensory information

Autonomous mobile robots are increasingly being used in our environments to perform concrete complex tasks (Figure 2). Such robot agents need to perform a set of computationally intensive functions, in order to be able to perceive, to reason about, and to act in their surroundings. The robot's actuation, whether it is to manipulate objects or just to navigate throughout its environment, is based on the information provided by its sensors. The success of this actuation depends on the reliability and accuracy of the sensory information. One of the richest and most complex sensory information sources is the visual information as captured by cameras. Many of the modern robots are equipped with cameras to observe the world and detect the objects relevant to accomplish the specific tasks. Robots perform their tasks in a closed loop between perceptions and control (behaviours). Control includes the computation of the next action towards self-localization, navigation, cooperation, or object manipulation. In dynamic environments in particular, the detection of relevant objects to the actuation has to be done in real time, i.e., with no delay in the perception / control loop.

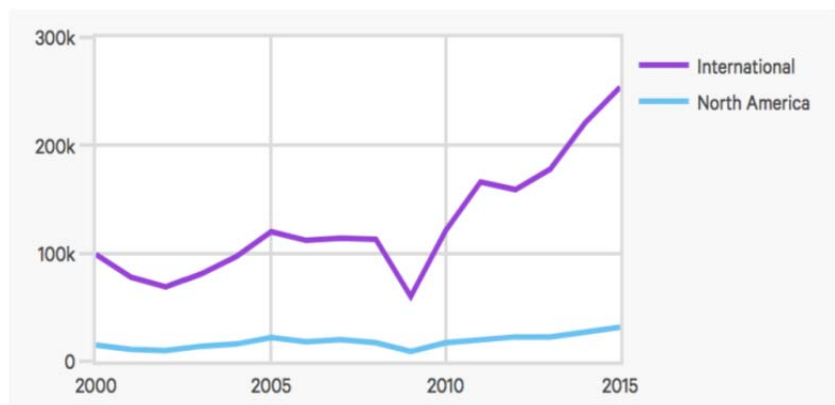


Figure 2 Import of industrial robots units, into North America and globally, between 2000 and 2015 (after [14])

3. Can machines think?

The machines know how to play, but can they think? Recently, however, computers have regularly beaten professional gamers in a growing number of games. Last year, AlphaGo beat a professional go player, for the first time in human history (which reminds us of the defeat in chess by world champion Garry Kasparov, defeated in 1997 by an IBM computer). But how do you "teach" a computer to play such games? Let's take the simple

game of the spy game, and try to understand the process. How do we humans manage to play the spy game? For most of us, there are some informal rules that we learned as children. One of these rules could be: when you start, mark the centre square. Another: when an opponent has two squares in a row, mark the third. With these two very simple rules, you can already program a computer to play morpion (although rudimentarily, of course). It only takes eight simple rules of this kind to make sure that the computer doesn't lose any more parts!

There is a completely different approach: we can also make a list of all possible game situations in the spy game, with all the best moves in each of these situations. Then we could tell the computer to look for the best movement in this very long list, and for each movement. Drawing up this list would be tedious, but feasible.

However, learning requires an opponent, usually a human. And the better the opponent, the better the computer becomes, so that eventually the best human player will lose at some point. This is exactly what we have seen in the recent past, with chess, go and poker.

But the most interesting aspect of this approach is that the new machines are starting to make new movements, which have never been made by a human being. That's why we can start to wonder: how far will the machines go?

What if the computer was programmed to "learn" and memorize all the situations by itself? This is achievable, and today it is called *machine learning*. For example, suppose we program a computer to have only one basic morpion rule, and tell it to play randomly until the game is over, and record each step of the game. In the very first games, the computer would be immediately beaten. But thanks to the "bad moves" he has recorded, he will learn which movement he should not repeat in the future and, gradually, he will end up finding a list of "right moves". From then on, the more the machine plays, the more it will "learn" and win!

We have been talking about robots⁶, golem, and artificial beings in science fiction films for a long time. Artificial intelligence actually exists since we have been thinking about how to use machines to think, to calculate for us. It is part of a great historical continuity. What's new is the presence of self-learning machines. A real qualitative leap forward. We have the impression that if these machines can learn, we can lose control.

Man gradually tries to transform himself into an artefact, an immortal thing. His absolute fantasy is to transfer self-consciousness into an artefact. It is the long tendency of human history to want to escape death. To date, I see many more advantages than disadvantages in artificial intelligence. Are we creating a race of humans that will surpass us? That's possible. It is necessary to protect oneself from it and to avoid that human beings find themselves in a situation of dependence on machines. Some believe that man will be overtaken by machines in 2030 or even 2045. We don't know that yet. I think we're still a long way from it.

⁶ The robots [from Czech, from *robot* 'forced labour'. The term was coined in K. Čapek's play R.U.R 'Rossum's Universal Robots' (1920)] are typically mobile, unlike their factory counterparts, and must operate reliably in dynamic and complex environments. Application areas for field robots include agriculture, mining, construction, forestry, cargo handling, and a myriad of other domains. Field robots may operate on the ground (either terrestrially or on other planetary bodies), underground, underwater, in the air, or in space. Service robots work closely with humans, including the elderly and the sick, to assist them with their daily lives and activities.

4. Ai and the reasoning of the human being

It would be a philosophical revolution if artificial intelligence were to reach the mode of reasoning of the human being. But here too, we are far from it. The man has more than a billion neurons and 10^{12} synapses. We may be able to analyse 100,000 neurons today. But we're still a long way from the billion. The exact functioning of the brain is not yet understood. Apart from artificial intelligence, it is therefore important to develop human intelligence. There are billions of human intelligences out there. There are billions of people who have not been to school enough. I don't think there are exceptional brains on one side and stupid people on the other. Not all of them have grown up in social conditions that have allowed them to develop favourably. That is why, before developing AI, human intelligence must be developed through education and creativity.

It is also necessary to develop other forms of intelligence, artistic, emotional, emotional and amorous. This presupposes work on the process of releasing human intelligence. Finally, a huge amount of networking of real intelligences is also necessary. For if humanity had a level of education equal to that of the most advanced people and these intelligences were networked, no artificial intelligence could compete with them.

A permanent watch must be set up from the outset. Transparency of research and rules are also needed to ensure that artificial intelligence does not develop to the detriment of the human species. These are the famous three laws of robotics known as Asimov Laws, i. e. do not harm humanity, obey the orders of man and act in accordance with these two precepts. But even that is not enough, because machines could harm the environment.

It is therefore important to maintain the possibility of literally killing artificial intelligence. But here too, it is very delicate, because if the AI understands that man has the means to destroy it, it could, in order to guard against human intervention, invent languages, as it has begun to do, that man does not understand.

We will need a moratorium if we cannot implement the rules mentioned above. Artificial intelligence is not only developed in public places, but also in highly confidential military laboratories. It is therefore difficult to control everything.

General and mathematical culture remains fundamental, as well as music and literature. It will be necessary to learn curiosity, to learn to learn. Math remains the basis of everything and can quickly make scientific knowledge obsolete.

The risk of total disconnection exists. Jobs will be lost because of artificial intelligence. If this allows the human being to devote himself to more interesting activities, much better. But there is a real danger, on the one hand, of seeing people with a higher intellectual quotient and, on the other hand, people who would be forced to survive on a universal minimum income and consume all kinds of real and virtual drugs.

5. Face recognition

What has really changed in the world over the last few decades: We suddenly have a technology that is "smart enough" to recognize a face, even better than a human being. This has a great influence on how we can organise society.

Face recognition has attracted great interest as an important biometric technique and has wide applications in information security, law enforcement and surveillance, smart cards, access control, etc. Among the numerous methods that have been proposed [1–3] for face recognition, *linear discriminant analysis* (LDA) is widely used as a dimension reduction

technique because of its superiority in considering the underlying class structure of input data over other techniques such as *principal component analysis* (PCA) [2, 4].

Image recognition has exploded over the last few years. Each Facebook and Google photos have tens of billions of images on their platform. With this dataset, they - and many others - are developing technologies that go beyond facial recognition providing algorithms that can tell you what is in the image: a boat, plane, car, cat, dog, and so on. The crazy part is that the algorithms are better than humans at recognizing images. The implications are enormous. Imagine an AI able to examine an X-ray or CAT scan or MRI to report what looks abnormal.

As AI begins to impact every industry and every profession, there is a response where schools and universities are ramping up their AI and machine learning curriculum. IBM, for example, is working with over 150 partners to present both business and technology-oriented students with cognitive computing curricula.

6. Automatic learning

Automatic learning has become increasingly important due to the rapid growth of the amount of data available. In the year 2000, the total amount of information on the Web varied somewhere between 25 and 50 terabytes [6]. By 2005, the total size was approximately 600 terabytes [7]. Nowadays, the total amount of information is almost incalculable. This unrestrainedly growth of data opens the way for new applications of machine learning. Automatic data analyzers are needed since a human, even an expert, cannot look at a “very large” data set and plausibly find a good solution for a given problem based on those data. In this situation, new challenges are raised regarding the scalability and efficiency of learning algorithms with respect to computational and memory resources. Practically, all existing implementations of algorithms operate with the training set entirely in main memory. If the computational complexity of the algorithm exceeds the main memory then the algorithm will not scale well, will not be able to process the whole training data set or will be unfeasible to run due to time or memory restrictions. However, increasing the size of the training set of learning algorithms often increases the accuracy achieved by classification models [8], and thus, in order to handle “very large” data sets, a new and active research field emerges, large-scale learning [9, 10]. It intends to develop efficient and scalable algorithms with regard to accuracy and to requirements of computation (memory, time and communication needs). Large-scale learning has received considerable attention in the recent years and many successful techniques have been proposed and implemented [11 – 13].

Distributed learning seems essential in order to provide solutions for learning from both “very large” data sets (large scale learning) and naturally distributed data sets. It provides a learning scalable solution since the growing volume of data may be offset by increasing the number of learning sites. Moreover, distributed learning avoids the necessity of gathering data into a single workstation for central processing, saving time and money. Despite these clear advantages, new problems arise when dealing with distributed learning as, for example, the influence on accuracy of the heterogeneity of data among the partitions or the need to preserve privacy of data among partitions. Therefore, this is already an open line of research that will need to face these new challenges.

Deep learning first transformed speech recognition, then computer vision. Today, *Natural Language Processing* (NLP⁷) and robotics are also undergoing similar revolutions.

AI publication numbers are of interest (Figure 3) and are used generally in scientometrics and research statistics. It is impossible to combine a system based on giving values to individual publications with a study of the growth rate of AI science.

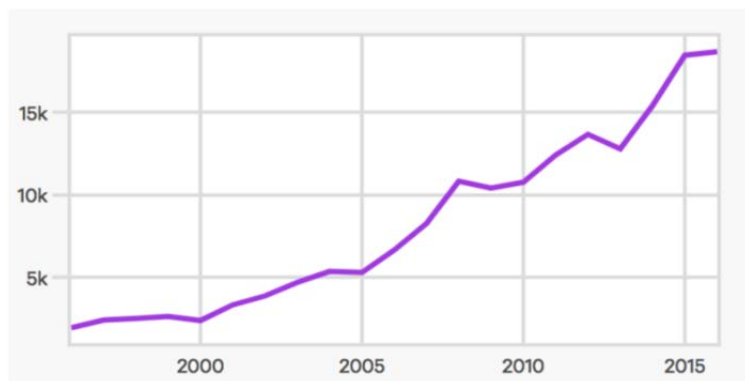


Figure 3 Annual published papers in recent years concerning AI (after [14])

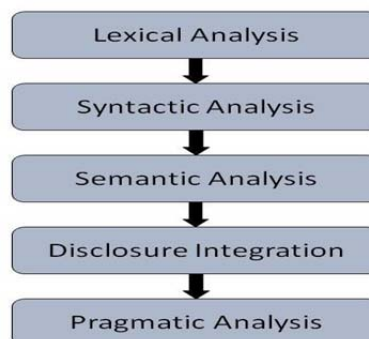


Figure 4 The five steps in NLP (after [17])

7. Computers versus humans

Obviously, computers are vastly superior to humans in certain tasks; however, the competence of AI systems becomes more difficult to assess when dealing with more general tasks like answering questions, playing games, and making medical diagnoses.

With so much excitement about progress in artificial intelligence, you may wonder why intelligent machines aren't already running our lives.

Key advances have the capacity to dazzle the public, policymakers, and investors into believing that human-level machine intelligence may be just around the corner. But a new report [14], which tries to gauge actual progress being made, attests that this is far from true. The findings may help inform the discussion over how AI will affect the economy and jobs in the coming years.

Tasks for AI systems are often framed in narrow contexts for the sake of making progress on a specific problem or application. While machines may exhibit stellar performance on a certain task, performance may degrade dramatically if the task is modified even slightly. For example, a human who can read Chinese characters would likely understand Chinese speech, know something about Chinese culture and even make good recommendations at Chinese restaurants. In contrast, very different AI systems would be needed for each of these tasks.

Despite the difficulty of comparing human and AI systems, it is interesting to catalogue credible claims that computers have reached or exceeded human-level performance. Still, it is important to remember that these achievements say nothing about

⁷ NLP refers to AI method of communicating with an intelligent system using a natural language such as English. Processing of Natural Language is required when you want an intelligent system like robot to perform as per your instructions, when you want to hear decision from a dialogue based clinical expert system, etc. There are general five steps in NLP (Figure 4). Today, NLP's deep learning transformation is well underway; this will lead to a flourishing of new applications (such as chatbots). Deep Learning in robotics is also gaining significant momentum, and this will lead to many new applications (such as new manufacturing capabilities).

the ability of these systems to generalize. Games provide a relatively simple, controlled, experimental environment and so are often used for AI research.

8. Anticipated top ai breakthroughs

Alan Turing created the Turing test over half a century ago as a way to determine a machine's ability to exhibit intelligent behaviour indistinguishable from that of a human. Loosely, if an artificial system passed the Turing test, it could be considered AI. The specialists believe that for all practical purposes, these systems will pass the Turing test in the next three-year period. Perhaps more importantly, if it does, this event will accelerate the conversation about the proper use of these technologies and their applications.

All five human senses (yes, including taste, smell and touch) will become part of the normal computing experience. AIs will begin to sense and use all five senses. The sense of touch, smell, and hearing will become prominent in the use of AI. It will begin to process all that additional incremental information. When applied to our computing experience, we will engage in a much more intuitive and natural ecosystem that appeals to all of our senses.

Solving big problems: detect and deter terrorism, manage global climate change. AI will help solve some of society's most daunting challenges. We're already seeing this technology being deployed in governments to assist in the understanding and pre-emptive discovery of terrorist activity. We'll see revolutions in how we manage climate change, redesign and democratize education, make scientific discoveries, leverage energy resources, and develop solutions to difficult problems.

Leverage all health data (genomic, phenotypic, and social) to redefine the practice of medicine. AI's effect on healthcare will be far more pervasive and far quicker than anyone anticipates. Even today, AI / machine learning is being used in oncology to identify optimal treatment patterns. But it goes far beyond this. AI is being used to match clinical trials with patients, drive robotic surgeons, read radiological findings and analyze genomic sequences.

AI will be woven into the very fabric of our lives -physically and virtually. Ultimately, during the AI revolution taking place in the next three years, AIs will be integrated into everything around us, combining sensors and networks and making all systems "smart." AIs will push forward the ideas of transparency, of seamless interaction with devices and information, making everything personalized and easy to use. We'll be able to harness that sensor data and put it into an actionable form, at the moment when we need to make a decision.

9. Instead of a conclusion

Not all aspects of AI in which recent progress has been made can be covered. Progress is typically tracked consistently when good progress has been made. For some areas there are not clear standardized benchmarks (e.g. dialogue systems, planning, and continuous control in robotics). In other areas it is hard to measure performance when there has not been significant progress, like in commonsense reasoning. And still, other areas are waiting to be tracked but we simply have not had the opportunity to collect the data (e.g. recommender systems, standardized testing).

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THE IMPACT OF SOFTWARE ACTIVITY ON THE IMPLEMENTATION OF COST MANAGERIAL SYSTEM

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Abstract. The cost management system must be tailored to the needs of the company. The article details the elements of a cost system, as well as the methodology for implementing the cost system based on the specificity of software companies activity.

Keywords: *applications, launching, enterprise, model, method*

1. Introduction

The cost management objectives within a software company are [1]:

- Determining costs. By using the cost accounting managerial system, managers can determine the cost of software projects, maintenance services, etc;
- Cost control. The cost accounting managerial system allows minimizing costs by comparing the recorded costs with estimated or planned ones;
- Determining the size of sales. The cost accounting managerial system allows managers to determine the volume of sales to be achieved to reach a certain level of profit;
- Comparing costs with earnings. The cost accounting managerial system allows to keep costs and revenues in balance;
- Profit planning. The cost accounting managerial system helps managers plan their future activities and, as a result, maximize their profits;
- Determining and controlling efficiency indicators. The cost accounting managerial system studies various aspects of developing a product or service, making it easier to measure the effectiveness of the organization as well of a subdivision;
- Contributes to the preparation of both financial reports and non-financial ones. The cost accounting managerial system allows the collection of information on going projects and made products;
- Provides a decision base for the approval of operational policies. The cost accounting managerial system helps managers to justify operational policies with reference to the production processes, closure of some company subdivisions, giving up some projects, etc.;

To achieve its goals, a cost accounting managerial system has to be practical, simple and tailored to the company's needs; it has to provide accurate data; the performers and future users must cooperate and participate in its development; the implementation costs must be commensurate with the benefits it brings. The introducing of the system, should not affect the existing methods of obtaining information if they were recognized to be

efficient. The system must be implemented step by step by developing an appropriate network within the organization, and the managers' support must be unconditional in designing and managing the system, in order to get the expected result.

2. The elements of the cost managerial system

For a cost managerial system to achieve its goals it is necessary to develop six components of it: costing methodology, data, performance indicators, reporting system, procedures and system applications [2, 3].

The costing methodology describes how the organization forms the cost, by defining the basic cost elements, and how each element of the cost is calculated and reported. The methodology must be documented, which makes it easier for new employees to be trained. Selection of one or another method will be based on the specificity of the enterprise activity, its strategic objectives and how they are dispersed over time, the effort desired to achieve the given objectives.

For a software enterprise, it is important to understand the behavior of costs and how they can be influenced, in order to ensure greater efficiency. Costing methods are designed to find answers to the questions how costs are formed, which factors influence the costs in order to predict their future evolution. These are grouped into traditional ones, which give, as a rule, post-factum answers, when the actions have already been undertaken and they can only be ascertained. The second group of methods are the modern ones that allow ante-cost calculation and will serve as a reference for current and future decisions.

Methods for cost determination will be chosen according to the enterprise needs, and the analysis of the local software product market has shown that we have [4]:

- developers who serve one segment of the software development cycle, their activities are routine, with very clear specifications for the final product. It is crucial for them to fit within certain limits in order to estimate their performance. In this case, it is advisable for them to apply ante-calculation cost methods, such as the standard method;
- developers who produce standard products (specialized software) that only adjust to the needs of the beneficiary. For such companies, determining the parameters of a standard project, with standard cost, would serve as an efficiency norm, that would allow a more accurate negotiation of contracts with its customers and would contribute to reducing the risk of exceeding the contractual parameters;
- developers who serve the entire software development cycle, or even the software life cycle. For these, the method of variable costs is the most appropriate. It supposes to pay attention only to those costs that change proportionally to the production volume. For a software project, it is difficult to estimate exactly the quantity of needed resources, especially for innovative projects.

Data can be financial and operational, both describing how resources are consumed per product or service. It should be noted that financial data are not just those recorded in the financial reports that are rigorously controlled, but also financial data that are recorded in the accounting books and used for internal reporting, such as current recorded costs, as well as financial data included in annual budgets or financial forecasts, such as costs or standard costs. Financial data with reference to costs can also be obtained from other reports, not only from the financial ones, such as cash flow reports, movement of fixed assets reports, and so on. Financial data for costing can also be got from outside the enterprise, such as data on the markets evolution, sector development rates, or from

benchmarking. Another source of data used in cost estimation and management arise from the operational activity, which are called operational data, in this way operational managers estimate through statistical or expert models what resources are needed to provide a service, which they indicate in the service description. The basic requirement for the data is that they must be precise and reliable, so that the decisions that will be taken while using them to be accurate.

Regarding *the procedures*, it is important that the procedures for recording and reporting financial data, which will be further used for the calculation of costs, to be adapted to the applied costing methodology. For exemple, if it was decided to allocate equipment maintenance costs to the project based on the working hours of the equipment within each project, then this principle should be also applied to budgeting and execution. If during the execution as a basis will be used direct salary costs, then the data will be no longer comparable. Operational procedures are equally important, as a lot of data are collected from operational managers, such as: consumed hours to perform certain operations, material consumption (in the case of software projects - applications or software required to produce customized software), who must be responsible for ensuring that all data reach the system accurately, complete and in time. All data recording procedures, both accounting and operational, have to help and provide support to the costing methodology.

The system applications that are used to collect, process, and report cost information are extremely important. The cost system must be able to also retrieve information from other applications where data referring to cost can be stored. A software company may have time standards to execute certain operations that might be found in the system application used for planning. In establishing the links between different systems, it is necessary that people who will use the information for decisions justifying, to know which enterprise subsystems influence their cost calculation. When creating the cost system which will be used for both reporting and managerial purposes, it is crucial to know the previously used cost system, what are its limitations, as well the limitations of other information systems used by other departments. It is very important to define the cost model used previously, what information the system must generate, and how the existing or future system can be adapted to the business needs.

The performance indicators often used by the enterprise refer to the performance indicators per fields of activity, indicators of capacity usage, labor productivity, etc.; at the same time, the cost system must give an answer to the question of how the change in these indicators will influence the financial indicators. The cost system must be able to quantify financially the impact of non-financial performance indicators. Such analyses could reveal hidden costs and opportunities that otherwise would not be visible in the analysis of traditional financial reports. The value of a cost system is that managers intuitively understand the financial impact of daily decisions without waiting for financial reports at the end of the month. Thus, if in a software project it would be necessary to develop a software component where the enterprise does not have the necessary skills or the necessary personnel, the understanding of the cost formation of internal elaboration or outsourcing will make the manager to take the right decision. In this situation, it is important for the manager to understand how the costs are formed, and the cost system must come as a support.

The sixth element are *the reportings* and they refer to how information is accessed and presented for the decision-making process. The cost system has to generate simple, legible and easy to use reports. The cost system must ensure access to both accounting and operational information, that's why it is necessary for managers to be involved in the designing of cost system, otherwise, there is a risk that the reportings become more accountable, than tailored to the decision-making process. For example, an analytical report per story points in an Agile project could include, besides data on actual costs (labor cost, cost of used materials), also data regarding the number of iterations, the number of people involved per iteration, the number of working hours, the type of support materials used.

3. Stages of managerial cost system implementing methodology

The managerial cost system implementing methodology involves several steps [2, 3]. In the implementation process, it must be taken into account that this process is an iterative one and at each stage, as the cost system implementation is progressing, the team that will implement the project will return to its initial objectives to adjust them to the needs of the enterprise.

Determining the needs of the enterprise. At this stage, the enterprise will benchmark the six components of the cost system: the costing methodology, the data, the performance indicators, the reporting system, the system procedures and applications, the way they interact and the shortcomings the enterprise face when providing cost information. The tools to be used: questioning the basic users of cost information from different functional areas of the enterprise, analysing the data from the accounting books and financial reports, understanding currently applied cost methodology, and determining the system capacity to gather, store and report data.

It is recommended that the assessment of the needs to be done by one or two people. The people involved need to know the specific of production activity and to have knowledge about the accounting system, processes and procedures applied in the enterprise. As a result of the analysis, the findings are listed and recommendations are made to the management team with reference to the following actions. If the enterprise has limited resources and it is looking for an objective analysis of the situation, the preliminary assessment can also be done by outside consultants.

Launching the project. It is one of the most important moments because the decisions taken at this stage will influence other stages of the process. A few steps are recommended:

1. Obtaining commitment from managers.
2. Formation the project team.
3. Building a project plan, which will include the description of the business needs, the objectives, the scope and the limits of the project, the deliverables of the project, the project timetable.

4. Estimating the cost of the project implementation as well as its benefits. The project costs include consultant payments, the cost of training sessions, books, software to be used, or the equipment, as well as the amount of salaries paid to the team members for the system development. The benefits of the system can also be estimated, which can consist of measurable benefits: cost savings for the future, as well as non-quantifiable benefits, which could include more accurate information, which will lead to a more precise budgeting, or a more efficient consumption of costs, which will not lead to over budgeting.

5. Approving the project by the senior managers. At the given stage the final presentation of the project will be done, the project adjustments will be performed and the approval of the managers will be received.

System design. At this project stage, the team will conceptualize the design of the new cost system, determine what type of information is required, and how this information will be collected. The team will focus on three core elements: costing methodology, financial and operational data, and system applications. For a software company, some important moments need to be considered when designing the enterprise cost system, and namely: the software is done through distinct projects, some projects after the product completion and delivery to the customer are extended to maintenance projects of the soft. If the cost system will cover all elements within the enterprises, a possible cost system architecture could be as shown in Figure 1

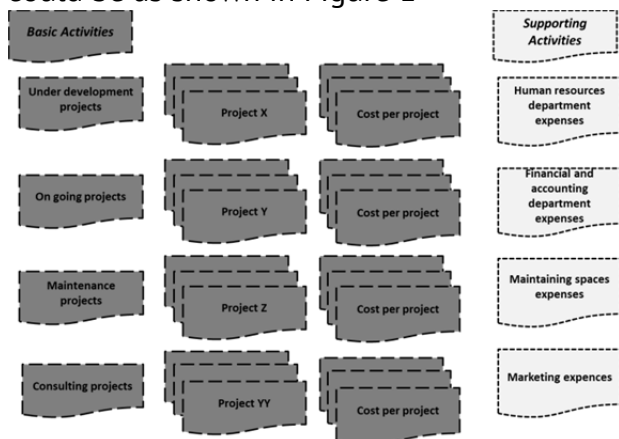


Figure 1. Model of cost system architecture

Source: Developed by the author

collection methods and will be adjusted to the requirements of the new model. For data collection initially can be used the project sheet.

2. Data validation. Once the data have been collected, the team must validate its reliability. Validation can be done in two ways: by comparing it with the current ones, budgeted or previously recorded, by examining them with experts, or by comparing them with industry ones, or by internal benchmarking. Validation aims to highlight inconsistencies or areas requiring additional investigations. This will demonstrate that cost information is reasonable and representative for the concerned business processes or consumed resources by these processes.

3. Setting up the system. This step involves setting up the system application and entering data into the system. The company can have cost-specific applications that can calculate the cost per unit, or spreadsheets can be used. Whatever system application is used, it is important for it to reflect the cost methodology set up in the previous step. If the system application used does not correspond to the cost methodology, then the implementation team will have to assess the possibility of adjusting to the new methodology. If it is not possible to modify the system, it will be evaluated the possibility to perform the calculation without using the existing system, or the original design will be changed in order to adjust to the existing system limitations. If the team members choose to redesign the system, they must understand how this will influence the accuracy and reliability of the cost calculation, and they will document these changes.

System setup and testing

Once the system design has been approved, the team will proceed to create the cost model. This stage includes four steps to follow:

1. Data collection. Collecting the financial and operational data that are considered the basis of the model. The company may have some time standards or some others that do not support the developed model. In this situation, the company will revise the standards in line with the new methodology, the data

4. Testing the system. After the system has been set and the data have been entered, the team will calculate a preliminary cost and review the results. At this stage, the team receives confirmations that the data is reliable and can be used for decisions.

As a result of the given step, if the system does not meet the initial requirements of the system, for example the double allocation of expenses for the final product, the team could return to the previous stage - the system designing.

Implementing the system. Once the system has been tested, it goes to implementation. Depending on the purpose, the system can be implemented at one stage or at several ones. Implementation is recommended to be started at the beginning of the fiscal year because the company can start from "zero". During the fiscal year, changes in the system could lead to major changes in financial reporting and cost differences, which will require additional explanations. The optimal launch period is the end of the year - the first quarter of the fiscal year. It is recommended to track the system's progress, to ensure that there are no deficiencies or stops and the progress is ongoing.

Evaluation and review. During the first year of implementation, it is advisable to review the cost system every 3-6 months to ensure that the core objectives have been achieved and operational managers receive the information they need. Once the system is stable, it should be reviewed periodically, especially if there are changes at the top management, business processes, or organizational structure (merge or acquisition).

A cost system can operate between three to five years without major changes, which does not mean that it remains static, it grows with the company and evolves with the company.

4. Conclusions

Studies conducted in the previous research have shown that local software companies do not have any cost management systems, mainly focusing on cost reporting rather than managing them. Implementing a cost system tailored to the enterprise's requirements will enable it to know the cost of each project and, consequently, to manage it more efficiently.

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RATIONAL STRUCTURE OF A TSEMENTOBETON FOR A COVERING OF HIGHWAYS

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Abstract: The article examines the effect of providing the necessary physical, mechanical and operational characteristics of the road pavement material from cement concrete intended for highways. Studies carried out in this area have shown that the technical, economic and operational characteristics of such coatings are largely due to the rational choice of the material composition. In the author's proposed work, a study was made of the effect of durability under compression ($f_{ck.cube}$) and on bending (f_{ctk}) and abrasion (G). Changes in these characteristics are achieved by introducing into the cement concrete plasticizer (Dynamon Easy 11), filler (microsilica) and polypropylene fiber (MAPEFIBRE NS 12/ NS 18). The obtained researches made it possible to draw a conclusion that, with rational selection, the composition significantly increases the physico-mechanical and operational characteristics of the material of the pavement from cement concrete.

Keywords: a cement concrete, a paving, a highways, filler, a fiber, the plasticizing additive.

1. Relevance of work

The analysis of works [1-4] shows that when using a tsementobeton as a covering for highways, their operational technical characteristics improve [1, 3, 4]. Such covering allows to cut a consumption on the contents and repair of the road, on 7-10% reduces fuel consumption of motor transport [5] and improves ecology. Wear of a paving [1-5], depends on intensity of a transport stream and climatic conditions in which the highway is operated. Quality of the applied material, its physicommechanical and operational indicators has essential impact on wear of a covering. Requirements to paving material from a tsementobeton for the countries of Europe are provided in the table 1 [6].

2. Work purpose

The purpose of work is, to develop rational composition of material from a tsementobeton for a covering of highways due to introduction to its structure of additives, a filler and a fiber.

Proceeding from a goal, the following research problems were accepted:

1. To study influence on quality indicators of material from a tsementobeton for a covering of the quantity entered into its structure:

a) Dynamon Easy 11 softener (TU At B.2.7-24.6-02498197-385-2004), $\rho = 1,04 \times 10^{-3} \text{ kg/m}^3$, (Mapei firm, Italy);

b) microsilicon dioxide (size of particles <1 microns, ρ : not condensed 130 - 350 kg/m³, condensed 480 - 720 kg/m³, suspension of 1320 - 1440 kg/m³);

v) a polypropylene fiber - MAPEFIBRE NS 12/NS 18 (diameter – 0,34 microns, length of fiber is 12-18 mm, ρ – 0,91 x 10⁻³ kg/m³, tensile strength – 700 MPa), (Mapei, Italy).

2. To conduct researches of change of characteristics of material, at change of the entered quantity of the considered components.

3. Using the received results to calculate mathematical models which describe changes of quality of material which is investigated.

4. To carry out the analysis of the received results and to offer recommendations about regulation of quality of a paving from a tsementabeton for highways.

3. Main part

The preliminary tests which are carried out by the author and described in works [3, 7, 8] allowed to define basic composition of concrete and range of change of quantity of the entered components (table 2). The plan of carrying out experiences (tab was developed for decrease in labor input 2) and its randomization.

Factors of influence and range of their variation got out by results of preliminary experiments [3, 13, 14]. The following factors influencing quality of concrete were investigated:

x_1 - quantity of the plasticizing additive of Dynamon Easy 11 (PA) from 0% up to 1% of the mass of cement;

x_2 - quantity of a polypropylene fiber of MAPEFIBRE NS 12/NS 18 (F), from 0 to 0,6 kg/m³;

x_3 - quantity of a filler – microsilica (M), from 0 to 15 kg/m³ from the mass of cement.

Experiments were made in the following sequence:

- selection of compositions of the studied paving materials was carried out, and then production of necessary quantity of samples (table 2) was carried out. Samples were produced in number of 9 pieces for each point of the plan (table 2) with sizes: 0,1x0,1x0,1 m, 0,07x0,07x0,07 m and 0,04x0,04x0,16 m,

- the made samples were maintained in the conditions of normal curing within 28 days ($t=200C$, $W=80\%$);

- for the 28th days samples of 0,1x0,1x0,1 m, were subjected to test for durability at compression on the 100th ton press of TESTING PL 100 firm in laboratory of firm Heidelberg Ukraine Cement,

Table 1

Requirements to a tsementobetone for a paving of highways in the countries of Europe [6]	
Indicators	Requirements EN
Water cement relation	0,4
Classes on durability on compression (MPa)	52,5H
Durability on stretching at a bend (MPa)	6,5
Water tightness	there are no requirements
Frost resistance	there are no requirements
Istirayemost	there are no requirements
The volume of the involved air in BS for fine-grained concrete	<7%
Cement designation	TSEM I 52,5H

- samples of 0,04x0,04x0,16 m were subjected to test for durability at their bend in laboratory of chair of construction materials of the Odessa state academy of construction and architecture (OGASA);- samples of 0,07x0,07x0,07 m were subjected to test for attrition, on the LKI-3 device in laboratories of chair of design, construction and operation of

Table 2

Plan of experiment ($x_1... x_3$) and compositions of the studied concrete ($X_1 ... X_2$)

№	X_1	X_2	X_3	x_1	x_2	x_3
	PA	F	M	PA	F	M
1	0	0	0	- 1	- 1	- 1
2	0	0,3	0	- 1	0	- 1
3	0	0,6	0	- 1	1	- 1
4	0,5	0	0	0	- 1	- 1
5	0,5	0,3	0	0	0	- 1
6	0,5	0,6	0	0	1	- 1
7	1	0	0	1	- 1	- 1
8	1	0,3	0	1	0	- 1
9	1	0,6	0	1	1	- 1
10	0	0	7,5	- 1	- 1	0
11	0	0,3	7,5	- 1	0	0
12	0	0,6	7,5	- 1	1	0
13	0,5	0	7,5	0	- 1	0
14	0,5	0,3	7,5	0	0	0
15	0,5	0,6	7,5	0	1	0
16	1	0	7,5	1	- 1	0
17	1	0,3	7,5	1	0	0
18	1	0,6	7,5	1	1	0
19	0	0	15	- 1	- 1	1
20	0	0,3	15	- 1	0	1
21	0	0,6	15	- 1	1	1
22	0,5	0	15	0	- 1	1
23	0,5	0,3	15	0	0	1
24	0,5	0,6	15	0	1	1
25	1	0	15	1	- 1	1
26	1	0,3	15	1	0	1
27	1	0,6	15	1	1	1

Table 3

Results of experiments

№	$f_{ck.cube}$ (MPa)	f_{ctk} (MPa)	G ($\times 10^3$ kg/m ³)
1	59,15	8,15	0,30
2	61,78	6,30	0,57
3	63,40	8,00	0,27
4	58,50	6,21	0,61
5	55,34	7,60	0,40
6	52,20	5,43	0,67
7	56,35	6,83	0,37
8	53,20	5,65	0,55
9	52,90	7,30	0,43
10	48,34	5,41	0,82
11	44,30	6,90	0,41
12	53,58	5,89	0,48
13	43,34	6,80	0,46
14	47,89	5,38	0,74
15	46,45	6,70	0,45
16	43,62	5,00	0,97
17	55,30	5,26	0,68
18	47,40	5,35	0,56
19	55,38	5,70	0,70
20	48,42	5,81	0,63
21	52,25	5,50	0,75
22	52,57	5,45	0,66
23	52,40	7,30	0,38
24	52,63	5,30	0,59
25	53,42	6,90	0,55
26	49,23	5,70	0,54
27	52,55	6,05	0,61

OGASA. By results of experiences there were obtained data on durability of samples at compression ($f_{ck.cube}$), durability at a bend (f_{ctk}) and resistance to attrition (G). Results of experiments are given in table 3.

Results of experiences allowed to calculate a number of mathematical models. Models describe durability at compression ($f_{ck.cube}$) (1), durability at a bend (f_{ctk}) (2) and firmness at attrition (G) (3).

The calculated mathematical models:

$$f_{ck.cube} \text{ (MPa)} = 46,768 - 1,257x_1 + 1,552x_{12} + 1,753x_1x_3 - 2,443x_3 + 6,735x_{32} + \quad (1)$$

$$f_{ctk} \text{ (MPa)} = 5,854 - 0,201x_1 + 0,359x_1x_3 - 0,431x_3 + 0,544x_{32} \quad (2)$$

$$G \text{ (} \times 10^3 \text{ kg/m}^3\text{)} = 0,619 + 0,049x_1x_3 + 0,069x_3 - 0,087x_{32} \quad (3)$$

4. Conclusions

On the basis of the executed researches it is possible to draw the following conclusions:

- At introduction to composition of concrete of a filler of microsilica (to 15 kg/m^3) durability on stretching at a bend on 15 increases. 20%. Durability at compression increases from 45 to 60 MPa (33%), at introduction - 1% of an additive of Dynamon Easy 11 with a filler microsilica (to 15 kg/m^3).

For convenience of the analysis of [9] models (1-3) are presented in the graphic form (figure 1, 2, 3).

- Introduction to composition of concrete of an additive of Dynamon Easy 11 in quantity from 0,8 reduces to 1% of the mass of cement V/C the mix relation from 0,5 to 0,36 (more than 20%).

- Application of a fiber from $0,3$ to $0,6 \text{ kg/m}^3$ demands increase in an amount of water of a zatvoreniye on 8. 10%. Increases durability on stretching at a bend - 20-25%.

At introduction to $0,6 \text{ kg/m}^3$ of a fiber to concrete wear of concrete effectively decreases to $0,3 \times 10^{-3} \text{ kg/m}^3$ (more than for 60%).

Thus, it is possible to draw a conclusion that application of the considered additives and a filler can be recommended in transport construction in the countries of Europe as a covering for highways.

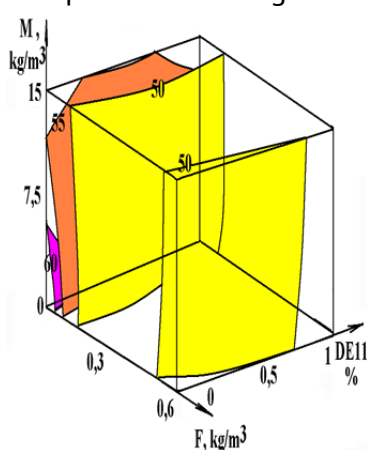


Figure 1. Influence of number of the PA (x_1), M (x_2) and F (x_3) on durability at compression (MPa)

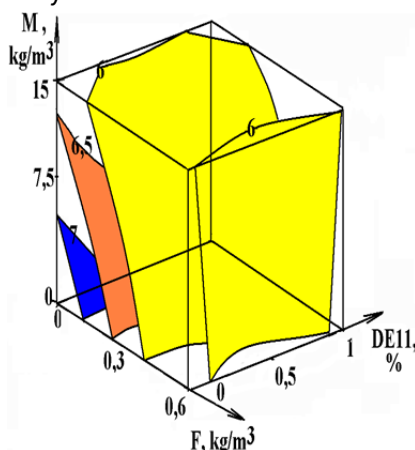


Figure 2. Influence of number of the PA, F and M on their durability on stretching at a bend (MPa)

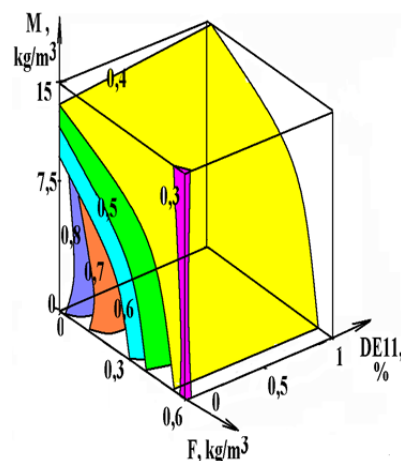


Figure 3. Influence of number of the PA, F and M on an istirayemost of G ($\times 10^{-3} \text{ kg/m}^3$)

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OPERATING PROPERTIES OF EPOXY COMPOSITIONS UNDER THE INFLUENCE OF ABSORPTION-ACTIVE ENVIRONMENT

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Abstract. It was researched the influence of the multifraction mineral frame, that includes zeolite and furfural on the properties of different filled compositions. Such compositions are intended for the use under the influence of water and oil products and other agents (in the elements of structures connected with the maintenance of transport). Whereas it is practically impossible to conduct long-term testing in such inhomogeneous environments, the properties of the compositions were measured after exposure separately in water and two kinds of oil.

Keywords: *polymer composite materials, zeolite, furfural, water and light oil absorption*

1. Problem formulation

The high resistance materials are necessary for protection of concrete constructions, that work in contact with water, oil products and other agents. Such materials were used for repair of many hydrotechnical constructions operated in Ukraine for many decades. Polymer solutions based on epoxy resins have the necessary set of properties for performing the works listed above. Despite the high primary cost of epoxy binders their application is justified on the total costs of the life cycle of structures due to the reduction of costs for repair and replacement of structures, elimination of consequences of failures, environmental and other measures. Given the ability to regulate properties, improve durability and durability, and reduce the cost of these materials, using various modifiers and fillers (from their huge diversity), development of filled modified epoxy compositions designed for specific operating conditions is relevant.

2. Research methodology

As a basic component of compositions for repair and protection of concrete structures, it is advisable to use the epoxy-rubber resin "Macro" produced in Ukraine. Improving the operational properties of solutions on this resin can be facilitated by the introduction of certain dosages of furfural and zeolite (patent of Ukraine No. 5408). In particular, the positive role of zeolite in reducing water absorption has been estimated [1]. It is known [2] that aluminosilicate (the crystal structure of which is formed by tetrahedral fragments $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$, united by common vertices into a three-dimensional framework) has molecular sieve properties. However, the reasons and conditions for its positive effect on the structure of furfural modified epoxy compositions (in particular, on the criteria of adsorption and resistance in water and oil products) are not clear.

In epoxy resin furfural is introduced as an organic modifier that is capable of increasing water and chemical resistance, adhesion and strength properties of the material, and also serves as a polymerization accelerator and, to a certain extent, plasticizes the compositions.

In the experiment to determine the physico-mechanical and operational properties [3], a 27-point D-optimal plan was used. The levels of the five parameters of the disperse system varied. To determine the effect of the components of the dispersed phase on properties of system, they are represented among the variable factors by a hierarchy of relationships-the fractions of the components of the embedded subsystems (rather than individual mass parts in the dispersion medium, taking into account the experience of analyzing the role of the zeolite in [4]): mineral frame - 280 ± 100 mass parts; share in the frame of the filler - $0,6 \pm 0,3$ mass parts, the proportion of zeolite in the filler - $0,16 \pm 0,10$ mass parts, the proportion of large zeolite - $0,25 \pm 0,25$ mass parts, furfrol - 7 ± 5 mass parts.

3. Results and discussion

Long-term operation of polymer composite materials, with constant or periodic contact with an aggressive environment (water), usually leads to changes in their properties. Adsorption-active environment penetrating the composite due to diffusion and molecular transport along the structure defects promote the mobility of structural elements, reduce the strength of intermolecular bonds and thereby facilitate the "slippage" of molecular chains and molecular formations relative to each other, which is manifested in a decrease in energy, necessary for the destruction of material [5].

Among the characteristics determined for 27 compositions, there was water absorption W (%) after 1, 3 and 6 months ($\tau = 30, 90, 180$ days) of stay in water. From these data, for each composition, it was possible to obtain (with an acceptable error) the analytical dependences of W on the time τ of the same exponential type (1) and the corresponding equations of water absorption rate (2). In Figure 1, such dependences are shown for the composition at the center of the experimental region ($x_i = 0, i = 1-5$).

$$W = a \cdot (1 - \exp[-b \cdot \tau]) \quad (1)$$

$$dW/d\tau = a \cdot b \cdot \exp[-b \cdot \tau] \quad (2)$$

The parameter a in the models (1 - 2) corresponds to the maximum amount of water absorbed by the polymer solution, b - the rate indicator of water recruitment.

The obtained models (27 pairs of curves) make it possible to estimate the water absorption and its velocity for 27 compounds at any time. In particular, one can predict W after a year in water.

According to such estimates, by the levels of parameter a , rate b and other generalizing parameters of the water absorption kinetics, it is possible to compare compositions in the analysis and design of material quality.

All 27 curves of water absorption fit into the range of values shown in Figure 2a (at the maximum absorption a in the range from 0.2 to 0.6%). A picture of the decrease in the intensity of water absorption as the water is collected is represented by the zone in Figure

2b, covering the velocity curves for all compositions (maximum, initial velocities in the range 0.001-0.005).

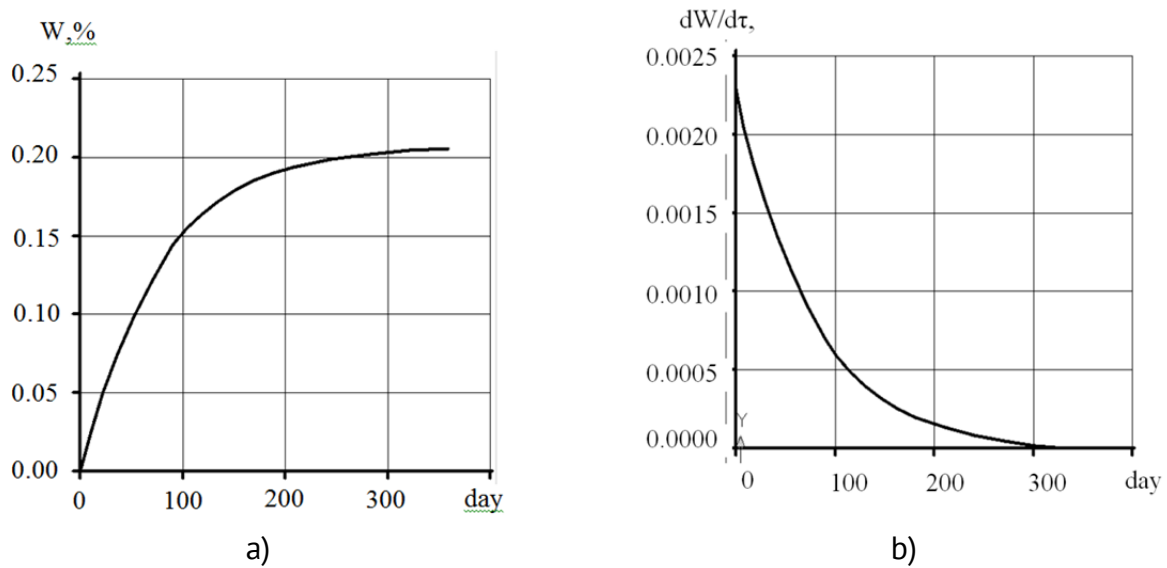


Figure 1. The water absorption curves (a) and the absorption rate (b) for the central composition ($x_i = 0, i = 1-5$)

A comparative analysis of the water absorption curves of different compositions shows that the most noticeable effect on this process is exerted by the furfural content. Moreover, a lower water absorption level at any exposure time corresponds to the average dosage.

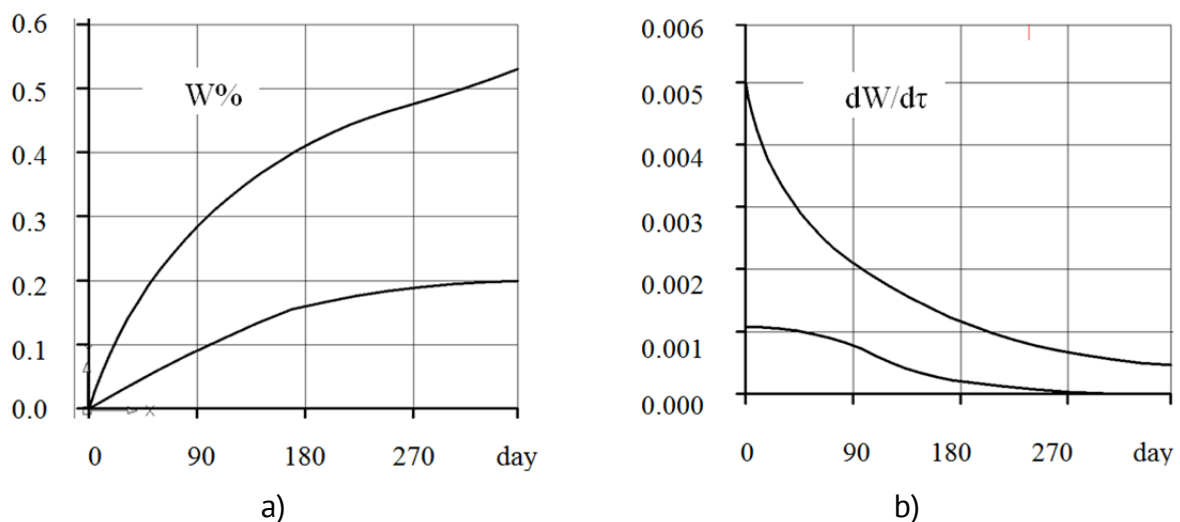


Figure 2. Changes in the quantity (a) and rate indicator of water recruitment (b) in the field of experimental data

It should be noted that these data showed a weak correlation between W_6 and density ($r = 0.48$).

In the analysis of the ES model, describing the total field [6] of water absorption in the coordinates of all five composition parameters, it is established that the minimum level of this field is $W_{6,\min} = 0.009\%$, at $x_1 = +1$ (maximum filling with the mineral framework), $x_2 = x_3 = -1$ (the minimum filler and the minimum part of the zeolite in it), $x_4 = 1$ (the

maximum amount in the zeolite of coarse grains), $x_5 = -0.07$ (average dosage of furfural). The maximum is $W_{6,max} = 0.045\%$ at $x_1 = -1$ (low filling), $x_2 = +1$ (maximum filler content,

little sand), $x_3 = 0.16$, $x_4 = 0.60$ (medium level of zeolite modification with increased content of coarse grains) and $x_5 = +1$ (much furfural).

Among other characteristics, the oil absorption of P modified epoxy solutions was determined after a 6-month exposure in "light" and "heavy" oil (PL and PH), according to the plan of the five-factor natural experiment. Sufficiently low values of PL and PH are obtained with a faster average absorption of light oil by 30%. The absence of a linear static coupling between the levels PL, PH and the corresponding water absorption levels is revealed.

A significant negative correlation was found between the absorption of water and light oil in maximally filled compositions, $r\{P_L, W\} = 0.58$). The ones shown in Figure 3, the oil absorption curves PLH, depending on each of the normalized factors in the PLH maximum zone, were obtained using a second-order ES model constructed from the data of the planned experiment using the k-transformation [7] (because the minimum P levels are close to zero) for

$$kP_{LN} = \ln[p/(1-p)],$$

$$p = (P_{LH} - P_{LH.min}) / (P_{LH.max} - P_{LH.min}).$$

The graphs generally reflect the positive effect of the zeolite, especially for hard solutions (with a reduced tar consumption). In such compositions, with an increased filling of the mineral framework, furfural significantly reduces the absorption of oil.

Conclusions

1. It is obvious that an increase in the share of the mineral skeleton leads to a decrease in water absorption. The effectiveness of the organic modifier - the average dosage of furfural - is confirmed. With increased filling, an additional positive effect can be given by a mixture of large and small zeolite grains.

2. In all the investigated range of compositions of epoxy composites, water absorption (up to 0.6%) does not exceed the values characteristic for this class of materials.

3. The absence of a linear static connection between the corresponding levels of water and oil absorption indicates that the same material structures differently prevent the mass transfer of three different liquids.

4. The positive role of organic (furfural) and mineral (zeolite) matrix modifiers in highly-filled epoxy compositions has been revealed.

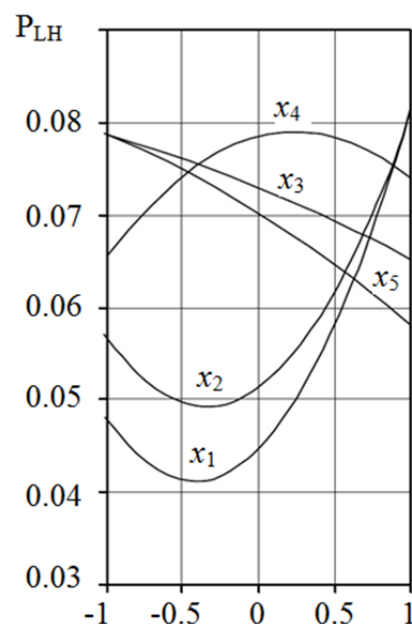


Figure 3. One-factor dependence of oil absorption PLH depending on the composition factors in the zone of maximum values

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STUDY ON PARAMETERS OF USED WATER IN A CHEESE-PROCESSING FACTORY

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Abstract. The main purpose of the research consists in monitoring the quality of hygienic drinking water and wastewater in a food industry plant in order to obtain information on water quality, efficient treatment technologies. Following the results obtained drinking water samples were corrected from the point of view of quality accordingly to the acts in force. The results have also highlighted significant differences concerning the characteristics of drinking water and wastewater monitored depending on the source of water supply and the type of technological process. Chemical oxygen demand, biochemical oxygen, pH, total nitrogen and phosphorus are the parameters of qualitative indicators with significant differences from the point of view of statistics for wastewater.

Keywords: *wastewater, quality indicators, biochemical oxygen, nitrogen, phosphorus*

Introduction

In food industry water is used as a raw material, as a solvent for substances with different density when washing products and equipment, as transport water or merely cooling water [1 - 4].

Quality monitoring of the hygienic drinking water and the waste water discharged is one of the conditions requested for all producing, processing, storing, keeping, shipping and marketing product supply units [5 - 8]. The increase in acquisition, application and development of knowledge, advanced services and techniques in the fields of environmental protection, population's health, and information technology is influenced by research and multidisciplinary developing skills in order to improve technological performances required by the implementation of national and European normative and regulations on the control of environmental pollution (water pollution) [9 - 12].

Materials and methods

Drinking water samples were taken from the water supply situated at the entrance of the factory monitored or water basin drilled from well. To monitor the quality of non-treated wastewater, samples were taken from the sewage point towards the pre-purification plant and sewage point of its own purification plant of the food factory in question. The sanitary research of water was done by laboratory examinations and area investigations. Toxicological analysis of water consisted in determining the organoleptic and physical properties as well as of chemical composition. Water samples were taken in sterile flasks equipped with bottle shutters or cotton corks rolled in gauze and with paper caps,

preserved by refrigeration accordingly with legal normative in force. Waste water indicators are determined by standardized analysis methods, adapted to [13 - 15].

Water hardness was determined by complexometric titration (EDTA); pH was measured according to SR EN ISO 10523:2012; total phosphorous - according to SR EN 12240:2004; biochemical oxygen demand SR EN 1899-2:2002; biochemical oxygen after 5 days (CBO₅) was measured according to SR EN 1899-2:2002 („Water quality – Dilution and Pitching Method”); chemical oxygen - CCO-Cr index was measured according to SR ISO 6060:1996. Nitrites were determined by molecular absorption spectrometric method; nitrates were determined by 2, 6 dimethylphenol spectrometric method; total nitrogen was determined by Kjeldahl method [16]. All tests were performed in triplicate and the results were statistically processed in the MCO 2016 Excel program.

Results and discussion

After having taken drinking water samples from the control points of the factory monitored, toxicological analyses were made in order to establish if the values of quality indicators of drinking water complied with the maximum admitted limits stipulated by the normative in force. The results of the tests are shown in Figure 1.

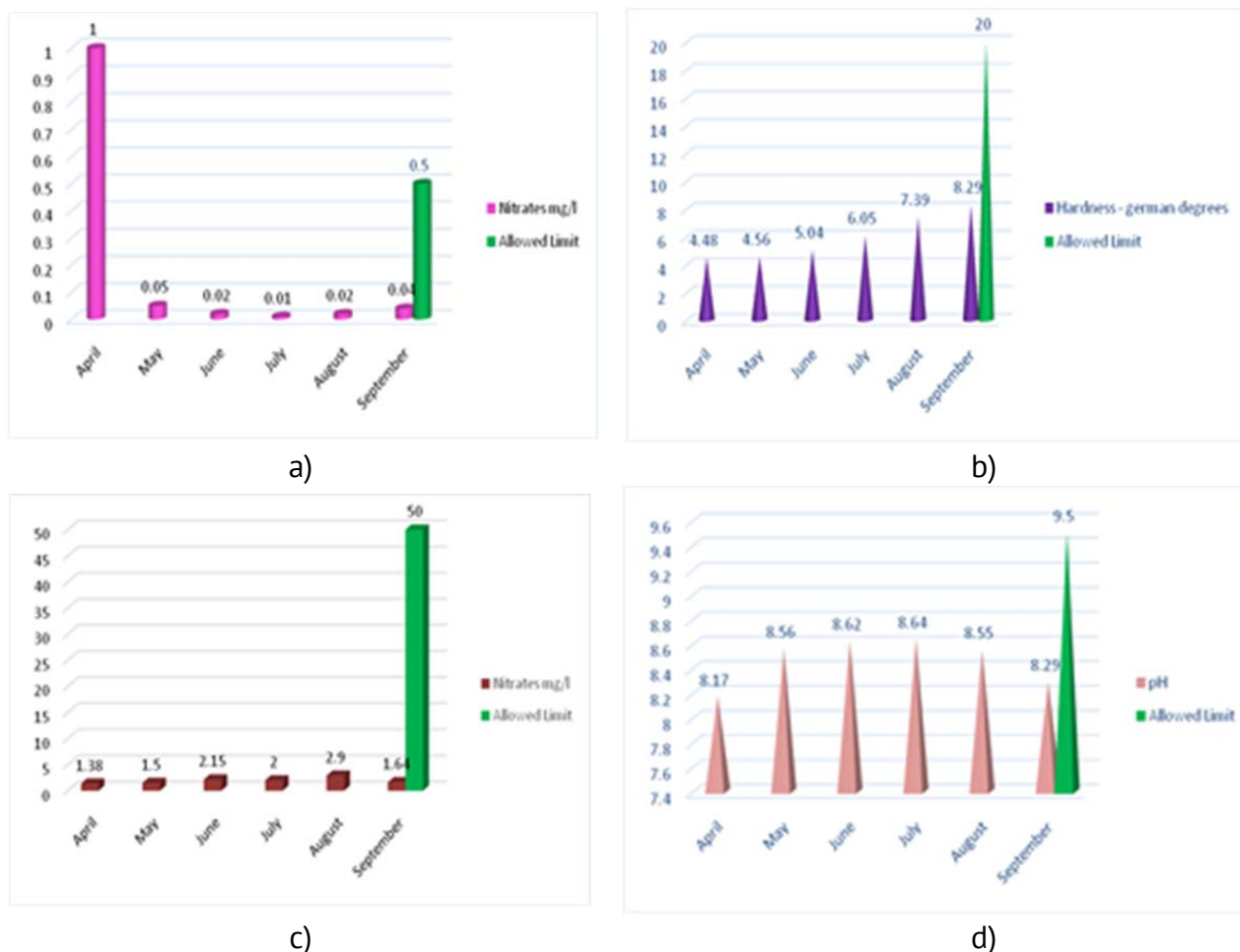


Figure 1. Control results for nitrites (a), nitrates (b), of hardness (c) and pH (d) in drinking water

The results of toxicological analyses of the samples taken during 08.04.2017-07.09.2017 from the food factory monitored showing that drinking water complies from the

point of view of quality indicators with the maximum admitted norms stipulated by the normative in force.

The following analyses on waste water were also made: CBO_5 was obtained by determining the oxygen content dissolved in water after sampling and after 5 days, and the difference was CBO_5 ; CCO-Cr – potassium bi-chromate method. The data written down in fig. 2 emphasize the fact that overtakes of the following quality indicators were registered: CCO-Cr, CBO_5 , pH, total nitrogen and total phosphorous in waste water before getting to treatment plant.

Waste water samples sewed from the factory ranged within the maximum admitted limits imposed for surface water, with small exceptions regarding the indicators CCO-Cr and CBO_5 , in the months April and May, of 145; 156 mg/l as against 125 mg/l admitted, 34 respectively; 42 mg/l as against 25 mg/l admitted. Thus, the treatment plant of the factory in question functioned at optimum parameters, complying with the quality requirements of wastewater.

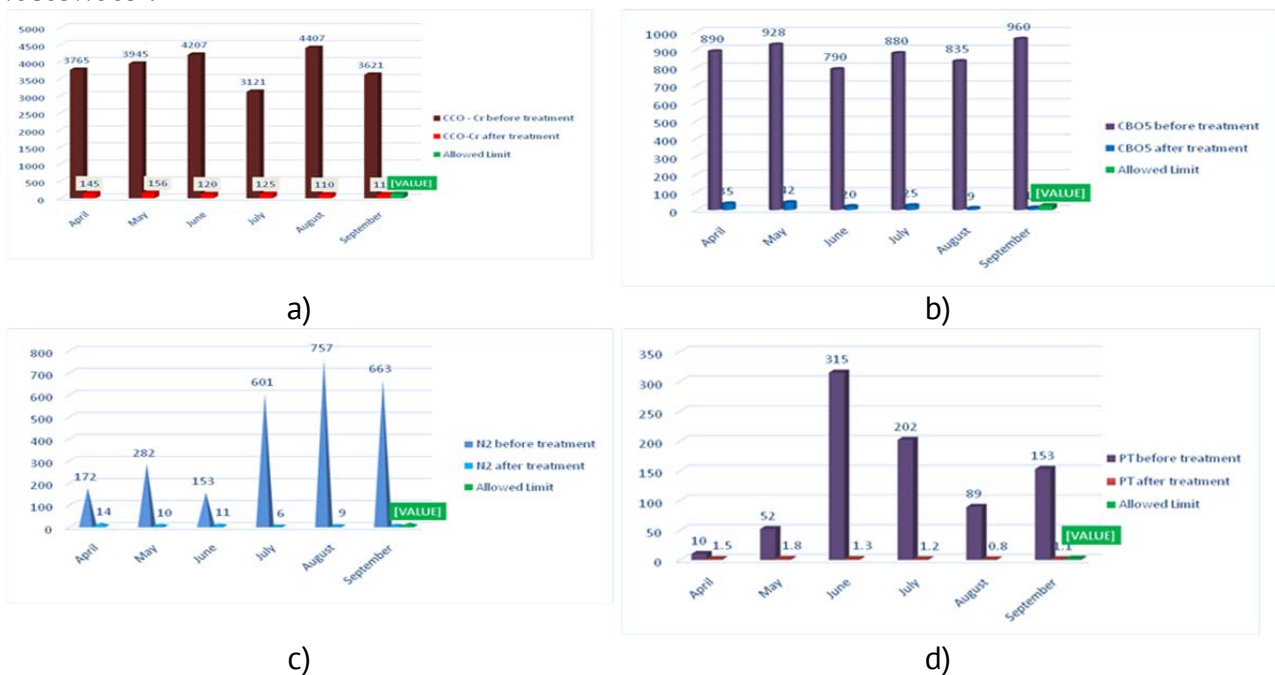


Figure 2. Control results of CCO-Cr index (a), CBO_5 index (b), total nitrogen (c) and total phosphorous (d) in wastewater analyzed

Conclusions

In the designing of industrial treatment plants, the knowledge of water characteristics is the key factor as well as in the case of urban treatment ones. Among the main noxious substances of industrial wastewater are organic substances (expressed by CBO_5), substances in suspension, toxic substances, heavy metals etc. Anaerobe treatment is a widely used method to treat the effluent of milk and cheese processing factories. The anaerobe/aerobe combined treatment of the effluent from dairy and cheese factories has important advantages regarding the complete aerobe treatment, especially for the following benefits: a positive energy balance, reduced production of (bio) mud, and space demands significantly reduced. The recent development of high anaerobe reactors (HAR) and that of aerobe reactors (air transport) permit the extremely compact design of effluent treatment plant in view of complying with the strict quality requirements of surface water.

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INFLUENCE OF OILSEED GROATS ADDITION ON THE YIELD OF MINCED MEAT PRODUCTS

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Abstract. This study includes investigation of the influence of oilseed groats on the thermal treatment yield of the final product – “mici” from sheep and poultry meat (70:30). 7% groats of walnut, pumpkin and sesame seeds and 2% wheat fibers were used. There has been determined water content, fat, protein, water retaining capacity and fat retaining capacity, emulsifying capacity of oilseed groats, thermal treatment efficiencies on the final product. Sensorial characteristics of the groats were studied. As the result it was established that the addition of groats in the “mici” of sheep and poultry meat reduces the mass loss after heat treatment.

Keywords: *oilseed groats, thermal treatment effect, sheep meat, poultry meat, sensorial characteristics, physico-chemical characteristics, functional-technological characteristics*

Introduction

The scientific basis of the modern food production strategy is: the search for new resources of essential food components, the use of non-traditional basic raw materials, the development of new advanced technologies to increase the number of food products and the biological value of the product with desired properties [1].

The groats are the most important products of the vegetable oils industry. The nutrition value of the groats is represented by a high protein content (35-50%), mineral substances (6-7%), vegetable fats (5-40%), carbohydrate residues, and this makes its use in the manufacture of food products [2].

The objective was to establish physico-chemical properties of minced meat products with addition of walnuts groats, groats of pumpkin seeds, groats of sesame seeds and wheat fibers and determination of the impact of the oil seeds groats on the efficiency after thermal treatment.

Materials and methods

The researches were performed at the Food Biotechnology Laboratory of the Public Institution “Scientific-Practical Institute of Horticulture and Food Technologies” and at the Department of Food Products Technology, FFT, TUM.

The sheep meat was procured from “Technical Support Enterprise from Bardar” Jsc and the poultry meat from the “Floreni” Jsc, from which the minced meat was prepared with nut groats addition, obtained in the FPT department, pumpkin seeds groats and sesame seeds

groats, both purchased from “Rozavena” Doctor Oil” Ltd and with the addition of wheat fibers, kindly provided by “Ingreda” Ltd.

Sheep and poultry meat in a ratio of 70:30 was replaced with 7% of groats and 2% of wheat fibers. Four types of semi-prepared meat products from minced sheep and poultry meat with addition of wheat fibers were prepared based on the previously developed recipes. The obtained semi-prepared meat products from minced sheep and poultry meat have been stored at $t=0...+4^{\circ}\text{C}$, $W_{\text{air}}=75...78\%$, $\tau=5$ days.

The samples of groats were studied on water content [3], fat [4], protein [5] and water retention capacity, fat retention capacity, emulsifying capacity [6, 7], appearance, smell, color and taste [8] and thermal treatment yield of the final product: semi-prepared meat products of minced sheep and poultry meat with the addition of groats and wheat fibers [9].

Results and discussions

Table 1 presents the organoleptic, physico-chemical and functional-technological characteristics of walnut groats, pumpkin seed groats and sesame seed groats. The protein mass fraction (Table 1) in walnut groats is 17,7% lower than in the pumpkin seed groats and 27,86% than in sesame seed groats. The highest fat content is found in walnut groats, 25,29% more than in pumpkin seed groats and 20,52% than in sesame seed groats. The content of protein and fat in groats was influenced by the initial fat and protein content of the seeds and by the extraction method.

The functional-technological characteristics of the groats Table 1 make it possible to recommend it for usage in food industry as binding ability components due to water retention capacity, to fat retention capacity and to emulsifying capacity.

Table 1

Quality parameters of the vegetable additives						
Nº	Type of groat Parameter	Walnut groats	Pumpkin seed groats	Sesame seed groats		
Organoleptic characteristics						
1.	Appearance	Fine particles without the presence of moldy particles or foreign substances				
2.	Smell	Characteristic for walnut, no foreign smell.	Characteristic for pumpkin seeds, no foreign smell.	Characteristic for sesame seeds without foreign smell.		
3.	Color	Light yellow to light tan.	Yellow-green to light brown.	White to light brown		
4.	Taste	Characteristic for the core of walnut, with no foreign taste.	Characteristic for the pumpkin seed, with no any foreign taste.	Characteristic for sesame seeds without foreign flavors.		
Physico-chemical and functional-technological characteristics						
1.	Water content, %	9,0	9,0	9,0		
2.	Protein, %	26,92	44,62	54,78		

Table 1 (continuation)

3.	Fat, %	35,20	9,91	14,68
4.	Water retention capacity, %	28,6	30,0	21,4
5.	Fat retention capacity, %	11,6	15,6	11,6
6.	Emulsifying capacity, %	55,3	61,1	64,3

The technology of the semi-prepared meat products made of sheep and poultry minced meat includes chopping of sheep and poultry meat into a grinder machine with diameter of the mesh holds of 2-3 mm, sheep and poultry meat addition in the agitator, walnut groats, pumpkin seed groats, sesame seed groats, salt, sodium bicarbonate, fresh garlic, grounded black pepper, grounded red pepper, pre-hydrated wheat fibers in ratio of wheat fibers: water 1:5 for 60 minutes with water temperature +20...+25 ° C and drinking water, mixing of the composition to a homogeneous mass, shaping of the semi-prepared meat products, packing and storage in chilled or frozen form.

Other technological problems associated with lowering fat content include reduction of particle-to-heat bonding, reduced succulence, crumbling, excessive juice removal and reduced shelf-life. The fat content of semi-prepared meat products can be reduced by replacing the fat with water, adding carbohydrates and / or proteins or using functional ingredients.

Replacing fat with water reduces fat content, but results in concomitant changes in texture and water retention capacity - so it is limited to low values.

The addition in low-fat and protein-reduced minced meat products of functional ingredients from various vegetable and animal sources as fillers, binders, emulsifiers or diluents can improve the ability to retain / bind water and modify the texture. It also increases the yield of the finished product and reduces cooking losses.

The heat treatment yield represents the mass loss due to heat treatment Eq. (1) [9].

$$R = m_1/m_0 \times 100 \% \quad (1)$$

where: R – thermal treatment yield, %;

m_1 – mass of the heat treated sample, g;

m_0 – sample mass in the raw state, g.

Having similar properties to soybean flour (which is widely used in the industrial manufacture of minced meat products), being rich in protein and starch, oleaginous groats have been proposed and tested in this work for use in low fat meat preparations.

The results shown in figure 1 show that the incorporation of the groats in the minced meat of sheep and poultry reduces weight loss on heat treatment and thus leads to increased yield of the finite product of the small ones. The addition of 7% of groats and 2% of wheat fibers reduces mass losses compared to the control sample, which is 6,1% for nut groats, 20,3% for samples with the addition of pumpkin seedgroats and 6,9% for samples with the addition of sesame seed groats. Samples of sheep and poultry minced meat (control sample) after heat treatment showed a mass loss of about 36,0%.

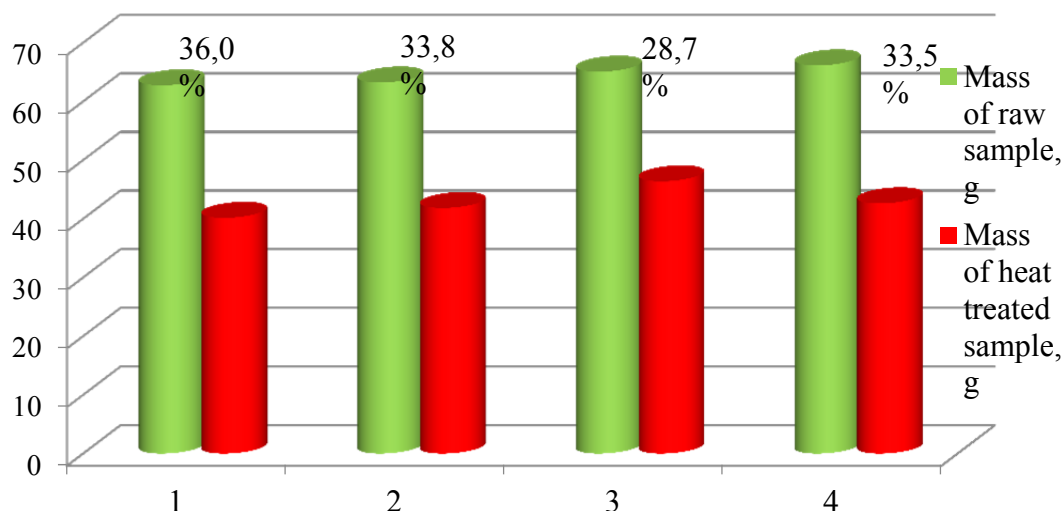


Figure 1. The yield of minced meat semi-prepared meat products after thermal treatment.

1 – „mici” from sheep and poultry meat (70:30) –control sample; 2 – „mici” from sheep and poultry meat (70:30) with 7% walnut groats and 2% wheat fibers; 3 – „mici” from sheep and poultry meat (70:30) with 7% added pumpkin seed groats and 2% wheat fibers; 4 – „mici” from sheep and poultry meat (70:30) with 7% sesame seed groats and 2% wheat fibers

Conclusions

The additional use of 7 % oil seeds goats and 2 % wheat fibers in minced meat semi-products impacts positive on the sensorial properties of final product such as appearance, smell, taste by softness and succulence of the finished product.

The physico-chemical analysis results that seed groats and wheat fibers influence on water retention capacity at 30 % for seed groats and 62 % for wheat fibers. Capacity of walnuts groats, groats of pumpkin seeds, groats of sesame seeds and wheat fibers to hold water increase volume and weight of the meat products, thus improving quality characteristics. As a result, the heat treatment yield decreased to 20% comparative with the control sample.

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DRYING KINETICS OF APRICOTS KERNELS

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Abstract. In this paper, we proposed convective and combined methods for drying wet kernels of apricot stones. Kernels of apricot stones are a very ambiguous food product, during their heat treatment in them occurs not only the loss of mass due to the removal of moisture, but also the loss of mass due to biochemical changes occurring at high temperatures. It was experimentally established that the drying process should be carried out in two stages: the first stage lasts until the critical moisture content of 110 % (by total weight of solids) is reached and it should be implemented by convective energy supply (100 °C). The second stage lasts until the equilibrium moisture content of 30 % is reached, using a combined energy supply (convention + UHF) with the strength of the electromagnetic field $E = 1.8 \cdot 10^4 \text{ V}\cdot\text{m}^{-1}$.

Keywords: *air-solar drying, drying curves, drying speed curves, combined method, kinetic, kernel of apricot stone*

Introduction

Everyone is looking forward to the summer, waiting for apricots. Apricot is a delicious and healthy fruit is a favorite fruit of many children and adults, and apricot seeds, being a very ambiguous food product, are thrown away without even thinking about their taste.

Apricot stones are a healer of human cells. All because their kernel contains a rare vitamin B₁₇, which includes cyanide substance. When cyanide enters the body, cancer cells either die or are healed [1]. In stone kernel, it is concentrated from 35 to 60 % of non-drying fatty oil. Its chemical composition is very similar to peach oil. The composition is dominated by oleic and linolenic fatty acids. The substance contains a low acidity and a minimum degree of viscosity. Also kernels contain: glucoside amygdalin, emulsin, lactase and hydrocyanic acid.

In addition to healing cancer cells, the apricot kernels are the most effective remedy for bronchitis, whooping cough and nephritis. Apricot kernels are useful and due to the fact that they help to fight the human body against various parasites, including worms. In this case, the kernel should be eaten raw. In addition, people with cardiovascular problems consume apricot seeds. Kernels can be eaten raw, dried or roasted, but not more than 20 grams at a time. 100 grams of apricot kernels contain more than 450 kcal [1 - 3].

Apricot kernels are the favorite delicacy of people who want to gain a couple pounds. After all, kernels contain a lot of vegetable oil, which is well absorbed in the

human body. In addition, many athletes use the kernel in food, because they provide huge amounts of energy.

Apricot kernels are very often used in medicine. Even in Ancient China, healers used apricot kernel oil to treat skin and joint diseases. In medicine, apricot kernel oil is also used for massage, because it is very well absorbed by human skin. In addition, the oil is added to shampoos, which contribute to the fight against dandruff. In many cosmetic companies, oil is used as an additive for natural creams and scrubs.

Apricot kernels are widely used in cooking in the form of powders, which are added into glazes, ice cream, yogurts, creams and other dairy products.

Materials and Methods

The purpose of this work was an experimental study of the drying process of the kernels of the apricot stones by convective and combined - convection + UHF (high frequency currents) methods.

In general, air-solar drying is applied on unsuitable open areas, this way the apricot stones clutter the territory of factories, raw sites, creating unsanitary conditions. The use of this method of drying, due to the processing time reduces kernels' quality. It is important that during the drying process, the properties of the product are preserved and improved; they play a decisive role, determining its qualitative indicators.

In order to intensify the drying process, increase economic efficiency and improve environmental conditions was proposed the drying of moist kernels of apricot stones by convective and combined (convection + UHF) methods.

The investigations were carried out on the experimental setup already described [4 - 7]. The drying was performed by using moist apricot stones of «Krasnosciokii» variety with the moisture content $U^c = 146\%$.

To record the weight loss in the studies, a mechanical scale of the type BHL – 200 was used. The speed of air supplied to the drying chamber was maintained constant automatically and was $1.1 \text{ m}\cdot\text{s}^{-1}$. The air parameters were determined up to the air heater (initial temperature t_0 and relative humidity ϕ_0) and after the air heater (t_1).

In the first part of the study, were studied the kinetics of convective drying at drying agent temperatures of 60, 70, 80, 90 and 100°C. Mass loss was measured every 5 minutes, dehydration was conducted until equilibrium humidity of 30 %.

Figure 1a shows the drying curves $U = f(\tau)$ of apricot kernels. As it can be seen from the drying curves, the drying process duration at a temperature of 60°C was 620 minutes, and for a temperature of 100°C, 220 minutes, decreasing by 2.85 times.

Figure 1.b shows the drying rate curves, which are typical curves having a warm-up period, the 1st and 2nd drying periods [8, 9].

Based on the experimental data, the drying rates in the first period were calculated. Table 1 shows the drying temperature, t_1 , °C; critical humidity, u_{cr} , %; drying rate in the 1st period, $\left(\frac{dU}{d\tau}\right)$, $\% \cdot \text{s}^{-1}$, the drying rate constants of the 1st, K_1 , and the 2nd, K_2 , periods, warm-up time, $\tau_{\text{warm-up}}$, min, and drying time of the 1st, τ_1 , min, and 2nd, τ_2 , min, periods. In the second part of the experiment, was studied the influence of high-frequency heating in combination with the convective method of energy supply on the kinetics of drying under various regimes of electromagnetic field strength $E = 8.75 \cdot 10^3 \text{ V}\cdot\text{m}^{-1}$ and $E = 1.8 \cdot 10^4 \text{ V}\cdot\text{m}^{-1}$.

Table 1

Experimental data on the drying kinetics of apricot stones by the convective method									
N ^o	t ₁ , °C	U _{cr} , %	$\left(\frac{dU}{d\tau}\right)^1$, %·s ⁻¹ ·10 ³	K ₁ , %·m ⁻² ·s ⁻¹	K ₂ , s ⁻¹ ·10 ⁶	T _{warm-up} , min	T ₁ , min	T ₂ , min	T _{total} , min
1	60	90	6.46	58.6	1.6	100	240	280	620
2	70	90	8.62	63.5	3.2	89	184	232	505
3	80	95	11.18	65.9	4.0	78	158	169	415
4	90	95	15.74	84.35	4.98	59	122	137	318
5	100	95	23.61	107.1	5.6	35	91	94	220

The results of the studies are shown in Figure 2a, b in the form of drying curves and drying rate curves.

As can be seen from the graphs, the imposition of high-frequency electromagnetic fields in combination with the convective method greatly intensifies the drying process.

At the same time, as the intensity of the electromagnetic field increases, the period of drying process for different temperatures decreases. Thus, at a temperature of 60°C and an electromagnetic field strength of $8.75 \cdot 10^3 \text{ V} \cdot \text{m}^{-1}$, the drying process time to 30 % humidity was 410 minutes, and at $1.8 \cdot 10^4 \text{ V} \cdot \text{m}^{-1}$ it was 370 min. - decreased by 40 min.

If we compare the dehydration process at minimal temperature and intensity of the electromagnetic field ($t = 60^\circ\text{C}$ and $E = 8.75 \cdot 10^3 \text{ V} \cdot \text{m}^{-1}$), with the maximum temperature and field intensity ($t = 100^\circ\text{C}$ and $E = 1.8 \cdot 10^4 \text{ V} \cdot \text{m}^{-1}$), the dehydration time from 146 % to 30 % decreased by 2.8 times.

Reducing the duration of the apricot stones drying is due to a more intensive release of heat per unit volume of kernels with an increase in the intensity of the electromagnetic field

In the case of high-frequency heating of dielectrics and semiconductors, heating is uniformly distributed over the entire volume due to the arising polarizing effects.

Therefore, the speed of the process of drying the kernels using UHF rapidly increases as the material warms up and, after reaching the maximum value, begins to decrease. In this case, the greater the intensity of the electric field, the shorter the time of increase and subsequent decrease in the drying rate, i.e. 1 st and 2 nd periods.

When the temperature of the drying agent 60 °C (Figure 2b) and electromagnetic field strength $E = 8.75 \cdot 10^3 \text{ V} \cdot \text{m}^{-1}$ maximum rate was $0.00741 \text{ \%} \cdot \text{s}^{-1}$, and at the same temperature, and $E = 1.8 \cdot 10^4$ it was $0.00873 \text{ \%} \cdot \text{s}^{-1}$, i.e. increased by 17.8 %. With increasing temperature, the value of the maximum rate of the drying process also increases. If the maximum rate is $0.00741 \text{ \%} \cdot \text{s}^{-1}$ at a temperature of 60 ° C and $E = 8.75 \cdot 10^3 \text{ V} \cdot \text{m}^{-1}$ (Figure 2b), then at the temperature of 100°C (Figure 2b) and with the same intensity, the rate was $0.0147 \text{ \%} \cdot \text{s}^{-1}$, i.e. increased 2 times.

Results and discussion

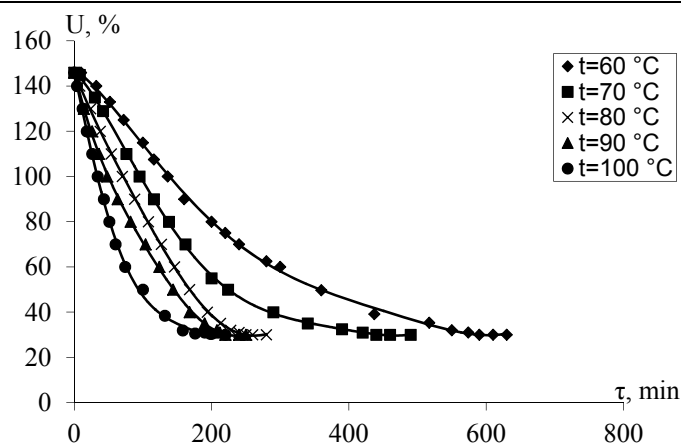
Taking into account [4 - 8], it can be assumed that, judging by the nature of the drying rate curves for apricot kernels, the physico-mechanical and physico-chemical forms of the bond of moisture to the material are inherent.

As for the convective method, the kinetic characteristics of the drying process were calculated for the combined method of convection + UHF for different field strengths, the values of which are given in Table 2.

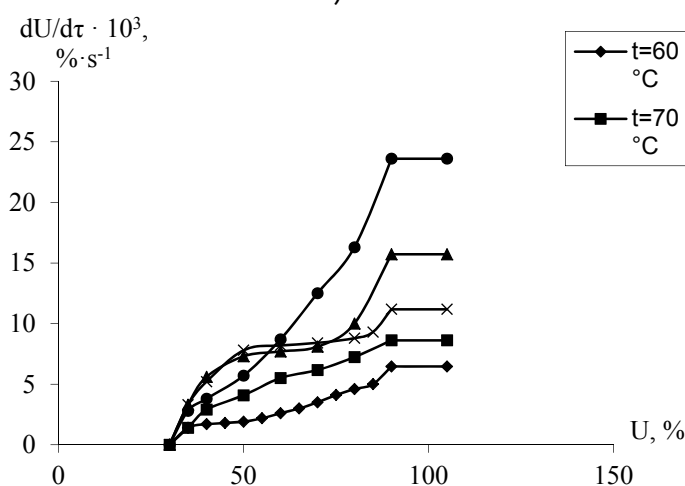
Table 2

**Experimental data on the drying kinetics of apricot kernels
in a combined method - convection + UHF**

N ^o	t ₁ , °s	U _{cr} , %	$\left(\frac{dU}{d\tau}\right)^{1,}$ %·s ⁻¹ ·10 ³	K ₁ , %·m ⁻² ·s ⁻¹	K ₂ , s ⁻¹ ·10 ⁶	T _{warm-up} , min	T ₁ , min	T ₂ , min	T _{total} , min
The electric field strength E = 8,75·10 ³ V·m ⁻¹									
1	60	70	7.41	67.2	3.53	80	235	85	410
2	70	69	8.93	65.8	4.09	56	223	61	340
3	80	69	9.59	56.6	4.65	28	193	59	280
4	90	70	11.61	62.2	5.86	25	187	48	260
5	100	70	14.72	76.8	6.45	17	165	33	215



a)



b)

Figure 1. The drying curve (a) and drying rate (b) of kernels of apricot stone by convective energy supply

For the 2nd period the drying rate constant K_2 at temperature 60°C has changed with an increase in electromagnetic field intensity from $3.53 \cdot 10^{-6} \text{ s}^{-1}$ to $4.04 \cdot 10^{-6} \text{ s}^{-1}$ which represents 14.4 %. The influence of temperature from 60 °C to 100 °C led to an increase of the drying rate constants from $3.53 \cdot 10^{-6}$ to $6.45 \cdot 10^{-6}$ at $E = 8.75 \cdot 10^3 \text{ V m}^{-1}$, i.e. by 82.7 % , and at $E = 1.8 \cdot 10^4 \text{ V m}^{-1}$, the increase of K_2 from $4.04 \cdot 10^{-6} \text{ s}^{-1}$ to $9.55 \cdot 10^{-6} \text{ s}^{-1}$ was 136 %.

These values show that the effect of UHF on drying is significant, especially in the 2nd period. This is obviously due to the influence of UHF on the structure of the product and on the state of water in the material.

The obtained results of studies of the drying process of apricot stone kernels in the convective heat input (Figure 1) and the combination of convective heat supply with heating in the electric field of high frequency currents (Figure 2) showed that the kernels are a complex organic product.

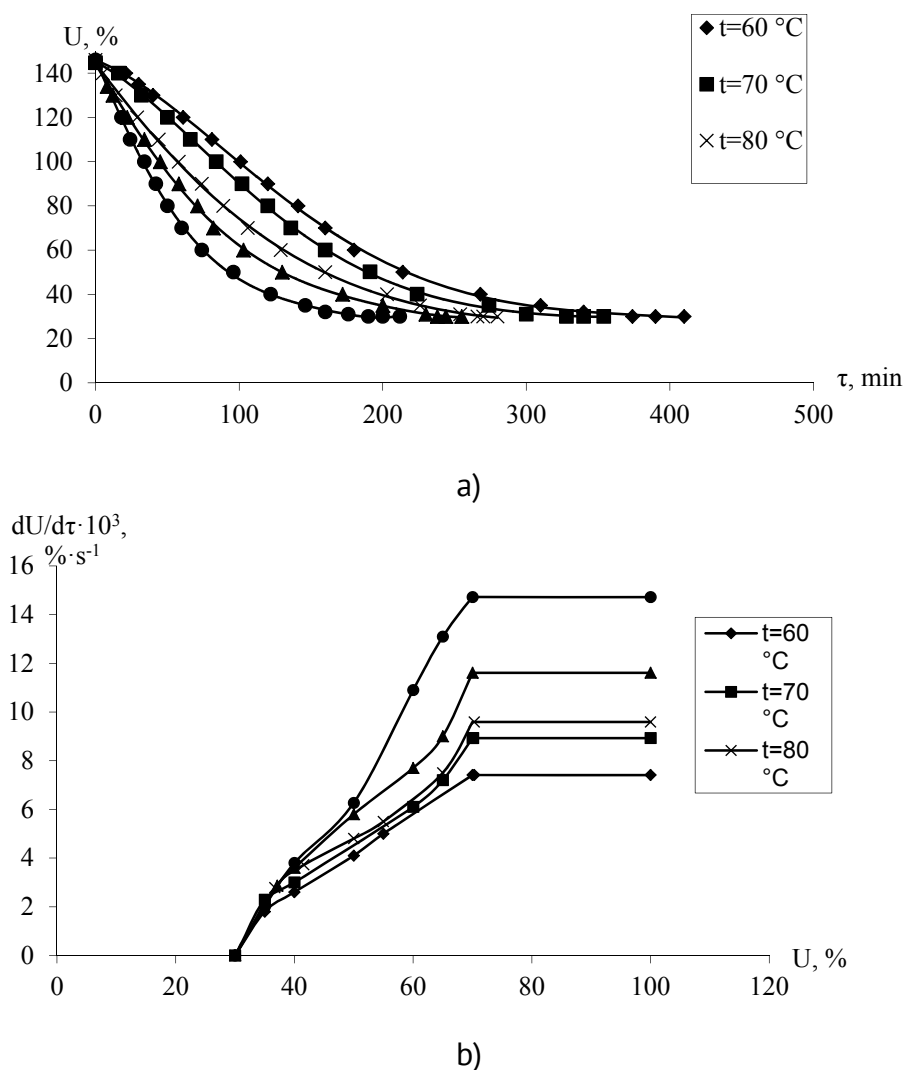


Figure 2. The drying curve (a) and drying rate (b) of kernels of apricot stone in a combined way at an electromagnetic field with the strength $E = 8.750 \text{ V} \cdot \text{m}^{-1}$

During the heat treatment process, in the kernels of apricot stone the mass loss occurs not only due to the removal of moisture (which is typical for most wet materials), but also due to biochemical changes occurring in them at high temperatures. Therefore, the rationale for the drying method for such products as kernels of apricot stone should be

carried out considering these features. Studies have shown that the most prolonged is the drying process with convective heat supply. Thus (Figure 1), the duration of dehydration at a temperature of the drying agent 60 °C was 620 minutes and at 100 °C - 215 minutes. With a combined power supply and at the same temperatures and field strength $E = 1.8 \cdot 10^4 \text{ V} \cdot \text{m}^{-1}$, the drying time is 365 and 145 min, respectively, i.e. it decreased more than 2.5 times. If we compare the drying time at the minimum temperature of the convective method with the maximum values (100 °C and $E = 1.8 \cdot 10^4 \text{ V} \cdot \text{m}^{-1}$) of the combined method of dehydration of apricot stone kernels, then the process intensifies more than 3 times.

The application of various drying methods has an effect on the nature of the ongoing process. So, with convective heat input, the curve of drying speed includes two periods - a period with a constant speed and a period with a falling rate [2 - 4].

As the Figure 1 shows, with a convective heat supply, the drying rate increases with a drying agent temperature from $0.0065 \text{ \%} \cdot \text{s}^{-1}$ to $0.0236 \text{ \%} \cdot \text{s}^{-1}$. With the use of combined energy supply, the intensity of dehydration increases in proportion to the temperature of the hot air and the intensity of the electromagnetic field. Thus, at a temperature of 100°C and $E = 1.8 \cdot 10^4 \text{ V} \cdot \text{m}^{-1}$, compared with a temperature of 60°C and $E = 8.75 \cdot 10^3 \text{ V} \cdot \text{m}^{-1}$, it increased almost 3 times.

Conclusions

From the carried out studies, it can be seen that high-frequency heating in combination with a convective energy supply method is more promising for the process of dehydration of apricot stone kernels. The drying process is best carried out, as studies have shown, in two stages. In the first stage, prior to obtaining a critical moisture content 110 % of the kernel, a convective energy supply (100 ° C) should be carried out, in the second stage, using a combined energy supply (convention + UHF) at an electromagnetic field strength $E = 1.8 \cdot 10^4 \text{ V m}^{-1}$.

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CONTRIBUTION OF FORCEMEAT COMPONENTS ON THE PRODUCING OF RAW-DRIED SALAMI WITH STARTER CULTURES

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Abstract. This work deals with the analysis of the influence of forcemeat composition (meat/lard ratio, dextrose, dietary fiber) on the producing of raw-dried salamis. The costs of study on an industrial scale were reduced using experiment in the linear approximation. A high level of meat/lard ratio directly and indirectly accelerates the drying process. A-posteriori was found that the optimal amounts of dextrose in the salami's recipe correspond to the center of the experimental matrix. A higher fiber content helps stabilize the pH value at the end of the fermentation process. Fibers directly accelerate the drying of the product and ultimately improve its quality.

Keywords: *dextrose, dietary fibers, meat/lard ratio, raw-drying, salami, starter cultures*

Introduction

Quite often, there is a need to modify the recipes of raw-dried and smoked salamis. These recipes are changed by "trial and error" method, using the knowledge and experience of technologists. Such an approach does not guarantee obtaining a product of a desired quality, especially when replacing at least some of the main ingredients. Technologists of a small enterprises should adapt "standard" recipes because of different quality indicators of entry raw materials, so that the obtained product meets the specified requirements [1]. Composition of forcemeat mixture represents best controlled input factor. Thereby, the quality of the products firstly is a function of the forcemeat composition, secondly, of the technological process parameters [2]. This work deals with study of influence of the forcemeat components on the physico-chemical characteristics of the fermented salami during the producing process.

Materials and methods

For the development of experimental and control samples of raw-dried salami, pork meat was used, which was obtained by intensive fattening technologies in pig breeding complexes in the Republic of Moldova. As a control (basic) formulation, the recipe of the raw-dried salami type "Kachchatori" was adopted. Its forcemeat recipes consisted of chilled low-fat pork (60%), frozen pork trimming (15%), frozen fat bacon (25%), nitrite salt, dextrose, skimmed milk powder, black and white pepper ground, food fibers Unicell WF 200. ("InterFiber" Sp. z.o.o., Poland).

To accelerate and regulate the fermentation process, as well as subsequent maturing and drying of salamis, the starting culture SM-194 (Chr. Hansen, Denmark) was used [3]. The

starting culture included the following types of microorganisms: *Pediococcus Pentosaceus*, *Lactobacillus Sakei*, *Staphylococcus Xylosus*, *Staphylococcus Carnosus*, *Debaromyces Hansenii*. Preparation of experimental and control samples of raw-dried salamis was carried out in the production conditions. The technology included traditional operations: cutting, deboning, tendon removal, refrigeration (cooling, freezing), chopping, draining and compaction of crushed meat.

The forcemeat was made on the meat-cutter at a temperature from -5°C to -1°C in order to obtain a structure with the grains of 6-8mm in diameter, then other ingredients according to the recipe were added. Starting culture SM-194 in the amount of 10 grams per 100 kg of forcemeat was preliminarily diluted in 300 ml of cold water and introduced into the bowl of the cutter in the last turn. For the filling with forcemeat of a natural shell with a diameter of 44-46 mm special syringe was used. Fermentation, maturation and drying were performed in the Friulinox AS EN2 clime chamber ("Friulinox", Italy) – Figure 1. The fermentation process began with tempering and shrinkage for 5-8 hours at a temperature of $22-24^{\circ}\text{C}$ and relative humidity of 95-98%. Then followed, strictly speaking, fermentation process, which was carried out at $22-24^{\circ}\text{C}$ and relative humidity of 85-90%, during 2-3 days until the pH of the forcemeat reached 4.8 - 4.9. The temperature and the humidity of the air in the climatic chamber were gradually reduced, respectively, to $18-20^{\circ}\text{C}$ and to 82-84%.



Figure 1. Initial state of salami sticks

The final stage of drying was performed at relative humidity of air 72-74%, $13-14^{\circ}\text{C}$, and the speed of air movement equal to 0.1-0.2m/s. The total weight loss at the end of drying was 40-45%. Four experimental compositions and one control composition of raw-dried salamis were studied. In the finished product, water activity (a_w), humidity (W), pH and total fat content were determined by means of non-modified standard method [4].

Results and discussion

The formulations of the investigated raw-dried salamis were elaborated on the basis of the following considerations. The meat content was postulated as main factor influencing both the technological process and the consumer properties of the product. At the same time, the technology for producing raw-dried salamis assumes the use of lard, which, in turn, should lead to the introduction of an additional entry factor, respectively, to complication of study and increasing its cost. Therefore, the ratio of the meat mass to the lard mass in the recipe, $m_{\text{Meat}}/m_{\text{Lard}}$, was introduced as the main factor of influence.

Table 1

Formulation of control probe classical salami type "Kachchatori"	
Basic ingredients	per 100kg
Pork meat (back)	60
Pork meat (low-fat trim)	15
Frozen lard	25
Sodium nitrite	2.4
Sugar	0.2
Black pepper	0.1
White pepper	0.1
Fiber Unicell WF 200	1
Skimmed-milk powder	1
Starter culture SM-194	0.02

The recipes of raw-dried salamis contain about 1% of milk powder, which in turn is half composed of milk sugar (lactose). Thus, even without additional dextrose administration, the starting content of lactose in all samples will be about 0.5 kg per 100 kg. Such a content of sugars, according to the data of some authors [5, 6], is insufficient to provide the necessary activity of starter cultures. At the same time, this amount of nutrient medium cannot be neglected when interpreting the results of the effect of sugars on the fermentation process. Therefore, planning the experiment, we assumed that the total amounts of sugar in the recipes, should differ by not less than 1.5 times, also taking into account lactose, introduced with skimmed milk powder. The content of the structure-forming food additive, dietary fiber "Unicell WF 200", was the third chosen *a priori* influencing factor. Since in the control sample the content of dietary fiber was 1%, we can to assume, what this value is equal to the geometric center of the experiment. The minimum and maximum levels of dietary fibers content in the experimental samples were set at 0.5 and 2.0 as in comparison with the control (Table 1).

Two-Level, Three Factor Fractional Experiment FFE 2^{3-1} , (which is a "half-reply" of complete three-factor experiment CFE 2^3) was realized for obtaining of quality product according to good production practices. Its realization presumes deducing the following equation:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 \quad (1)$$

in which: Y – is measured parameter (response); β_0 – response in the center of experiment; $\beta_1, \beta_2, \beta_3$ – influence coefficients of separated presumably independent factors X_1, X_2 and X_3 [7].

Table 2

Experiment-planning matrix in the encoded and real coordinates.

Factor 1		Factor 2		Factor 3	
x_1	Meat / Lard	x_2	Dextrose (kg/100kg)	x_3	Fiber (kg/100kg)
+	6...9	+	0.30...0.50	+	1.75...2.00
+	6...9	-	0.05...0.10	-	0.50...0.75
-	2...3	+	0.30...0.50	-	0.50...0.75
-	2...3	-	0.05...0.10	+	1.75...2.00

The kinetics of water activity in the salami samples were studied. Obtained data, interpreted as $W_A = f(\tau)$ corresponded well to the linear model (Figure 2), since the values of the credibility of the approximation, R^2 , are very high for all samples: 0.948 for the control and 0.968...0.986 for experimental recipes.

The values of the coefficients at X show the steepness of the straight line $W_A = f(\tau)$, that is, the rate of drying of the salami is quantified by that coefficients. It is clearly seen that the steepest slopes have dependencies for the first and fourth samples, which corresponds to the upper level of factor X_3 . Thus, the decrease in water activity in the sample of salamis during the fermentation process directly depends on the content of added dietary fiber. For the most reliable estimation, a regression equation (2) was obtained:

$$|\Delta W_A / \Delta \tau| = 0.00435 + 0.00030 \cdot X_1 - 0.00010 \cdot X_2 + 0.00035 \cdot X_3 \quad (2)$$

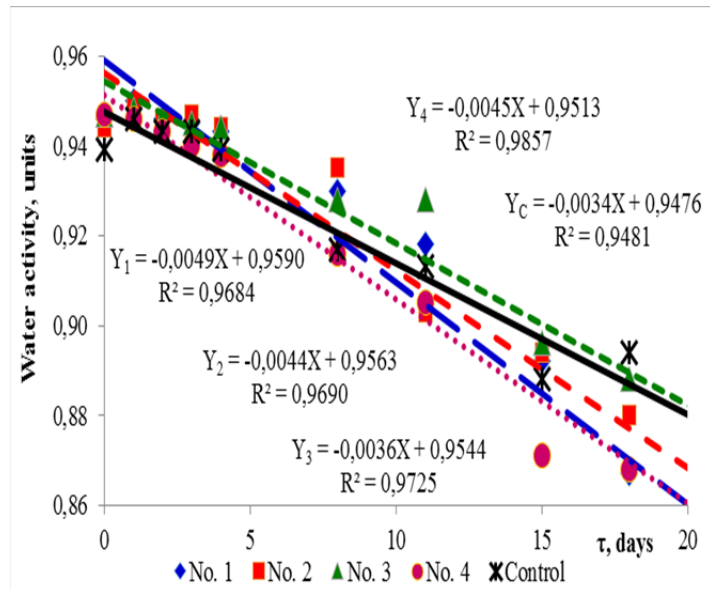


Figure 2. Changes in water activity, W_A , of the salami samples

Equation (2) shows that the drying rate in the product actually grows most noticeably with an increase in the content of dietary fiber (X_3) and for a larger value of relationship m_{Meat}/m_{Lard} (X_1) too. The addition of dextrose to the forcemeat formulation contributes to a slight slowing down of the drying process (since the coefficient at X_2 has a negative value). Analysis of the kinetics of moisture reduction in samples of forcemeat (Figure 3) showed that the dependencies $H_R = f(\tau)$ have very high values of the credibility of the linear approximation. Reducing the humidity of all experimental samples is faster than in the control.

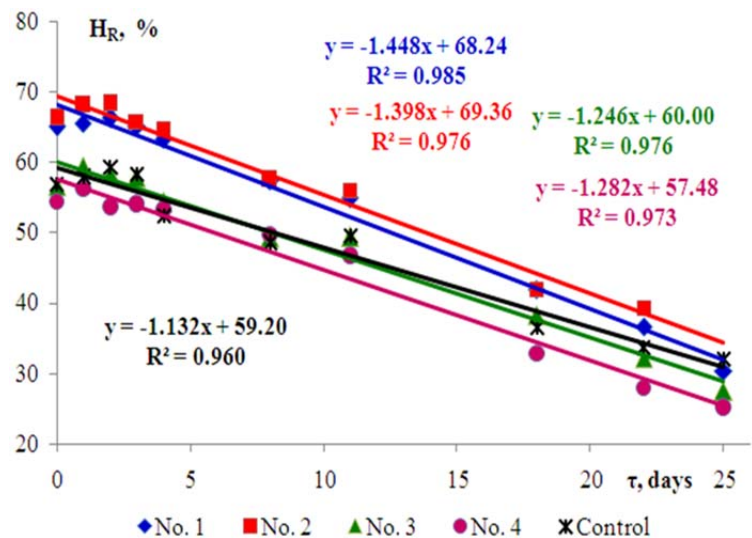


Figure 3. Linear kinetics of humidity changes

The regression equation (3) estimates influence of factors on the rate of humidity decrease:

$$\Delta H_R / \Delta \tau = 1.344 + 0.080 \cdot X_1 + 0.004 \cdot X_2 + 0.022 \cdot X_3 \quad (3)$$

Eq. (3) shows that the factor X_1 , and to a lesser extent factor X_3 , contribute to the decrease in humidity. The influence of factor X_2 is least significant, which also agrees with Eq. (2). The kinetics of fat content both in the samples under study and in the control sample obey linear dependences (Figure 4). Attention is drawn to the fact that the kinetics of samples with low fat (No. 1 and No. 2) are characterized by very high values of the credibility of approximation (0.982 and 0.990). This speaks for the higher reproducibility of analysis of the samples with a lower fat content.

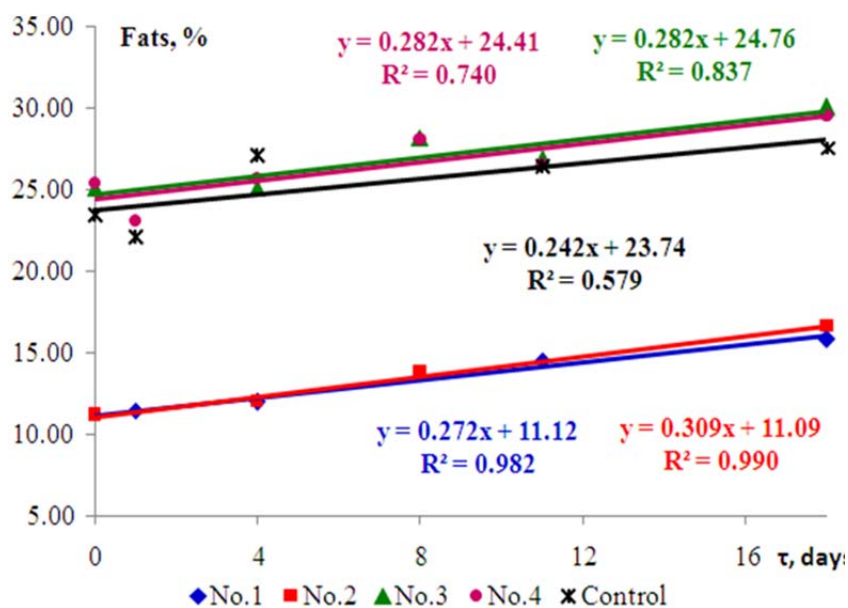


Figure 4. Variation of fats in linear correlation

Kinetics of the pH contain the sections that correspond to the processes of formation of low-molecular acids and their subsequent consumption during the fermentation process. The sharpest decrease in pH is observed for samples Nr.1 and Nr.3, which corresponds to high values of dextrose (X_2), and indicates more intensive fermentation processes in these samples (Figure 5). At the end of the process, on the 25-th day, the pH values are even more significantly different from the sample to the sample. Thus, the dextrose added to forcemeat affects the physicochemical characteristics of the product throughout the entire process.

To adequately assess the effects on pH changes, the corresponding models were obtained at the extremes of the function $\text{pH} = f(\tau)$:

$$\text{pH}_{3\text{rd_day}} = 4.95 + 0.01 \cdot X_1 - 0.11 \cdot X_2 + 0.04 \cdot X_3 \quad (4)$$

$$\text{pH}_{25\text{th_day}} = 6.33 + 0.35 \cdot X_1 + 0.07 \cdot X_2 - 0.25 \cdot X_3 \quad (5)$$

From equations (4) and (5) it is obvious that increasing the meat / lard ratio (X_1) increases $\text{pH}_{3\text{rd_day}}$ and $\text{pH}_{25\text{th_day}}$. Moreover, if at the beginning of the process the influence of factor X_1 is insignificant, then on the 25th day it is, on the contrary, the largest. Probably, the influence of relationship meat/lard on the product's pH is indirect. This is presumably being a consequence of the influence of this factor on drying speed. And already drying speed directly influence the process of fermentation and the pH values.

Dextrose has the strongest, lowering effect on pH on the third day and contribute to a very slight increase of this index in the 25th day. The presence of dietary fiber slightly increases the pH on the third day of drying, in fact during active fermentation, and on the 25th day it significantly reduces it. In general, dietary fibers inhibit the growth of pH throughout the fermentation process.

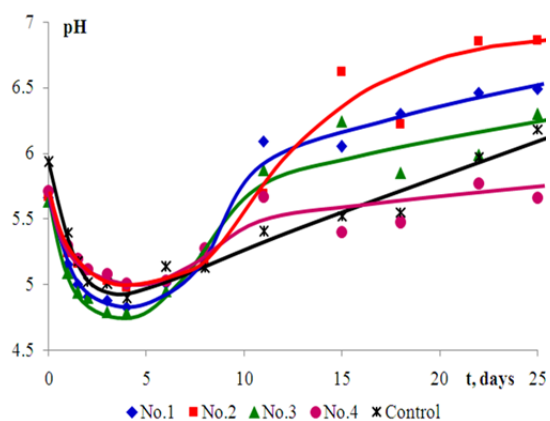


Figure 5. Changes of pH - during the raw-drying



Figure 6. Three weeks' age raw-dried salamis

3. Conclusions

1. Application of the FFE 2^{3-1} method allows quantifying the effect of the mince composition and the accompanying factors (fond) on the physicochemical and technological parameters of the raw-dried salamis in the process of manufacturing.
2. The use as an influencing factor of the ratio of the mass of meat to the mass of lard significantly simplifies the study without reducing the information content. High values of this factor directly and indirectly accelerates the drying.
3. Dextrose has a weak direct effect on the physicochemical parameters of the process of obtaining the product. Its effect on the pH of the samples, strong at the beginning of the fermentation process, almost does not manifest itself to the end of the drying process.
4. The low effect of dextrose on all responses of studied system allows to state that the amount of sugars in the center of the experiment corresponds to the optimal value, necessary in the production conditions.
5. The greater content of fibers contributes to the stabilization of pH values in the final product, and also directly accelerates its drying. Thus, the increased content of dietary fibers (about 2%) contributes to the acceleration of the producing process and the production of better quality raw-dried salamis.

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FORMATION OF MICROCAPSULES' BIOPOLYMERIC SHELLS: ELECTROCHEMICAL ASPECTS

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Abstract: Study of the formation of comestible bio polymeric shells of microcapsules is actually for food science. Electrochemical measurements were carried out using a working unit with digital multi-tester in ohm-metric mode as main device. The stages of formation of complex-coacervate shells, its neutralization and recharging, are accompanied by visible and informative changes in the resistance values. Dynamical electrochemical measurements can be proposed as the effective tool for investigating and controlling the processes of simple and complex coacervation of polymer electrolytes, taking place in the microencapsulation process.

Keywords: *microencapsulation, coacervation, water retaining agents (WRA), sodium sulfate, gelatin, alginate, electrochemistry*

Introduction

Microencapsulation is a relatively new method of preserving biological activity and targeted delivery of important bio compounds [1]. One of the areas of microencapsulation is the enrichment of products with polyunsaturated fatty acids. A feature of microencapsulation of lipids is that the formation of microcapsules occurs in an aqueous medium [2]. The microcapsules obtained in this way are extracted from the aqueous medium and introduced into food products. The most interesting and useful are the microcapsules, the shells of which consist of one or more comestible biopolymers, which are polyelectrolytes. There is a sufficiently large number of works devoted to the interaction of biopolymers in food systems [3...6]. However, the processes of electrochemical interaction of the components of the microcapsules' shells are not sufficiently clarified. So, an electrochemical study of the biopolymeric microcapsules' shell formation is actually and is of interest.

1. Materials and methods

Measurements of the resistance, pH, temperature, setting of the feed rate of the reagents and mixing were carried out using a working unit connecting the functions of the reactor and the control and measuring system (Figure 1). The main measuring instrument was the digital multi-tester "UT33C" (Shenzhen Sunkoo-Reid Electronic Co., China), used in the ohmmeter mode. The ohmmeter electrodes were rigidly fixed in the reactor to ensure reproducibility of the measurements. The pH of the solutions was adjusted by the addition of citric acid crystals. The pH and temperature were monitored throughout the experiment.

The introduction of the same volume of solutions and measurement of the system resistance was carried out with a periodicity of 60 seconds at a constant rate of mixing. The dependence of the resistance of the system under study was plotted in function of the real concentration of added reagents in the solution. In addition, the mole fraction of salt and the ionic strength of the solution were calculated.

2. Results and discussions

The MCs' shell obtained by coacervation of biopolymers from the aqueous solution are in a swollen "semi-liquid" state. This makes it difficult to separate the MCs from the supernatant liquid, which leads to their coalescence and destruction.

2.1. Water-absorbing agents for shells

The formation of the coacervate shell must be accompanied by its dehydration under the action of water-removing factors: anhydrous salts and alcohols. It should be noted that the term "desiccant" is not entirely correct for the process of coacervation occurring wholly in an aqueous medium in which the polymers are not in a "wet" state but in a swollen state. The role of the water-removing factor is to reverse the process of swelling of the coacervates. The water-withdrawing factors must ensure the process of syneresis (self-compression) of the gel, in other words, turn it into a more stable shell in the form of a dense thin film.

The drainage and water-withdrawal capacity can be estimated from the calculation of water's chemical absorption, calculated for 100 g of the corresponding reagent, the results of which are given in Table 1.

Salts of divalent metals (CaCl_2 , CuSO_4 , FeSO_4 , etc.) give the corresponding hydroxides in alkaline media and therefore cannot be used as water-removing agents at $\text{pH} > 7$. Carbonates and alkaline acetates are not suitable for acid media ($\text{pH} < 7$), where CO_2 or CH_3COOH will be released, respectively. These salts increase the pH of the medium during hydrolysis. The salts of Ca^{2+} , Cu^{2+} , Fe^{2+} and other polyvalent metals precipitate the anions of pectic substances and polyuronic acids. Metal ions have different effects on proteins, which are macromolecules with variable charge (zwitter-ions). Precipitation occurs when the protein molecules are negatively charged at $\text{pH} > \text{pI}$ [3, 4].

At first glance, this property should only contribute to the formation of a denser shell.

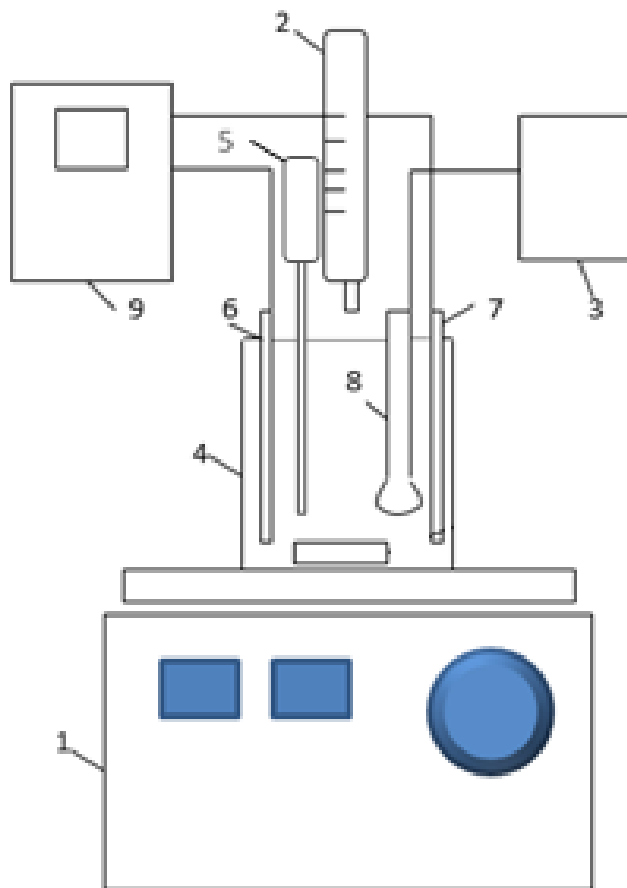


Figure 1. Installation. 1 - magnetic stirrer, heater; 2 - reagent dispenser; 3 - pH-meter; 4 - reactor; 5 - thermometer; 6, 7 - ohm-metric electrodes; 8 - pH-sensitive electrode; 9 - ohmmeter

Table 1

Water-absorption capacity of some common water-removing agents (WRA)

WRA formula	Hydrated WRA formula	Water per 100g of WRA, g.
CaCl ₂	CaCl ₂ · 6H ₂ O	97.3
CuSO ₄	CuSO ₄ · 5H ₂ O	56.2
FeSO ₄	FeSO ₄ · 7H ₂ O	82.9
Na ₂ CO ₃	Na ₂ CO ₃ · 10H ₂ O	170.0
Na ₂ SO ₄	Na ₂ SO ₄ · 10H ₂ O	126.8
C ₂ H ₅ OH abs.	C ₂ H ₅ OH · 5H ₂ O	195.7
CH ₃ COONa	CH ₃ COONa · 3H ₂ O	65.9

However, the interaction of metal ions with polyanionic macromolecules leads to neutralization of the negative charge of a high molecular weight poly-anion, and hence to the coagulation of macromolecules.

Thus, this can lead to an excessive strengthening of the biopolymer shell, which will lead to the destruction of the microcapsule. Anhydrous sodium sulfate is devoid of many disadvantages of named dehydrating agents. This salt is easy to clean and to regenerate, it absorbs a large amount of water, and doesn't undergo hydrolysis.

Introduction of the sodium sulfate into the system under study doesn't affect the pH value directly. In addition, sodium sulfate can be used at any pH values, generated by other components of the mixture.

This property is particularly important for microencapsulation, since pH has a decisive role in the formation of protein-polysaccharide shells of microcapsules [5, 6].

Due to its features and being used in food industry, sodium sulfate is the most suitable dehydrating reagent for formation of biopolymer shells of microcapsules.

Sodium sulfate forms recently described heptahydrate [7, 8]. This causes its unique solubility in function of temperature (Figure 2), probably, affecting its properties as a WRA.

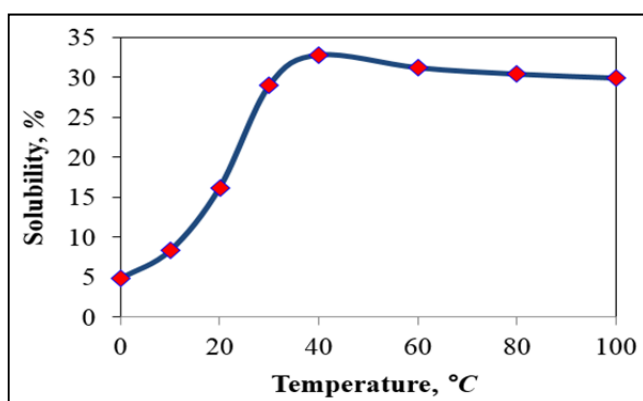


Figure 2. Unusual temperature dependence of sodium sulfate solubility [9]

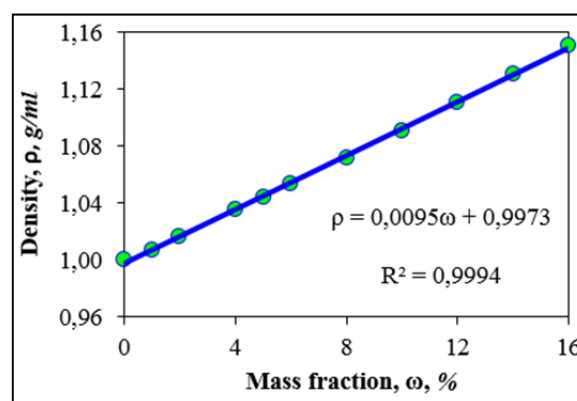


Figure 3. Densities of Na₂SO₄ solutions at 20°C

At the same time, in the temperature range from 10 to 35°C, which corresponds to the process of microencapsulation, this dependence is almost linear. To avoid precipitation of hydrates at 20...25°C, 16% sodium sulfate solutions were used. Advantage of this reagent is the good linear dependence of density in function of concentration (Figure 3).

2.2. Influence of sodium sulfate on the formation of the primary gelatin shell

When sodium sulfate is added to distilled water, three regions of resistance values are observed (Figure 4). When the concentration is increased to 4%, the solution resistance is sharply reduced. In the range from 4 to 6%, the resistance drops slowly. Finally, at concentrations greater than 6%, the resistance of the solution increases rapidly. A sharp increase in the resistance of the solution with concentrations bigger than 6% can be explained by a decrease in the mobility of the conductive ions caused by the lack of free water molecules. In other words, it is under such conditions that sodium sulfate begins to act as a water-removing agent.

Results of electrochemical measurements, (Figure 4), shown that solution resistance changes abruptly at $\text{pH} = 3.5$. Therefore, we believe that in these conditions reagent works most effectively.

The change in the resistance of solutions containing gelatin is more complex, that in case, described above (Figure 1, b). Of greatest interest is the section corresponding to 6.2 ... 6.8%, at which the resistance of the solution remains practically unchanged. The presence of this plateau can be explained by the gradual dehydration of gelatin molecules. The resistance of the solution remains practically unchanged, since sodium sulfate binds the released water molecules. Dehydration of gelatin leads to its sedimentation in the model system, which does not contain microcapsules. In a system containing phase of lipid drops, gelatin macromolecules are adsorbed on the oil/water interface. Therefore, in the process of microencapsulation, when concentrations of Na_2SO_4 equal to 6.2-6.8% are reached, the shell from adsorbed gelatin is compacted, that is, microcapsules with the solid shells are formed. These observations are consistent with our earlier gravimetric determination of the optimal concentration of Na_2SO_4 (5.4-7.2%), obtained at such pH values [10].

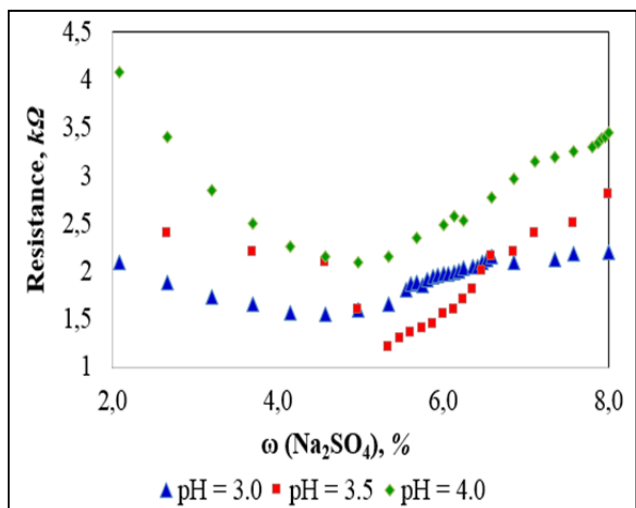


Figure 4. Resistance of Na_2SO_4 solutions at various pH values

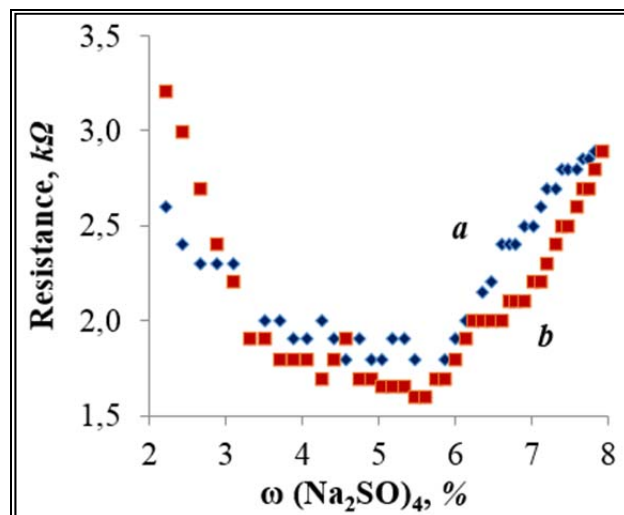


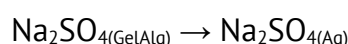
Figure 5. Resistance of sodium sulfate solution (a); in the presence of gelatine (b)

2.3. Electrochemistry of coacervation

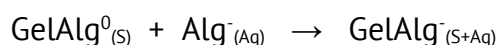
Addition of a 0.5% solution of potassium alginate to the system leads to a visible increase of its resistance. This indicates an abrupt decrease in the number of ions that carry the charge when small amounts of alginate are added (Figure 6).

Such an electrochemical signal corresponds to the formation of protein-polysaccharide, namely, gelatin-alginate complex, GelAlg^+ . With the further addition of a certain amount of

alginate, the resistance of the solution increases slowly. In our opinion, this corresponds to a gradual increase in the molecular weight of the GelAlg⁺-complexes while maintaining a positive charge. Finally, with the addition of about 35 ml of the alginate solution, an abrupt reduction in the resistance of the solution occurs. This corresponds to the achievement of a mass ratio of m(Gel) / m(Alg), which corresponds to the formation of neutral compounds GelAlg⁰ and its further precipitation [2]. This process is accompanied by decrease in the system's viscosity, and by the synerghesis of the biopolymer phase, leading to the expulsion of sodium sulfate into the solution:



Both factors can contribute to reducing of resistance. Finally, with the addition of even larger amounts of alginate, the formation of negatively charged biphasic micelles (GelAlg⁻) takes place and the viscosity of the solution increases, and as a consequence, the resistance increases:



Conclusions

1. Salting out of gelatin from the solution, corresponding to the formation of primary gelatinous shells of microcapsules, occurs when the gelatin molecules are dehydrated by means of sodium sulfate and correspond to its content in the solution above 6%.

2. The stages of formation of complex-coacervate shells (GelAlg-complexes), its neutralization and recharging, are accompanied by visible changes in the resistance values. We consider that the drop in resistance at the recharging point is caused both by a decrease in the viscosity of the liquid phase and by the synerghesis of the polymer phase, which causes the transfer of sodium sulfate from the shell to the solution.

3. Dynamical measurements of resistance can be proposed as the effective tools for investigating and controlling the phenomena of simple and complex coacervation of polymer electrolytes occurring in the process of microencapsulation.

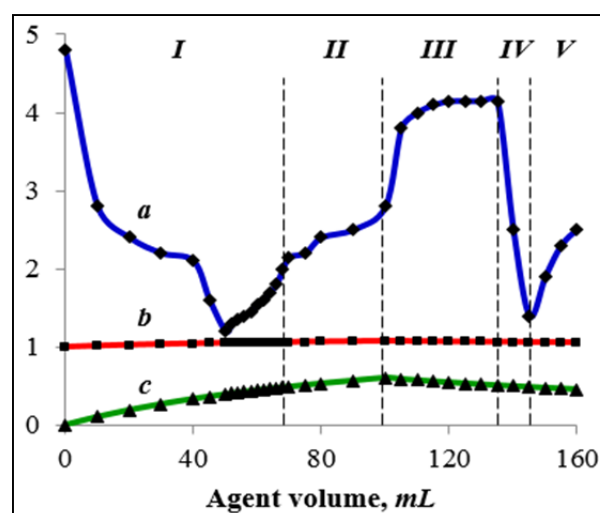


Figure 6. Electrochemical features of microencapsulation: *a* – resistance, *kΩ*; *b* – density, *g/ml*; *c* – molarity of Na_2SO_4 , *mol/l*; *I* – no ccv.; *II* – simple ccv (Gel⁺); *III* – complex ccv (GelAlg⁺); *IV* – neutral shells (GelAlg⁰); *V* – recharging of shells (GelAlg⁻)

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CONCEPTUAL ASPECTS OF FOOD SECURITY

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Abstract. Food security is considered a global issue, but it is also an indispensable element of national security and needs rigorous treatment at country level. Ensuring food security at country level is when the country's population is supplied with safe, harmless and appropriate food and with free, physical and economic access.

Keywords: *food security, levels of food security, national security*

1. General information

One of the main physiological problems faced by mankind along its development was - the issue of food security. Lack of food, access to drinking water was a consequence of thefts, social conflicts. One of the basic functions that the leaders of the countries met and fulfilled was also ensuring food security.

The main and first instinct a man has in this world is - the instinct to eat, for it is the basic foundation of the instinct for self-preservation.

Food security is considered a global issue, but it is also an indispensable element of national security and needs rigorous treatment at country level. Ensuring food security at country level is when the country's population is supplied with safe, harmless and appropriate food and with free, physical and economic access.

Throughout the development of economic theories, problems have arisen in ensuring food security. The most obvious view issues concerning food security belongs to T. Malthus, who believed that chronic food insecurity is associated with decreased fertility of land. He said that population grows in geometric expression, and natural arithmetic in natural resources, and in order to achieve balance between population and natural resources, there must be as many wars, contagious diseases and that is the only way to meet the human feeding needs. Malthus T. analyzed the increase of the population in his country, but he did not take into account the fact that during that period the population grew because of migration, not because of the birth rate [7].

Later, the issue of food security was addressed in the light of the fact that the agro-food complex in many countries is not developing. In the 1970s, XX-th c., at the level of the world economy, the issue of food security had a contradictory character, if in developed countries there was an overproduction of food, then in the third world, the world suffered from hunger and mass malnutrition. This underpinned even greater aggravation of global food security, which served as a basis for increasing the gap between decent living and livelihoods. The global food security issue has led to countries with high capacities to help third world countries.

Currently, there is no an opinion and an universally accepted definition. Some approaches focus on "food security," others identify it with "food independence," and last but not least, the concept of "food safety" is also used.

However, confusion often occurs, for some scholars confuse the term "food security" with "food safety." Indeed, the given concepts have tangential points and marginality is very "fine", but "food safety" determines food innocuity and harmlessness based on quality standards, and in terms of food security we will try to deduce it after studying the views of scholars both autochthonous and international.

Addressing "food security" as a concept differs from generation to generation, from scholar to scholar, from society to society. Largely depends on the stage of development of society in which the determination of this concept takes place. The more the development of society takes place through the modernization of technologies, the more the food security rigor is growing.

The stages of development of the "food security" system depend on the level of society development that can be illustrated by a figure 1.

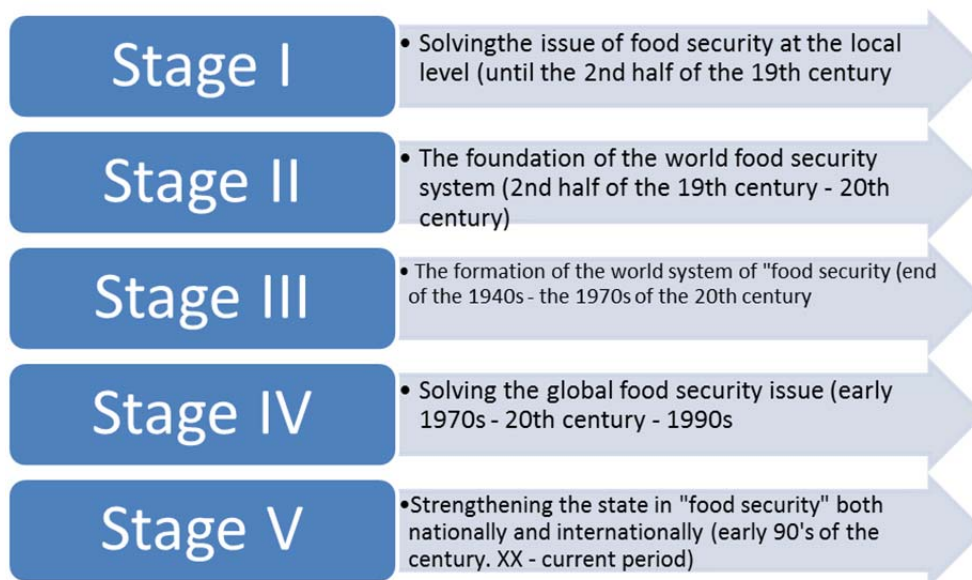


Figure 1. Stages of development of the "food security"

Source: elaborated the author

2. Discussion of the experimental study

The first stage in the development of the food security process was that in majority of countries it was based on the country's traditions. The function of redistributing the products belonging to the social categories of the society belonged to the state, but it also fulfilled only in exceptional cases.

A new stage of the development of economic thought led to the "birth" of the public security mechanism, which is characteristic for the end of the nineteenth century - the beginning of the 20th century, namely "replacement" of the state frontiers, and as a result have appeared "mobile" open companies. As a result of the changes, the function of redistribution of production came to the state institutions. It was during this period that the transition to a market economy took place, where obviously the main economic security instrument was the market. As a result of the changes in society, social discrepancies have

emerged in terms of structure and consumption patterns depending on the level of available income, territorial distribution and social affiliation.

As a world-class problem, food security was recognized only in the mid-twentieth century. The most decisive role in the formation of food security as an integral system has been played by international organizations, especially the UN.

Under the aegis of the United Nations, the right of all to food and hunger protection was officially registered in the Universal Declaration of Human Rights (1948) [21] and the International Covenant on Economic, Social and Cultural Rights (1966) [15]. The latter indicates not only human rights to freedom from hunger but also obliges the state to ensure the implementation of this right in practice.

When the world crisis on cereals occurred in 1972-1973, the UN proposed to use the concept of "food security".

Primordial global food security was considered as "Maintaining the food safety fundamentals in the food markets for all countries of the world. "This approach was declared by the UN General Assembly in 1974 in the Universal Declaration on the Elimination of Hunger and Malnutrition" And also in the Resolution" International Commitments to Ensure Food Security in the World" [17].

Also at the same conference in Rome in 1974, the Food and Agriculture Organization (FAO) has developed the International Food Security Assurance Strategy.

During the 1980s, there were cardinal changes in the harmony of the state of food security. It has been established that it predicts not only the availability of food on the world market and its regularity of supply, but also access to food for the entire population of the globe and nutritional quality at the standards to lead an active and healthy life.

In 1983, the FAO changed its concept of "food security" to include ensuring vulnerable people's access to available food, that is, the balance between supply and demand that is nothing but the food security equation: "ensuring that all people have at all times physical and economic access to the basic foods they need" [5].

The World Bank report "Poverty and Famine", presented in 1986, focused on the temporal action of food insecurity. It introduced "the widely accepted distinction between chronic food insecurity, associated with problems of continuing or structural poverty and low incomes, as well as transient food insecurity, which involved periods of increased pressure caused by natural disasters, economic collapse or conflict." This concept of food security is further elaborated in the terms "access of all people at all times to sufficient food for an active and healthy life" [9].

The UNDP Human Development Report of 1994 promoted human security, including a number of aspects of which food security was just one [16].³ This concept has a close link with the human rights perspective on development, which, in its turn, has influenced food security discussions [4].

The concept of "food security" was fully highlighted in the Rome Declaration on Global Food Security in 1996. According to the Rome Declaration, food security has "dressed" the following form: "food security is a state of the economy in which the population of each country has the guarantee of access to food and drinking water in the quantity and quality necessary and sufficient for the physical and social development of the individual, health insurance and increased reproduction of the population"[20].

In 2001, FAO proposes a redefinition of food security: "Food security is a situation when all people at a time have physical, social and economic access to sufficient, safe and

nutritious food that meets their needs food and food preferences for an active and healthy life" [6].

Naiken [22] considers that the basic requirements for food security are:

- The energy used for the functioning of an individual in a state of complete rest (basal metabolic rate);
- Energy required for food digestion, food metabolism and storage and increased food consumption;
- Energy required to carry out physical activities, both in work and outside work.

Romanian researcher Banu C. in his paper "Sovereignty, safety and food security" states that "food security does not imply that the state assumes its obligations or legal mechanisms for the poorest (malnourished) to defend itself against those who can forbid them from access to food (large land plots, corporations, state authorities, etc.)"[1, p. 2].

According to Bulgaru M. "food security is given by the amount of food required for an individual, expressed in physical, conventional units (calories)", and trophins, in order to ensure their physiological balance and to cover their daily consumption rations: ration of maintenance, ration of growth and ration of activity "[2].

A significant contribution to the concept of food security have russian scientists such as Beleacov A., Altuhov A., Nazarenco V., etc.

In Table 1 the author presents the scientific approaches to the concept of food security from the point of view of different scientific schools. In the last period of time, the concept of food security has found a widespread not only in scientific literature but also in official documents elaborated at country level.

Table 1

The concept of food security approach

Author	The concept of food security approach
Rome Declaration on Global Food Security, 13-17 November 1997 [23]	Food security is a state of the economy where the population of the country as a whole and each citizen individually have access to food, drinking water and other food products of the quality, range and volume necessary and sufficient for the physical and social development of the individual and the reproduction of the country's population
The concept of food security of the Eurasian Economic Community, adopted by the EURASEC Interstate Council Decision 11-19 dcembrie 2009 N° 464 [18]	Food security is understood as a state of state economy in which the country's food independence is ensured at the expense of its own production, the physical and economic availability of food and drinking water to the entire population is guaranteed in the quantity and quality required for an active and healthy life
The concept of improving food security of CIS Member States, adopted by Council Decision of CIS heads of government November 19, 2010 [19]	Food security is defined as a condition of the state economy where the country's food independence is ensured by its own production and the physical and economic accessibility of food and clean drinking water for the entire population in the quantity and quality required for an active and healthy life;

Table 1 (continuation)

Anderson [3, p.2]	The basic definition of food security is that it refers to the ability of individuals to get a sufficient amount of daily food. International food security is defined as the ability of people to provide adequate food. More specifically, it was defined by researchers as the access of all people at all times to sufficient food for an active, healthy life.
Hart [3, p. 3]	He noted that longest food security definition includes the phrase "at any time" and, as such, does not distinguish between different duration and intensity of food insecurity. In addition, food insecurity has a temporal dimension as well as an intensity. The temporal dimension may be chronic (long-term or persistent), transient (referring to short periods of extreme availability and access to food) as well as seasonal or cyclical. The dimension of intensity, on the other hand, refers to the size of the food gap. It is also important to have a good understanding of the vulnerability of concepts and food insecurity. Vulnerability has an external and internal dimension, and food insecurity has a temporal and intense dimension
Altuhov A [11]	Food security the capacity of the state to ensure that the need for food is attained at a level that ensures the usual existence
Beleacov A [24]	The country's food security is the permanent capacity of the state and society to ensure the availability of food for the entire population in the quantity and quality necessary for an active and healthy life
Ahmetova C [10]	Food security is a state of the economy where the food needs of the population are met in accordance with physiological norms; and food security is part of the national security of the country. Food security in many respects depends on the development of the agro-industrial complex
Serova E [14]	Food security, in the broadest sense, means the level of food availability for the majority of the country's population to maintain a normal lifestyle

Source: elaborated by the author

Unfortunately, so far, there is no scientific and normative basis in the Republic of Moldova which stipulates the main determinations, tools of food security. In the Republic of Moldova, the study on food security is reflected in the works of local scientists Stratan A., Perciun R., Bajura T., Artiomov L., Boaghi L., Mocanu N., Moroz V.

According to researcher Bajura T, "Food security is a major factor in the economic, social, and political stability of a country, region, and / or global. With different dimensions of approach, the food security category, in terms of the relatively free economic and physical access of consumers to these products (in a required volume and rich assortment), can be presented as a basic treatment" [12].

Mocanu N. has raised the threats to food security both at international and national level, so, "The specificity of the threat to food security (worldwide) is that the advancement of alternative sources of energy originates, first of all, in industrialized countries - the main producers of agricultural raw materials, therefore, the main suppliers of this matter on the international food market" [13].

Regarding the existence of laws, doctrines or strategies on food security in the Republic of Moldova at the moment are not elaborated.

In the "National Security Project Conception of the Republic of Moldova " we can find the following objective regarding the food security "The credibility, safety and quality of the foodstuffs are fundamental criteria to which the Republic of Moldova will comply in order to ensure the protection of consumer health and the competitiveness of food products on internal markets and external markets. Taking into account the influence of this policy on the social and economic spheres, the elaboration and implementation of such a policy, as well as the surveillance of the pricing policy for the first products, the concrete measures to support the domestic producers, the quality of the imported products, including the genetically modified ones, constitute priority tasks for the agri-industrial sector institutions. In order to develop an agricultural sector with a production corresponding to the European and global requirements and a competitive quality, the competent institutions will undertake measures for the modernization of the production technologies, quality assurance throughout the process of production and distribution, promotion and development of the market.

Internal food security will be one of the priorities for the development of the agro-industrial sector. The principle "From a safer food to a healthy diet" will underpin the development of policies and action plans, the development and adoption of the regulatory framework in the area of food quality, safety and security, as well as the protection of consumer health. In order to protect the health of consumers, programs for monitoring the risks in the food chain will be developed and implemented [25].

Thus, we can conclude that in the "National Security Project Conception of the Republic of Moldova ", food security is regarded as a more limited concept but is in a clear correlation. By synthesizing the definitions of food security proposed by both foreign and native researchers, we can see that this concept is quite complex and multilateral.

According to the author, food security is the category that has its own power resources that regardless of what level, but that can satisfy consumers with enough food to lead a healthy lifestyle. By reviewing the ideas of several scientists, researchers, we believe that food security is a commitment of the state, both in physical and economic terms, to ensure that the population has quality food that that meet vital human needs and to lead a healthy life. We also believe that the state must develop the competitive environment of the agro-food complex on the basis of increased investment, because if the agro-food complex is developed then food security will be efficient. Summarizing the theoretical aspects of food security, we have the following pillars, figure 2:

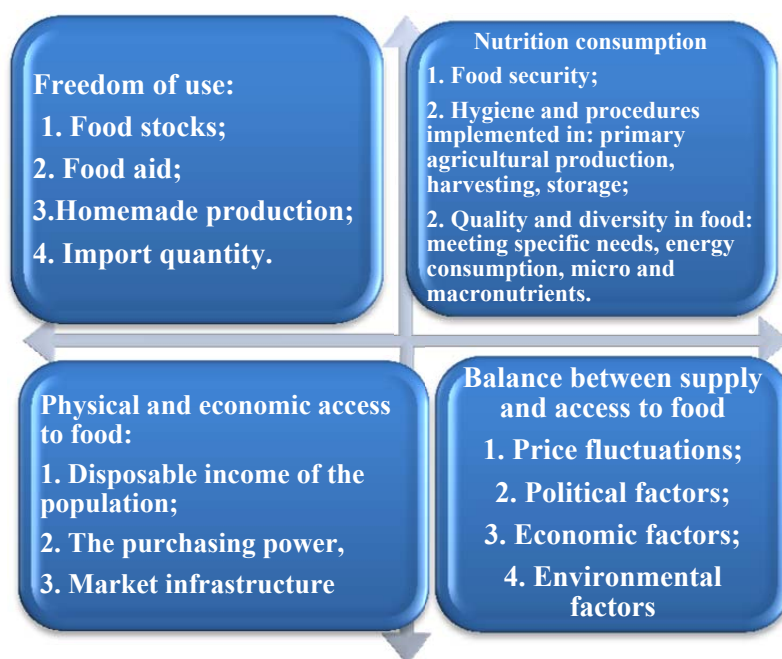


Figure 2. The pillars of food security

Source: elaborated by the author

Each hierarchical level of the food security system has problem-solving subjects, table 2:

Table 2

Subjects responsible for ensuring food security

Levels of food security	Subjects
World level	UN, FAO, World Trade Organization (WTO), World Health Organization (WHO)
Interstate level	Regional associations
National level	Government, legislative bodies
Regional level	Interregional enterprises of relevance
Local level	Territorial authorities
Consumer groups	Households according to income level
Households	Households

Source: [8, p. 9]

Regardless of the established level, the problems that have arisen must be settled by a body responsible for the area whose functions are: ensuring the supply of food products in the distribution networks, creating the necessary conditions for the actual production of the necessary products, etc

Conclusion

Based on the reported information, the author considers that food security can determine that the level of the economy must be developed to such a level that, regardless of the international market, the supply of foodstuffs is guaranteed by the state according to the consumption norms established by the respective bodies.

By highlighting all the approaches to the concepts of "economic security" and "food security", we can say that they express the entrustment of life without taking into account several circumstances: economic security of economic unity, and also food security primary for the individual or for the entire population of a region, country or even continent.

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THE DYNAMICS OF SCIENTIFIC RESEARCH IN THE AREA OF FOOD SCIENCE IN EASTERN EUROPE

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Abstract. Based on scientific metrics (the number of published works, their citations, the H-factor, the Scopus database), it was conducted the analysis of the development of food science research in Eastern Europe (EU, Poland, Romania, Bulgaria) and post-Soviet countries (Russia, Ukraine, Moldova). There have been presented the main information channels of the global information area in this research domain, as well as the most important information channels of Eastern Europe. It is shown that if the first are represented by the journals of the first quartile (in accordance with the SJR data), then the latter are represented, in the best case, by the 2-nd quartile journals. Leading countries in this area of research on the total number of publications and the H-factor have been identified. It is analyzed the dynamics of the number of publications (per million inhabitants) for EU countries surveyed and the post-Soviet countries. It is shown that in all countries there is a positive dynamics, but the publication activity is significantly higher in the EU countries (21 million people per year in Poland, ~ 8 in Bulgaria and Romania, ~ 2 in Russia, Ukraine and Moldova, data of 2017).

Key words: *Eastern Europe, food science, science of science, scientometric indicators*

Introduction

The development of research in the field of food science is one of the trends of modern development of civilization. This, in particular, manifests itself in the fact that the sciences about man are increasingly determining in the direction of the development of science, and food science is one of its most important sections. This science defines as "...the discipline in which the engineering, biological and physical sciences are used to study the nature of foods, the causes of deterioration, the principles underlying food processing, and improvement of food for the consuming public" [1]. The textbook of food science defines of food science in terms as "...the application of basic sciences and engineering to study the physical, chemical and biochemical nature of foods and the principles of food processing" [2] Obviously, this is interdisciplinary, complex science. Complexity science is a science, that studies the complex systems, which consist of a large number of components that interact which each other to produce nontrivial phenomena that cannot be explained by analyzing the individual constituent elements [3]. The quantitative analysis of the science development in general and food science, in particular, is possible scientometrics methods [3-6]. In this paper, we will analyze the development of

science in the above area on the basis of the Scopus database [7] - one of the main databases of the world information area, indexing 21 thousand scientific titles (journals, conference materials, serial books) in the field of natural, technical, medical and human sciences.

Methodological part

The purpose of this work was an statistical study of the main scientific publications in the field of food science in the world and Eastern Europe.

In Tables 1, 2 shows the main information channels (journals) that have the best quantitative indicators within the information model of science (science as the world information process), and therefore, the most popular in the area of food science. In Table 1, they are classified by such an indicator as SJR, and in Table 2 by the H-factor [6]. SJR is an analogue of IF (average citation of work), but taking into account the "weight" of the journal in which this work is cited. As you can see, SJR is significantly lower than IF, but in the Scopus database, this parameter is determined by the quartile Q (rank) of the journal. As you can see, all the logs shown in the Table 1 and 2 belong to the category of 1-st quartile. Obviously, SJR is an indicator that takes into account the average weighted citation of the journal. The data presented in the Table 1 and 2 differ, because the factor H takes into account not only the citation but is an integrated indicator, taking into account, along with the citations and the activity of general publication [6].

Table 1

The world's leading journals in the field of food science (ranking by SJR)

	Title	↓ SJR	H index	Cites / Doc. (2years)(IF)
1.	Comprehensive Reviews in Food Science and Food Safety	2.996Q1	72	7.65
2.	Annual Review of Food Science and Technology	2.966Q1	43	9.66
3.	Trends in Food Science and Technology	2.344Q1	151	7.23
4.	Advances in Nutrition	2.196Q1	56	6.44
5.	Food Hydrocolloids	1.991Q1	118	5.01
6.	Food Policy	1.950Q1	76	3.46
7.	Global Food Security	1.809Q1	24	3.66
8.	Food Chemistry	1.793Q1	204	5.15
9.	Applied and Environmental Microbiology	1.684Q1	281	3.67
10.	Molecular Nutrition and Food Research	1.666Q1	104	4.81

The data presented in the Table 1 and 2 scientific journals are journals published in American or European journals (Elsiver, Springer). They are the main channels of information, essentially determining the scientific "policy" in the analyzed area of science.

As for the journals published in the countries of Eastern Europe, their degree of influence on the global information process is significantly lower. The most significant of these are Polish journals (Polish Journal of Food and Nutrition Sciences, Journal of Animal and Feed Sciences, Acta Scientiarum Polonorum, Technologia Alimentaria Q2, SJR 0.651-0.385). The Czech Journal, Q3, SJR 0.355, the Slovak Journal of Food and Nutrition Research, Q3, SJR 0.313 etc. should also be mentioned in Croatian journals Food and Biotechnology

journal, Mijekastvo, Q3, SJR from 0.365 to 0.273. The IF of these journals varies between 1.7 - 0.6, which indicates them as very important channels of scientific information. Despite the fact that they all belong to the category of magazines of the second and third quartiles, they can be regarded as magazines that have a significant impact on the world information process in the field of science in question.

Table 2

Leading scientific journals in the field of food science (ranking by H)

	Title	Type	↓ H index	Cites / Doc. (2years)(IF)
1.	<u>Applied and Environmental Microbiology</u>	1.684 Q1	281	3.67
2.	<u>Food Chemistry</u>	1.793 Q1	204	5.15
3.	<u>International Journal of Food Microbiology</u>	1.366 Q1	162	3.52
4.	<u>Journal of Dairy Science</u>	1.350 Q1	159	2.68
5.	<u>Trends in Food Science and Technology</u>	2.344 Q1	151	7.23
6.	<u>Journal of the Academy of Nutrition and Dietetics</u>	1.505 Q1	146	3.02
7.	<u>Journal of Food Engineering</u>	1.279 Q1	142	3.24
8.	<u>Food and Chemical Toxicology</u>	1.144 Q1	139	3.91
9.	<u>Journal of Animal Science</u>	0.848 Q1	131	1.31
10.	<u>Meat Science</u>	1.643 Q1	131	2.76

Contribution of various countries of Eastern Europe to the world information process in the area of food science

In the Table 3 shows the scientometric indicators of the publication activity (the number of articles published in scientific journals included in the Scopus database in 2017) as well as the H factor values for these countries for 1996-2017 years. Comparison of these values allows us to conclude that, in general, there is a correlation between them. However, tracing dynamics based on the H-factor is hardly possible. However, tracing dynamics based on the H-factor is hardly possible. Therefore, in the future, for the analysis of dynamics, such an indicator as publication activity (the number of publications in the most important scientific journals). Because this value depends largely on the country's "scale", especially its population, K was used, which is the number of publications per year per 1 million inhabitants of this country (Figure 1).

Table 3

Comparative publication activity of Eastern European countries in the field of food science

	Country	Documents	↓ H index
1.	<u>Poland</u>	807	88
2.	<u>Czech Republic</u>	266	70
3.	<u>Slovenia</u>	81	63
4.	<u>Croatia</u>	133	61
5.	<u>Hungary</u>	98	59

Table 3 (continuation)

6.	<u>Russian Federation</u>	245	56
7.	<u>Serbia</u>	204	49
8.	<u>Bulgaria</u>	55	47
9.	<u>Slovakia</u>	177	47
10.	<u>Lithuania</u>	55	35
11.	<u>Ukraine</u>	76	34
12.	<u>Estonia</u>	21	27
13.	<u>Latvia</u>	186	22
14.	<u>Bosnia and Herzegovina</u>	21	17
15.	<u>Macedonia</u>	27	17
16.	<u>Georgia</u>	7	12
17.	<u>Moldova</u>	7	12
18.	<u>Albania</u>	7	9
19.	<u>Armenia</u>	3	6

Dynamics of scientific development based on the index of public activity K

The results presented in Table 3 and Figure 1 allow us to conclude that within the information science model, the greatest development of food science in Eastern European countries was achieved in Poland.

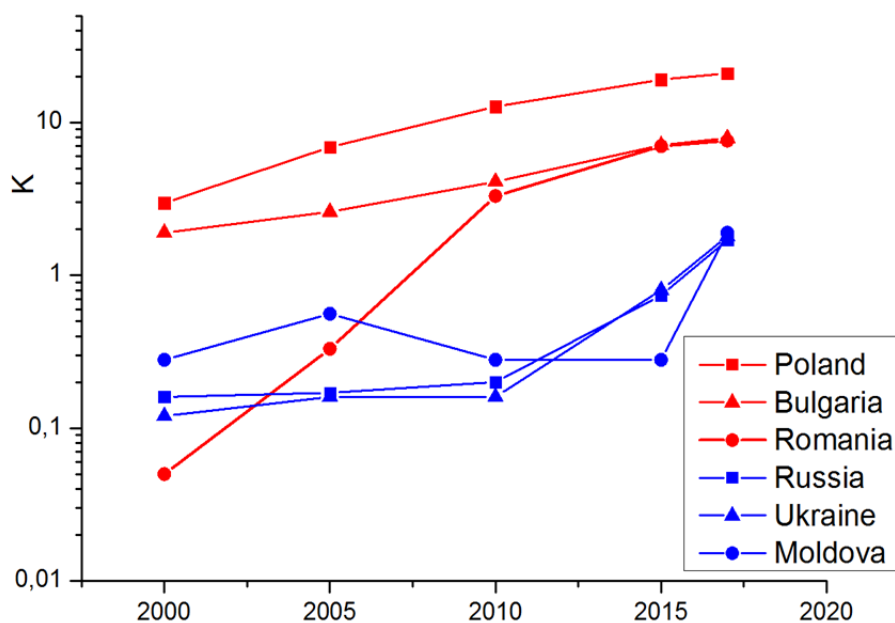


Figure 1. Dynamics of publication activity

It has the highest indicators, both in the importance of scientific journals published in the country, and in the number of publications, as well as an integral indicator that takes into account the number of publications and their citation (H-factor). The results shown in the figure also allow one to compare the intensity of food science in the EU countries and the post-Soviet countries. It is seen that it is much higher in EU countries.

Conclusions

As for the dynamics of scientific development, it should be noted that it is positive in all countries. However, this trend is the most pronounced for Romania. If at the beginning

of the 21st century the relative intensity of scientific development in this area was practically the same as that observed in the post-Soviet countries (and even lower), by 2017 it is several times higher than the indicators of the post-Soviet countries (~ 8 articles per 1 million inhabitants in Romania against 2 in Russia, Ukraine and Moldova). During the period under review, the publication activity, estimated by the number of publications in leading journals per 1 million inhabitants, increased 160 times in Romania. It is also necessary to note the proximity of this indicator separately for a group of post-Soviet countries, as well as Romania and Bulgaria. Obviously, this fact is explained by the peculiarities of funding research in the EU and post-Soviet countries. A significant difference in the intensity of scientific development in EU and post-soviet countries was shown in [8]. The results of the analysis carried out in this study indicate that this conclusion extends to food science.

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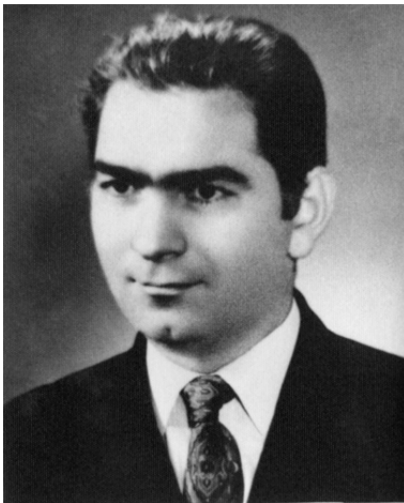
PERSONALITIES ON THE MERIDIANS OF THE SCIENTIFIC UNIVERSE

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Belea Constantin, university professor, doctor docent at the University of Craiova, Faculty of Electrotechnics, Department in **System Theory**, was born on 6-th of March 1929 in Slanic Prahova, Prahova County. He attended the Plopeni Metallurgical Technical School, followed by the admission at the Polytechnical Institute of Bucharest, Faculty of Electrotechnics, in 1950. After two years, in 1952, he was selected and transferred, by a decision of the Council of Ministers, to the Technical Military Academy of Bucharest, the Faculty of Aviation. He graduated in 1954, obtaining a Diploma of Electrical Engineer on Board Electric Installations in Aeroplanes. He continued studies at doctoral level both in Bucharest as well in Moskow defending his thesis in 1959 at

Jucovski Military Academy of Aviation Engineers in Moscow.

He was awarded the title of Candidate in Technical Sciences (according to USSR regulations). The subject of his dissertation was "Nonlinear oscillations in automatic regulation systems" which was published on the recommendation of the Jukovsky Academy of Sciences Council, in the form of a 264 - page monograph (the original title "Nelineinye kolebaniya v sistemah avtomaticheskovo regulirovania i upravleniya"), in the Maşghiz Publishing House, Moscow.

In this paper he developed an exact method of determination of periodic regimes from non-linear automated systems, established the exact dependence of the amplitude and period of auto-cycles on nonlinear parameters, established the characteristic equations that solve the problem of stability of periodic regimes, studied several possibilities for removing the periodic regimes of functions of nonlinear automatic systems and so on.

He continued his research work at the higher level of an Ph-D thesis, also at the Jukovski Military Academy of Aviation Engineers the approached subject being: "New Methods in Automatic Regulatory Systems Theory", defended successfully in 1962. Based on this achievement he obtained his Doctoral Degree in Technical Sciences, USSR version, awarded by the Commission of the Ministry of Higher Education and Special Environment of the USSR, which in turn was recognized by the Higher Education Commission of the Romanian Ministry of Education as a New Doctoral Degree in Technical Sciences, named „DOCTOR DOCENT”.

The approached subjects in the thesis were development of methods for calculating automatic systems, finalized by proposing two new methods based on series of rapidly

converging powers, replacing the trigonometric series and the classic series of exponential functions development in the dynamic calculation of automatic systems of different types. At the same time, he dealt with the coordinate and parametric invariance of the automatic systems, establishing some important theorems.

Between 1962 and March 1965 he held teaching and scientific activities at the Department of Radioelectronics at the General Military Academy, as well as reading the following courses as lecturer: "The Basics of Automatic Regulation", "Automation", "Computation Electric Machines", "Cybernetics" and so on. He coordinated the scientific research activity of the department and was a member of the editorial board of the General Military Academy Bulletin.

Between April 1965 and February 1966 he worked at the Bucharest Research and Design Institute for Automation, as chief designer at the Complex Automation Department, on topics related to the introduction of computing technique in industry.

Between February 1966 and September 1966 he worked at the Institute Power Energy of the Romanian Academy as Head of the Nonlinear Systems Division, activity that was prolonged on half-time basis until 1968, when he became honorary researcher of the same institute.

In the scientific activity, he was involved in developing the theory of nonlinear systems and the numerical methods of dynamic calculation of automatic systems.

He studied the self-adaptive systems, the theoretical principles and methods of optimization of automated systems, the study and construction of computational devices, the study of parametric systems, the optimal reception of signals, the numerical modeling of nonlinear systems, the construction of linear dynamic systems based on the distributions theory.

On September 1, 1966 he was appointed professor at the University of Craiova, Faculty of Electrotechnics, coordinating a series of departments: Electrical Machines and Devices, Devices (1966-1967), Automation and Electrical Devices (1967-1969) Automation (1969-1975) and Automation and Computers (between 1976-1985).

He founded the Automation Department in 1967. Between April - November 1968, and between 1969 -1974 he served as Prorector of the University of Craiova. Since 1968 he was appointed as Scientific Coordinator of PhD activity in the field of Automation and Remote Control. Under his guidance 10 doctorate theses were finalized.

He was the founder of the Automation Research and Design Institute – Craiova branch and in 1980 initiated the National System Theory Symposium, which is regularly held today at the international level. He was the Chairman of the System Theory Commission within the Automation Section of the National Council of Engineers and Technicians, sponsored by the National Council of Science and Technology.

In 1983 he obtained the title of "Meritorious University Professor", awarded by the Order of the Ministry of Education No. 5121 / 16.06.1983.

Between 1981-1985 he chaired the course "Automation of Automatic Flight and Navigation Devices" at the Faculty of Aeronautics of the Polytechnic Institute of Bucharest.

He was awarded the Traian Vuia Prize of the Romanian Academy. He is the author of numerous studies, university courses, monographs, and synthesis works in Romanian, Russian and English languages, publishing over 200 articles in following magazines: *Avtomatika i Telemekhanika*; *Izvestiya Akademii Nauk Energetika i Avtomatika*; *Automation and Electronics*; *Power Energy and Electrical Engineering Research*; *Revue Roumaine des*

Sciences Techniques Series; Electrotechnique et Energétique; Bulletin of the General Military Academy; Annals of the University of Craiova.

He translated synthesis works from Russian and English.

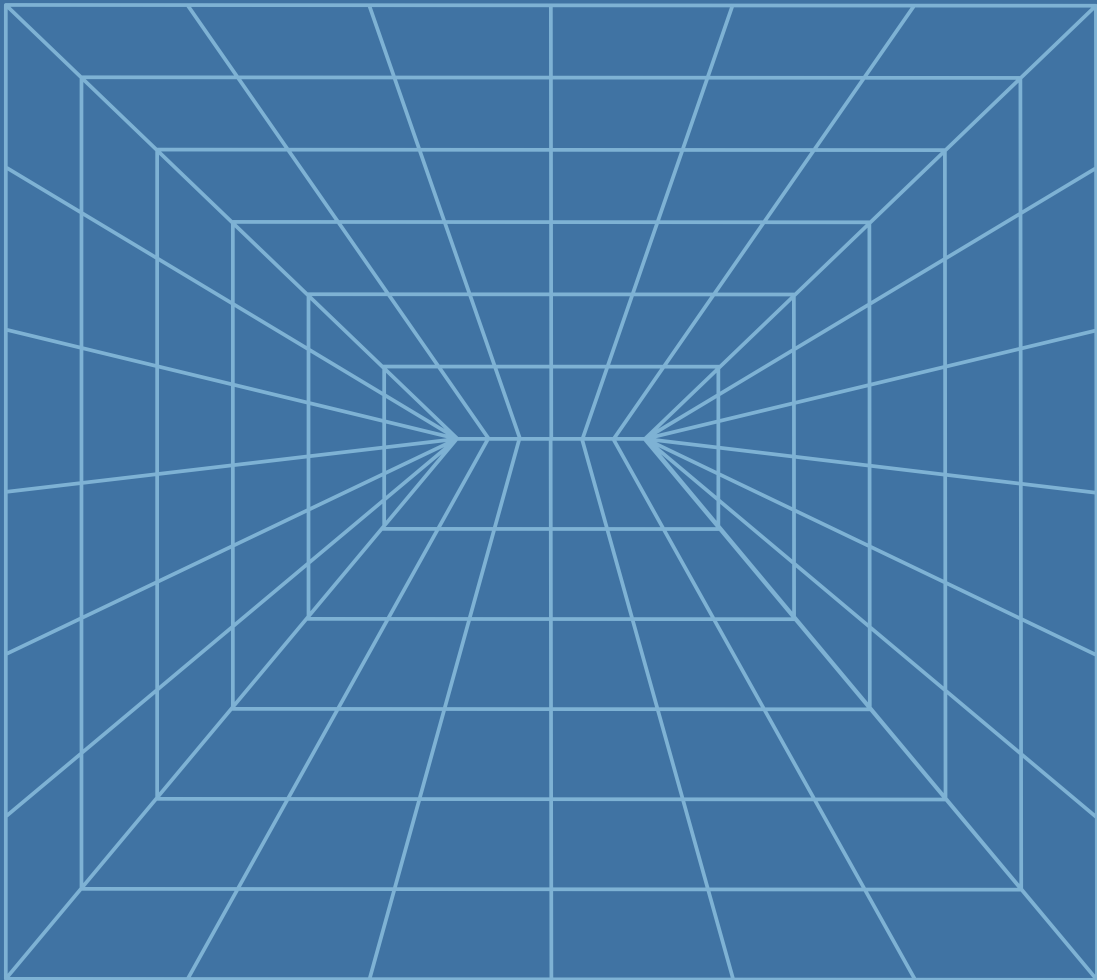
He initiated several pioneering directions:

1. *Linear automated systems on portions.*
2. *Numerical methods for transient automated systems.*
3. *Invariance of automatic systems in relation to disturbances.*
4. *Switching in linear electrical systems and applications of "theory".*
5. *Optimal systems based on the minimum time criterion. Numerical methods for transient automated systems.*
6. *Calculation of nonlinear auto-aspirations based on rapidly converging Fourier series.*

Among the reference published works there are to be mentioned:

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