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Introduction

The very idea of European Young Engineers Conference arrived in year 2011, during Students Scientific Club meeting. We were wondering, how we can develop our work and how to provide a new, attractive and easy way to exchange knowledge and experience between young people. People who, like us, believe, that science and engineering are the best ways to develop.

Ever since, we work very hard to make our Conference better and better. After previous editions, we can say that event like EYEC is still highly desired. Our goal was to create a possibility for young scientists to show their work for public. For many of EYEC participants, our conference was the first step in their career. Thanks to EYEC’s scope, friendly atmosphere and high level of presented research, we believe that it is the best way to start or continue your scientific career.

During the EYECs’ second edition we come up with an idea to provide our participants more space to present their scientific work. Since 3rd edition of EYEC we issue the EYEC Monograph, our very first and the most important piece of written work. In this book you can find the most promising, important and reviewed papers of European Young Scientists. We hope, that this book you are holding will be the first step in career of each and every of participants of our conference.

The book, as well as conference, covers following matters:

- process engineering
- chemical engineering
- process equipment
- biomedical engineering
- nanotechnologies & nanomaterials
- bioprocess engineering
- environment protection
- material engineering
- other engineering disciplines

We hope you will find the papers within this book highly interesting and important, as we do.

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The Editorial Team of EYEC Monograph is extremely grateful for the effort and work of Scientific Committee put on the reviewing process of all the manuscript published in this book. Right after authors, without your work this book would not be created. Thank you.

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Scientific Commission

Prof. Tomasz Sosnowski, PhD – chairman

Vice-Dean for Scientific Affairs of the Faculty of Chemical and Process Engineering at Warsaw University of Technology.

He received his PhD (in 1997) and DSc degree (habilitation, 2006) from Warsaw University of Technology for the research related to dynamic interfacial phenomena and their relevance for hydrodynamics and mass transfer in the human respiratory system. He was a post-doc fellow at Lovelace Respiratory Research Institute in Albuquerque, USA (1999-2000) where he worked on aerosol systems for drug delivery by inhalation. From that time problems of chemical engineering applications in biomedicine have remained his main field of scientific activity.

Prof. Sosnowski is an author of more than 60 scientific papers in JCR journals and more than 200 other scientific publications (journal papers, book chapters, conference communications). In 2010 he published a book "Respirable aerosols and inhalers" (in Polish; 2nd edition in 2012) which was focused on the application of engineering methods in designing of medical inhalers, analysis of aerosol flow and particle-lung interactions. He is a co-author of 3 granted patents and several patent applications. He is also a scientific expert of European Medicines Agency (EMA – London), a member of the Managing Commitee of the European Initiative COST MP1106, and a member of the Committee of Chemical and Process Engineering, Polish Academy of Sciences (PAN).

Anna Jackiewicz, PhD

She graduated from the Faculty of Chemical and Process Engineering of the Warsaw University of Technology in 2004. Her master thesis was appreciated by the Award of the Ignacy Łukasiewicz Grant Fund of PGNiG S.A. for the best Master's thesis. In November 2010, she received a PhD degree and her Doctoral thesis entitled "Investigation into filtration of aerosol particles in inhomogeneous fibrous filters" was distinguished by the Faculty Council and by the jury awarding the Fiat grants. Dr Anna Jackiewicz has been employed by the Warsaw University of

Technology as Assistant Professor since 2011. She is the supervisor of the filtration laboratory at the Department of Integrated Processes Engineering.

Dr Anna Jackiewicz is co-author of 50 papers published in periodicals and conference materials. She has presented her research results at 14 international and 10 national conferences. She received scholarships for distinguished Ph.D. students in the field of science and research and scholarship for young scientists awarded by the Centre for Advanced Studies, Warsaw University of Technology, and by the Marshal of the Mazowieckie province. In 2011, she was granted an individual Award of the Rector of the Warsaw University of Technology for scientific achievements. Her profile was presented at the exhibition entitled “Maria Skłodowska-Curie in the Service of Science Yesterday and Today” at the European Parliament in Brussels. Since 2012 Dr Jackiewicz is the manager of the Leader III project from the National Centre for Research and Development. She was awarded first place in the project called “Internship as a success of a scientist”, intended to strengthen the cooperation between researchers and enterprises.

Her scientific interests: separation processes of gas-solid and liquid particles, filtering media design, modeling of filtration in fibrous filters, techniques for aerosol generation and detection, materials science.

Anna Zalewska, PhD

She is a specialist in the field of Explosives and has a well-established expertise in the detection of explosives vapors. Master thesis made at the Central Police Headquarters Forensic Laboratory. The aim of this study was to develop the effective methods of the extraction of the trace amounts of explosives from clothes. Doctoral studies, carried out in the Department of Energetic Materials at the Department of Chemistry, Warsaw University of Technology. She defended doctoral thesis on “New possibilities of the screening mobile devices in the detection of the explosives” and she is an assistant professor at the Military Institute of Chemistry and Radiometry, where she is a specialist in the field of trace analysis especially by ion mobility spectrometry and differential ion mobility spectrometry. She participated and giving a speech in international trade fairs and many conferences.

Zoltan Kovács, PhD

Dr Kovács holds the position of associate professor at the Department of Food Engineering at the Corvinus University of Budapest, Hungary.

He earned his Ph.D. degree on Chemical Engineering from the Institute of Process Engineering at the Johannes Kepler Universitaet Linz, Austria. Prior to his current position, he had worked as senior scientist at the Institute of Bioprocess Engineering and Pharmaceutical Technology of the University of Applied Sciences Mittelhessen, Giessen, Germany. He has been a regular reviewer for reputed scientific journals, published 3 book chapters, over 20 peer-reviewed papers in top journals, 60+ papers in conference proceedings, and filled one patent application. He has received distinctions from the European Membrane Society, the Association of German Engineers, and since 2013 he is a Marie Curie Researcher. He has participated to and is responsible for many out-of-campus projects with industrial partners in the field of bioprocess and membrane technology design and development.

Kamil Wojciechowski, PhD, DSc

He is currently employed as an associate professor at the Faculty of Chemistry, Warsaw University of Technology (WUT). He earned his PhD in analytical chemistry from WUT (Poland) in 2001. Until 2007, he was employed at the University of Geneva (Switzerland) as a faculty member (maitre assistant) before returning to WUT. He worked in laboratories of University of Twente (Netherlands), Paul Scherrer Insitute (Switzerland), Brookhaven National Labs (USA), Argonne National Labs (USA) European Synchrotron Research Facilities (France), Rutherford Appleton Laboratory (UK), and others. He co-authored about 50 peer-reviewed scientific papers, 3 book chapters and 4 patents. He is currently head of the doctoral school of the Faculty of Chemistry at WUT.

Alessandro Benedetti, PhD

More information about dr Benedetti in section: Invited Lectures.

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Invited lectures

Prof. Gyorgy Marosi, PhD

He is a full professor at the Department of Organic Chemistry and Technology of the Budapest University of Technology and Economics. He is also a leader of the Technology of Pharmaceutical, Environmental and Safety Materials Research Center.

He has received his M.Sc. (1981) and his postgraduate diploma in the field of Processing and Application Technology of Plastics (1985) from the Technical University of Budapest. He has obtained his C.Sc. (1991) from the Hungarian Academy of Sciences and the Technical University of Budapest, Ph.D. (1996) and habilitation (1999) from the Budapest University of Technology and Economics and D.Sc. (2003) from the Hungarian Academy of Sciences.

Prof. Gyorgy Marosi is an experienced researcher in the field of biomedical materials, fire retardancy of polymers and polymer composites. He also specializes in multicomponent systems Raman + AFM characterization and computer control of organic chemical technologies.

Prof. Gyorgy Marosi is a member of two Committees of Hungarian Academy of Sciences and three Hungarian scientific societies. He is also a chairman of three international conferences and a member of Scientific Advisory Board of ten conferences. He also coordinates four European and sub-coordinates eleven national projects. He is a member of editorial board of following journals: “Polymers for Advanced Technologies”, “Express Polymer Letters” and “Polimery” and a guest editor of the “Polymer Degradation and Stability”, “Macromolecular Symposia”, and “Polymers for Advanced Technology”. He has more than 280 publication in international journals.

Among many other awards, he was honored in 2014 with Szentgyorgyi Albert prize and in 2008 with Zoltan Csuros prize. He has attended following academic scholarships: Szechenyi Professorial scholarship (2000-2003), Melbourne (Florida, USA) (2002), Lyon (France) (1996), Cambridge (Great Britain) (1991), Duisburg (Germany) (1991), Palermo (Italy) (1989).

Prof. Marosi will present a lecture about: **Recent Biomedical Advancements Utilizing Advanced Polymer Technologies**

Polymer technologies, developed for engineering applications, are getting more and more widely used for answering challenges of pharmaceutical and medical fields. For example controlled release of certain drugs can be achieved by using supercritical CO_2 assisted extrusion. Sudden release of hardly soluble drugs requires formation of amorphous solid dispersion with high surface area. Electrospinning technology is a feasible way for this purpose. Surface engineering of polymers with advanced gas phase methods is required for optimizing the applicability of medical implants. The technology of 3D printing has been recently extended to the field of tissue engineering resulting in breakthrough in the applicability of stem cells. All of these technologies require severe control, for which purpose Raman microspectrometry serves as a feasible way.

Prof. Tomasz Ciach, PhD

He is the Head of the Department of Biotechnology and Bioprocess Engineering at the Faculty of Chemical and Process Engineering at the Warsaw University of Technology. Prof. Ciach received his MSc (1991) and PhD (1996) from Warsaw University of Technology. He also studied at the Faculty of Biology of the University of Warsaw. He obtained habilitation (2010) from Warsaw University of Technology for the research related to nanotechnology and biomedical engineering.

Only in last five years he wrote over 27 scientific publications concerning such topics as drug delivery, biomedical materials and nanotechnology. Prof. Ciach has over 280 citations and is a member of editorial boards of scientific magazines such as “Journal of Drug Delivery Science and Technology” and “Journal of Biomaterials Applications”.

Prof. Ciach received an award for scientific achievements from the Rector of Warsaw University of Technology three times (in 1999, 2002 and 2011). He was also rewarded with Tadeusz Sendzimir medal by the Association of Polish Inventors and Rationalizers in 2015 and with a gold medal on the World Exhibition of Innovation, Research and Technologies, Eureka in 1998. Prof. Ciach is a co-author of over 12 patents and several new patent applications. Majority of his work focuses on biodegradable polimaterials and their medical application and methods of receiving various nanoparticles.

He is an author of two technologies currently applied in industrial practice: drug eluting coatings for coronary stents and biocompatible low friction coatings for urological catheters. He is also the founder of three university spinoff companies: NanoVelos – nanoparticles for cancer treatment, NanoThea nanoparticles for cancer diagnostics, and NanoSanguis – synthetic blood and systems for organ transplantation.

Prof. Ciach will present a lecture about **"Nanomaterials for medical applications"**

Nanotechnology is a new emerging science which focuses on the objects smaller then a fraction of micrometer. It promises to solve various problems from medicine to energy supply. Especially medical applications of nanotechnology are promising a lot, from cancer cure to longer life. This is probably because the whole cellular machinery is of the same size range. Cell membrane receptors and receptor – ligand interaction are happening in nanometric size range, protein folding process as well. The most advanced, up to date, digitally controlled protein manufacturing nanorobot, ribosome, has about twenty nanometer size. To interfere with this structure in the controlled manner it is possible if we employ structure of the similar sizes. To produce such structures we can employ same interactions which governs natural world of the cell interior – self assembly processes. In the lecture process of nanoparticles and nanocoatings for medical applications will be presented.

Alessandro Benedetti, PhD

Researcher in the MARECO CNR-IENI sea marine station, located in Bonassola (SP, Liguria, Mediterranean sea) also responsible for management of the CePAS-Bonassola office, a public structure by the Bonassola Municipality and CNR-IENI for the divulgation of sea environment peculiarities consisting in stormy waves formation and watching.

He received his PhD in Environmental Science from Università degli Studi di Milano). Dr Benedetti's research is currently related to surface and material behavior in different seawater environments (e.g. effects of different seawater environments on superhydrophobic surfaces, Al and Fe alloys, cathodic protection of steel in shallow euphotic seawater).

He is also involved in the 'wave watching' activity which links science and education. He took part in research related to development of high resolution models for description/forecast of meteomarine dynamics of the Bonassola bay (cooperation with Univeristy of Genoa) and sea-wave motion measurement by accelerometric/sysmologic techniques (collaboration with National Geeophysic and Vulcanology Institute). Beside a number of scientific papers he also published a book "Wave Watching – lo spettacolo delle mareggiate in Liguria" (S. Gallino, A. Benedetti, L. Onorato. Ed. Hoepli, 2011)

Dr. Benedetti will present a lecture about **"The waves of Bonassola: show, science, education"**

Bonassola is a touristic village on the ligurian coast (Mediterranean sea, Italy), 80 km from Genoa and close to the Cinque Terre UNESCO Human Heritage. Here CNR-IENI has installed in 1993 a sea marine station, the MARECO CNR-IENI sms, devoted to research in eco-compatible marine technologies.

About meteo-marine phenomena, the stormy waves impacting on the 6 km shoreline comprising the villages of Levanto, Bonassola and Framura are spectacular as no other in the ligurian region. This depends on the effective combination between swell building and surf emphasizing factors as wind exposition, fetch, coastal bathymetry and physiography. Even around these premises, scientific and educational activities has been developed and integrated in recent years.

The University of Genoa and the INGV-AGI collaboration investigate the marine behavior of the Bonassola bay with innovative techniques. The activity of the Genoa University consists in coastal monitoring by processing images provided by digital video cameras in order to validate high resolution predictive models, as a proper tool to risk assessment and coastal management. The INGV-AGI activity consists in measuring wave parameters through a new method called OS-IS (Ocean Seismic-Integrated Solution) which exploits the seismic signal induced by the sea waves. OS-IS is installed inside the MARECO CNR-IENI sms with no part in the sea, making the system more reliable and affordable than the traditional systems (e.g. buoys).

Finally, CNR-IENI and the Municipality of Bonassola divulge the unicity of the wave exhibition basing on the aforementioned scientific grounds. From a touristic point of view, this proposal has been demonstrated to be as qualifying as attractive. In parallel, education is developed as well: the ‘wave watching’ practice is proposed merging the show of the waves and the safety of the watcher in accordance to information and rules deduced by the achieved knowledge.

Marta Bojarska, PhD

She graduated from the Industrial Biotechnology at Faculty of Chemistry, Warsaw University of Technology in 2010. In March 2015, she received a PhD degree at Faculty of Chemical and Process Engineering, Warsaw University of Technology. During her PhD studies her work was awarded on international conferences by European Membrane Society. Dr Marta Bojarska is a postdoc in Professor Mathias Ulbricht group at Faculty of Chemistry at University of Duisburg-Essen since July 2015. She is a co-author of over 20 papers published in periodicals and conference materials. In 2015 she was granted a Lider VI project from the National Centre for Research and Development.

Her scientific interests are: membrane preparation, characterization of membrane properties, membrane modification via nanoparticles, photocatalysis, antibacterial properties, materials science.

Dr. Bojarska will present a lecture about **“Membranes in automotive climate control systems”.**

Jakub Bujalski, PhD

He graduated in 1997 from University of Nottingham, (UK) with a MEng in Chemical Engineering. In 2003 he received his PhD in Chemical Engineering from University of Birmingham (UK), titled: “Computational fluid dynamic modelling of stirred reactors: power, baffle stresses, mixing times and semi-batch precipitation”. From 2003 to 2006 he joined the CFD group at CSIRO Minerals (Australia) as a Post Doc Researcher where he worked on CFD modelling of hydrometallurgical mineral extraction processes.

From 2006 he is based in Norway as a Principal Engineer in the Process Modelling and Control Department at the Yara International’s Innovation Research and Development Centre. His current focus is on the use of CFD in the fertiliser process industry to optimise the existing plants as well as new equipment design. He is an author of over 100 internal research reports focusing on improvements in the production of fertilisers and a number of conferences and journal publications. His current research interests are in CFD modelling of large scale industrial processes with a special focus on the nitrophosphate fertiliser process.

Dr Bujalski will present a speech about: **“The use of CFD modelling in the fertiliser process industry, challenges and opportunities”**

Due to the construction of the chemical plant it is difficult to visualise the system (flow patterns and phase separation) during normal operation. For this reason Computational Fluid Dynamics (CFD) has been found to be a useful tool in process industry by providing information on the flow patterns inside the equipment during normal and abnormal operation.

Over the years CFD technique has moved out of research environment and has slowly penetrated the conservative approach of the process industry and is becoming an essential part of the industry research and development. With the current and future computational power, CFD gives the research engineer the possibility of analysing more complex physics in industrial scale equipment and is no longer just used of simulation of “what if” scenarios in change in geometry and operational load.

By showing a number of case examples from the different process unit operations that are used in the fertiliser production the presentation will detail the challenges faced in using CFD for process plant equipment as well as highlighting the useful contribution of the CFD simulation tools in improving the operating performance in existing system, as well as an investigative tool in determining the root cause of unplanned plant shutdowns.

Articles

Probabilistic simulation of fire scenarios using Monte Carlo analysis

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***Keywords**: fire modeling, Monte Carlo, FDS, uncertainty, sensitivity analysis*

ABSTRACT

Mathematical techniques are integral methods used for fire modeling nowadays. Traditionally, fire models in enclosures and estimation of fire consequences have been performed by means of deterministic models. These can be characterized by a given set of input variables, which always lead to the same prediction – given set of outputs. However, in many cases user can define input variables within a range of values based on common knowledge, generally accepted practices in the field or even may use a best guess. That is why in this paper other approach will be presented – instead of creating a model, in which single point estimates of outputs are produced by single point estimates of inputs, it will be shown that a distribution of output variables can be produced by sampling distributions of input variables.

This probabilistic approach can be achieved by a number of techniques. The most simple one would be to take into account uncertainty and distribution of input variables varying them manually within some allowable range. However, in more complex cases it is needed to use Monte Carlo techniques – a method of performing multiple experiments by means of random sampling of variables within given probability distribution. What is more, when performing Monte Carlo analysis, it is needed to select the most relevant input variables, which should be investigated. This can be done using sensitivity analysis, which allow to analyze whether the output parameters are sensitive to changes in input parameters and to determine which input parameters contribute most to the uncertainty in fire model.

This paper discusses current capabilities of quantifying user uncertainty in fire modeling by means of Monte Carlo analysis. Present state of art in probabilistic Monte Carlo analysis of fire scenarios will be presented – regarding both zone models and FDS simulations. The most relevant results will be discussed – which input variables are the most sensitive and how uncertain is the output data to variations in the input variables. Finally, recommendations for future work will be given.

INTRODUCTION

Giving an overview of historical development of fire modeling it can be stated, that the earliest investigations were focused on better understanding of complicated physical and chemical interactions in fire dynamics, including fluid dynamics, thermodynamics, radiation, combustion and others. At this early stage experiments provided the most important observations and measurements and theoretical models tried to develop a mathematical description of these physical phenomena. In this way were created deterministic fire models, which can describe processes in compartment fires using mathematical expressions based on physical and chemical ground. Within years deterministic fire models evolved from basic, simplified analytical models of fire growth to more advanced zone models and finally, the most complex field models. First zone models were developed in 1970s and were based on the most basic one-zone approach. Next, zone models were upgraded to multi-zones and multi-compartment models. Finally, in the late 1980s appeared early field modeling approach and developed dynamically within next decades. In 2000 first version of Fire Dynamics Simulator (FDS) was released, which is nowadays the most common code for field fire modeling around the world.

Mathematical techniques in fire modeling have certainly come a long way and regardless of used model type, nowadays there is a high confidence in codes ability to model transport phenomena. McGrattan [20] stated that it is currently possible to solve mass, momentum and energy conservation equations reliably, as long as valid source terms and boundary conditions are given. Valid input data under the constraints of the model, in which assumptions and parameter values are included, are in this context elements with crucial importance. In the traditional deterministic models described above, a given set of input variables is incorporated into the model, which always lead to the same prediction – given set of outputs. However, in every fire model there is a degree of uncertainty. There are many classes of possible uncertainties, like uncertainty in resources, in assumptions and decisions made by a user solving the problem, errors in the model used for calculations and finally uncertainties in the input data, which will be mainly discussed in the paper. All the possible uncertainties lead to one conclusion - fire model predictions should not be used in engineering applications uncritically.

There is a number of techniques, which deal with the uncertainty of the system. In a deterministic approach single point estimates of inputs produce single point estimates of outputs. In an uncertain system, like fire spread model in a compartment, these single point estimates are the most likely values of the uncertain variables. Other traditional approach is to use range estimates, for which we typically calculate three scenarios: the best case, the worst case and the base (most likely) case. In this approach a range of outcomes can be shown, however it is impossible to determine the probability of any of these outcomes and to take into account interdependence between inputs or impact of different inputs relative to the outcome. That is why all approaches based on determining input parameters allowable range and varying them manually within it can be used only for very simple cases. In complex ones, like fire modeling, it is needed to use more sophisticated methods. Monte Carlo (MC) technique is one of the most popular techniques in scientific modeling and is based on performing multiple experiments by means of random sampling of variables within given probability distribution. It is a practical method of combining deterministic fire models with probabilistic treatment of model variables. Monte Carlo application in fire engineering is not an innovative approach – there is a number of researches known, in which this probabilistic method was used to model risk to human life, model fire in buildings or to study the role of uncertainty in fire regulations. However so far Monte Carlo applications were based mainly on rather simple, zone models, as the use of more complex, field models, was too expensive in terms of computational computer power. As in recent 10-20 years computers CPU increased dramatically, nowadays it seems to be finally possible to apply probabilistic techniques, like Monte Carlo method, to these more advanced numerical models.

The paper proceeds by providing brief description of most popular computational methods in fire modeling and some background to the MC modeling, before presenting current state of art in probabilistic Monte Carlo analysis of fire scenarios – concerning both simpler zone models and more advanced numerical simulations and concluding with the significant findings.

CALCULATIONAL METHODS IN FIRE MODELING

There is a range of computational tools for fire analysis in rooms and other enclosures. In this section three most acknowledged calculation methods in fire modeling will be briefly described, namely hand calculations, zone models and computational fluid dynamics code – Fire Dynamics Simulator.

Hand calculations

Hand calculations, sometimes called as specialized fire dynamics routines, are simplified procedures that require minimum data and information to solve a problem (often a narrowed one). Since the governing equations for heat and mass transfer are rather complex, numerous simplifications need to be made when performing hand calculations. As a consequence, the quality of results cannot be expected to be as high, as in more complex computational methods. However, manual calculation methods can provide relatively good estimation of considered fire effects, e.g. prediction of time of flashover, ignition time or heat release rate. Their advantage is that the underlying physics is being transparent and they are fast to execute. What is more, manual calculations results can show whether it is necessary or not to perform more detailed analysis [7].

Zone models

Zone models, also known as control volume models, solve the conservation equations for distinct regions – control volumes. It is assumed that within the control volume conditions are uniform at any time. As a result, a control volume has one temperature, one gas concentration and one smoke density. Number of zone models is known nowadays, varying in how detailed is the treatment of fire phenomena [1]. Depending on the required accuracy there can be different amount of control volumes within the model. In the most common zone fire model, the room is divided into two layers (zones) – hot upper layer and cold lower layer. Calculations give us estimations of most important conditions in both layers as a function of time. When it is needed to improve the model accuracy, additional zones can be added, for example for the fire plume or the ceiling jet. Two-layer approach has origin in observation of real-scale fire experiments, where such a layering was noticed – hot gases always collect at the ceiling and fill the compartment from the top. Even though there might be some small differences within the layer in various experiments, they can be considered negligible compared to the dissimilarity between the layers. Thus, zone models are proved to produce fairly realistic simulation under most typical conditions [13].

As mentioned before, there is a number of zone models widely used nowadays. One of the most popular is Consolidated model of Fire Growth And Smoke Transport (CFAST) model developed by the National Institute of Standards and Technology and used e.g. in fire reconstructions and in litigation procedures. Next acknowledged model is BRI2, which was developed in Japan and which is broadly used for risk analysis at Factory Mutual Research Corporation. Other models in use include Compbrn, FIRe Simulation Technique (FIRST) and LAVent. CFAST model will be shortly described below, as it will be a subject of further analysis in the paper.

CFAST was first released in 1990 and the aim was to give researchers and fire engineers a computer code, which is relatively easy and has low computational requirements. This zone model code is a lumped-parameter code – each room is divided into two lumped-parameter volumes. In the lower layer originates fire, which entrain air into a smoke plume and transport heat and mass into the upper layer. With time, as more mass is transported into upper layer, it grows downward. If it grows down below any opening, like a window or a doorway, heat and mass can be transported into other compartments – this makes possible to compute fire spread between floors. Other features of CFAST model include possibility of modeling fire either as a source of heat or with an elementary combustion model. User can define its basic parameters, e.g. rate of pyrolisis, chemical composition of the fuel, combustion products, based on which CFAST combust the fuel, taking into account amount of available oxygen. What is more, unburned fuel can be transported within compartments where it can continue burning [7]. In the picture below can be found simplified overview of a two-layers zone model.

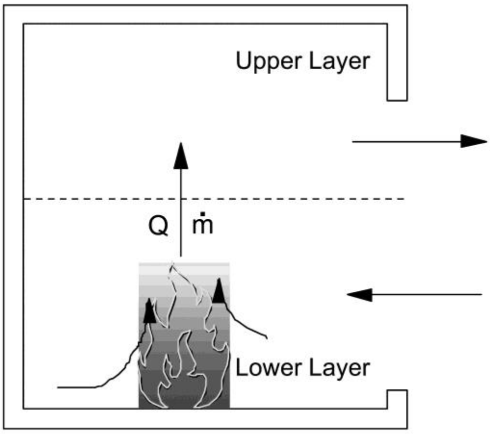

Fig. 1. Two zone model overview [7].

Computational fluid dynamics models – FDS

Computational fluid dynamics models (CFD), also referred to field models, are based on an approach, which divides an enclosure into a large number of elemental volumes. It can be said that zone models with its compartment division into two layers (zones) were just a start in fire modeling. Fire engineers knew that dividing compartment into smaller and smaller zones will increase dramatically the accuracy of fire predictions and that was the ground for field models development. Fundamental governing equations of mass, momentum and energy transfer are being solved between these small volumes to predict fire consequences within the enclosure. CFD codes were originally developed to solve complex fluid dynamics issues. This family of models can be considered as a micro approach to fire modeling [12].

Compared to zone models, field models require extensive computer power and more detailed understanding of fundamental physical phenomena, like turbulence and combustion kinetics. However, because of advance in computer technology over the last decade, field models have become more accessible and are one of the most common type of codes in fire modeling nowadays. Still, it needs to be emphasized that after all input parameters describing compartment geometry and fire parameters are placed in the model it takes down to few minutes for a zone models to be run, while days, weeks or even months to obtain results from CFD simulation. Lentini claims that in fire engineering there is a place for both type of models, however its choice should be based on type of required simulation. For example, multiple scenarios can be run using a zone model and in this way one or two scenarios can be selected for field modeling [14].

The most popular CFD model in fire engineering is Fire Dynamics Simulator. It was developed by National Institute of Standards and Technology in USA and first released in 2000 in order to solve fire-driven flows both in enclosures and in the ambient. It calculates numerically a large eddy simulation form of Navier-Stokes equations appropriate for low-speed, thermally driven flow, with an emphasis on smoke and heat transport from fires. Navier-Stokes equations are reduced from their full form to a thermally expandable, multi component perfect gas form, which eliminates acoustic waves. Because of modified form of Navier-Stokes equations –"low Mach number" equations, which are being used, a high-speed solver is capable of solving transient flows for a large number of volumes in a relatively short time compared to other CFD codes. This solver uses a fast Fourier transform method for direct solving of pressure equations, while in typical CFD schemes they must be solved iteratively.

Complete description of methods, equations and schemes used in FDS can be found in [21]. To give short information about main FDS features it could be stated that turbulence is being modeled by Smagorinsky form of Large Eddy Simulation (LES) and combustion is modeled with mixture fraction based model. This model assumes that combustion is mixing controlled and that there is infinitely fast reaction of fuel and oxygen. Mass fractions of all the products and reactants can be derived from the mixture fraction using state relationships. Finally, radiative heat transfer is solved using radiation transport equation for a non-scattering gray gas by means of Finite Volumes Method.

MONTE CARLO METHOD

In this section a method of quantifying user uncertainty in fire modeling will be described, called Monte Carlo method. Monte Carlo technique is a method of performing multiple experiments by means of random sampling of variables within given probability distribution. This random sampling of parameters uncertainty space is replacing point calculation carried out by conventional, deterministic methods. As stated already in the paper, in deterministic models, a set of zero-uncertainty parameters is taken and transformed into a zero-uncertainty prediction set. However, all sources of simulation input data are subject to uncertainty. These include inaccuracies and indeterminancies of initial conditions, lack of knowledge about phenomenological model, uncertainties in describing the physical reality and other approximations in mathematical model, not being part of investigation in this paper. To make sure that we are drawing conclusions about real environmental process and not some artefacts resulting from model uncertainty, a statistical comparison between uncertain model predictions and uncertain observations is needed and Monte Carlo technique is one of the simplest method of implementing it. Its simplicity lies in regarding a deterministic simulation as a single realization random process and then building statistics of this process by performing multiple simulations [1].

To understand methodology of Monte Carlo simulation, typical steps performed in such an analysis can be described [26]:

- *Static model generation* – every MC simulation starts with developing a deterministic model, which can be considered as a base case and in which the most likely (base case) values of input parameters are used,
- *Input distribution identification* – when deterministic model is ully developed, risk components can be added to the model. As described above, it is considered here that the risk originates from the probabilistic nature of input parameters, that is why in this step it is needed to develop underlying distributions of input parameters. Identifying input distributions for the simulation model, often called a distribution fitting, is well known problem and many fitting routines can be adapted to identify the most suitable probability distribution for a given set of data, e.g. Chi-square, Kolmgorov-Smirnov, Anderson-Darling tests [6],
- *Random samples generation* – when all distributions of input parameters are collected, a set of random samples from these distributions can be generated. One set of the input variables is used in the deterministic model to provide one set of output variables. Next, this step is repeated – in this way a number of sets of random samples is generated and all possible output values are collected. This part can be called a core of Monte Carlo simulation and is described more detailed below,
- *Analysis and decision making* – after all output values from simulations are collected, a statistical analysis of this data is performed.

Implementation of Monte Carlo methods requires sampling from given probability distributions of input variables, which may be very difficult and expensive in analysis and computer time [22]. Indeed, selecting the values of input variables for simulation should be done with a great care to make sure that desired information will be obtained from the code. There are many methods of selecting the values of input variables, in [23] are described three methods, which seems to have most considerable appeal to the authors, namely random sampling, stratified sampling and Latin hypercube sampling. Random sampling is the most basic sampling technique and is based on choosing a sample randomly from the input values, so that each input value has the same probability to be chosen for the sample. In stratified sampling all areas of the sample space are divided into disjoint intervals. Then simple random sampling is applied to each interval. Finally, Latin hypercube sampling is based on similar approach of sampling each interval of sample space, but leads even further. The way of selecting n different values from each of k variables X1, …, Xk will be described based on [27]. At first, a sample space is divided into n disjoint intervals on the basis of equal probability. Then, one value from each interval is selected at random according to the probability density in the interval. The n values obtained for X1 are paired in random manner with n values of X2. The n pairs are combined in random manner with n values of X3,forming n triplets and so on. Authors suggest to think of Latin hypercube sample as forming a (n x k) matrix of input where ith row contains specific values of each of the kth input variables, which are used on the ith simulation. In this way it is ensured that each of input variables Xk has all portions of its distribution represented by input values [23].

There are many advantages of using Latin hypercube sampling. When the output is dominated only by few components of X, this method ensures that each of those components is represented in fully stratified manner, regardless which one is truly important [23]. Stein [25] showed that Latin hypercube sampling decreases the variance of simulation compared to the simple random sampling as long as the sample size is larger than the number of variables. What is more, the reduction increases with the degree of additivity in random variables on which depends simulated function. However, drastic decrease in variances of the probability integrals in fire simulations should not be expected. Reason for this is the fact that in this type of simulations results are often a strongly non-linear function of the input variables.

To sum up, Monte Carlo technique is considered as rather straightforward method for accounting simulation uncertainty – it does not require any assumptions or approximations. Main advantages of the method are that the convergence rate does not depend on the number of independent random variables and that it is so exact. Main disadvantage is the fact that it requires large number of simulation for complicated problems and so large CPU time. Even though techniques of improving the convergence rate exist, e.g. Latin hypercube sampling, it is still considered by some as not applicable in most of problems currently studied in CFD [19].

MONTE CARLO SIMULATION OF FIRE SCENARIOS

According to [17] there are two main reasons of using Monte Carlo simulations in fire engineering – to deduce the probability or to propagate the uncertainty. In recent years Monte Carlo simulations have been used to model risk to people in building fires [28], fire risk assessment of a domestic houses [8], evacuation life safety in assembly halls [18], human behavior in office building fires [9], probability of deaths in fires caused by toxic gases inhalations [29], to study the role of uncertainty in improving fire regulations [24] and others. Some computer tools have been developed, which include the possibility of using Monte Carlo technique – CRISP model, which determines stochastic aspects of entire fire scenarios [9] and CESARE-RISK [29], which can be used to identify cost effective design solutions for building fire safety systems. However these tools and researches are based on simple zone models, mainly two-zones schemes and easily done hand calculations, as the use of more advanced, CFD models has been too expensive to compute. As the computational resources has significantly increased within the last 10 years, now it seems to be possible to include in Monte Carlo simulations in more advanced models, not only the simple zone ones. According to [14] CFD models in fire safety engineering of large buildings have already replaced the zone ones. However it seems that still not many research has been done on computing probabilistic Monte Carlo simulations with these advanced fluid dynamics models. In this paper a review of state of art in probabilistic fire simulations using Monte Carlo method and more advanced field models will be done.

Monte Carlo analysis of user uncertainty in FDS – research on Lund University in Sweden

There has been a research on Lund University in Sweden regarding connection between FDS and risk analysis by means of performing Monte Carlo analysis [16]. According to the authors it was the first attempt to implement Monte Carlo technique directly on FDS code. The main objective was to determine the level of uncertainty when using FDS and to show how the choice of input variables affect the results of FDS simulation. One fire scenario was chosen as the basis for all the simulations with input parameters representative for a real case. It was decided to choose a well-documented fire experiment in a typical multi-room building. Afterwards the most important input parameters were determined by means of both qualitative reasoning and sensitive study with one input parameter at a time variation. Next step was to find the input parameters distribution. Finally, the input variables were sampled randomly within the determined distributions and simulated using FDS code. Simulations were done both by varying input variables independent of each other and by varying all chosen input parameters. Only one output variable was investigated, namely visibility along a path, which is regarded as one of the most common criterion in fire safety engineering.

Based on output variable investigated – visibility along a path qualitative reasoning was made to choose input parameters affecting it the most. Then, for the chosen parameters a sensitivity study was conducted by varying parameters around an estimated value by a factor of approximately 0,5 to determine the difference in visibility. As a result, three parameters were chosen to have the most impact on the results, namely mass extinction coefficient, soot yield and Heat Release Rate (HRR). Next step, finding reasonable distributions of these input variables was according to the authors one of the most time consuming and challenging work done. Based on over 800 simulations performed main conclusions were as follow: when all three input parameters were varied simultaneously there is a significant spread in the output data – at a height of 1,4m above the floor there is a 35% probability that the visibility is equal or exceeding 10 meters. This means that if a FDS user would select a value of HRR, soot yield and mass extinction from the acceptable ranges there is 35% probability that the results would be acceptable. According to the authors it cannot be expected that FDS users will apply presented method in the practical work due to its time consumption, however the main recommendation is to be very careful about any decisions concerning input variables and it is highly recommended to perform informed sensitivity analysis whenever any input parameter is questionable. Another conclusion might be to use safety margins as possible approach to ascertain that the simulation results are conservative enough.

Two-Model Monte Carlo Simulations

Two-Model Monte Carlo Simulation is a technique developed by Hostikka [10], [11]. It can be regarded as an "intelligent" method of accelerating the convergence of Monte Carlo simulation, when more demanding fire schemes, like CFD, are used. It combines fast to simulate zone modeling with CFD modeling of potentially higher physical resolution and is therefore called Two-Model Monte Carlo (TMMC). Underlying assumption of the model is that the ratio of the results obtained by zone and CFD models has smooth variations when moving within points of the random space. In this way, when at some point of the random space a result is obtained for the more accurate model, it is possible to scale the result in its neighbourhood for the less accurate model. Actual Monte Carlo is based on calculating results for all the scaling points of random space directly, which is computationally very demanding, while here more efficient way of improving the model accuracy is used.

TMMC technique was used to develop Probabilistic Fire Simulator tool (PFS) at VTT Technical Research Centre of Finland. Originally the tool was used in the projects concerning fire safety of nuclear power plants, with time its application became much wider, including fire safety in large building and ships. PFS can be used to compute the distributions of fire model output variables and the sensitivities of the output variables to the input by means of rank order correlations. Implementing rank order correlations allows the user to identify both the modelling parameters and the physical properties that have the most influence on the results.

Various test were carried out to check the performance of the TMMC model, described in [11]. CFAST model was used as the less accurate one, while the more advanced one was the Fire Dynamic Simulator. CFAST results were then scaled with FDS results and compared with full Monte Carlo analysis performed with FDS (as it is impossible to compare high number of scenarios with any experimental data). The outcome of the tests is that a good accuracy of the technique can be achieved when there is a knowledge on the relative importance of the random variables and based on this information are placed the scaling points. When such a knowledge is not available, the random space should be divided uniformly in all dimensions and the number of necessary scaling points may be very high. What is more, it should be ensured that the physical time series, that are used to calculate the scaling functions are not limited by artificial or unphysical reasons. If such a limitations exist it may prevent the convergence of the TMMC distributions.

Sensitivity analysis of Fire Dynamics Simulation

In previous sections two approaches were described of combining Monte Carlo method with advanced methods of simulation of fire scenarios. Both methods showed that sensitivity analysis is very important step in the simulation methodology. Therefore research carried out at the Aalborg University in Denmark concerning sensitivity analysis of Fire Dynamics Simulation will be presented [2]. Sensitivity analysis was performed on a benchmark case corresponding to a fire scenario in a domestic size room. The purpose of the work was to investigate the most important input parameters and in this way to optimize work with FDS. In the research screening method of Elementary Effects was applied. This method can be considered as an extension of a derivative-based screening method – screening method with global characteristics. The method determines elementary effects on the model of input factors calculated within the factor's range of variation. Model sensitivity to each factor is then evaluated by the mean value and standard deviation.

To choose significant input and output parameters for the analysis initial "pre-screening" was made in the work based on literature and experience. Then, a number of 40 FDS simulations were performed according to the method of Elementary Effects. As a results it was found that FDS shows very significant sensitivity to a high number of input parameters. It was found that it is possible that deviations of 100% of an output parameters may occur in case of varying input parameters within the possible range. Detailed results from the screening sensitivity analysis can be found in the paper [2]. What is the most important, authors state that fire dynamics simulation results should never be accepted and applied in practice without performing proper sensitivity analysis. It is highlighted as well that sensitivity screening results leads for the importance of uncertainty estimation.

One more recent work on sensitivity analysis of complex problems in fire protection engineering should mentioned. In the paper [5] FDS model and evacuation model are evaluated multiple times varying input parameters according to probability distributions found in the literature. A detailed methodology is presented, including two steps of the analysis. First step is a significance test for the correlation between the input variables and the outcome. Second step is a stepwise regression analysis. Detailed description of the method can be found in the paper.

Other approaches

So far in the paper Monte Carlo technique was described as being applicable for probabilistic fire simulations. However, opinions can be found stating that due to high computational costs Monte Carlo technique is not applicable to CFD probabilistic models. Such an opinion can be found in [4]. In the paper author suggests alternative approach to Monte Carlo technique, namely an adaptive response surface method based on moving least squares. The method is used to minimize the number of required solver solutions and according to the authors allows a very fast evaluation of the model reliability. It is said that for complex CFD models number of necessary evaluations is much lower compared to Monte Carlo analysis. To further decrease the number of simulations performed authors recommend proceeding sensitivity analysis and identification of the input parameters relevance. Also preliminary scan of random space is suggested for the sensitivity analysis to be able to focus on the narrower, most relevant sampling area. In the work it is again concluded that there is a very limited available data for the stochastic fire models and system components. Detailed data on some parameter uncertainties and distributions is missing and so controlled assumptions have to be made. Still, it is said that estimating distributions is more appropriate approach compared to estimating deterministic values.

DISCUSSION AND CONCLUSIONS

Deterministic numerical models are essential tools in modern fire protection engineering. Zone models were extensively used in the last decades, however their reliability and accurateness in some applications were questionable. That is why, when the computational computer power increased dramatically, in recent years more complex field models, based on computational fluid dynamics, started replacing the zone ones and nowadays they seem to have major role in fire simulation in practice.

Why deterministic fire modeling is not enough? Because every fire model is a subject to uncertainty. There is a problem, known in the scientific environment as the problem of GIGO (Garbage In-Garbage Out), which basically means that the quality of model output is determined by the quality of input. In this context, uncertainty and sensitivity analysis can be concerned as a method of estimation a degree of validity of a simulation model. What is more, there is a common statement in fire protection society, that the most critical link in the process of using computer fire simulation is the user. It is essential that the user is aware of possible uncertainties and take into account the possibility of failure during the design process. That is why even though conventionally simulations are performed by means of deterministic models and fixed input parameters selected by the user, alternative, probabilistic approach should be propagated, which makes possible to incorporate into analysis all relevant variables and uncertainties. The main disadvantage of probabilistic models, compared to deterministic ones, is required long computational time. Nowadays however, with dramatic increase in computer power or even cloud computing as new paradigm in information technology, computer requirements are becoming less of a barrier.

Recommended probabilistic technique in this paper is the use of Monte Carlo analysis – a general technique of performing multiple simulations using random sampling of input variables which belong to given probability distribution. The use of Monte Carlo analysis in fire engineering is not an innovative approach and a number of successfully implemented applications of this probabilistic method was presented in the paper. However, for many years the method was mainly applied to coarse, zone models and the application in more advanced fire models was unpractical due to the computational cost. Nowadays, when the field models are replacing the zone ones, there is a need to apply the probabilistic manner to more sophisticated solutions.

Even though there is a very limited research on applying Monte Carlo to CFD fire models, as a fairly new method, the review of most important work in this subject was given. Different ways of implementing Monte Carlo to advanced computer models were presented - explicit application of Monte Carlo to FDS models and alternative, intuitive approach - Two-Model Monte Carlo analysis, which allows to combine two models: the coarse, zone one and accurate, field one in the same simulation. In TMMC simulations are initially performed using both models in relatively small number of points of the random

space. Next, full Monte Carlo is performed using the faster but less accurate model, and the results are corrected using the scaling functions. In this way the convergence of the model is significantly accelerated.
As the computer power capabilities improve dramatically, implementing probabilistic manner to very advanced fire models needs to be developed. Methods that already exist should be, according to their authors, simplified and the theoretical basis should be further investigated. General trend is to decrease the number of scaling points to shorten the computational time and make the techniques more applicable in practical engineering work. All of the researchers in the subject highlight the difficulties in finding reasonable distributions of the input parameters and the need for further investigations in this topic. All in all, it seems that the probabilistic approach in advanced fire simulations is on very early stage at the time.

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The physicochemistry methods used in criminalistics

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ABSTRACT

Criminalistics is a lawful education which was created in the late nineteenth century. It uses many methods to work against the crime events. The most often used are the physicochemistry methods. The object of interest which is analyzed by this methods is called a criminalistics trace.

In this article we characterized and compared some analytical methods used in criminalistics, viz., microscopy, spectroscopy, chromatography and electrophoresis, so it can be useful to study analytical chemistry and criminalistics.

INTRODUCTION

Analytical chemistry is the study of the detection, identification and quantification of the components (called also analytes) present in the test sample. We say about an qualitative analysis when we want to know what chemical elements are in the sample and about quantitative analysis which determines the amount of this elements, all of them or just a certain. Structural analysis gives an information of functional groups and the spatial arrangement of the atoms in molecules. Analytical chemistry also determines what chemical changes taking place within the analyzed compounds and gives an information of speciation [1,2].

Analytical chemistry has an important role in the development of many fields of science and technology. It is widely used in industry, in the monitoring and control of pollution, medicine and many others [1-3].

Criminalistics is one of the application of analytical chemistry. Many chemical methods can help in the identification of unknown materials found at a crime scene.

Criminalistics is a lawful education which was created in the late nineteenth century. The father of this education is an Austrian criminal jurist Hans Gross. In 1893, he release the book titled ‘Handbook for Coroners, police officials, military policemen, et cetera’ (original German title is ‘Handbuch für Untersuchungsrichter, Polizeibeamte, Gendarmen, u.s.w.’). Of course the crime and ways of catching criminals were known much earlier, however this event is believed to be the beginning of criminalistics [4-6].

Despite the fact that this form of an education is very young, it has so many definitions – general (‘criminalistics detects a crime’) and very detailed. Nowadays, criminalistics can be defined as a practical education, on the basis of which it is possible to recognize, detect, prove and prevent the crime. It also divides on technique, tactic, strategy, methodology and theory of criminalistics [5-7].

Criminalistics uses many methods to work against the crime events. The most often used are the physicochemistry methods. The object of interest which is analyzed by the physicochemistry methods is called a criminalistics trace. This is a residue after some incident and it has to be revealed, collected and protected before an analysis. Glass, alcohol, fiber, lacquer, soil, clothes, all biological traces which contain DNA, explosives, drugs and many other subjects can contain the criminalistics traces. The police laboratories use many methods to analyze the criminalistics traces. There are spectroscopy, chromatography, electrophoresis or microscopy methods [8].

This article is a collection of fundamentals of criminalistics and various analytical methods, its characteristic and comparison.

MATERIALS AND METHODS

In this section we characterized and compared a few analytical methods, like gas chromatography or mass spectrometry.

Gas chromatography

Generally accepted definition of chromatography (nomenclature of the International Union of Pure and Applied Chemistry, IUPAC) reads as follows:

Chromatography is a physicochemical method for the separation in which the components separated are distributed between two phases - one of which is stationary (stationary phase) while the other (the mobile phase) moves in a particular direction [9].

The gas chromatographic separation of a mixture of compounds is based on their distribution between the stationary phase and a mobile phase, which in gas chromatography is gas. The mobile phase moves the components of the mixture through the column. The chromatographic process is based on the migration of samples which are in the form of steam, through a column packed with a stationary phase. The stationary phase can be a solid or a liquid.

Typical gas chromatograph consists of a receptacle or a generator of carrier gas, flow regulator, carrier gas purifier (desiccant and deoxidizer), an injector, the chromatographic column, a detector, a thermostat and a computer.

The gas chromatograph works as follows: carrier gas from a receptacle is run by a flow regulator, carrier gas purifier and injector where it is directly inject to the column chromatography and further to the detector and to the atmosphere.

The sample is injected by using of a syringe or injection loop, in the injector is evaporated and goes into the carrier gas flow and then to column chromatography. In the column is separation of the individual components of the sample that passed through the column successively goes to the detector generating the analytical signal. The signals after amplification are stored in computer memory in the form peaks - the chromatogram.

The entire system - from the injector to the detector - is in the thermostat, the temperature of each component is determined using the appropriate controls [10].

Chromatographic analysis can provide qualitative information in the form of characteristic retention parameters and quantitative information in the form of peak areas [1].

UV-VIS spectrophotometry

UV-VIS spectrophotometers are used to measure absorbance in wavelength function in in the range of 200 to 800 nm (ultraviolet range at a wavelength of from 200 nm to 400 nm, visible range – from 400 nm to 800 nm). The basic elements of spectrophotometers are the source of radiation, an optical system (monochromator), measuring cuvette, a detector for measuring the radiation intensity and the recorder and the computer [1,11].

Radiation sources can be for a range of UV – deuterium lamp, for a range of VIS – tungsten filament lamps, halogen lamps, or tungsten-halogen lamps and for the entire range of UV-VIS – high pressure xenon arc lamps.

The monochromator consists of a radiation splitter and two narrow slots. Among monochromators stands out prisms and diffraction gratings.

Samples are placed in a transparent cell, also called a cuvette. The cuvettes are rectangular vials (for special purposes are also used cylindrical cells) with lids, which are placed before the measurement of the test sample (in the form of a dilute solution of analyte in a solvent of low absorbance over a range of wavelengths).

The intensity of the radiation passing through the sample must be recorded after processing an electrical signal. Due to the low beam energy generally spectrophotometric detector should also fulfill the function of the amplifier. The ultraviolet and visible light detectors are used as the device whose operation is based on a photoelectric effects. These include photocells, photomultipliers, photoresistors and photodiodes.

The UV-Vis spectrophotometer works as follows: radiation from the light source passes through the entrance slit, then passes through the monochromator where is cleaved, then starting slot ‘out’ as a narrow band of the cleaved part of the spectrum directly to the sample. After passing through the sample beam is directed to the detector, where the conversion of light into electrical impulses, which are then recorded and processed [1,9,11-13].

Quantitative interpretation of the results of spectrophotometric can be done in various ways, by an algebraic method or calibration curve [12].

Microscopy

The microscope is a traditional tool in the study of physical properties of criminalistics traces. The ability to zoom allows accurate analysis of surface features and sometimes also the inner structure. Once a simple, uncomplicated construction, today microscope is a device increasingly sophisticated, giving more and more research opportunities. There are many types of microscopes; in criminalistics greatest recognition are:

> stereoscopic or stereo microscope – it has the simplest construction and it is easy to use, gives even 125-fold magnification, allows to obtain a three-dimensional, non-reversed image of the object observed which is entirely sufficient;

> comparison microscope – two stereo microscopes are connected to a single comparison eyepiece and this type of microscope allows to observe two different objects lying next to each other in the same time, it is an excellent tool for comparative analysis;

> scanning electron microscope – is characterized by high resolution, zoom to as much as 500000 times and high sharpness, not only serves to magnify the observed object, but also to analyze its ‘interior’ [14].

Mass Spectrometry

The essence of mass spectrometry is measuring the mass to charge ratio (m/z) to determine the amount and type of chemical elements present in the sample. A mass spectrometer consists of a sample injector, an ion source, an accelerator, a mass analyzer and a detector.

1. Depending on the state of matter and the volatility of the sample there are several ways of sample’s injection.
2. In the ionization chamber take place ionization and fragmentation particles. Ionization is to create a positive ion, or electron detachment (one or more) of atoms/molecules, whereas fragmentation is the breakdown of the resulting ion to different fragments (parts) electrically neutral or positively charged. There are several ways ionization - the simplest and most commonly used electron ionization, chemical ionization and ionization electric field.
3. In the analyzer takes place the separation of ions according to their mass and charge. There are three basic analyzers - analyzers static (the magnetic analyzer

with single or double focusing), dynamic analyzers (the time of flight analyzer) and resonance analyzers (quadrupole mass analyzer).

4. As a detector in mass spectrometry the most commonly used is ion collector.

Mass spectrometry is most widely used in the analysis of organic and inorganic compounds. It allows to get maximum information on the test substance, if it is in the pure state. The spectra of contaminated compounds are difficult to interpret, so it is necessary to find a pre-separation method (fractionation). Unfortunately, it is destructive for the sample, however, thanks to the possibility of testing materials of small size, this problem is partially solved. Mass spectrometry is therefore a very accurate method, highly sensitive and allows analysis of a large amount of sample components without the need for prior separation [15].

Capillary Electrophoresis

Electrophoresis name comes from a combination of two words – electro- and Greek '*phoresis*' (transfer). The basis of electrophoretic techniques varies electrophoretic mobility ionic compounds (a charged) in an electric field.

Construction of the capillary electrophoresis apparatus is not complicated. It is composed of two vials of electrolyte (buffer), wherein the ends of the capillary and two platinum electrodes are immersed. On the cathode side there is a detector and on the anode side there is injector of samples. The capillary tube may be placed in the thermostat.

In the capillary electrophoresis due to the small volume of capillary (up to 2 ml) very important issue is the application of repetitive, small volume of samples, in order not to cause a reload of the excessive volumes. In practice, usually it is applied to a few to several nanoliters of sample.

There are several methods of injection a small amount of sample to the apparatus. One of them is carried out by use of a small pressure difference between the inlet and the end of the capillary. For this purpose, the pressure at the inlet of the capillary or vacuum pressure at its outlet. In some designs it is also used siphoning, a slight difference that is generated by increasing the capillary immersed in the sample vial, above the level of the final vial.

Capillary electrophoresis has many advantages distinguish it from other instrumental methods. Using this technique can analyze very small sample quantities. This method is also characterized by high efficiency, selectivity, short analysis time, the ability to automate the process, and to prepare the sample for analysis it has to be diluted [9].

DISCUSSION AND CONCLUSIONS

Microscopy gives the opportunity to study surface features, and sometimes the internal structure of samples, does not allow for qualitative and quantitative analysis. This technique can be tested samples of very small sizes, both organic and inorganic; it is a non-destructive method – not have any effect on the sample. Using this method police officers can identify for example tests shells and missiles [16].

Other (characterized in this work) analytical methods allow to analyze the chemical composition of the samples.

Using mass spectrometry, we can analyze samples of organic and inorganic gaseous form, but this analytical technique in contrast to microscopy, is a destructive technique. However, due to the possibility of testing materials of small size, this problem is partially solved. The result of the analysis carried out on a mass spectrometer, a mass spectrum, which is characteristic for each compound. Analyzing them, it is possible to determine molecular weights and formulas summary of the test substances, which will help to understand their structure and composition; thanks to these spectra it is possible to identify unknown substances. It is a method accurate, characterized by high sensitivity, thanks to mass spectrometry can analyze a large amount of sample components without the need for prior separation.

The capillary electrophoresis apparatus is less complicated in structure in comparison with the mass spectrometer, a gas chromatograph or UV-VIS spectrophotometer. This method allows quantitative and qualitative analysis of organic and inorganic samples, however it is destructive; this method is characterized by high efficiency, selectivity, speed testing and the ability to automate the process and the analysis of very small sample amounts.

Gas chromatography is also a destructive method, it makes possible to analyze samples of the organic and inorganic compounds in gaseous form in trace amounts. This allows for qualitative and quantitative analysis. As in the case of capillary electrophoresis it is possible to automate the process.

Chromatographic analysis is rather fast, we can get results in few minutes. In Central Police Crime Lab in Warsaw it is possible to quantitative analysis of amphetamine sulfate by gas chromatography. They have accreditation No. AB 596 by the Polish Centre for Accreditation [16].

UV-VIS spectrophotometry, as gas chromatography or capillary electrophoresis allows analysis of small quantities of organic and inorganic compounds. Samples are placed in the apparatus in liquid form. Using this analytical method obtain qualitative and quantitative information about the tested substances; an additional advantage is the ability to automate the research process [5].

In conclusion, physicochemical methods used in the laboratory police to detect criminalistics traces are useful because of their sensitivity, automation and test speed and objectivity of the result. In addition, the study of organic and inorganic substances, with the possibility of quantitative and qualitative analysis, are effective and extremely useful in detecting criminalistics traces. For the analysis of criminalistics traces, one of the most commonly used test methods is gas chromatography or GC/MS which is coupled with a gas chromatograph mass spectrometer. Actual forensic technologies are so advanced at helping to solve crimes, for example Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), High-Speed Ballistics Photography, Magnetic Fingerprinting and Automated Fingerprint Identification (AFIS) [17].

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Jasmonates as new active substances in pharmaceutical and cosmetic industry

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***Keywords**: jasmonates, methyl jasmonate, tumour therapy, anti-aging cosmetics*

ABSTRACT

In recent years there has been observed an increasing interest in the use of natural compounds in both cosmetic and pharmaceutical industry. Phytohormones are natural compounds that regulate plant growth [1]. Jasmonates are a class of phytohormones, that has been recently used as an active substance in compositions for skin care and treatment. Jasmonic acid and its derivatives may be used in anti-aging products, because they stimulate epidermis desquamation and reduce both wrinkles and discolorations [2,3]. It is also believed that jasmonates have antiparasitic and anti-inflammatory potential [4,5]. Moreover, they are able to suppress proliferation and induce the apoptosis of tumour cells [6]. This review covers the synthesis, biological activities and use of jasmonates in medicine, pharmacy and cosmetology. A concise overview of the available information of the use of jasmonates in both pharmaceutical and cosmetic industry may provide insights for future research in this area and gives hope for the development of new active substances in related fields.

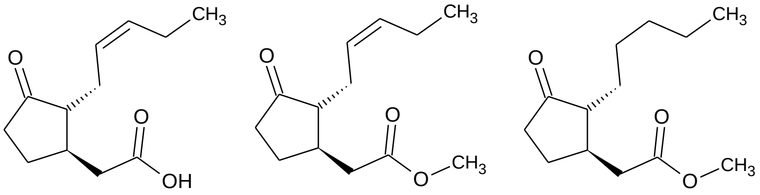
CHARACTERISATION OF PHYTOHORMONES

The therm „hormone" is derived from Greek, meaning „set in motion" [7] and was coined by Ernest Starling in 1905 [8]. In general, there are five major classes of plant hormones: abscisic acid, auxins, cytokinins, gibberellins and ethylene [1]. Other identified plant growth regulators include i.e. salicylic acid, polyamines, brassinosteroids and jasmonates (jasmonic acid and its derivatives). Phytohormones are signal molecules that are produced within the plant in extremely low concentrations and are responsible for plant growth and development process. They affect gene expression and transcription levels and cellular division [9]. It is important to notice, that not every plant growth regulator is a plant hormone. According to Kopcewicz et al. [1] the criterion for including a chemical compound to plant hormones is the ability to cause a physiological effect in concentration that not exceed 10^{-6} mol L^{-1}. The another criterion is widespread occurrence of particular substance in plants. After being transported to desired tissue, hormones may cause an immediate effect or they can be stored in cells to be released later. Storage is not the only way to decrease an excessive amount of already-formed hormones. The can be also inactivated or modified by their coniugation with carbohydates, amino acids or peptides [10].

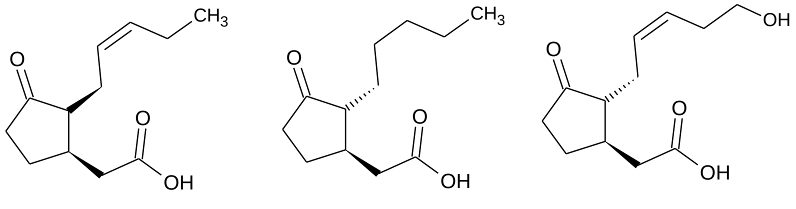
BIOSYNTHESIS AND BIOLOGICAL ACTIVITY OF JASMONATES

Jasmonic acid (JA) and its derivatives such as methyl jasmonate (MeJ), methyl dihydrojasmonate (MeDHJ) (Fig. 1), 7–iso–jasmonic acid, 9,10–dihydrojasmonic acid and 12–hydroxyjasmonic acid are members of the jasmonate group [9]. MeJ was isolated for the first time in the year 1962 from the essential oil of *Jasminum grandiforum L.* and *Rosmarinus officinalis L* [11]. Jasmonic acid is one of the most abundant jasmonate. The biosynthesis of JA takes place in cell membrane and involves combinations of a number of enzymatic biosynthetic pathways. The substrate in this synthesis reaction is linolenic acid [12].

Jasmonates play a significant role in plant resistance to insects and pathogens, therefore they are called „stress hormones”. They can also modulate aspects of fruit ripening, root growth, tendril coiling and production of viable pollen. These phytohormones represses genes encoding proteins involved in photosynthesis as well as activate genes encoding vegetative storage proteins [13].



(-)-JA MeJ MeDHJ



(+)-7-iso-JA 9,10-dihydro-JA 12-hydroxy-JA

Fig. 1. The structure of jasmonic acid and its derivatives.

THE USE OF JASMONATES IN COSMETIC INDUSTRY

Jasmonic acid and its derivatives have found application in cosmetics. Many patent publications reveal various cosmetic activity of jasmonates. They were used to inhibit hair loss and to stimulate the growth of human keratin fiber. They were also applied to increase hair density [14]. Moreover, jasmonic acid and its derivatives were also used as depigmenting agents [3]. In other patent jasmonic acid derivative such as 3-hydroxy-2-pentylcyclopentaneacetic acid was used to stimulate epidermal renewal and to promote desquamation of the skin. This compound was applied to reduce the signs of skin ageing and to smooth the skin of the face [15]. Compositions comprising of at least one (dihydro)jasmonic acid derivative were also used to stimulate the production of the lipids that form sebum and therefore to treat dry skin [16].

Recently, one of the derivatives of jasmonic acid, sodium tetrahydrojasmonate with trade name LR2412 has been developed to reduce the visible signs of aging. To determine the biological activity of this compound, both *in vitro* and *in vivo* studies were performed. Franz diffusion cell was used to investigate the penetration of LR2412 on human skin. The studies proved that LR2412 reached viable epidermis and superficial dermis. Within the upper layers of the stratum corneum LR2412 accelerated desquamation and enhanced the mechanical properties. Moreover, the positive effect of LR2412 on deposition of fibrillin-rich microfibrils in the papillary dermis in clinically photoaged volunteers was confirmed *in vivo* studies using a patch test. Additionally, the clinical study proved that the facial wrinkles were reduced [17]. The effect of sodium tetrahydrojasmonate on an *in vitro* reconstructed skin model (EpiskinTM) was also ivestigated. results obtained by the quantitative real time polymerase chain reaction (RT-qPCR) technique showed an increase in hyaluronan synthase 2 and 3 expression. Furthermore, an increase in hyaluronic acid deposits concentration in basal and suprabasal layers of the epidermis was observed [18].

THE USE OF JASMONATES IN PHARMACEUTICAL INDUSTRY

Jasmonates may by a feature of pharmaceutical industry, because they are ascribed to have antimicrobial, antioxidant, anti-inflammatory, anti-nociceptive and anticancer activity [19]. The use of jasmonic acid and its derivatives in pharmacology has been already known in prior art.

Jasmonates in tumour therapy

According to result of studies, jasmonates are able to supress proliferation and induce the apoptosis of tumour cells in diseases such as leukemia, melanoma, neuroblastoma, and moreover lung, colon, prostate and breast cancers [6,20,21]. Methyl jasmonate was found to be the most active anti-cancer derivate among natural jasmonates [22]. MeJ was studied in topical application for precancerous and cancerous skin lesions. It was observed, that three out of eight patients exhibited positive responses, two of them had complete recovery and one had a recurrence of the lesion three months post treatment [23]. Additionaly, he results of *in vitro* and *in vivo* studies on the potential anti-tumour effects of MeJ showed that jasmonic acid methyl ester acts against various tumour cell lines, moreover it was studied that that administration of MeJ with common chemotherapeutic drugs (such as cisplatin, adriamycin and taxol) and glycolysis inhibitors may be effectively used in cancer therapy [20].

Antiparasitic and anti-inflammatory potential of jasmonates

To determine the antiparasitic potential of jasmonates, Gold et al. [4] performed *in vitro* studies on selected major human blood parasites: a unicellular parasite *Plasmodium falciparum* (protozoan parasite causing malaria in humans) and a multicellular helminth *Schistosoma mansoni* (parasite causes the disease schistosomiasis which is one type of helminthiasis) [24, 25]. It was found that jasmonates are cytotoxic toward both parasites, however multicellular tested parasite is more prone to jasmonates activity. According to results of the studies performed by Vilela et all. [26], MeJ showed antiparasitis activity also against *Trichomonas vaginalis* (protozoan parasite and the causative agent of trichomoniasis, by inducing both time- and dose-dependent reduction in the number of living organisms [27]. It was also investigated that MeJ was found to be cytotoxic towards a metronidazole-resistant strain of *T. vaginalis* [28].

Inflammation is part of the complex biological response of body tissues to harmful factors, such as irritants, pathogens or damaged cells [29]. The potential anti-inflammatory activity of jasmonates was studied by Dang et al. [5]. The results of *in vivo* studies of activity of methyl jasmonate derived from the red alga *Gracilaria verrucosa* showed, that MeJ anti-inflammatory potential is similar or even more effective than prostaglandin-like compounds. Verbitski et all.[30], presented the results of *in vitro* studies, that revealed methyl 4,5-didehydrojasmonate anti-inflammatory activity that is comparable to that of the most potent natural anti-inflammatory prostaglandin 15d-D. Moreover, the modification of MeJ α-carbone atom with chlorine or bromide gave derivatives being much more potent than natural anti-inflammatory prostaglandins, however chlorine derivative would be more desirable with respect to safety [5,31].

SUMMARY AND DISCUSSION

According to the literature review presented above, it can be concluded that jasmonates are phytohormones that have interesting cosmetic and pharmaceutical activity. It is believed that jasmonates are able to reduce visibe signs of aging, stimulate epidermis renewal and enhance its desquamation. Moreover, these compounds stimulate hyaluronic acid synthesis, so they may be used in the treatement of visible signs of skin aging. Jasmonates have plant origin and may replace chemical active components of cosmetics with similar biological activity. Jasmonic acid and its derivatives give also hope for natural tumour therapy. They may be useful in leukemia, melanoma, neuroblastoma, lung, colon, prostate and breast cancers treatment. Moreover, these plant hormones may be used as natural anti-inflammatory medicine. Additionaly, jasmonates are believed to have antiparasitic activity (*S. mansoni* and *P. falciparum*). Oral administration of MeJ may be helpful in malaria treatement, whereas topical use of this jasmonate may be useful in trichomoniasis therapy. Although the biological activity of jasmonates on human body has not been fully investigated yet, they seem to be a promising natural active components of pharmaceutical and cosmetic formulations. Methyl jasmonate is found to be the most useful substance in pharmacology among all jasmonates. To sum up, jasmonates may be used in pharmaceutical and cosmetic compositions to enhance the activity of other active substances or as natural replacement of chemical compounds with similar biological action.

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The influence of the molecular weight of polymer on the morphology of polylactide-based membranes for tissue engineering

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ABSTRACT

Cell cultures are an important aspect of tissue engineering (TE). TE is a field whose main aim is to support regeneration of damaged, difficult to regenerate tissues. The scaffolds are the main and the latest issue of this science. Scaffolds are a medium for cell culture characterized by a highly developed, three-dimensional spatial structure. One form of scaffolds are semi-permeable membranes.

The experimental results of the preparation of semi-permeable membranes for cell cultures were presented. The effect of the molecular weight of polylactide and the addition of pore precursors (polyvinylpyrrolidone) on the morphology of the membranes and on functional their properties were studied.

INTRODUCTION

Tissue engineering is a field whose main aim is to support regeneration of damaged, difficult to regenerate tissues. The latest issue of this science are scaffolds. They are characterized by a highly developed three-dimensional spatial structure created by a network of interconnected pores. Scaffolds are a modern spatial physical medium for cell cultures used in the therapy of damaged tissues. Additionally, studies have shown that the scaffolds imitate very well the natural conditions in tissue, compared with traditional methods of cells cultures (e.g. Petri dishes, liquid medium). For this reason, in recent years scaffolds have become a popular part of research subjects [1÷3].

Scaffolds are generally in the form of semi-permeable membranes, which provide delivery of nutrients to the cells and evacuation of metabolites outside the scaffold. Membranes in tissue engineering are mainly made of biodegradable polymers, natural and synthetic. Natural polymers used in the preparation of scaffolds are collagen, elastin, chitosan or gelatin. The advantage of these polymers is that the products of their degradation are nutrients for cells. The disadvantages of membranes made from natural polymers is that they produce poor mechanical properties. Synthetic polymers have improved functional properties and are easily processed [3, 4]. The most popular synthetic polymers in tissue engineering are polyesters such as a polylactide (PLA), poly-ε-caprolactone (PCL), polyglycolide (PGA) or copolymers thereof [4, 5]. These polymers are characterized by biocompatibility and biodegradability and are well-tolerated by organisms. Moreover, these compounds and their degradation products are non-toxic to the organism cells. Additionally, they are subject to hydrolytic degradation, firstly to the building monomers which are physiologically present in organisms of mammals and secondly to CO_2 and water, products of physiological metabolism that are easily excreted from the organism [5÷7].

Polyesters differ in the time of hydrolytic degradation. The longest time (in organism, pH 7,2) is taken by poly-ε-caprolactone (more than 2 years), the shortest – polyglycolide (a few months). The time of hydrolysis of polylacitde is middle falls between PCL or PGA, under 2 years. This time, for a given polymer, increases with the length of carbon chain. Probably in feature, it is possible to control, to some extent, the degradation time of the whole scaffold by choosing an appropriate polymer with a specific molecular weight [5÷9]. This feature has also an influence on the functional properties of membranes used as implants for the regeneration of damaged tissues [10÷15].

There are many techniques for the preparation of polymer membranes. One of these techniques is a method of "wet" phase inversion (Fig. 1). It is characterised by the simplicity and ease to preparation and in that there is no need for any complex device. For example it is based on the pouring of the membrane-forming polymer solution onto an inert base (e.g. glass plate) and on the subsequent immersion thereof in a coagulation bath consisting of nonsolvent of polymer. It is important that the solvent and nonsolvent are miscible. After polymer coagulation, the membrane is taken out of the coagulation bath and dried. The use of a pore precursor is a variant of this method. For this purpose, other polymers (e.g. polyvinylpyrrolidone, poly(ethylene glycol)) or non-organic salts with appropriate crystal diameter are mainly used. Pore precursors are removed out from the structure of the already coagulated membrane. It takes place in the coagulation bath with an additional wash bath depending on the solubility of the precursor used [16÷20].

MATERIALS AND METHODS

Materials

Poli-L-lactide (PLLA) of M_n 86 000 g/mol NW 2003D, PLLA of M_n 53 000 g/mol NW 3051D and PLLA of M_n 43 000 g/mol NW 3251D were produced by Nature Works. Poly-L-lactide of M_n 43 000 g/mol, M_n 17 500 g/mol and poly-D-L-lactide (PDLLA) of M_n 30 000 g/mol (30% D centers content) were produced by Faculty of Chemistry of Warsaw University of Technology. Polyvinylpyrrolidone (PVP) of M_n 10 000 g/mol was produced by Sigma Aldrich. Chloroform and methanol were produced by POCh SA. Ultrapure water with 18.2 MΏcm conductivity was obtained using MiliQ device.

Preparation of the membrane-forming solution

The solutions of all polylacides with the addition of pore precursor (polyvinylpyrrolidone) and without it, were prepared. Firstly, solution of polylactides in chloroform with 3,5cP viscosity were obtained. Polymers were dissolved in organic solvent during 24 h with constant stirring using a magnetic stirrer without heating. Polyvinylpyrrolidone was added after complete dissolution of PLLA (minimum 24 h) in weight ratio 50:50. Subsequently the stirring was continued for the next 24 h.

Preparation of membranes

The polilactides solutions in chloroform with addition of pore precursor (polyvinylpyrrolidone) and without it, were poured onto a glass base. Thickness of solution on a base was 0,4 mm. The membranes were gelled in methanol. The membranes were dried after polymer coagulation and removal of pore precursor.

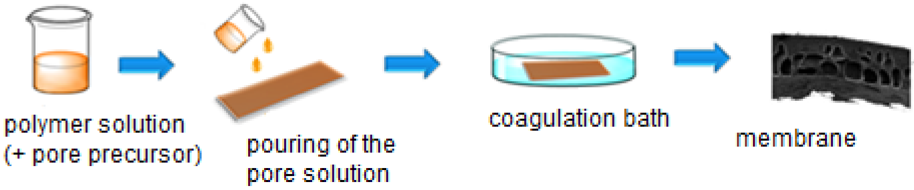


Fig. 1.“Wet” inversion phase method [21]

Analytical methods

The viscosity of polylactides solutions in chloroform was analysed using viscosimetric method in a capillary viscometer. The viscosity was measured by a flow time of a given quantity of liquid by a suitably calibrated capillary tubes with a known pressure difference.

The morphology of cross-sections for membranes and both surfaces was analysed using Scanning Electron Microscopy (SEM) on Hitachi TM1000. Samples of the membranes were immersed in ethanol and then fractured in liquid nitrogen. After drying, the membrane samples were coated with 7–10 nm thick gold layer using K550X Sputter Coater. Samples coated with gold were analysed in 300x and 1000x magnifications using 15 kV acceleration voltage.

RESULTS AND DISSCUSION

As a result, twelve kinds of semi-permeable membranes were obtained. For the preparation of the membranes six polylactides of different values of molecular weight were used. For every kind of polylactides, the influence of pore precursor was examined.

PLLA of M_n 86 000 g/mol

The membranes obtained from polylactide of M_n 86 000 g/mol are presented in Fig 2. The lower surface (located on the side of the glass plate used as a base) contains small oval pores with a diameter of below 3 to 5 μm. The cross-section of the membrane is characterized by the presence oval pores with diameter of 5–15 μm. The upper surface is more porous, than the lower one. Moreover, the pores are bigger – their size is in the range from about 5 to 10 μm. The other pores on this surface are covered with a thin covering layer.

PLLA membranes prepared by adding polyvinylpyrrolidone as a pore precursor are presented in Fig. 2. The lower surface, contains multiple oval pores with a diameter of below 5 to 15 μm. On the upper surface there are many more pores compared with the lower one. Their size is bigger, and is in the range from about 2 to 20 μm. The other pores on the upper surface are covered with a thin covering layer. The cross-section of the membranes is characterized by numerous pores with 5–15 μm diameter. Between them there are present bigger pores with diameter of 20–30 μm. It is important that on the walls, especially of the bigger pores, there are smaller pores, below 5 μm. This is a very important feature for cells because the perforation of inner pore walls enables the migration of nutrients and metabolites.

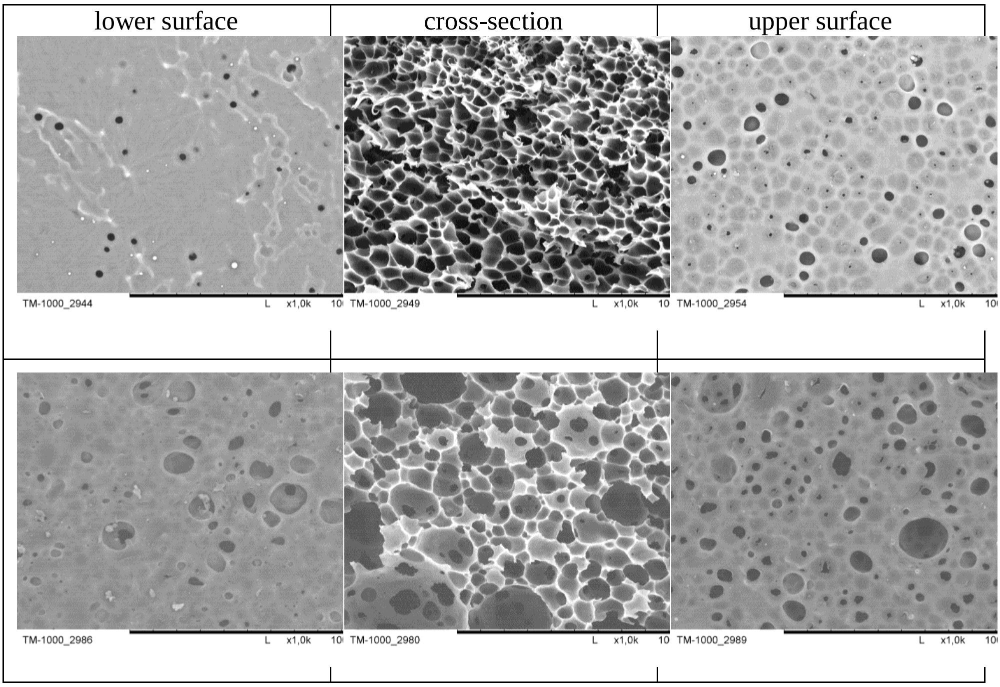


Fig. 2. SEM photomicrographs of membranes obtained from PLLA of M_n 86 000 g/mol (up) and membranes obtained from PLLA of M_n 86 000 g/mol with the addition of PVP (down)

PLLA of M_n 53 000 g/mol

The morphology of membranes obtained using polylactide of M_n 53 000 g/mol is shown in Fig 3. The structure of lower surface is irregular. The pores are very rare, unevenly distributed and small (about 1 μm). The cross-section of membranes and the upper surface contain small pores with a diameter of about 5 μm. In the cross-section, the shape of the pores is spherical and on the upper surface – irregular. The disorderly structure of the membranes with small pores is unfavourable for cell cultures. The number of pores on both surfaces and in the cross-section is significantly smaller, than in the membranes obtained using PLLA M_n 86 000 g/mol.

The membranes prepared with the addition of the pore precursor are presented in Fig 3. The lower surface is characterized by the presence of unevenly distributed pores with an irregular shape and a diameter of 2–10 μm. In the cross-section, the size of the pores is the biggest, having a diameter of about

20 μm. The upper surface is similar to the lower, with the difference that the pores are bigger, their size is 5–30 μm. Moreover, a lot of the pores on this surface are covered with a thin covering layer. This surface also contains cracks.

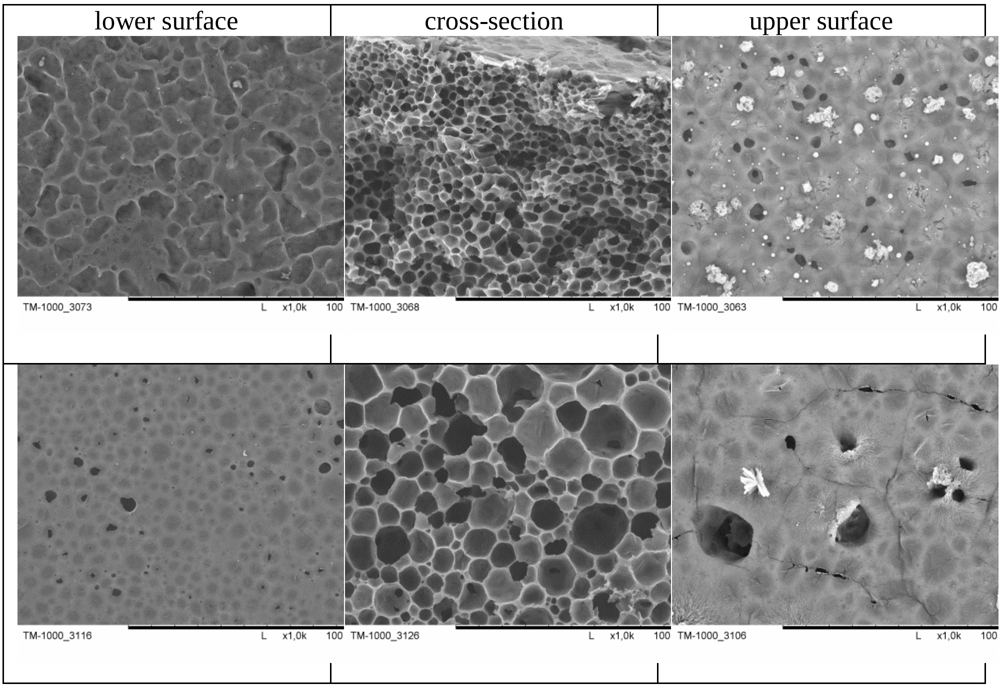


Fig. 3. SEM photomicrographs of membranes obtained from PLLA of M_n 53 000 g/mol (up) and membranes obtained from PLLA of M_n 53 000 g/mol with the addition of PVP (down)

PLLA of $\mathbf{M_n}$ 43 000 g/mol

Morphology of membranes obtained with PLLA M_n 43 000 g/mol are presented in Fig 4. The irregular lower surface contains rare small pores (about 1 um). In the cross-section are spherical pores with a diameter of 5–10 um. The morphology of the upper surface is similar to the lower. The number and size of the pores on both of surfaces is smaller than in the membranes obtained using PLLA of M_n 86 000 and 53 000 g/mol.

The membranes obtained with the addition of PVP as the pore precursor are shown in Fig. 4. The lower surface is characterized by plenty of, small pores (1–5 μm), that are unevenly distributed. The cross-section contains pores with an irregular shape and size from 2 to 25 μm. On the upper surface the shape of the pores is asymmetric and their sizes vary from 5 to 15 μm. The addition of the pore precursor increases the porosity of both surfaces and the size of the pores.

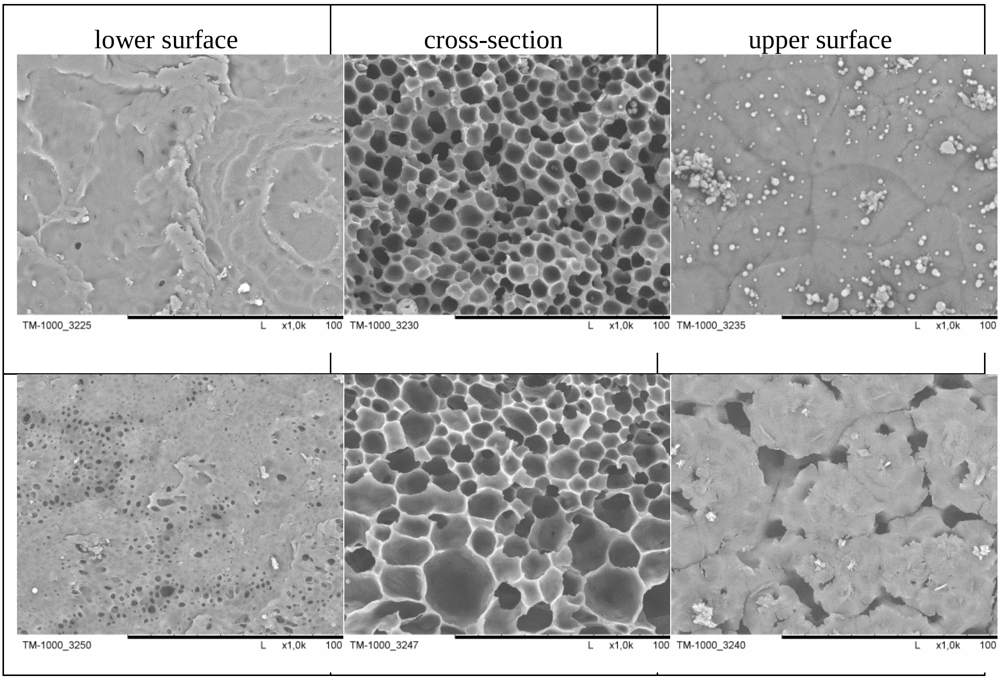


Fig. 4. SEM photomicrographs of membranes obtained from PLLA of M_n 43 000 g/mol (up) and membranes obtained from PLLA of M_n 43 000 g/mol with the addition of PVP (down)

PLLA of M_n 37 000

The morphology of the membranes prepared with polylactide of M_n 37 000 g/mol are presented in Fig. 5. The lower surface is characterized by rare, irregular pores with a diameter of 2–10 μm that are distributed between structures similar in shape to a block. These structures probably have an influence on the fragility of the membranes and decrease their functional properties. In the cross-section the pores are oval with a size of 5–15 μm. The number and size of the pores on the upper surface is similar to the lower.

The addition of the pore precursor caused the loss of block structures (Fig. 5). The lower surface contains small pores (2–5 μm) that are mainly are covered with a thin covering layer. In the cross-section, pore sizes are different and vary from 5 to 20 μm. Moreover, the biggest pores have perforations of in their inner walls. This is very important feature for cell cultures, because it allows for the migration of nutrients and metabolites. The addition of the PVP is favourable, because it causes an increase in the number of the pores on the upper surface. The shape of the pores on this surface is asymmetric and elongated, their size is 3–10 μm.

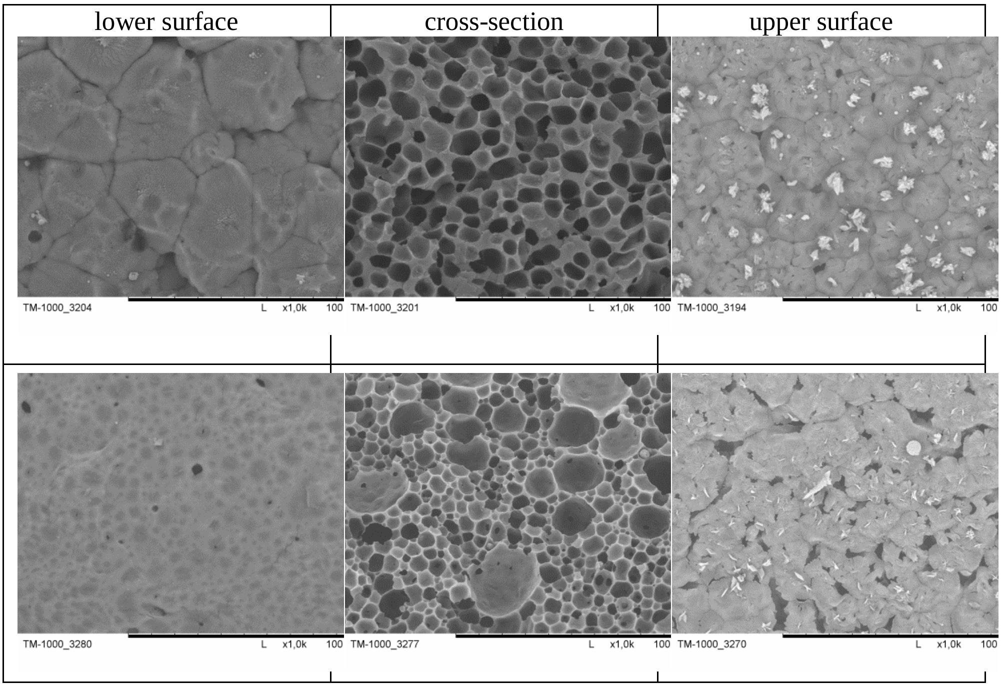


Fig. 5. SEM photomicrographs of membranes obtained from PLLA of M_n 37 000 g/mol (up) membranes obtained from PLLA of M_n 37 000 g/mol with the addition of PVP (down)

PDLLA of M_n 30 000 g/mol

The membranes manufactured with PDLLA of M_n 30 000 g/mol with the addition of the pore precursor, and without it, are friable and breakable. Their functional properties are weak. These disadvantages can be caused by the low molecular weight of polymer and the contents of D center in carbon chain.

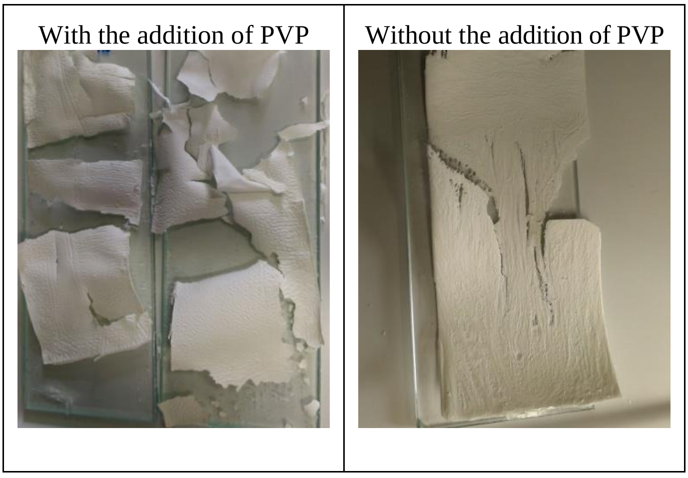


Fig. 6. Photographs of membranes obtained from PDLLA of M_n 30 000 g/mol

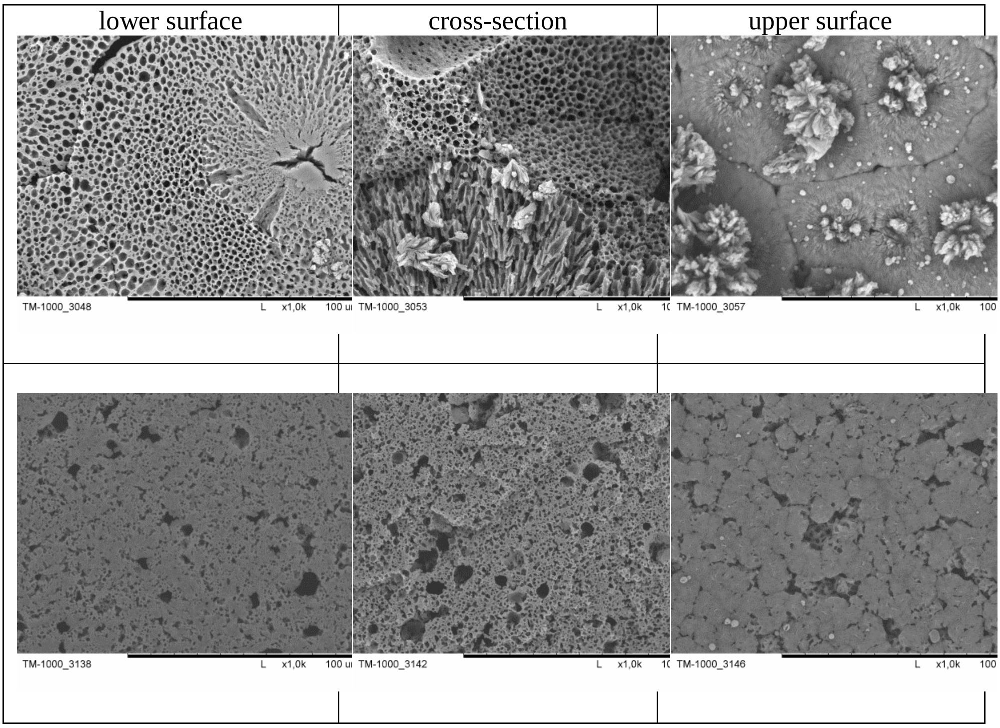


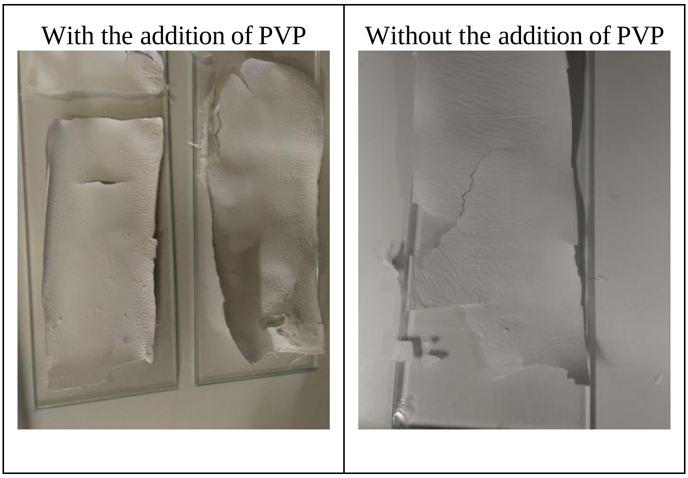
Fig. 7. SEM photomicrographs of membranes obtained from PDLLA of M_n 30 000 g/mol (up) and membranes obtained from PDLLA M_n of 30 000 g/mol with the addition of PVP (down)

The lower surface contains cracks and small spherical pores (about 3 μm). The cross-section of the membranes is characterized by the presence of oval or elongated pores of 3 μm in diameter. On the upper surface the pores are very rare, their size is the same as in the cross-section and on the lower surface. Moreover, the upper surface contains crystallites, which are probably polylactides with short carbon chains.

The membranes obtained with the addition of PVP, contain on both surfaces and in the cross-section numerous very small pores (about 2 μm), between which are some bigger ones with a diameter of 10 μm. The shape of these pores is irregular. The addition of PVP organizes the morphology of the membranes (lack of crystallites and differences in the shape of the pores).

PLLA of M_n 17 500 g/mol

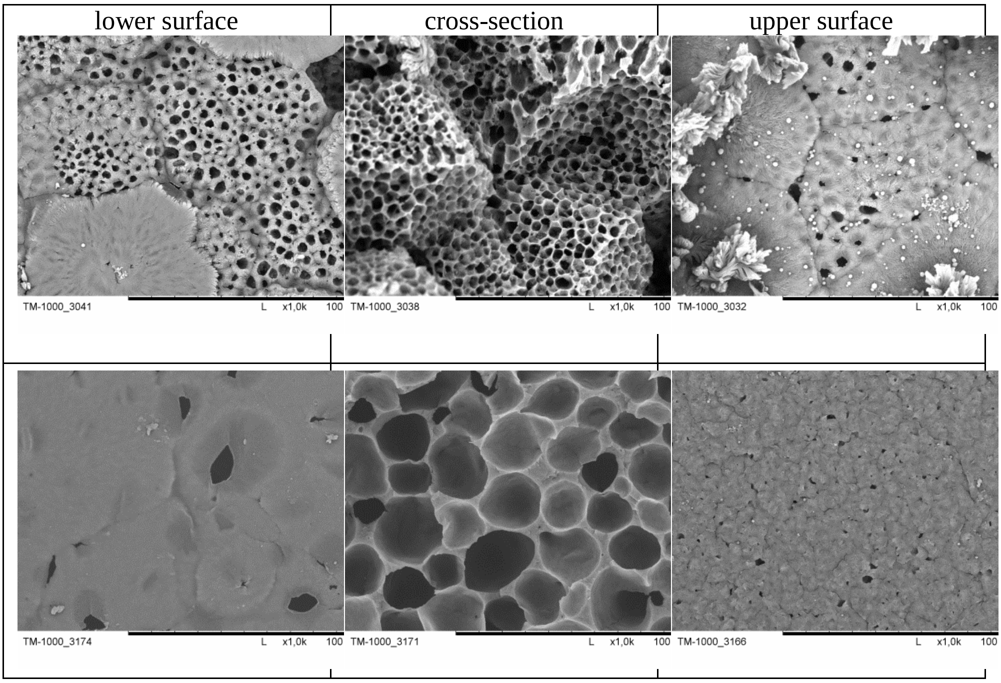
The membranes prepared with PLLA of M_n 17 500 g/mol using the pore precursor and without it are characterized by weak functional properties.



With the addition of PVP

Without the addition of PVP

Fig. 8. Photographs of membranes obtained from PLLA of M_n 17 500 g/mol



lower surface

cross-section

upper surface

Fig. 9. SEM photomicrographs of membranes obtained from PLLA of M_n 17 500 g/mol (up) and membranes obtained from PLLA of M_n 17 500 g/mol with the addition of PVP (down)

The morphology of these membranes is disorderly, similar to the membranes prepared with polylactide of M_n 30 000 g/mol. Both surfaces and the cross section contain block structures and rare, small pores (about 5 μm) of irregular shape. On the upper surface crystallites are present.

Here, as in the case of PLLA of M_n 30 000 g/mol, the addition of PVP organizes the morphology of the membranes (lack of crystallites and block structures). The lower surface contains rare pores, with irregular, elongated shapes and in size from 2 to 10 µm. In the cross-section are oval pores, with a diameter of 15–30 µm. On the upper surface are very small pores, ranging in size from 0,2 to 2 µm.

FINAL REMARKS

The influence of the molecular weight of polylactide on the morphology and functional properties of the semi-permeable membranes was examined.

The results show that :

- The membranes obtained from PDLLA of M_n 30 000 g/mol or PLLA of M_n 17 500 g/mol have insufficient properties for tissue engineering. They are friable and breakable, practically they do not form membranes at all. Their common feature is the presence of block structures.
- These structures probably have an influence on the bad functional properties of the membranes. Block structures are also observed in the case of PLLA of M_n 37 000 g/mol. For this reason, although membranes made from this polymer have the correct structure, there are doubts connected with their functional and mechanical properties.
- The addition of the pore precursor is favorable for the morphology of the membranes. In the membranes obtained with the addition of PVP, the upper surface is much more porous. Moreover, the pores are larger in size.
- Additionally, polyvinylpyrrolidone promotes the formation of perforations in the inner walls of the pores. The first of these features, allows for the entry of cells inside the membrane, and the second allows for the migration of nutrients and metabolites.
- The addition of PVP promotes the organization of the morphology of the membranes that are made from polylactide of low molecular weight (resulting in lack of crystallites and differences in the shapes of the pores).

Based on the above conclusions, it is found that semi-permeable membranes for application in tissue engineering can be made with polylactides of molecular weight larger than 37 000 g/mol. Moreover, it was observed that with the growth of the molecular weight of polymer, the porosity and the size of the pores increased. Additionally, in order to obtain a better morphology of the membranes, PVP should be added to the polymeric solution.

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Use of organic compounds in solar batteries

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***Keywords**: organic photovoltaics, solar cells, P3HT*

ABSTRACT

This paper presents the preliminary investigations of the activity of few organic low molecular weight compounds mixtures with P3HT (poly(3-hexylthiophene))in organic solar cells. The photovoltaic properties of those compounds as an active layer in organic solar cells at the configuration ITO/PEDOT:PSS/active layer/Al (tin-doped indium oxide/polystyrenesulfonate-doped poly(3,4-ethylenedioxythiophene)/active layer/aluminum)under an illumination of 1.3 mW/cm2 were studied. Seven kinds of devices which differ in the composition of their active layers were fabricated. By introducing different compounds into the mixture, a quantum efficiency of the structures at 0.37 % was obtained.

INTRODUCTION

One of the greatest challenges for contemporary man is to provide energy for all the inhabitants of Earth. Today the total power consumption of electric energy by the world population is estimated at about 13.5 TW, with at least one billion people having no access to it. 85% of all electricity is produced by burning fossil fuels whose production is increasingly expensive and detrimental to the environment. Also wind and water power plants have unfortunately a negative impact on the environment. While electricity produced from nuclear reactions is admittedly the least expensive, it is accompanied by the serious problem of radioactive waste. Therefore, the photovoltaic effect is claimed to be a solution. It seems that the use of inorganic cells has reached its limits and for the last few years increasing the efficiency of commercial solar cells virtually has not been achieved. Furthermore, the cost of producing them is relatively high. This is primarily due to the high cost of the process of making the crystals which requires high temperatures and, therefore, a large amount of expensive energy.

The solution seems to be the use of photovoltaics based on organic materials [1]. The advantages of organic compounds are that they are inexpensive to manufacture, easy to process, flexible, have a multitude of shapes and textures, and also exhibit partial light transmittance. In Poland photovoltaic cells based on organic compounds were made for the first time in the Cracow University of Technology in the Institute of Physics in 2001.

These were multi-layered cells made on a glass substrate with an ITO layer acting as an electrode collecting positive charges, an active layer made of a mixture of P3HT: polypyrrole and an aluminum electrode collecting negative charges and at the same time reflecting light quanta in the direction of the active layer. The efficiency of the photovoltaic structure was at 0.05%, which was perhaps not such a big achievement, but gave hope for better results in the future. Currently, the efficiency of organic solar cells produced in the laboratory of the Institute of Physics, Cracow University of Technology in a collaboration with the Polish Academy Sciences in Zabrze is 6% [2]. Although better efficiency, even 15% and 19.3% [3,4], has been obtained in some other laboratories in the world, the results apply only to hybrid cells that contain also inorganic elements.

Nonetheless, new kinds of materials which would be equally or even more efficient are still sought. For this purpose, seven kinds of different materials were measured. The preliminary results and possibilities of increasing the photovoltaic effect for those devices are presented in this paper.

THE MODEL OF THE PHOTOVOLTAIC PHENOMENON OCCURRING IN ORGANIC COMPOUNDS

A photon absorbed by an active layer in a photovoltaic cell creates an exciton, which migrates in the layer and either undergoes recombination or, if it hits an appropriate potential difference in the structure, is separated into free charges. Such a potential difference is generated at the interface of two different compounds, wherein one is a donor and the other an electron acceptor. Then, the charges are guided to the electrodes, whose work function is respectively lower for positive charges and higher for the negative. There are energy losses in these processes associated with the recombination of charges during their passage to the electrodes and on the electrodes themselves. Therefore, the materials for the active layer should be chosen in such a way that their energy level difference provides effective separation of the charges (Fig. 1).

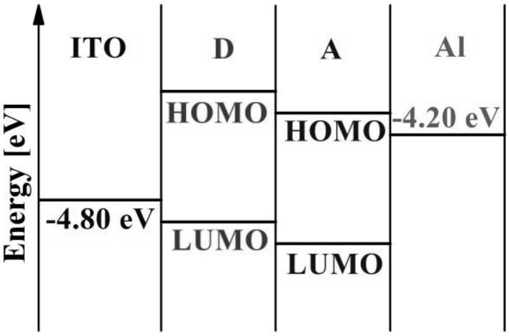


Fig. 1. The energy structure of a basic photovoltaic cell.

Fig. 1 presents the energy levels of the individual components of a photovoltaic cell. An electron donor D, in this case, is also an absorber of light quanta. An electron passes from D to the acceptor A, smashing the exciton at the same time. Subsequently, charges migrate to the electrodes, whose work function is at the appropriate energy levels to ensure the collection of charges.

A case where an absorber of light quanta is the acceptor A (Fig. 1) is also conceivable. In such a situation the positive charge, that means a hole, passes to the donor and then to the electrode. The negative charge is transferred in this case to the second electrode through the LUMO levels of the acceptor directly. Unfortunately, the mobility of holes is generally less than electrons, which causes the effect of exciton recombination to be more probable and, therefore, the photovoltaic effect appears to be less effective than the one described previously above. However, each time the structure of the energy levels must enforce separation of charges from the exciton and their transfer to the electrodes.

MATERIALS AND METHODS

As it is shown in Fig. 2 the following materials were used for the construction of an active layer in a photovoltaic cell: poly-3-hexylthiophene (P3HT), fluorene, 2-chloro-5-nitropyridine (pyridine), 7-hydroxy-coumarin (coumarin), a complex of 8-hydroxyquinoline and zinc (complex) and 2,2' bipyridyl (bipyridyl). In addition, two commercial compounds were used: Radiant Color NV HMS34 yellow dye (dye) and Uvitex NaClO4 (Uvitex). All of these materials have suitable energy levels, allowing the absorption of a photon (i.e. mainly P3HT) and creating a structure which gives a potential difference at the interface of the molecules, enabling separation of exciton charges, meaning a transfer of the electron to the acceptor (Fig. 1).

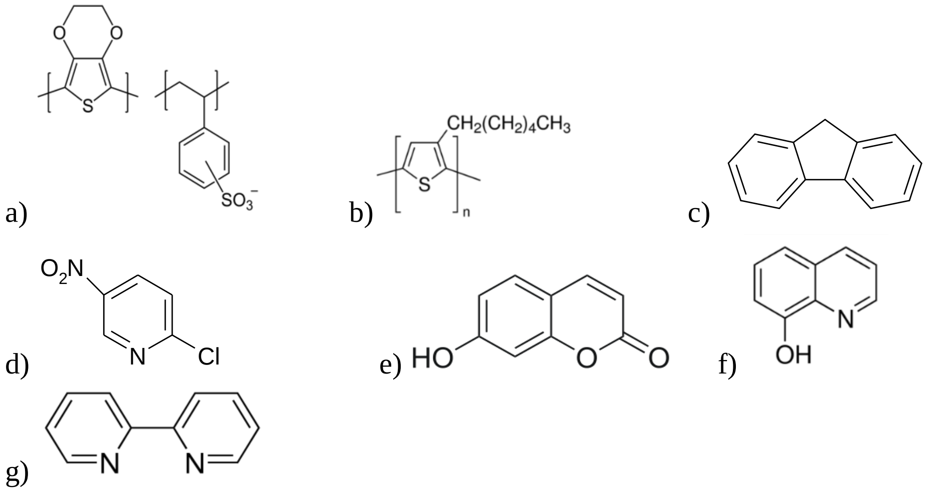
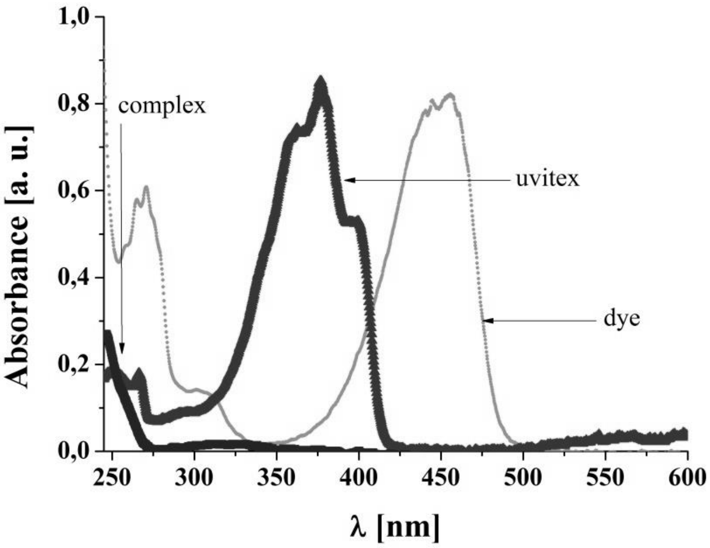


Fig. 2. Organic compounds used to create the photovoltaic cells: a) PEDOT:PSS, b) P3HT c) fluorene, d) 2-chloro-5-nitropyridine (pyridine), e) 7-hydroxycoumarin (coumarin), f) a complex of 8-hydroxyquinoline and zinc (complex),g) 2,2'-bipyridyl (bipyridyl)

The organic compounds used in the construction of the photovoltaic structure exhibit absorption in the UV range (Fig. 3); only P3HT absorbs in the range of solar light emission [5] with a maximum at 500 nm.

a)



b)

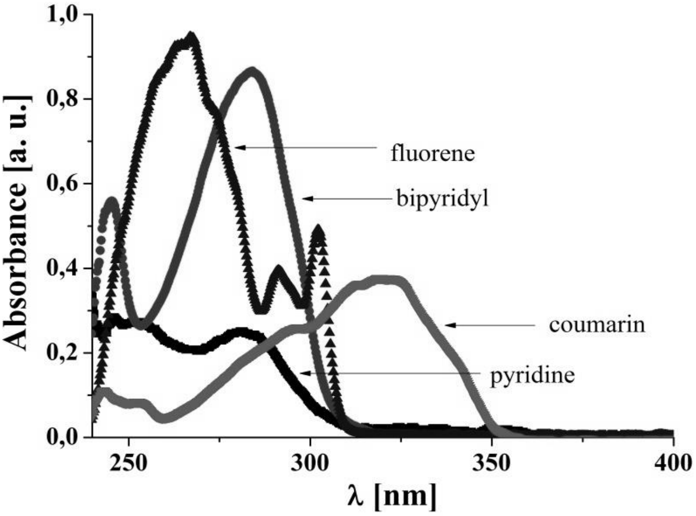


Fig. 3. Absorption of organic compounds used in the production of photovoltaic cells.

Thin layers were made by the spin coating method which means that the solvent solutions were applied on a rotating substrate. The speed of rotation can be changed and depends on the thickness of the layer which needs to be obtained. A lower value of rotations per minute results in thicker layers obtained and a higher value results in thinner layers. Speed also depends on the solvent and material. During the rotations the solution is spreading on the substrate by centrifugal force and the solvent evaporates. After spin coating, the layers can be dried in a vacuum oven in order to remove solvent residues and atmospheric moisture.

The aluminum contacts were evaporated in a high vacuum chamber (10^{-6} mbar) by thermal evaporation.

EXPERIMENT

The photovoltaic cells created in the laboratory had the structure shown in Fig. 4. On a glass substrate coated with ITO (indium tin oxide) a layer of PEDOT:PSS was fabricated by spin-coating (polyethylene dioxythiophene: polystyrene sulfonic acid) from an aqueous solution (layer thickness ranging from 70 to 80 nm). The substrate prepared in such a way was then dried at 120 °C in a vacuum oven for 30 min. Subsequently, the active layer was fabricated by spin-coating. The layer consisted of a mixture of P3HT polymer (regioregularpoly(3-hexylthiophene)) and another chemical (Table 1) having a weight ratio of 1: 1. The aluminum layer was applied by vacuum evaporation (thickness 100 nm). All structures presented in this paper were prepared in the same way, i.e. the sequence of layers was the same, the weight ratios of the components were identical (1: 1) and the layer thicknesses were almost the same. Thickness measurements were performed with a VASE® ellipsometer for each layer – for the active layer, the thickness ranges from 105 nm to 115 nm.

The structure prepared in this experiment was subject to a photovoltaic examination – determining the current-voltage characteristics: the so-called ‘light’ (that is, when a photovoltaic cell is illuminated) and ‘dark’ (without illumination), according to the measurement scheme shown in Fig. 4. For the measurement of characteristics, a computer-controlled Keithley 2400 sourcemeter was used. The solar cell was exposed to an illumination of 1.3 mW/cm2.

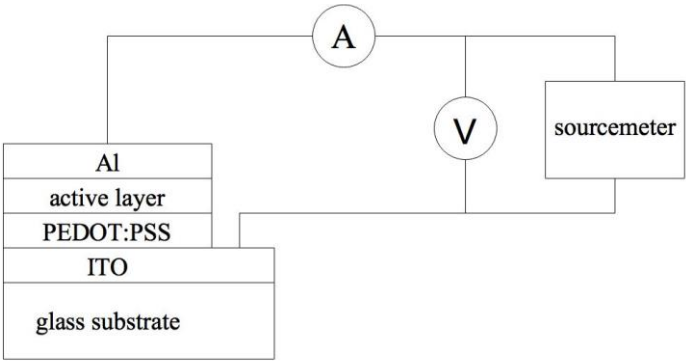


Fig. 4. The scheme of the measurement system of photovoltaic cells

The characteristics for the devices were determined by the use of current-voltage curves: open-circuit voltage U_{OC}, short-circuit current J_{SC} and the maximum power P_m that can be obtained from the examined solar cell. In addition, fill factor FF and the efficiency of the PCE photovoltaic cell were calculated using the following formulas:

the PCE:

$$PCE = \frac{P_m}{P_{light}} * 100\%$$

the fill factor:

$$FF = \frac{P_m}{U_{oc} * J_{sc}}$$

RESULTS

Fig. 5 shows exemplary current-voltage J-V characteristics of the devices. The results obtained are shown in Table 1.

The nature of all J-V curves of the structures examined is similar, which indicates similar values of parallel and serial resistance at the MΩ level, which appear in Shockley's model of photovoltaic diodes. In this model, the relation between the current and the voltage is described by the formula:

$$J = (J_L - \frac{U}{R_{sh}}) \frac{R_{sh}}{R_{sh} + R_s} - J_0 \frac{R_{sh}}{R_{sh} + R_s} \left(e^{\frac{U - JR_s}{nkT/q}} - 1 \right)$$

where:

JL - the density of current flowing upon illumination of the system

J0 - the constant of current flowing through the ideal diode in Shockley's model

Rs- series resistance

Rsh – parallel resistance

n =1

k – Boltzmann constant

T = 300 K work temperature

q - the electron charge in C

The high series resistance existing in the examined structures also results in a relatively low current, which can be obtained from the photovoltaic cell.

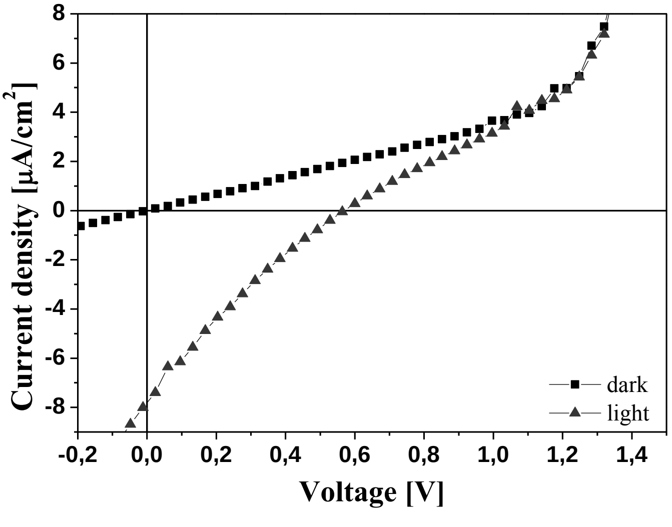


Fig. 5. J-V characteristics of the organic photovoltaic cell of the ITO/PEDOT:PSS/active layer/Al structure for an active layer made of a mixture of complex:P3HT.

Table 1. The characteristics of the photovoltaic cell of the ITO/PEDOT:PSS/active layer/Al structure illuminated (1.3 mW/cm2)

Active layer	**J_{SC} [μA/cm^2]**	**U_{OC} [V]**	**FF**	**R_{SH} 10^4 [Ω]**	**R_S 10^4 [Ω]**	**PCE [%]**
Fluorene:P3HT	3.72	0.462	0.22	8.52	9.47	0.029
Uvitex:P3HT	12.8	0.196	0.30	1.90	0.638	0.057
Dye:P3HT	4.72	0.089	0.33	2.22	0.149	0.011
Pyridine:P3HT	140	0.149	0.23	0.0889	0.0926	0.365
Coumarin:P3HT	6.44	0.490	0.26	7.88	6.56	0.063
Complex:P3HT	7.70	0.569	0.21	5.33	34.2	0.071
Bipyridyl:P3HT	5.66	0.541	0.21	7.12	9.48	0.050

It should be noted that the devices were not encapsulated which caused their faster degradation. Exposure to oxygen and humidity results in an abrupt increase in resistance which further causes the dramatic current reduction of those devices. Such low efficiency observed in those cells is caused by a high value of R_S resistance which has strong influence on the I_{SC} value. Also a high R_{SH} resistance value has an impact on the PCE - it causes a lower value. Furthermore, if the resistance R_S and R_{SH} are in the same order, this reduces the fill factor FF of that device.

The presented data confirm that a pyridine:P3HT structure has the best quantum efficiency of the photovoltaic cell, amounting to 0.37%. Although the result is not sensational, it shows the possibilities of the present compound. In each of them P3HT is the donor. Its absorption occurs in the visible range and the energy gap is equal to 2 eV, which means that such a system does not absorb the entire range of solar emission. Such an energy gap provides the maximum possibility of obtaining a light conversion factor at approximately 30%, which greatly limits the use of such a structure.

CONCLUSION

The research results prove that the structures presented in this paper have the photovoltaic effect, but at this stage they are not directly suitable for commercial application and they require further investigation. In order for these structures to show greater efficiency the thickness of the layers [6] and the weight ratios of the individual components need to be changed, and one more component of appropriate energy levels HOMO and LUMO needs to be added.

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The impact of modifications of the Krakowiec clays on their thermal expansion ability

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Keywords: *Hot-stage microscopy, Smectite modifications, Krakowiec clays*

ABSTRACT

The effects of modifications of the clay rocks containing smectite on their thermal expansion have been studied at the example of the Krakowiec clays from Wola Rzędzińska, Hadykówka and Łukowa (south-eastern Poland). Hot-stage microscopy (HSM) was employed combining a dedicated procedure of digital image analysis. The chemical modification included the treating with an soda addition and acid activation. The investigations of thermal expansion have shown that the acid activation of clays causes improvement of expansion ability. An soda addition is favorable as it considerably lowers the firing temperature of the firing product.

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INTRODUCTION

Lightweight aggregates (LWAs) are characterized by a bulk density not exceeding 1200 kg/m^3. They are usually manufactured from mineral raw materials, such as clays and clay shales, and also from some by-products of high-temperature technologies, for instance fly ashes and slags [1]. Keramsite (LECA – lightweight expanded clay aggregate) is produced of clay raw materials that on heating reveal a 5- to 6-fold increase of their volume due to evolving gases [2]. The product is composed of pellets with hard, sintered surface, while their interior is porous, light and resistant within a certain range.

Thermal expansion occurs when mineral phases present in clay rocks have a pyroplastic state at high temperature and while a pressure of evolving gases is sufficient to increase the volume of closed pores [3]. These processes take place after exceeding the range of firing of the clay rock, at temperatures above 1100°C. Under such conditions, clay-derived pellets become softer and expand, while their surface layer becomes sintered [4]. The gases evolving on heating depend on the mineral composition of the clay rock and result from decomposition of clay minerals, decomposition of minor minerals such as carbonates (calcite) and sulphates (gypsum), and also from high-temperature redox reactions. They include [1]: CO_2 (carbonate-derived), SO_2 (sulphate-derived) and O_2 (derived in reduction of iron oxides).

Krakowiec clays are the most important ceramic raw materials of southeastern Poland that are used for the production of brick products in many brickyards located in such places as Wola Rzędzińska and Markowicze.

Moreover, these clays are more and more often seen as materials useful for production of insulating screens protecting natural environment against penetration into soil of all kinds of contaminations [5]. Krakowiec clays have very diverse mineral composition with prevalent content of clay minerals such as: illite, chlorite and smectite.

Only few references to their suitability for the production of lightweight aggregates exist in the literature. Considering clay rocks, their suitability to manufacture keramsite is controlled mainly by their expansion index *S*. It is the ratio of the volume of the sample expanded to the sample volume prior to firing. The proposed studies except to determine this parameter for the raw materials in their natural state allow to describe the effect of modification of sulfuric acid and soda ash on the thermal expansion.

SAMPLE MATERIALS

The investigations were conducted on the krakowiec clays from Harasiuki, Wola Rzędzińska and Łukowa (SE Poland). They are represented by three samples – A, B and C – collected from active pits (numbering in accordance with the order given above). Their detailed characteristics were presented in Panna et al. [5], while the most important clay parameters related to the context of this paper have been compiled below (Table 1).

Table 1. Selected parameters of the Krakowiec clays sampled in the Harasiuki (A), Wola Rzędzińska (B) and Łukowa (C) deposits

Sample symbol	Smectite content [%]*	Other mineral phases **	Content of particles [%] ***	
			< 1 μm	<0,5 μm
A	21	chlorite, illite, quartz, calcite, dolomite	29,1	10,6
B	23		31,0	20,8
C	24		61,3	30,1

* determined using sorption of TETA Cu(II) [5]);
** determined using X-ray diffractometry;
*** determined using grain size analysis with a SediGraph 5100 apparatus.

The starting samples (A, B and C) were dried and milled in a laboratory ball mill. Three of them (batch I) were sodium modified by: adding into each 5% (in relation to the dry mass) of Na_2CO_3, physical activating the wet samples with a mechanical mixer, 30-day homogenizing, renewed drying and renewed milling. The sodium-activated derivatives were labeled with the symbols A1, B1 and C1. The other batch was composed also of three samples, whose 100-g milled increments were activated with 10% solution of H_2SO_4 and homogenized for 30 minutes with a mechanical mixer. After retaining them for 24 hours in a climatic chamber at 80°C and a relative humidity H_r of 90%, they were again dried and milled. These derivatives were designated as A2, B2 and C2.

METHOD OF INVESTIGATIONS

The course of thermal expanding of natural and modified clay raw materials was traced applying hot-stage microscopy (HSM). Using a HSM microscope it was possible to determine the temperatures corresponding to characteristic changes of the shape and the surface area of the samples observed continuosly in their transversal cross-sections. The images were used to observe whether the sample material expands on heating and, if it does, to record the temperatures of its characteristic changes, i.e. of firing, softening, expanding, melting and flowing. These data form the basis to establish the temperature ranges of the firing process of the expanded product.

Considering the difficulties in a precise recording of specific technological temperatures and determining the expansion coefficient *S*, the author used the novel method of determining the progress of thermal expansion with the MATLAB software, version 2013b. It facilitates a continuous measuring of the surface area of the geometrical figure being a transversal cross-section of the sample being heated. The proper procedure of image analysis [6,7] measures and records the thermal changes of the sample cross-section in relation to the cross-section of the starting sample in the function of temperature.

The samples for the HSM were made with a hand press from a disintegrated (<0.25 mm) material as tablets with a diameter of *ca* 2 mm and a height of *ca* 4 mm. The measurements were carried using a hot-stage microscope Misura HSM 3M (Italy) at the heating rate 10 K/min.

RESULTS AND DISCUSSION

The changes of the surface area *S* of the samples in the course of their heating compared with the surface area S_0 of the samples at the starting temperature were determined analysing the digital images recorded under a hot-stage microscope; they are presented in Figure 1. Detailed characteristics of the thermal expansion are presented (Table 2) – which are determined as in case of sample A (Fig. 1) – as the following parameters:

- the temperature of the beginning of expansion t_p. Assumed as the temperature at which the cross-section area of the sample after its softening and a further volume increase reaches back the volume of the starting sample, i.e. the cross-section of the initial sample;
- the temperature of the maximum expansion t_k, at which the sample size is the biggest and, at the same time, the sample is the highest;
- the temperature range of firing *I*; determined as the difference between the t_k and t_p temperatures;
- the expansion of the sample, expressed as $S_t/S_0 \cdot 100\%$, where S_t is the sample cross-section area at the temperature of measurements t_k, and S_0 the cross-section area of the natural sample.

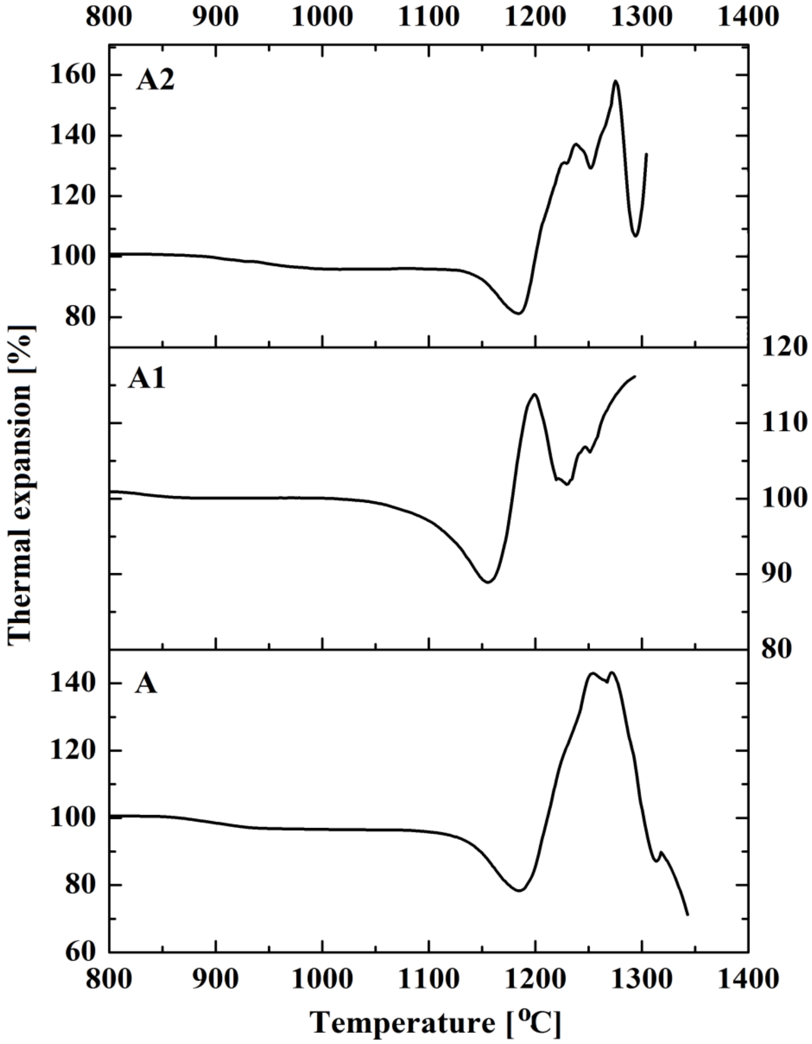

Fig. 1. Expansion values of the clay from the Harasiuki deposit (natural sample A and the products of its modification: samples A1-A2) in the function of the temperature of sample processing: A1 – sample activated with 5% (by weight) of Na_2CO_3, A2 – sample activated with 10% solution of H_2SO_4.

The highest value of expansion about 155% reached the sample A2 (after acid modification of the clay from Harasiuki). Other raw materials showed a smaller thermal expansion. A presence of the stepwise changes recorded on the curves of the volume increase (Fig. 1) can be explained as a result of cracking the vitreous coats on the tablets tested, accompanied by beginning of their softening. Low values of the firing temperature ranges of the remaining clay rocks from south-eastern Poland (especially for samples after sodium activation) are probably associated with the presence of some amounts of sodium feldspar (albite) that congruently melts at a temperature of 1118°C [8]. A significant content of the liquid phase with low viscosity results in the cracking of the coats at lower temperatures due to a high pressure of vapors evolved on heating. The gases are products of the reduction of iron oxide [$Fe_2O_3 \rightarrow 2FeO + \frac{1}{2}O_2$] and the transformation of the decomposition products of clay minerals into a mullite-like phase. At higher temperatures the latter phase recrystallizes into mullite. In the final phase composition of the fired mullite is accompanied (according to X-ray analyses) among others by cristobalite, a product of the decomposition of smectite [7,9]. Clay minerals and hematite are main sources of the gases evolving in the process of thermal expansion, the latter mineral being finely dispersed in the raw clay material.

Table 2. Selected parameters of the thermal expansion process of the samples (determined on the basis of HSM microscopy)

Sample symbol*	Temperature of the beginning of expansion t_p [°C]	Temperature of the maximum expansion t_k [°C]	Temperature range of firing I [°C]	Expansion ($S_t/S_0 \cdot 100\%$) of the samples at the t_k temperature
A	1210	1261	51	145
A1	1176	1196	20	114
A2	1199	1278	55	155
B	1202	1219	17	129
B1	1181	1195	14	106
B2	1197	1221	10	137
C	1210	1232	22	135
C1	-*	-*	-*	98
C2	1196	1212	16	140

* the sample did not returned to its initial height

The volume increase of sodium modified samples occurs at lower temperatures (maximum swelling ratio of approx. 1200°C), in view of the role of the large amount of flux (5% Na_2CO_3). However, the resulting melt has a lower viscosity and the expansion process ends – in comparison with started samples – at lower temperatures.

Treatment with sulfuric acid results in a slight improvement of expansion of samples, for example from 145% to 155% for clay with Harasiuki (sample A2). It is a result of the induction of a reducing atmosphere inside fired pellets connected with form gypsum by reaction of sulfuric acid with calcite. At high temperatures (about 1200°C) occurs SO_2 emissions. In this case the reduction of the iron oxide is combined with the releasing of molecular oxygen [6].

SUMMARY

The following conclusions can be made on the basis of HSM studies:

- Krakowiec clays have a low thermal expansion ability;

- The favorable values of thermal expansion are caused mainly by high contents of fine-grained smectite and also hematite. These minerals are the source of gases evolved on heating above 1000°C, initiating this process;
- It has been determined that an addition of 5 wt.% of sodium carbonate considerably decreases the firing temperature ranges but also reduces the ability to thermal expansion. It is connected with the introduction of too much liquid phase characterized by a low viscosity;
- Treatment with sulfuric acid results in a slight improvement in expansion of the samples due to the introduction of a reducing atmosphere inside the materials. This is associated with SO_2 emission.

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Polylactide scaffolds in tissue engineering

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ABSTRACT

Tissue engineering was once considered as a branch of biomaterials science. Nowadays it is an interdisciplinary field that allows reconstruction of damaged tissue by seeding multiplied host's cells onto the scaffold and implanting them into places of injury. Scaffolds are 3-dimentional porous constructions, made of polymeric or ceramic material. One of the most common scaffold materials is polylactide, a biodegradable and biocompatible polyester, easily obtained from natural, renewable sources. The aim of this paper is to highlight polylactide biomedical properties and summarize the state of art. It presents polylactide-based scaffolds used in cartilage, bone, nervous and vascular tissue regeneration.

INTRODUCTION

Tissue engineering was once a branch of biomaterials science, but since this discipline is constantly growing it is now considered as a separate category. Human body has a natural ability to repair its damaged parts and the goal of tissue engineering is to enhance the healing processes rather than to replace it. Host's cells are implanted to its body again in a way that should induce proliferation and tissue growth.

Cells are seeded onto and implanted in scaffolds – three-dimensional porous structures.

TISSUE ENGINEERING

Tissue engineering is an interdisciplinary field, combining material science, medicine, biology and chemistry. It is inspired by natural healing processes and seeks opportunity to enhance them.

The tissue engineering route is described in Fig. 1. It contains collecting patient's specific cells, which are then seeded and multiplied. Sometimes genetic engineering is used to increase cells' proliferation. After that cells are applied on a medium and implanted to patient body [1].

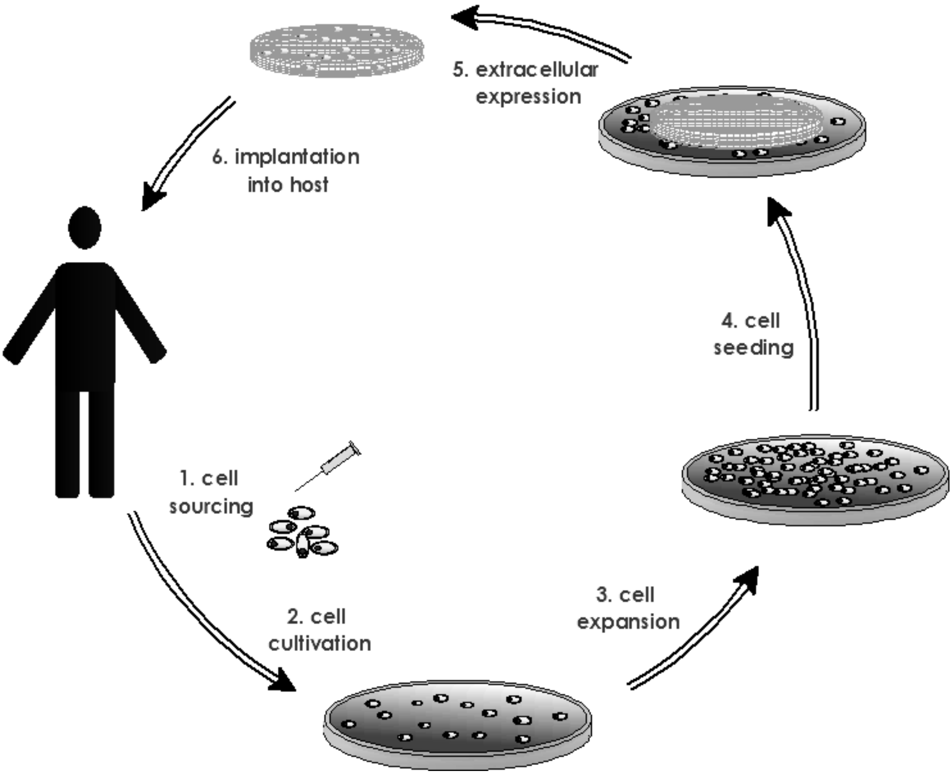

Fig. 1. Overview of tissue engineering process.

Implantation of cells in scaffolds causes natural wound healing response. The body responds to any tissue damage in a complex. During the process damaged tissue's remains have to be utilized and organism's homeostasis has to be restored. The process, unsupported, can be long and quite fragile.

Main concerns

Tissue engineering is based on positive interaction between cultured cells, scaffold and host organism. That implies several requirements.

First of all, scaffolds are implanted directly into patient's organism, so it is important that their material is biocompatible and will not alert the immunological system. Good cell adhesion is also mandatory [2].

Secondly, each kind of tissue is made from specific type of cells. The goal of tissue engineering is to encourage their proliferation. To ensure exclusive multiplication, bioactive factors are used (Fig. 2). Growth factors and antibiotics can also be delivered through scaffolds.

Apart from biological issues, scaffolds must possess appropriate mechanical properties, mostly depended on implementation area. They can be obtained through composites or using copolymers.

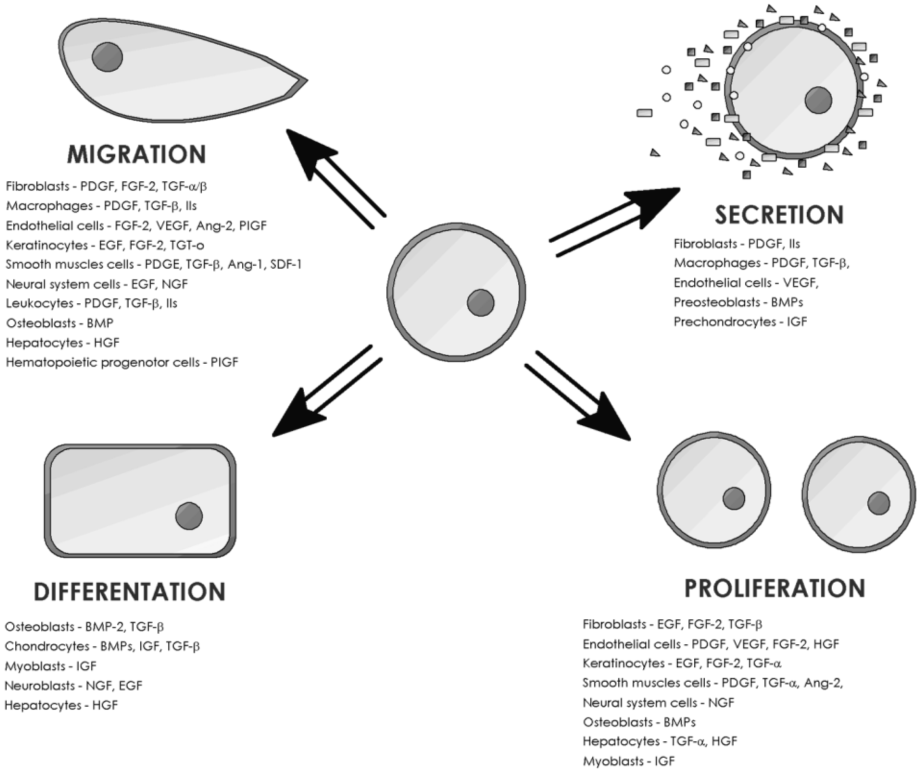

Fig. 2 Common bioactive molecules that regulate cell behaviour.

Scaffolds

Scaffolds are artificial three-dimentional structure with great porosity. They should stimulate cell growth. To do so, pore size must correspond with cultivated tissue cells size.

Materials used for scaffolds are often biodegradable – that allows to avoid unnecessary, invasive procedures of scaffold removal. This condition can be fulfilled using polymers such as polylactide and its copolymers.

Sometimes implantation of permanent structure is required. One of the non-polymeric materials used in production of this type of scaffolds are carbon nanotubes.

POLYLACTIDE SCAFFOLDS

Polymeric scaffolds are made from both natural and synthetic polymers. Natural polymers used in scaffolds are mostly protein-based and polysaccharide-based.

Most common protein-based polymers are: natural collagen, gelatin (denaturated collagen) or fibrin. On the other hand, commonly used polysaccharide-based polymers are: hyaluronic acid, chitosan and alginate [3]. They are widely used in regenerative medicine because they increase cells growth, they are biodegradable and highly water-soluble. Nevertheless, they have troublesome disadvantages too. As animal derivative they are less available, difficult to isolate and there is a risk of an immunogenicity. Also mechanical properties of natural-polymer-based materials are unexceptional.

Polylactide as a scaffold material

One of synthetic polymers used in scaffold preparation is polylactide. Polylactide is a polyester with lactic acid as a monomer, which is an α-hydroxyacid. The polymer can be obtained via direct polycondensation of lactic acid or via ring opening polymerisation of its dimer - lactide. It is biodegradable and degrades to non-toxic products [4]. It is allowed for medical applications by Food and Drug Administration.

Mechanical properties can be adjusted by modification of polymer structure. Both lactic acid and and its polymer are optically active, so stereoregularity of polylactide can differ, influencing its properties, e.g. crystallinity. PLA is often copolymerized with non-degradable but biocompatible polymers (eg. poly(ethylene glicol), PEG) to increase strength of the material.

Cartilage scaffolds

Cartilage is a flexible tissue that can be found in bones, rib cage, ears, nose, bronchial tubes and intervertebral discs. It consists of cells called chondrocytes and collagenous extracellular matrix, which is rich in elastine and proteoglycan. The main problem is that cartilage does not contain any nerves or blood vessels. That makes the healing process difficult and elongated in time, because nutrients from digestive system have to be delivered to cartilage through diffusion. Secondly, chondrocytes do not linger in the matrix but exist in small areas called lacunae and cannot reach injured areas. Damaged place is being covered in fibrocartilage, which is a scar tissue. Cartilage restoration is one of the most important challenges for tissue engineering.

There are many papers about cartilage regeneration. For example, Pilarek *et al.* created polylactide scaffolds containing perfluorodecalin (PFC) as a liquid carrier for respiratory gases[5]. This scaffold was made via elecrospinning of PLA fibers. Chondrocytes have to be cultured in high cell density, hence the risk that cells will suffocate on their own metabolic products and the tissue will die. Pores, at first big enough to drain those products, may get clogged in time, which hinders their effectivity.

It is known that chondrocytes supported on a scaffold can be shaped similarly to natural cartilage cells, however due to their simplified structure their mechanical behavior differs from natural mature cells. Camareo-Espinosa *et al.* produced multilayer polylactide scaffold to mimic natural regeneration environment [6]. All three layers of their scaffold were based on composites containing polylactide

Bone scaffolds

Bone tissue is a type of dense connective tissue. Osseous tissue creates a hard external layer of bone (Fig. 3). Bone marrow is located within the bone core. Between those two layers there is spongy bone tissue, where red and white blood cells are produced. Bone interior is made of organic substance – collagen and mineral substance – hydroxyapatite. This construction allows bone to be hard yet lightweight.

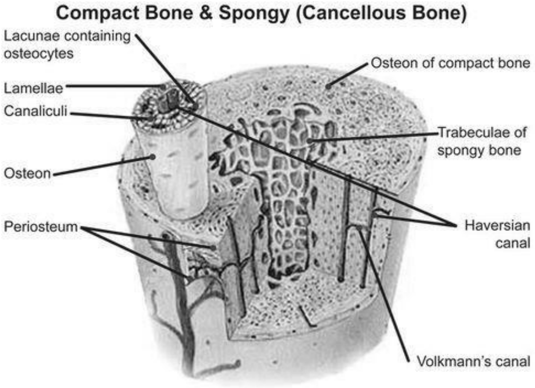

Fig. 3. The structure of bone [7].

Bone tissue is made of osteocytes and osteoblasts, which, same as chondrocytes, reside in lacunae. If necessary, bones are grafted with titan screws, which is an expensive procedure that requires further surgical removal. That creates an opportunity for polylactide scaffolds, which are already used in clinical trials.

Wing-Yuik Ip and Sylwester Gogolewski [8] compared polylactide scaffolds in bone regeneration in various forms: membranes, 3-D large sponges, chips and injectable pastes with marrow blood and osteoinductive component. Scaffolds were made of pure PLA, or combined with autogenous bone marrow, or in combination with bone graft. This way amount of autograft necessary to harvest before implanting was minimalized. Simultaneously, antibiotics like vancomicin were delivered. The addition of nanosize hydroxyapatite further improved mechanical properties of the materials.

It was proved that polylactide-based scaffolds provide a microenvironment for proliferation and expression of osteoblastic phenotype [8]. For example, polylactide scaffolds were succesfully implemented in a 85 year old patient. In this case, scaffolds replaced previously introduced bone-grafting, because after two months' patient slipped and broke the bone in close proximity to the previous injury.

Nervous system scaffolds

Nervous tissue is made of conducting cells, neurons, and supporting cells, neuroaglia. Single neuron has many dendrites and one, long axon (Fig. 4). Axon is covered in block segments of protective myelin. Spaces of axon not covered by myelin are called nodes of Ranvier. Whole axon covering is called neurilemma, a layer crucial to regeneration process. In peripheral nervous system myelin is produced by Schwann cells. In central nervous system myelin is produced by oligodendrocytes, but neurilemma does not occur and fibers do not regenerate.

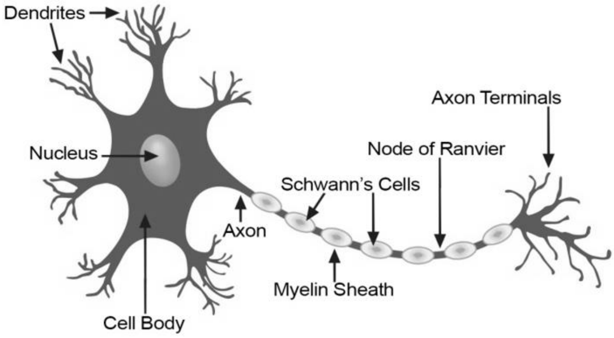

Fig. 4. Structure of typical neuron [9].

The importance of nervous system cannot be questioned. It provides brain activity, homeostasis and muscle control. Neurons are amitotic, which means they do not replicate through mitosis but though direct cell division. When neurons are damaged, neural connection is disrupted and electric impulses cannot be transferred.

Marquette *et al.* used polylactide scaffold for peripheral nervous system regeneration [10]. The trials have included 20 rats. PLA foam was used as a scaffold. Different technology of scaffold production resulted in their various morphologies. Poly(vinyl alcohol), (PVA) was used as a hydrophilic coating to increase cell adhesion. It is worth noting that it did not affect cells' proliferation, regardless of PVA amount. After one month neurons reconnected in all animals. Even gentle traction did not disconnect them.

For now, the best medical solution for nerve regeneration is still autografting. However, results for synthetic nervous scaffolds are promising and under further development. They plan to cover polylactide scaffold with conductive polymers such as polypyrrole to boost neurons' differentiation.

Cardiovascular scaffolds

Cardiovascular system, also known as circulatory system, is an organ that circulate blood trough organism. The most important elements of this systems are: heart, blood, and blood vessels. There are three types of blood vessels: arteries, veins and capillaries. Arteries transport blood from heart to capillaries, and veins transport blood in opposite direction. Capillaries are responsible for delivery of oxygen, water and nutrients to tissues.

Cardiovascular disease is the most common cause of death [11]. It is commonly treated by bypass grafts surgery, but only vessels with diameter more than 5 mm can be treated that way.

Korean researchers were testing whether polylactide scaffold is compatible with blood and if it can be used in vascular treatment [12]. Their scaffold was enhanced with non-biodegradable ePTFE (poly(ethylene terephthalate)). They also reported other successful applications of biodegradable polyesters in vascular tissue engineering. Authors show that the results are positive (Fig. 5), although they suggested tissue-engineering cells *in vitro* before implanting them to avoid thrombosis forming.

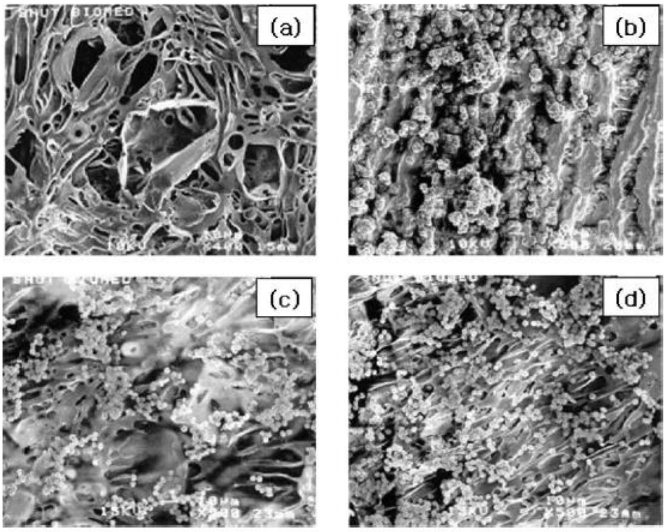

Fig. 5. SEM observation of blood cells adhesion on polylactide scaffold in short-term blood perfusion: a) before perfusion, b) after blood perfusion, c) albumin-absorbed surface, d) fibrinogen-absorbed surface [12].

CONCLUSIONS

Polylactide scaffolds are widely used in tissue engineering. Some of their advantages are mentioned in Table 1, however the most important ones are biodegradability and biocompatibility of the polymer.

Table 1. PLA in various tissue engineering.

Tissue	Produced by	Previous alternative	PLA scaffolds advantages
cartilage	chondrocytes	collagen scaffolds	better mechanical properties,
bone	osteocytes, osteoblasts	titan screws, bone grafting	better biocompatibility, no need for scaffold removal, do not contain magnetic metals (e.g. patient can still be scanned via MRI)
peripheral nervous system	Schwann cells in neurons	autografting	no need for many procedures and traumatizing donor tissue
cardiovascular	blood cells: erythrocytes, leukocytes	bypass grafts	vessels less than 5 mm in diameter can be cured

Great progress was made since the concept of degradable polymeric tissue scaffold was born. Cell adhesion is one problem that we became aware of and are trying to overcome now. Nowadays scaffolds are also enhanced with antibiotics or other additives.

There is no universal scaffold for tissue engineering. Desired properties are determined by tissue type and its cells. Mechanical properties can be easily modified in polymeric scaffolds, which places them amongst most promising and universal materials.

Even though polylactide scaffolds are currently only at the stage of clinical trials, they will probably be widely utilized in future medicine.

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Analysis of predictive methods to calculate heat transfer coefficient during flow boiling of NH_3

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***Keywords**: ammonia, heat transfer, predictive methods, boiling, refrigerant*

ABSTRACT

Because of European Union regulations common used in refrigeration and air-conditioning systems refrigerants from HCFC group are or will be forbidden. Because of that scientists are looking for other refrigerants as a replacement. There are two groups of refrigerant proposed to use: new synthetic refrigerants and natural refrigerants. In the second group can be mentioned carbon dioxide, propane, isobutene and ammonia.

Designers of refrigeration systems need to use calculation methods to predict heat transfer coefficient. In literature can be found a lot of calculation methods to predict heat transfer coefficient, but most of them are prepared for synthetic refrigerants. In order to verify possibility of using those methods the paper present analysis of some existing methods to calculate heat transfer coefficient during flow boiling of ammonia. For analysis Guerrieri and Talty, Mumm, Liu and Winterton, Kenning and Cooper and Kutateladze methods were used. Also proposed own new method to predict heat transfer coefficient of ammonia boiling inside channels. Methods were analyzed by use of mean absolute error, average deviation and number of data within ±50%.

Nomenclature

Bo - boiling number
G - mass flux
M - molar mass
P - pressure
Pr - Prandtl number
r - enthalpy
Re - Reynolds number
q – heat flux
x – vapour quality
α- heat transfer coefficient
ρ – density
η – dynamic viscosity
λ – thermal conductivity

Subscripts
2F - two phase
c – liquid
co – considering the total vapour-liquid flow as liquid flow
g – gas/vapour
wo – pool boiling

INTRODUCTION

Due to European Union Regulations (EC) No 842/2006 of 17 May 2006 on certain fluorinated greenhouse gases and (EU) No517/2014 the refrigerants from group HFC and HCFC are limited and could be forbidden in near future. To describe influence of substances on environmental there are used special factors ODP and GWP. ODP is Ozone Depletion Potential which describe how many more times this substance depletes ozone layer in comparison with R22, for which ODP value was assigned the indicator of 1,0. GWP is Global Warming Potential. This factor describe the impact of substance on various compounds for greenhouse effect. This factor is related to carbon dioxide with GWP value was adopted as 1,0. Because of the influence of HFCs and HCFCs refrigerants on environmental scientist are looking for other refrigerants as a replacement. There are proposed two groups of refrigerants. First of them is new synthetic refrigerants, because of that high group of scientist considers that this is not good choice. The use of synthetic refrigerants may be also limited by still stringent regulations. The second group is natural refrigerants. Amongst natural refrigerants should be mentioned carbon dioxide, hydrocarbons like propane and isobutene, water as well as ammonia.

Natural refrigerant were used in first refrigeration systems, but in the 30s of XX century were replaced by synthetic refrigerants which had a higher performance that natural refrigerants. A noticeable impact on the environmental of synthetic refrigerants has caused renewed interest in natural refrigerants. Ozone Depletion Potential and Global Warming Potential of ammonia are both equal zero, that mean it have no influence on environmental. It is similar to other natural refrigerant which as opposed to synthetic substances occur in environmental. Ammonia is a flammable and explosive substance, but it shows higher values of heat transfer coefficient than the other natural refrigerants. Special sensors can be used to detect leakage of ammonia, which provide to safety use of this effective refrigerant.

For purposes of designing efficient refrigeration and air-conditioning systems designers have to use calculation methods to predict heat transfer coefficient. Development of the method to calculate heat transfer coefficient during boiling of refrigerants inside channels is complicated because of flow structure changes. This changes cause the occurrence of various physical phenomena and make it difficult to make mathematical description of the phenomenon of boiling in channels. Picture 1 presents changing of flow structures during boiling inside horizontal channel.

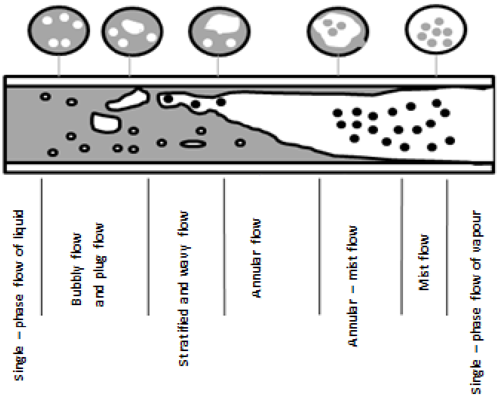

Fig 1. Structure changes during refrigerant boiling inside channel

As can be seen at Fig. 1. At first single-phase refrigerant flow into the channel. Uniform heating the walls of the channels cause that bubbles appears at the walls. Because liquid phase temperature is lower those bubbles condensate. When liquid rich sufficiently high temperature bubbles stops to condensate and they are flowing inside liquid. This is bubbly flow. Increasing the amount of bubbles cause they are connecting together to form plugs. This is plug flow. Increasing the amount of vapour cause that flow stratify – vapour is flowing at top of channel and liquid is flowing at bottom of the channel (stratified flow). Higher velocity of vapour in comparison with velocity of liquid can cause that wave would appear (wavy flow). With increasing vapour quality this flow will change to annular flow – vapour flow in the center of channel and liquid flow at the walls forming thin film. In horizontal flow liquid film is thinner at the top of the channel than at the bottom (as shown at picture 1). It is the result of gravity. This effect does not occur in vertical flow. Much higher velocity of vapour that velocity of liquid cause that droplets of liquid are detached from liquid film and they are flowing in the vapour phase – this structure is called droplet flow or mist flow. The film on the wall evaporates causing drying. After evaporates the whole volume of liquid occurs single- phase flow of vapour. It should be mentioned that can be specify five types of heat exchange mechanism: convective heat transfer of single-phase liquid flow, nucleate boiling which occur during bubbly and slug flow, convective evaporation in stratified and wavy flow as well as in annular flow, evaporation during wall dryout and single-phase vapour flow. It is important because calculation methods are developed for a specific heat exchange mechanisms.

Existed correlations were mostly developed for synthetic refrigerants. That's the effect of common used of synthetic refrigerants especially from CFCs in XX century. Calculation methods were prepared to improve efficiency of evaporators in refrigeration and air-conditioning systems. There is need to verify possibility of using those methods to predict heat transfer coefficient for ammonia boiling inside channels. It is also necessary to develop calculation methods to predict heat transfer coefficient especially for natural refrigerant's like ammonia.

The present paper has been divided into the following sections: abstract; introduction; analysis of calculation methods where is presented database of ammonia boiling data, described existing calculation methods and own new calculation method to predict heat transfer coefficient during boiling inside channels, it is presented analysis which were taken into account the number of point in range within ±50% and statistical analysis of calculation methods which contains average standard deviation and average relative error. At the end of this paper there are present summary and conclusions.

ANALYSIS OF CALCULATION METHODS

Database

For analysis it was prepared database compared 375 data of ammonia boiling inside channels taken from literature [1-3]. Data compared the wide range of conditions: inner diameter d= 3÷20 mm; mass flux G = 20÷600 kg/(m^2s), heat flux q = 15÷60 kW/m^2 and saturation temperature t = -10÷10 °C. Inner diameter of the channel were taken in this range to take into account only conventional channels. Lower inner diameter cause the other flow structures and physical phenomena and because of that mini and microchannels can not be dealt together with conventional channels. Limiting value of conventional and minichannels is 3mm. This inner diameter were also included in this analysis by taking into account Pamitran [1] experimental data. Analysis of calculation methods to predict heat transfer coefficient for mini and microchannels will be the subject of a separate paper. Detailed conditions of experimental data collected in database are presented in table 1. Wide range of conditions is used, because it is necessary to find one method to predict heat transfer coefficient of boiling ammonia for different constructions of heat exchanger.

Table1. Detailed condition of experimental data in database

Author	d, mm	G, kg/(m^2s)	q, kW/m^2	t, °C
Pamitran [1]	3	100÷600	15÷60	0÷10
Witczak [2]	20	55÷100	16,808	-10
Zurcher [3]	14	20÷120	15,1÷32	4

Pamitran [1] conduct experimental research about heat transfer of ammonia, carbon dioxide and propane. The research were conduct in horizontal, electrical heated steel tubes of length 2,0m for whole range of vapour quality.

Witczak's research were conducted on industrial refrigeration circuit to analyze influence of heat-flow parameters on heat transfer coefficient for horizontal and vertical pipes. There was also examined influence of immiscible oil on heat transfer coefficient during ammonia boiling. The research were conduct for vapour quality x from 0,10 to 0,89.Reserch also take into account pressure drop of ammonia boiling inside horizontal and vertical channels. Zurcher [3] examined ammonia, R134a and R407C in horizontal smooth tube. The research were conduct to develop new flow pattern map of ammonia and improve Kattan's [4] flow pattern map for R134a and R407C. Flow structures were observed through the glass part of the test section. All of presented experimental data shows that trend of heat transfer coefficient changes are similar to those which occurs for synthetic refrigerants.

Calculation methods

In literature can be found a lot of calculation methods to predict heat transfer coefficient of refrigerants inside channels. Most of them where developed for synthetic refrigerants and for small range of heat transfer conditions (mass flux, heat flux and saturation temperature). In order to use existing calculation methods to predict heat transfer coefficient during the design of evaporators developers need to know which methods can predict heat transfer coefficient with expected accuracy. Dutkowski [5] and Witczak [6] have reviewed calculation methods for determining heat transfer coefficient during boiling inside channels and minichannels. They're draw attention for some methods which were taken to analyze in this paper. Calculation methods to predict heat transfer coefficient were developed for various heat transfer mechanisms, because of that they're results can be drastically different from each other. Analysis compared five heat transfer coefficient calculation methods which are often cited in literature: Guerrieri and Talty [7], Mumm [8], Liu and Winterton [9], Kenning and Cooper [10] and Kutateładze [11] and one own new calculation method prepared especially for presented data.

Kutateładze method [11] is based on asymptotic model:

$$\alpha_{2F} = \sqrt{1 + \left(\frac{\alpha_{wo}}{\alpha_{co}}\right)^2} \cdot \alpha_{co} \tag{1}$$

where α_{wo} and α_{co} are calculated from:

$$\propto_{wo} = 55 P_{zr}^{0,12} (-log P_{zr})^{-0,55} M^{-0,5} q^{0,67} \tag{2}$$

$$\alpha_{co} = 0{,}023 \frac{\lambda_c}{D} Re_{co}^{0,8} Pr_c^{0,4} \tag{3}$$

Reynolds number is determined for mass flux of two-phase flow mixture from:

$$Re_{co} = GD/\eta_c \tag{4}$$

Liu and Winterton [9] method is based on Kutateładze method and is defined by:

$$\alpha_{2F} = \sqrt{(E\alpha_{co})^2 + (S\alpha_{wo})^2} \tag{5}$$

α_{wo} and α_{co} are calculated like in Kutateładze method from (2) and (3), respectively. Factors E and S are calculated from:

$$E = \left[1 + xPr_c\left(\frac{\rho_c}{\rho_g} - 1\right)\right]^{0,35} \tag{6}$$

$$S = 1/(1 + 0{,}05E^{0,1}Re_{co}^{0,16}) \tag{7}$$

Mumm [8] method was developed for convective boiling in horizontal channels and is calculated from:

$$\alpha_{2F,K(P)} = \left[4{,}3 + 5\cdot 10^{-4}\left(\frac{\rho_c}{\rho_g} - 1\right)^{1,64} x\right] Re_{co}^{0,808} Bo^{0,64}\alpha_{ck} \tag{8}$$

This method was create for boiling water Reynolds number in this method is also defined by (4) and boiling number Bo is determined by:

$$Bo = q/Gr \tag{9}$$

Guerrieri and Talty [7] method also was developed for convective boiling. Authors used organic substances as benzene, heptane, methanol and the other. This method is defined as:

$$\alpha_{2F,K} = F\alpha_{ck} \tag{10}$$

where

$$\alpha_{ck} = \alpha_c = 0{,}023\frac{\lambda_c}{D}Re_c^{0,8}Pr_c^{0,4} \tag{11}$$

$$F = 3{,}4\left(\frac{1}{X_{tt}}\right)^{0,45}. \tag{12}$$

X_{tt} is Lockhart-Martinelli parameter:

$$X_{tt} = \left(\frac{1-x}{x}\right)^{0,9}\left(\frac{\rho_g}{\rho_c}\right)^{0,5}\left(\frac{\eta_c}{\eta_g}\right)^{0,1}. \tag{13}$$

Reynolds number in (11) is calculated for mass flux of only liquid flow by full diameter of channel from:

$$Re_c = \frac{G(1-x)D}{\eta_c}. \tag{14}$$

Kenning and Cooper [10] conducted experimental research on water. In Kenning and Cooper methods heat transfer coefficient is calculated from:

$$\alpha_{2F,K} = E\alpha_{ck} \tag{15}$$

in this formula α_{ck} is calculated like in Guerrieri and Talty method from (11). E parameter is defined as:

$$E = 1 + 1{,}8\left(\frac{1}{X_{tt}}\right)^{0,87}. \tag{16}$$

It was prepared own new method to predict heat transfer coefficient during ammonia boiling inside channels. This method is based on convective boiling mechanism like in Guerrieri and Talty method. Own new method was prepared especially for the data from presented in this work database to take into account wide range of heat transfer conditions. Heat transfer coefficient is calculated from (10) and α_{ck} from (11). Factor F is defined as:

$$F = 2\left(\frac{1}{X_{tt}}\right)^{0,48} \tag{17}$$

Similar like in Guerrieri and Talty method Lockhart-Martinelli parameter should be calculated from (13). Reynolds number in α_{ck} is also calculated for mass flux of only liquid flow by full diameter of the channel from (14).

Analysis of calculation methods

It was calculated number of point within ±50% for all analyzed calculation methods. Results of this analysis provide to conclusions that the highest number of point within ±50% gives Guerrieri and Talty [7] and own new method with 60% and 58% of point in the range, respectively. Liu and Winterton [9] method as well as Kenning and Cooper [10] method gives 49% of points in the range ±50%. Kutateładze [11] and Mumm [8] methods gives respectively 47% and 42% of point within this range.

Fig. 2. present comparison between experimental and calculated heat transfer coefficient for different calculation methods. As can be seen in picture Guerrieri and Talty [7] as well as Kenning and Cooper [10] methods over predict some experimental data of heat transfer coefficient. Guerrieri and Talty [7] method over predict heat transfer coefficient for low values of vapour quality. This may be due to the fact that this method was prepared for convective boiling. From analyzed methods Mumm [8] method best describes a trend of changes heat transfer coefficient, but this method over predict experimental heat transfer coefficient for low vapour quality and under estimate heat transfer coefficient of the points in range of high vapour quality. Own new method under estimate some points of experimental heat transfer coefficient.

Kutateładze [11] methods results over predict heat transfer coefficient of ammonia boiling inside channels especially for high value of vapour quality. It can be seen that the different methods predict well heat transfer coefficient in different vapour quality. It is possibly related to flow structures appears in the other conditions. It seems that creating methods taking into account flow structures improve predictions of heat transfer coefficient of ammonia. The differences of calculated and measured values are really high and because of that the comparison of measured and calculated by this method heat transfer coefficient is not shown on picture.

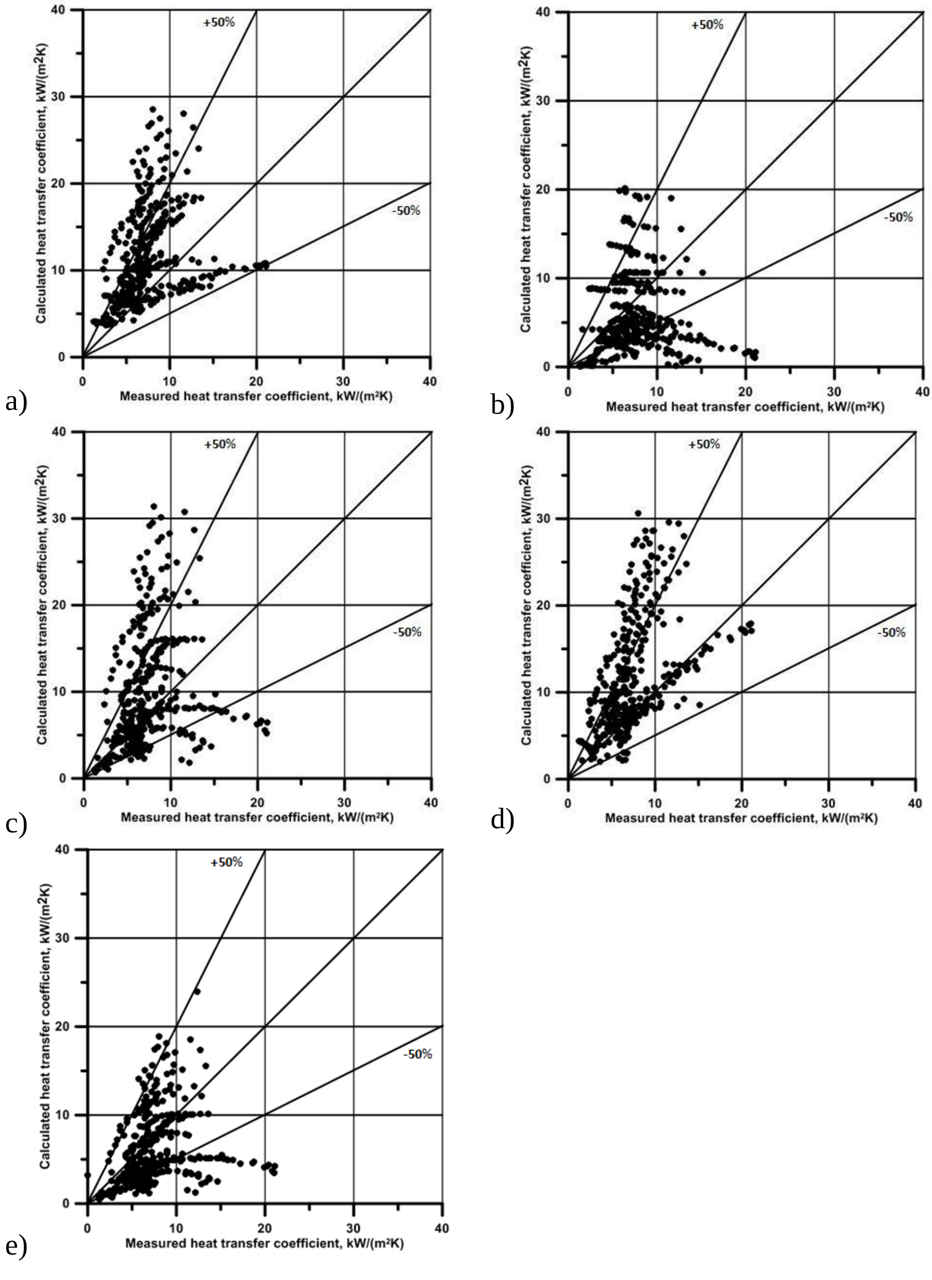

Fig. 2. Comparison between experimental and calculated heat transfer coefficient of ammonia boiling inside channels for various calculation methods a) Liu and Winterton[9], b) Mumm[8], c) Guerrieri and Talty[7], d) Kenning and Cooper [10] e) own new method

In order to assess the accuracy of the calculation methods the statistical analysis were also made. This analysis included calculations of the average relative error and the average standard deviation. Average relative error is defined as:

$$\overline{\delta\alpha_{2F}} = \frac{1}{N}\sum_{i=1}^{N} \delta\alpha_{2F,i}\ . \tag{18}$$

Average standard deviation is calculated from:

$$\sigma(\delta\alpha_{2F}) = \left[\frac{1}{N}\sum_{i=1}^{N}\left(\delta\alpha_{2F,i} - \overline{\delta\alpha_{2F}}\right)^2\right]^{0,5} \tag{19}$$

Statistical analysis of all examined calculation methods are compared in table 2. As can be seen in the table the lowest average standard deviation present Mumm method and own new method with values 0,14 and 0,16. Guerrieri and Talty method also showed low average standard deviation (with value 0,40) in comparison with the other methods. All methods present high value of average standard deviation. The worst results of statistical analysis present Kutateładze method with average relative error and average standard deviation values significantly higher than unity. This mean that this method can not be used for calculating heat transfer coefficient of ammonia boiling inside pipes.

Table 2. Statistical analysis of examined calculation methods.

Calculation method	$\overline{\delta\alpha_{2F}}$	$\sigma(\delta\alpha_{2F})$
Kutateładze [11]	1,59	7,98
Liu and Winterton [9]	0,67	0,76
Mumm [8]	0,14	0,75
Guerrieri and Talty [7]	0,40	0,89
Kenning and Cooper [10]	0,67	0,80
Own new method	0,16	0,61

SUMMARY AND CONCLUSIONS

Paper presented calculation methods to predict heat transfer coefficient during ammonia boiling inside horizontal channels. Existing calculation methods from literature were not made for ammonia boiling, but for other refrigerants mainly for synthetic refrigerant.

Analysis of calculation methods to predict heat transfer coefficient during ammonia boiling inside channels show that:

- The highest number of data within ±50% were obtained for Guerrieri and Talty method, but this method overpredict heat transfer coefficient for low vapour quality.
- The lowest average relative error were obtained for Mumm method with value 0,14 and for own new method with value 0,16.
- All analyzed methods showed high values of average standard deviation.
- The own new calculation method to predict heat transfer coefficient show good result of number of points in range within ±50% - 58% and low average relative error -0,16 in comparison with other calculation methods. It also present lowest average standard deviation, but it is still too high.
- High values of average relative error and average standard deviation cause that it is still need to looking for good calculation method to calculate heat transfer coefficient of ammonia boiling inside horizontal channels.
- It is planned an attempt new calculation method to predict heat transfer coefficient of ammonia boiling inside channels for wide range of condition taking into account flow structures.

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KAPITAŁ LUDZKI
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Surfactant-based extraction of plant origin compound

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ABSTRACT

At the turn of the last years there has been a growing number of new cosmetic products in which the essential active ingredients are plant-derived substances. Ever since prehistoric people used products with extracts from plants as cosmetics. The main focus of this paper is new methods for obtaining biologically active substances from plant origin (the object of interest are the polyphenols) – surfactant-based extraction. The Cloud Point Extraction and the Micelle-Mediated Extraction will be shortly reviewed.

INTRODUCTION

Modern methods of obtaining biologically active substances from plants are currently the most popular research topics that are dynamically developing. Extracts obtained from plants are widely used in food, cosmetics, pharmaceuticals, or in aromatherapy. More and more people are interested in dietary supplements that contain ingredients, which come from natural sources and aren't synthetically produced. One of the most interesting group of compounds, which can be obtained in the process of extraction from plant are polyphenols (in particular flavonoids). These compounds are widely used in medicine [1, 2].

Polyphenols are organic compounds from the group of phenols, which contain at least two hydroxyl groups, which are attached to the aromatic ring. These compounds can be found in all plants [1].

Biologically active plant based compounds, which have high purity can be obtained in the extraction process. This process involves the isolation from plant material the substances that we are interested in by using various kinds of solvents. Several methods of extraction has gained interest because of its innovation and speed of the process, for example micellar extraction [2].

The extraction, which is often carried out under different conditions (hot, cold, with a variety of factors enabling i.e.: microwaves, ultrasound) is one of the basic methods of obtaining active substances from the plant material.

STATE OF THE ART

Extraction (term used in pharmacy) is the separation of medicinally active portions of plant tissues by using solvents, which are selective. The extraction techniques allow to separate the soluble plant substance and leave behind the insoluble cellular marc [2]. Plant-derived products are complex mixtures of metabolites, which are in a liquid or semi-solid form, or (after removal of the solvent) in the form of a dry powder. They can be used orally and external as infusions, decoctions, fluid extracts, pilular (semisolid) extracts or powdered extracts, tinctures. These preparations have been popularly called galenicals, the name comes from Galen, a Greek physician. The purpose of standardization extraction, where the herbal medicines are obtained, is to achieve the therapeutic portions of the substance and to eliminate unwanted substances by using the selective solvent known as menstruum. So obtained extract, after standardization, can be used as medicinal agent (in the form of tinctures or fluid extracts). It can be also processed to be incorporated in any dosage forms such as tablets or capsules. All of these products contain a complex mixture of many medicinal plant metabolites. Among these are alkaloids, glycosides, terpenoids, flavonoids and lignans. Also the obtained extract can be use as a modern drug, after further processing of it by a various fractionation techniques, which allow the isolation of individual chemical entities [2].

Micelles – formation and solubilization

Surfactants or surface-active agents are the substances, which have a specific chemical structure. They are amphiphilic molecules that comprise distinct hydrophobic and hydrophilic moieties (Fig. 1) – a polar or ionic group is connected to a long hydrocarbon tail, which can be linear, branched or containing aromatic rings [3].

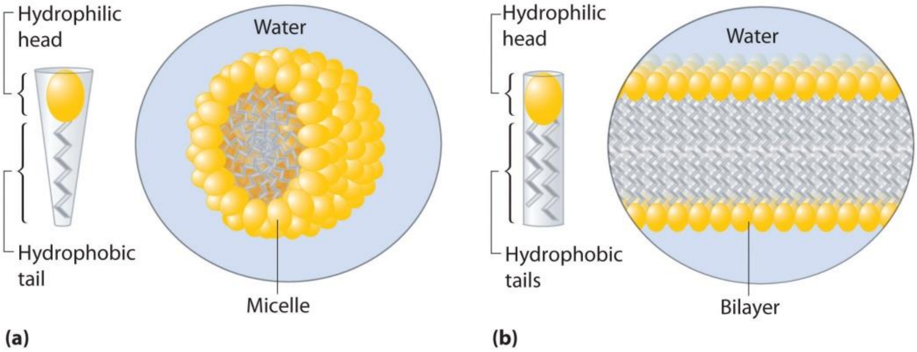

Fig. 1. The structure of micelle (a) and bilayer (b) [4].

The surfactants in their solutions, which have low concentrations exist as monomers. The minimum concentration of surfactant in the solution required for forming aggregates (called micelles) that are in dynamic equilibrium with the monomers in the bulk aqueous solution. This concentration is called the critical micelle concentration (CMC). The micelles can adopt a variety of shapes, ranging from roughly spherical to ellipsoidal (oblate or prolate). The interior region of the micelle contains the hydrophobic moieties of the surfactant molecules and the outer surface consists of the hydrated hydrophilic groups along with any bound water molecules [5].

One of the most important properties of surfactants is solubilization. This process helps substances, which are sparingly soluble in water and those insoluble in water to dissolve in water. It can occur because the water concentration decreases from the surface towards the core of the micelle, with a completely hydrophobic core. These aggregates exhibit an interfacial region separating the polar bulk aqueous phase from the hydrocarbon-like interior. As a result, micellar solutions consist of a special medium in which hydrophobic, amphiphilic or ionic compounds may be solubilized and reagents may be concentrated or separated in aqueous solution. Consequently, the spatial position of a solubilized drug in a micelle will depend on its polarity: non-polar molecules will be solubilized in the micellar core, and substances with intermediate polarity will be distributed along the surfactant molecules in certain intermediate positions [6,7].

Surfactant-based extraction

Micellar extraction is one of the alternative methods for classic extraction and one of the latest methods of obtaining biologically active compounds from plant origin. In this extraction process an aqueous solution of a surfactant is used instead of an organic one.

There are known two methods for the micellar extraction of biologically active plant based compounds : Cloud Point Extraction (CPE), Micelle-Mediated Separation (MMS).

CPE is an environmental friendly extraction technique that was first used by Watanabe and coworkers in 1976 [8]. Firstly CPE was used for preconcentration of trace-metal ions. In recent years this technique has been intensively developed and it was used as a primary isolation step in purification of proteins. Since then, this interesting process have been developing its potential and finding different applications. A recent publication by Paleologos and coworkers provides fundamentals, methodology and applications of the CPE technique [8].

Cloud point (CP) is the temperature below which an aqueous solution of a water-soluble surfactant becomes turbid. The cloud point system refers to the phase transfer of certain non-ionic surfactants from a clear homogenous solution to a cloudy system. The solutions of non-ionic surfactants are heated to above the cloud point and of anionic and cationic surfactants are cooled below the temperature of cloud point[3].

The extraction process of CPE is very simple. Firstly, the surfactant or its concentrated solution is added to the prepared sample containing a sample with biologically active compounds, which are the analytes to be extracted and preconcentrated. The final surfactant concentration must be above its CMC, because of ensuring formation of micelle aggregates. Analytes can reside in the hydrophobic domain of the micelles in a surfactant-rich phase or in the palisade/interface layer of it before being extracted and preconcentrated [3]. Secondly, the temperature needs to be changed by raising it or lowering and/or added salt or other additives to obtain phase separation. Next the system is mixed by gravity settling or centrifugation. And in the result the analytes are preconcentrated in a small volume of surfactant-rich phase. Depending on the density of the surfactant-rich phase, it can be at the bottom or the top. The substances, which are preconcentrated, in the surfactant-rich phase are sometimes viscous, and that sometimes may require dilution with aqueous or an organic solvent, other analytical methodologies [3,8].

The second extraction techniques is Micelles Mediated Separation, which consists of two stages. The first step is Micelles Mediated Extraction. In this step, the extraction solvent is the solution of surfactant, which has a concentration higher than the Critical Micelle Concentration. Next, the micelles start to form in the solution and the extraction process from plant material occurs [8,9].

The next step in the MMS is Cloud Point Concentration (CPC), a concentration of the solution at the cloud point. Any surfactant (anionic, cationic, nonionic) dividing the solution into two phases:

a) a surfactant-rich phase with the extracted substance,
b) an aqueous phase.

The CPC method is most often used with non-ionic surfactants, but this requires additional heating of the solution to phase separation.

If we want to obtain the best results in the MMS technique (MME part) it should be taken under consideration several parameters, which can be optimized. First of them is the pH. For organic molecules the pH is the most critical factor, which regulates the partitioning of the target analyte in the micellar phase. It is especially important for ionizable species, such as phenols and amines. They are achieving the maximum extraction efficiency at pH values where the uncharged form of the target analyte prevails. Recently the researchers created very effective method of extraction charged analytes in the CPE technique [8]. Second important parameter is the concentration of surfactant in solution. It is very hard to conduct the extraction process with easy phase separation, maximum extraction efficiency and analytical signal. The analytical signal is observed to deteriorate due to due to increase in a final volume of surfactant, which causes the preconcentration factor (the ratio of phase-volume) to decrease. When surfactant concentration is decreased from that recommended, accuracy and reproducibility will change for the worse, because the surfactant-rich phase would not allow to reproduce measurements of extraction and separation [8].

In conclusion all micellar extraction techniques are safe, economical and simple. The additional advantage of them is that in them are used nontoxic solvents, so that the extracted substances can then be consumed by people.

MATERIALS AND METHODS

Quercetin belongs to a group of flavonoids (3,5,7,3',4'-pentahydroxyflovonol) and it is one of the widely used pharmaceutical flavonoids compound. It generally occurs in plants and in food such as tea, juices, wine or honey. Quercetin has many properties, which have positive effect on humans health. It is considered to be a strong antioxidant due to its ability to scavenge free radicals and bind transition metal ions. Quercetin may help protect against heart disease and cancer. It can also help stabilize the cells that release histamine in the body and thereby have an anti-inflammatory and antihistamine effect [10].

The second flavonoid, which was used in experiment is rutin. Rutin (rutoside, quercetin-3-O-rutinoside, sophorin) is the glycoside between the quercetin and the disaccharide rutinose. Rutin possesses anti-inflamatory and anti-spasmodic properties. It prevents cancer and protects the liver. Also it helps absorb more vitamin C, which prevents cell oxidation. So the rutin is widely used in pharmaceutical industry [11].

Two surfactants were chosen for the experiment, in which the rutin and quercetin was extracted. One of them is Tween 80 (TW80) also known as Polysorbate 80. Tween 80 is an nonionic surfactant, which is often used in foods and cosmetics. It is derived from polyethoxylated sorbitan and oleic acid. The hydrophilic groups in this compound are polyoxyethylene (polyethers groups), which are polymers of ethylene oxide [12]. Tween 80 is the most commonly used surfactant and it has been shown to enhance solubility of compounds leading to increased absorption of drug candidates [13]. It is used commonly as emulsifier in foods.

The second surfactant is Triton X-114 (TX114). This is a nonionic, octylphenol ethoxylate surfactant with good wetting and detergency properties. Triton X-114 has a low cloud point temperature at 22^0 C. It is used in extraction, because it separates into detergent and aqueous phase above the clouding point.

Triton X-114 can be used to separate hydrophobic from the water-soluble hydrophilic moieties [14, 15]. TX114 is widely used in food industry as emulsifier.

The water solutions of :

- quercetin ($C_{qe}=10^{-4}M$) and Tween 80 ($C_{TW80}=10^{-6}M – 5x10^{-3}M$)
- quercetin ($C_{qe}=10^{-4}M$) and Triton X-114 ($C_{TX114}=10^{-6}M – 5x10^{-3}M$)
- rutin ($C_{ru}=10^{-4}M$) and Tween 80 ($C_{TW80}=10^{-6}M – 5x10^{-3}M$)
- rutin ($C_{ru}=10^{-4}M$) and Triton X-114 ($C_{TX114}=10^{-6}M – 5x10^{-3}M$)

were prepared. Next their absorption spectra were measured at 293K with the Helios γ spectrophotometer.

RESULTS AND DISCUSSION

Figure 2 a) and b) show that the maximum peak of the quercetin in the examined solutions is about λ = 375 nm. The most appropriate concentration of Triton X-114 to extraction of quercetin is $5x10^{-4}M$ and respectively for Tween 80 is $5x10^{-3}M$. From the obtained spectra of quercetin in Tween 80 micelles the amount of extracted 3,5,7,3’,4’-pentahydroxyflovonol increases with the increase of the concentration of surfactant in the solution.

Figure 3 a) and b) present the UV-Vis spectra for examined water solutions with rutin. The maximum of the absorption of rutin is about λ = 350 nm. The increases of the concentration of Triton X-114 in the solution causes increase of the amount of the extracted rutin. Above this concentration the amount of rutin in the extract decreases. The most appropriate concentration of Triton X-114 to extraction of rutin is $5x10^{-4}M$. Whereas the most appropriate concentration of Tween 80 is $5x10^{-3}M$. For the rutin in Tween 80 micelles the amount of extracted polypheonol mostly increases with the increase of the concentration of surfactant in the solution.

More effective surfactant to extraction of the quercetin is Triton X-114 , which is shown in Figure 2 b). Moreover the surfactant, which is better in extraction of rutin is Tween 80 ($C_{TW80}=5x10^{-3}M$) (Fig. 3 a)).

Both surfactants used for the extraction allow to obtain extracts of the examined substances (quercetin and rutin). Moreover both of used surfactants find the application in food production, so they can be widely used to extraction of quercetin and rutin.

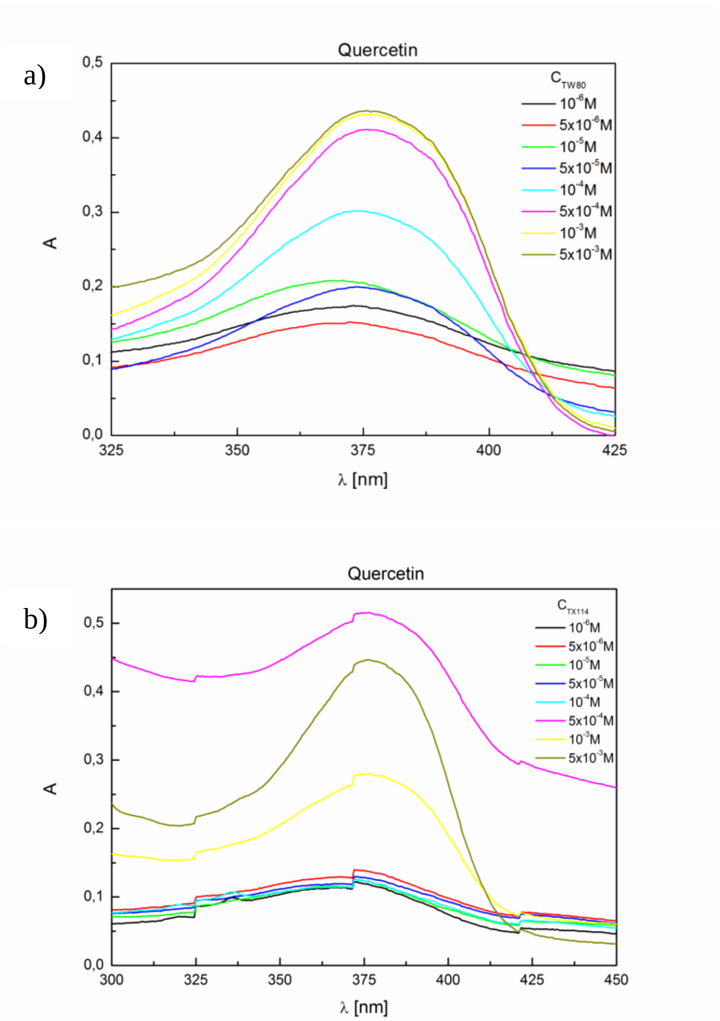

Fig. 2. Absorption spectra of rutin (10^{-4}M) in a) TW80 ($C_{TW80}=10^{-6}$M - $5x10^{-3}$M) and b) TX114 ($C_{TX114}=10^{-6}$M - $5x10^{-3}$M) micelles.

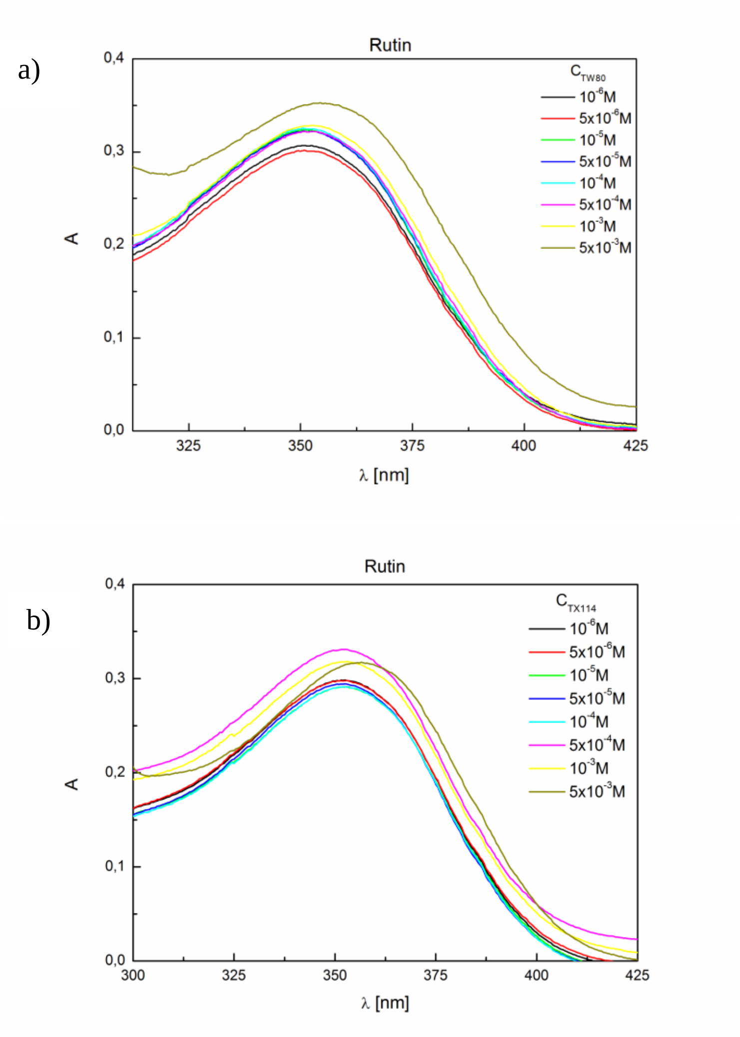

Fig. 3. Absorption spectra of rutin (10^{-4}M) in a) TW80 ($C_{TW80}=10^{-6}$M - $5x10^{-3}$M) and b) TX114 ($C_{TX114}=10^{-6}$M - $5x10^{-3}$M) micelles.

SUMMARY

At the turn of recent years are experiencing dynamic development of techniques for extracting biologically active compounds of plant origin. These techniques allow for simple, fast and low-cost effective sourcing of substances which later are used widely in food, cosmetic and pharmaceutical industries.

The micellar extraction techniques have many benefits, so researchers can used them to obtain high quality biologically active plant based compounds.

Tween 80 and Triton X-114 are the surfactants, which can be successfully used in extraction of biologically active compounds (poyphenols).

Quercetin and rutin can be extracted with the use of this surfactants. With use of Tween 80 we can obtain more of the extracted substance than with the use of Triton X-114. On the other hand the concentration of the Triton X-114 used in the process of extraction is lower than of Tween 80.

The negligible consumption (and subsequent waste generation) of organic solvent in surfactant-based extraction allows to highlight their green character. The surfactant-based extraction are still under development so the extraction of polyphenols by this technique is very interesting for the researchers.

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A comparative analysis of mills and grinding internals applied in comminution operations

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The article presents the characteristics of four types of mills with regard to the selection of grinding media. Milling is a process depending on many factors related both to the construction of the grinding plant and the nature of the material to be fragmented. Properly selected device parameters affect the effectiveness of its work both technologically and economically. The mills are devices used in the processing of raw materials [1].

Selection of the mill and its technical parameters determines the products' degree of fineness. A very important role to play in the grinding process is the proper selection of grinding media parameters such as the diameter and material.

Selection of appropriate grinding media allows to improve energy efficiency and to increase the efficiency of the process. Electromagnetic mill stands out in this ranking. Shredding system in the device with the control unit, allows the grinding of dry or wet raw materials in a closed cycle, with the possibility of a very wide selection of grinding media's movement speed with different frequencies [1]. The ability to control the size of the dosing feed and grinding media, ongoing analysis of particle size and the operating status of the mill and the flow of recycle will allow the full and far more effective activation of the mechanical properties of the grains with specific physical and mechanical parameters (size, shape, area and energy surface, surface properties), and also significantly increase the grinding capacity and reduce energy consumption. Grinding of raw materials is the operation widely used in many industries, from mineral processing to the chemical industry, constructions, foods, cosmetics and pharmaceuticals [1]. Therefore, one have to deal with diverse expectations for the fineness and characteristics of the product after crushing. Description of the process is very complex and depends on many factors such as: the size and form of the crushed grains, the arrangement of the material in grinding chamber, device technological parameters of the mill, the physicochemical properties of the material, the trajectory and speed of the particles [1]. It can be represented as effects on the material or seeds by means of pressure exerted by the grinding element, which results in cracking and degradation into smaller components [2].

A high energy comsumption of the grinding operation causes that this issue is the subject of many scientific and industrial research from around the world [3].

Selection of the mill and its technical parameters determines the fineness of particles that can be obtained. The grinding is also used for processing mineral aggregates, and the yield is strognly dependent on the type of feed [3]. Considering the case of a particular material, the final efficiency of grinding is affected by the moisture content of the feed and its particle size distribution of the feed. Therefore, a direct comparison of various types of mills is difficult and their performance difficult to scale. It is worth noting parameters such as performance and energy consumption of various types of grinding plant, because they are essential for the initial assessment of the mill suitability for specific applications [3,4].

The mills are used in the processing of raw materials. In Table 1 some mill types are listed, and they will be presented later in the article along with the type of grinding media used.

Table 1. Various mills along the type of grinding media.

Equipment type	**Grinding media**
Vibratory	The grinding process takes place between the free grinding mediums, usually balls, rarely rods and the inner portion of the chamber.
Ball or rod mill	The mill can be filled with of various grinding mediums such as grinding rods, spheres and cylpepses. Ore lumps can be also used and then we have to deal with self grinding.
Isa Mill	Low-cost materials as the grinding medium, such as discard smelter slag, screened ore particles and river sand or ceramic grinding medium as well if required.
VertiMill	The grinding media can be varied with a wide range of alternatives, depending on the application and the process requirements, for example: Aluminum Oxide, Aragonite, Barite
Electromagnetic	Mill is filled with loose the rod-shaped very small diameter grinding mediums. Grinding media are selected according to the particle size of the particulate material.

Characteristics of selected mills and grinding media used in them

The selection of grinding media is very important because it directly affects the grinding process and the resulting quality of the final material. Properly selected device parameters affect the effectiveness of its work, which directly comes from the selected technology, e.g. in classic drum mills - ball or rod - the movement of grinding media is caused by the rotation of the drum mill (cylindrical operating chamber filled with grinding mediums). However, in the mills with loose grinding mediums: gravity, vibration, electromagnetic, planetary or rotary-vibration, the grinding process is being affected by the kinematic parameters of movement of grinding media, such as their:

- velocity,
- energy,
- the number of mutual collisions,
- the number of collisions between grinding medias and lined chamber [5].

For some mills, one can intuitively predict how the chamber motion parameters can affect the movement of the grinding media and consequently – the grinding process. As an example, in the vibratory mills the higher value of the frequency and amplitude of the vibration, the grinding process will be more intense. However, it is difficult to determine in this way the optimum degree of filling of the chamber, which has a significant influence on the milling process. The aim of the constructor when designing this type of mill is to accept only those maximum values of oscillating motion, at which the milling process will have the highest efficiency and the greatest mill durability (least maintenance and operation probems) – all that at the lowest possible investment and operating costs [5].

Vibratory mill

Vibratory mills are among the mills with loose grinding mediums that energy is spent on the process of grinding received from the chamber that vibrates at a certain frequency and amplitude. They are characterized by diversified structure and technological opportunities. Grinding can be carried out in one of environments – an air or liquid, at reduced or elevated temperature, in a batch or continuous operation mode [6]. Vibratory mills have beed used in most of the technology of powders production with different physical properties. These mills are used for a various particle size, but mainly: fine - grain size of the ground product below 50 ÷ 100 microns; very small - less than 10 to 20 microns and colloidal - less than 1 ÷ 5 microns [6]. The process of grinding in vibratory mils, as in ball mills, occures between the free grinding mediums, usually balls, rarely rods with a length similar to the length of the chamber and between the grinding mediums and the inner surface of the chamber wall. Grinding media of other shapes, such as, for example cylpepsy are rarely used.

Ball mills

In this type of mills, conventional grinding of mineral particles occures by removing the layers of material by moving grinding media. Drum mills are used for grinding of a variety of materials, for wet and dry products. A fine or very fine particle are obtaineed. In the case of dry grinding, there is a fairly serious limitation of shredded materials humidity. Generally, it is required that in the case of grinding in a ball mill humidity should not exceed 3-5%. The disadvantage of this type of mill is a high energy consumption, and parts replacement due to a cladding or attrition of the grinding media [7]. This solution results in low efficiency of the process due to the high loss of energy supplied to the grinding media, which only marginally reflects in the actual grinding process. There is no control over the shape of obtained particles, which often means a low technological value of the product.

Drum mill is the general name assigned for mills made in the form of a rotatable drum for varying a length (L) to D (diameter). The mill can be filled with the various grinding media such as rods, spheres and cylpepses [7]. For grinding can also be used lump ore and then we have to deal with self-grinding. If only lumps of ore are used, the technology is called self-grinding or autogenous grinding. If ore lumps and a little spheres (less than is needed for normal grind) are being used, then we are dealing with the self-grinding or half-autogenous grinding [7].

The grinding of the material takes place as a result of the rotation of the drum arranged horizontally. Under the influence of the rotational movement, the grinding media is carried to of a specified height, dependent primarily on the size of the grinding media, the type of facing surface and rotational speed, then at some point the centrifugal force produced by the rotation of the drum is no longer sufficient and balls roll down on the top layer of balls [9]. Grinding is mainly caused by the abrasive nature of the traffic grinding aids. If the rotational speed of the mill increases, the grinding media are beginning to be carried above the point where they previously started to roll away. As a result of further movement of the mill, grinding medias finally pulled away from the drum and falls down on the parabola, hitting the top of a layer of grinding bodies lying at the bottom and rolling after the top layer to the bottom. In this case, the grinding is done primarily through attrition by cascading balls and hitting by falling balls. After crossing a certain speed of rotation of the drum (critical speed), the centrifugal force becomes so large that the grinding media "stick" to the drum and rotate with it, not doing the grinding [7]. Ball mills are used for over 200 years. They are applied mainly for the preparation of powders for chemicals and minerals. In most cases, ball mills are being used [1] [4]. In this kind of mills it is very difficult to obtain a particle size smaller than 10 um [7]. This is due to the low energy of grinding media, which is a result of the operation of the mill, and the accompanying process of grinding detrimental effects – coating and agglomeration. Grinding can be intensified in these mills, by the choice of value of technological parameters, i.e. the degree of filling of the chamber, a set of grinding bodies, construction liner, suitable aeration chamber and the use of a substance weakening the negative effects of coating and agglomeration, also known as grinding activator, but some substances can adversely affect the ground material and may also increase costs of production of powder [10]. These mills are used in grinding systems operating in an open or closed cycle [10].

Mills with mixed grinding medias

Mills with mixed grinding medias, depending on the type of the mill and its technical solution allows to carry out a grinding operation on both dry and wet conditions. For example, so-called mixed mills (Agitated Mill - SAM) by Metso, allow both dry and wet grinding. The maximum feed grain size should not exceed 1 mm, and the particle size of the product is about 2 micrometers [11].

Stirred Media Grinding Mill, also manufactured by Metso, can be operated in open or closed loop, and particle size of the feed and the product is the same as in case of the SAM mills.

According to the manufacturer data, Isa Mill can obtain a particle size less than 15 microns at a lower cost than any other existing technology, but also enables the milling to less than 7 microns in a practical and economical way. Due to the principle of operation, it appears that there are no obstructions that allows to obtain the same particle size as the SAM and SMGM mills [11].

In the case of VertiMill feed grain size should not exceed 6 mm. The mill is designed for precise post grinding or for the preparation of lime milk. Due to the special purpose of this mill, grinding technology in this device will be discussed separately [14].

IsaMill is a new fine grinding technology developed by Mount Isa Mines Ltd (MIM), a major international mining company based in Australia. IsaMill mill is a device with a completely different design than previously used in the mills, non-ferrous metals industry. It is a mill with a horizontal stationary mixing chamber equipped with a fast-rotating grinding disks for propelling the grinding medias closed in the grinding chamber [14]. Such construction makes possible to obtain high power density, and as grinding medias river sand, slag or ceramic beads can be used [11]. The mill is characterized by relatively low energy consumption compared with ball-mills. The main disadvantage of these solutions is relatively large footprint comparing to the electromagnetic mill, and thus the investment costs [11].

Electromagnetic mill

Electromagnetic mill is a device in which ferromagnetic grinding medias are moved intentionally by produced rotating electromagnetic field which serves as an energy carrier. The basic elements of the mill is an inductor of rotating magnetic field, placed in the axial position of tubular working chamber. The chamber is filled with about 20% ferromagnetic grinding mediums. They should be chosen accordingly to the particle size of the raw material [12].In the case of large variation of raw material grain size, a blend of grinding medias of different sizes is recommended. Any change in the size of the grinding media adapts to the physical properties of the raw material and the desired final fineness of the product [4]. One of the advantages of the electromagnetic mill is the possibility of intensification of many processes by carrying out grinding in the area in which the effect of the electromagnetic field rotates the vortex of ferromagnetic rods (grinding medias) with a suitable ratio of length to diameter [12],[15]. The mill operates efficiently in terms of both a highly hydrated materials and in low humidity conditions, less efficient milling (even about 70% of the optimal results) happens in case of a material with a moisture content between 15%–30% especially if it has high viscosity [15]. The electromagnetic mills are suitable for the continuous operation. In contrast to conventional mills (ball, rod, or cylpeps), the housing of the mill is stationary, and the grinding (or mixing) takes place in the working chamber, inside which moves a small ferromagnetic elements - called. grinding medias. The effectiveness and efficiency of the process conducted in such a mill is dependent on the proper selection of the physical parameters of the structure and process parameters such as flow rate of feed (residence time), particle size of the input, the speed and intensity of the rotating electromagnetic field, temperature, humidity, and other parameters of the workpiece (e.g. . the lithological composition) [13].

SUMMARY

The article shows a cross section through four different types of mills. At the design stage of mill the appropriate selection of the parameters of grinding media is very important. They have a significant impact on the economic assessment. Among the other described solutions, electromagnetic mill stands out in terms of performance, usage possibilities and energy efficiency. Silesian University of Technology and the University of Science and Technology in Krakow are designing electromagnetic mill. Shredding system of the electromagnetic mill with a reasonable control system will allow the grinding of dry or wet raw materials in a closed cycle, with the possibility to choose a very wide selection of speed of movement of the grinding medias of different parameters. The ability to control the size of the dosing feed and grinding media, ongoing analysis of particle size and the operating status of the mill and the flow of recycle will allow obtaining a well defined properties of the obtained grannular media with specific physical and mechanical parameters (size, shape, surface area and surface energy, surface properties), and also significant increase in grinding efficiency and energy savings.

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Comparison of numerical methods for inverse Laplace transform to solve of gas flow problems

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Keywords: *numerical methods for inverse Laplace transform, numerical efficiency, solve of gas flow problems, CAS-program*

ABSTRACT

In this paper we examined three numerical methods for inverse Laplace transform: the Gaver-Stehfest, the Durbin and the Koizumi methods and they applicability to solving of a gas flow model. The measurement unit, its application as well as its useful model were described in details in a work [1]. All the algorithms could be used to solve this problem. Methods worked very well, but the Gaver-Stehfest method was the most effective. Calculations were performed with the use of the CAS program type (Maple®).

INTRODUCTION

The Laplace transform is a useful 'tool of mathematics' to solve of ordinary and partial differential equations, and integral equations in many areas of sciences e.g. mathematics, economy, physics, engineering mathematics, computational sciences.

The Laplace transform of the function *f(t)* is expressed as follow:

$$\mathcal{L}\{f(t)\} = F(s) = \int_0^\infty f(t)e^{-st}dt \qquad (1)$$

where *s* is a complex variable known as the Laplace variable.

The inversion formula of Eq. (1) can be defined as:

$$f(t) = \mathcal{L}^{-1}\big(F(s)\big) = \frac{1}{2\pi i}\int_{\sigma-i\omega}^{\sigma+i\omega} F(s)\cdot e^{st}ds \qquad (2)$$

where σ is the contour of integration, which is to the right-hand side of singularities of F(s).

The inverse transform can be made by using the properties of Laplace transform, as well as by employing tables of Laplace transform and computer programs(e.g. Maple, Mathematica). Unfortunately, an analytical inversion can be difficult or even impossible to obtain, then numerical methods of inverse Laplace transform could be used. There are many (over 100) algorithms for the numerical inversion of Laplace transforms. According to literature reports e.g. [2, 3, 4, 5], a suitable method should be chosen for any problem under consideration.

Algorithms for the numerical inversion of Laplace transforms are split into four categories [6]:

- Fourier series expansion
- Laguerre function expansion
- combination of Gaver functional
- deform the Bromwich contour

DESCRIPTION OF THE PROBLEM

The Gaver-Stehfest method

This numerical method was first introduced by D. P. Gaver but it was later improved by H. Stehfest. It is a simple algorithm for the numerical inversion of the Laplace transform which has been used in mathematics, chemistry and many engineering applications e.g. fluid flow problems [7, 8, 9].

Time domain solution is approximated by [10]

$$f(t) = \frac{\ln 2}{t} \sum_{k=1}^{N} V_k \cdot F(k \cdot \frac{\ln 2}{t}) \tag{3}$$

where V_k is described by the following equation

$$V_k = (-1)^{k+\frac{N}{2}} \sum_{j=(\frac{k+1}{2})}^{\min(k,\frac{N}{2})} \frac{j^{\frac{N}{2}}(2j)!}{\left(\frac{N}{2}-j\right)!j!(j-1)!(k-j)!(2j-k)!} \tag{3a}$$

The parameter N is the number of terms used in Eq. (3). N must be an even integer, it should be chosen by trial and error method. The precision of calculation depends on the parameter N. If N rises, accuracy of results, increases first and then the accuracy declines due to round-off errors [6].

The Fourier-series method

In this paper we have also presented methods which are based on the Fourier series expansions. These methods were first used by Dubner and Abate in 1968 for the numerical inversion of Laplace transforms. The Fourier series technique is based on a freedom in choosing the contour over which the inverse Laplace transform may be evaluated and it provides the basis for a powerful computational method in determining the inverse integral. Next the inverse integral is converted into the Fourier series [11].

This technique can be described by:

$$f(t) = \frac{e^{at}}{T}\{\frac{1}{2}F(s) + (-1)^k \sum_{k=1}^{N} \mathrm{Re}(F(a + \frac{k\pi i}{T})) \tag{4}$$

- *The Durbin method*

Durbin approximated a formula (4) by expressing the function f(t) in terms of Fourier cosine and sine series [8, 12]:

$$f(t) = \frac{2e^{at}}{T}\{\frac{1}{2}\mathrm{Re}\big(F(s)\big) + \sum_{k=1}^{N} \mathrm{Re}\left(F\left(a + \frac{k\pi i}{T}\right)\right)\cos\left(\frac{k\pi t}{T}\right) -$$
$$- \sum_{k=1}^{N} \mathrm{Im}\left(F\left(a + \frac{k\pi i}{T}\right)\right)\sin(\frac{k\pi t}{T})\}\} \qquad (5)$$

- *The Koizumi method* (5)

The second method we shall consider is *Koizumi's method*. Koizumi approximated a formula (4) by writing the function f(t) in Fourier sine series, what may be summarized [8]:

$$f(t) = \frac{2e^{at}}{T}\{\frac{1}{2}\mathrm{Re}\big(F(s)\big) - \sum_{k=1}^{N} \mathrm{Im}\left(F\left(a + \frac{k\pi i}{T}\right)\right)\sin(\frac{k\pi t}{T})\} \qquad (6)$$

T is the time interval; *Re* means the real part of a complex function.
The parameter *a* is chosen as

$$a = \alpha - \frac{\ln E}{2T} \qquad (7)$$

where *E* is the error tolerance, *α* is the real part of the leading pole of the function F(s) [12].

RESULTS

The aim of this work is to investigate and comparison the accuracy of described, numerical methods for solve of the model of real gas flow process.

The scheme of the measuring system is presented in Figure 1.

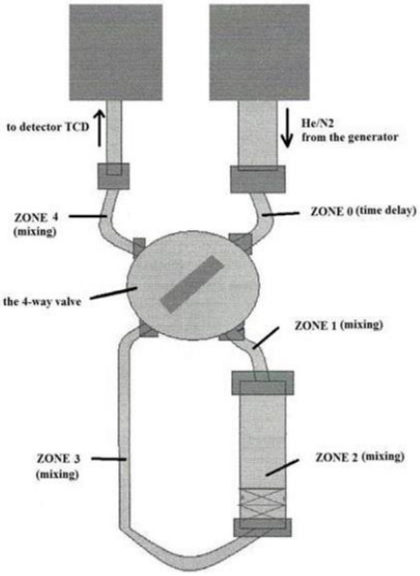


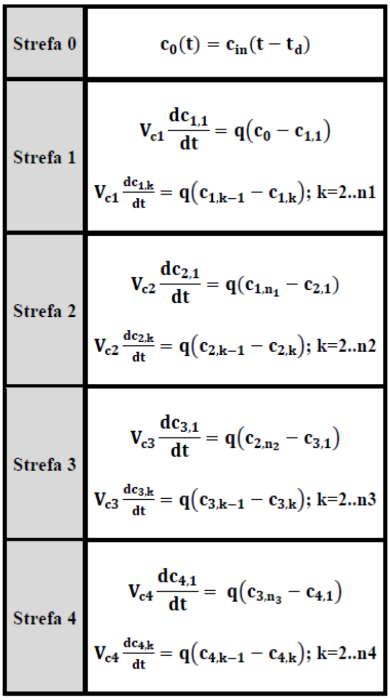
Fig. 1 The schematic representation of the measuring system.

The measuring system consists of the following elements, the 4-way valve, thermal conductivity detector (TCD), steel and empty column, pipes connected the mentioned elements. The unit was divided into five zones. In order to identify the type of mixing, the zones of this system were divided into *n* cells. Number of cells in each zone may be different. One cell in the zone corresponds to the ideal mixing in zone. Infinite number of cells in the zone corresponds to the plug flow. The proper *n* values were determined by trial and error method to obtain the best fit between model solution and experiments. The best fit was determined on the basis of minimal value of sum of squares of differences between calculations and experiments. Description of the experiments were described in details in [1].

Mass balance of the process

Mass balance of the nitrogen in each zones and for the number of cells of *n* leads to the following a system of ordinary differential equations (Table 1).

Table 1. Mass balance of the process.



Strefa 0	$c_0(t) = c_{in}(t - t_d)$
Strefa 1	$V_{c1}\frac{dc_{1,1}}{dt} = q(c_0 - c_{1,1})$ $V_{c1}\frac{dc_{1,k}}{dt} = q(c_{1,k-1} - c_{1,k})$; k=2..n1
Strefa 2	$V_{c2}\frac{dc_{2,1}}{dt} = q(c_{1,n_1} - c_{2,1})$ $V_{c2}\frac{dc_{2,k}}{dt} = q(c_{2,k-1} - c_{2,k})$; k=2..n2
Strefa 3	$V_{c3}\frac{dc_{3,1}}{dt} = q(c_{2,n_2} - c_{3,1})$ $V_{c3}\frac{dc_{3,k}}{dt} = q(c_{3,k-1} - c_{3,k})$; k=2..n3
Strefa 4	$V_{c4}\frac{dc_{4,1}}{dt} = q(c_{3,n_3} - c_{4,1})$ $V_{c4}\frac{dc_{4,k}}{dt} = q(c_{4,k-1} - c_{4,k})$; k=2..n4

(8)

In Table 2 presented initial conditions which were formulated for each zone.

Table 2. The initial conditions.

Strefa 1	$c_{1,1}(0) = c_T;\ c_{1,k}(0) = c_T;\ k=1..n1$
Strefa 2	$c_{2,1}(0) = c_T;\ c_{2,k}(0) = c_T;\ k=1..n2$
Strefa 3	$c_{3,1}(0) = c_T;\ c_{3,k}(0) = c_T;\ k=1..n3$
Strefa 4	$c_{4,1}(0) = 0;\ c_{4,k}(0) = 0;\ k=1..n4$

(9)

We obtained the following equation which is the solution of the model in Laplace domain:

$$c_{4,n4} = \frac{1}{s} \cdot \left[\left(\frac{q}{n4 \cdot V_{c4} \cdot s + q} \right)^{n4} \left(\frac{q}{n3 \cdot V_{c3} \cdot s + q} \right)^{n3} \left(\frac{q}{n2 \cdot V_{c2} \cdot s + q} \right)^{n2} \left(\frac{q}{n1 \cdot V_{c1} \cdot s + q} \right)^{n1} \cdot \right.$$

$$\left. \cdot c_{in} + \left(\frac{q}{n4 \cdot V_{c4} \cdot s + q} \right)^{n4} \cdot c_{in} \right] \cdot e^{-t_d s} \qquad (10)$$

where:

$c_{4,n4}$– outlet concentration of gas, measured by TCD detector

q - gas flow [dm^3/min] (10)

c_{in}- gas concentration in inlet to zone 0 [mol/dm^3]

V_{ck}- volume of a single cell in *k*-th cell [dm^3]

$c_{j,k}$ - gas concentration in *j*-th zone, in cell *k* [mol/dm^3]

t – time [min]

t_d - time delay [min]

c_T- concentration of pure gas [mol/dm^3], = 0.03906 [mol/dm^3]

P – pressure [Pa]

R_g – gas constant [$J \cdot mol^{-1} \cdot K^{-1}$]

T – temperature [K].

Concentration $c_{4,\,n4}$ is the outlet concentration and it is measured by TCD detector. Parameters n1, n2, n3, n4 are numbers of cells in each of zones.

The inlet concentration is described by

$$c_{in} = \begin{cases} 0 \text{ for } t < 0 \\ c_T \text{ for } t \geq 0 \end{cases}$$

t_d is time delay and it is given by

$$t_d = \frac{V_0}{q}$$

where:

V_0 - the volume of zone 0.

Eq. (10) was solved using the Gaver-Stehfest, the Durbin, and the Koizumi methods. Computations were done for following parameters: gas flow – 0.04 dm^3/min., the temperature - 308 K, the pressure - $1 \cdot 10^5$ Pa. Numbers of cells in each of zones: n1=1, n2=40, n3=1, n4=1. All calculations were carried out using Maple® with precision up to 50 decimal digits and an number of measurement points equal 70. Results are shown in Tables 3-5 and on Figures 2-6.

Table 3.Calculation results for the Gaver-Stehfest method.

The Gaver-Stehfest method			
	N=8	**N=14**	**N=24**
The average absolute errors	2.1757E-03	8.8109E-04	5.4328E-04
The average relative errors	1.0220E-02	4.1387E-03	2.5519E-03

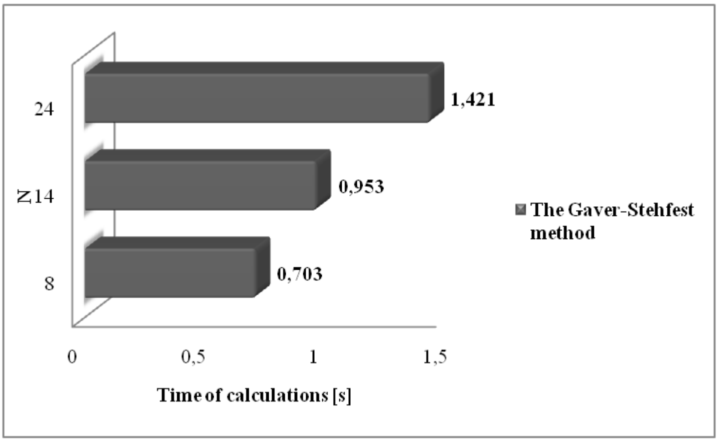


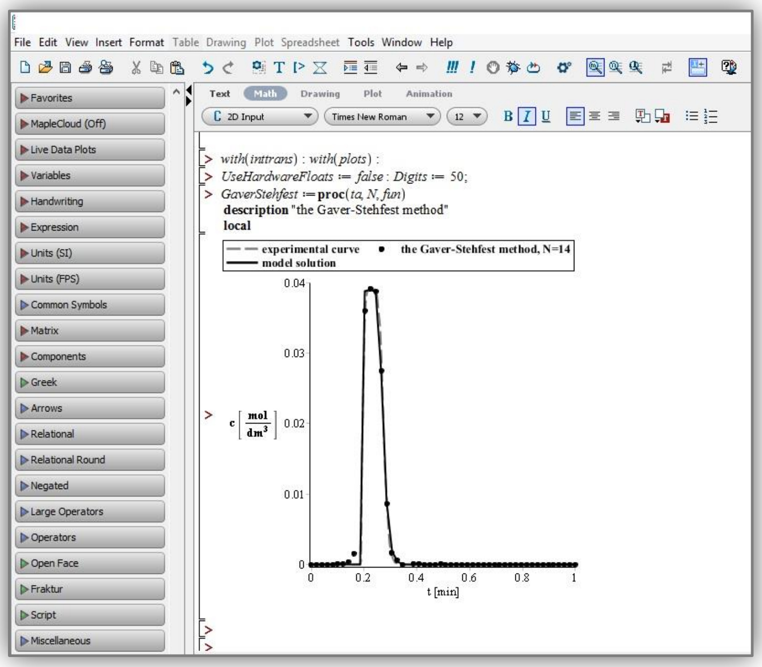
Fig. 2 Impact of parameter N on time of calculations in the Gaver-Stehfest method.

Table 4.Calculation results for the Durbin method.

The Durbin method			
	N=100	**N=500**	**N=1000**
The average absolute errors	5.8871E-04	6.6632E-05	1.9516E-05
The average relative errors	2.7653E-03	3.1299E-04	9.1676E-05

Table 5.Calculation results for the Koizumi method.

The Koizumi method			
	N=100	**N=500**	**N=1000**
The average absolute errors	7.8485E-04	9.3324E-05	2.8888E-05
The average relative errors	3.6867E-03	4.3837E-04	1.3569E-05



```
> with(inttrans) : with(plots) :
> UseHardwareFloats := false : Digits := 50;
> GaverStehfest := proc(ta, N, fun)
  description "the Gaver-Stehfest method"
  local
```

Fig. 3 Screenshot of program Maple®. Numerical, theoretical and experimental profiles gas concentrations for 0.04 dm^3/min. The Gaver-Stehfest method.

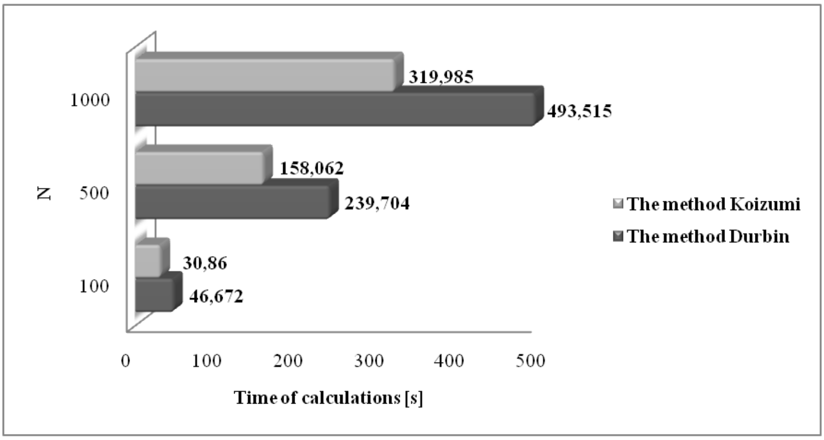
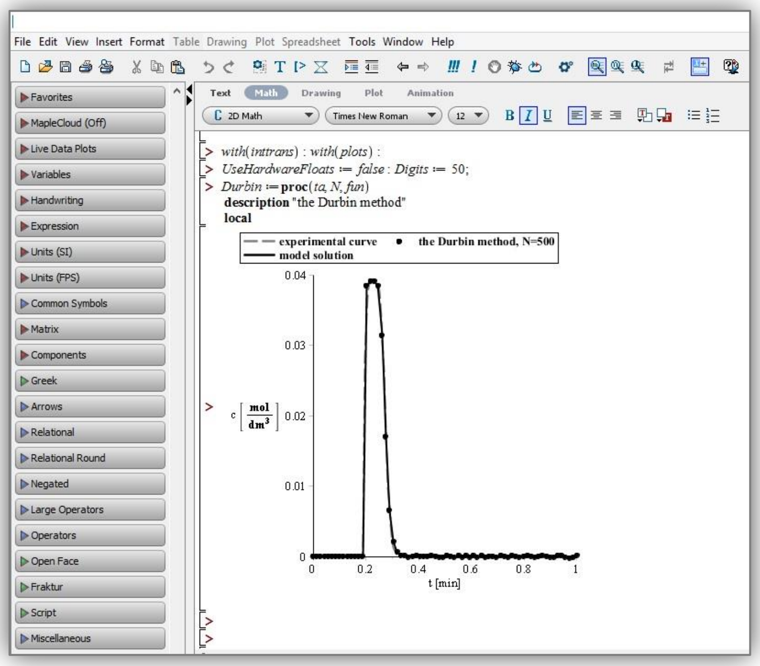
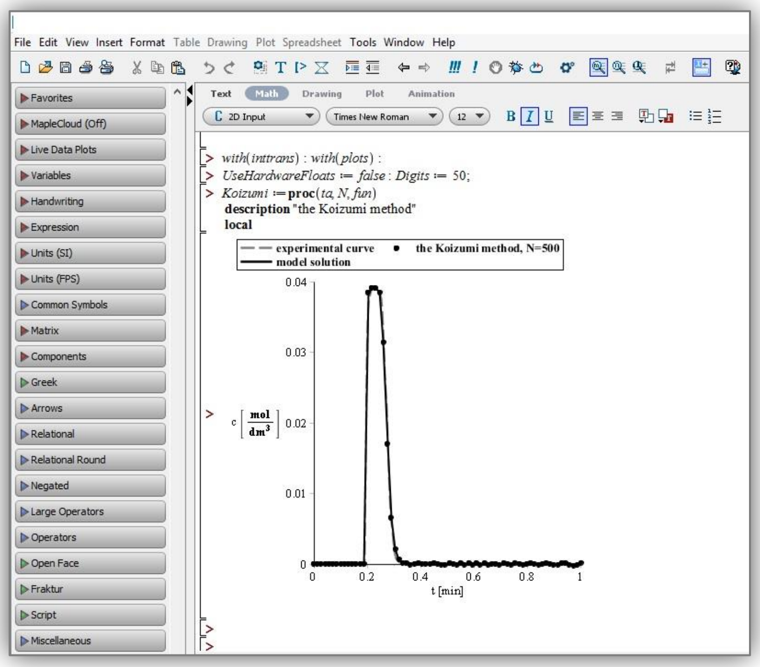


Fig. 4 Impact of parameter N on time of calculations in the Durbin and Koizumi methods.



```
> with(inttrans) : with(plots) :
> UseHardwareFloats := false : Digits := 50;
> Durbin := proc(ta, N, fun)
  description "the Durbin method"
  local
```

Fig. 5 Screenshot of program Maple®. Numerical, theoretical and experimental profiles gas concentrations for 0.04 dm^3/min. The Durbin method.



```
> with(inttrans) : with(plots) :
> UseHardwareFloats := false : Digits := 50;
> Koizumi := proc(ta, N, fun)
  description "the Koizumi method"
  local
```

Fig. 6 Screenshot of program Maple®. Numerical, theoretical and experimental profiles gas concentrations for 0.04 dm^3/min. The Koizumi method.

The tests show, that all methods presented are suitable for solution of the analyzed problem – the mathematical model related with gas flow through the measuring system. The methods have similar accuracy. Using the Gaver-Stehfest method, one can solve the gas flow problem with slightly higher accuracy than the other methods. For this method, the average absolute error is equal to 8.8109E-04 and average relative error is equal to 4.1387E-03 for N=14. For other methods, we obtained the average absolute error only for N=500. Moreover, the Gaver-Stehfest method is also faster (time of calculations t=0.953s for N=14) than the Durbin method (time of calculations t=239.704 s for N=500) and the Koizumi method (time of calculations t=158.062 s for N=500). The method based on a Fourier sine series expansion (the Koizumi method) is faster than the method Durbin.

CONCLUSIONS

We have found that presented numerical methods for inverse Laplace transform were appropriate to solve analyzed problem, but the Gaver-Stehfest method proved to be the most effective computational.

APPENDICES

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Abstracts

Preparation of macroporous hydrophobic flat-sheet PVDF membranes via vapor induced phase separation

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Keywords: *contactor membrane, vapour induced phase separation, polyvinylidene difluoride, macroporous, hydrophobic*

The aim of this work is to prepare hydrophobic and highly porous polyvinylidene difluoride (PVDF) membranes with high porosity and tunable and narrow barrier pore size distribution in the range from ~0.1 to ~1 µm using the vapor induced phase separation (VIPS) technique.

Polymeric membranes can also be obtained via other phase separation methods, such as non solvent induced phase separation (NIPS) or thermal induced phase separation (TIPS). In contrast to the latter ones the here used VIPS method is not widely used in industrial scale. During the process the cast film of the membrane polymer solution is exposed to humid air prior to immersion in the coagulation bath. It promises interesting ways for influencing important membrane characteristics. Factors like relative humidity, exposure time to humid air or airflow velocity influencing mass transfer can be used for tuning VIPS conditions, so that a macroporous membrane with high porosity, isotropic cross section and narrow barrier pore size distribution can be achieved.

So far, membranes with several of the desired properties have already been prepared in lab-scale. Dependencies of porosity and pore size of the above mentioned parameters have been evaluated. Interestingly, the temperature at which the polymer is dissolved plays a more important role in the VIPS process than in the traditional NIPS process. It has been found that after higher dissolution temperatures a so called nodular structure is formed, which leads to problems in the membrane forming process during the final immersion in the non-solvent.

As a perspective, it will be interesting to explore to what degree it is possible to tune all desired characteristics of the membranes by the VIPS process parameters. Additionally, membranes which can withstand plasma post-treatment for increasing the hydrophobicity are of interest.

Material left after supercritical camomile extraction as precursor of adsorbents of liquid phase pollution

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***Keywords**: camomile, activated carbons, physical activation, iodine adsorption, organic dyes removal*

Activated carbons are porous materials that behave as powerful adsorbents because of their high surface area, adequate pore size distribution, and variable characteristics of surface chemistry. Thanks to strongly developed porous structure, activated carbons show very good sorption properties, both from liquid and gas phase, that is why they have been applied in many areas of industry. Broadening range of their use leads to increased demands for carbonaceous adsorbents, which stimulates the search for new carbon precursors. Therefore, the aim of this study was to check the usefulness of residue after supercritical extraction of camomile as precursor of low cost activated carbons as well as characterization their sorption properties toward organic and inorganic pollutants from liquid phase.

The starting material was residue after supercritical extraction of camomile in the form of powder with size range of 0.10 – 0.65 mm and moisture content in air-dry state of 4.9%. At the beginning, the precursor was subjected to pyrolysis process. The samples were heated (10ºC/min) from room temperature to the final pyrolysis temperature of 500 and 700ºC. In the final pyrolysis temperature, samples were kept for 60 min and then cooled down in an inert gas atmosphere. Then products of pyrolysis were next subjected to physical activation. This process was carried out at temperature of 700 and 800ºC under a stream of carbon dioxide at a flow rate of 0.250 L/min, for 60 min.

The activated carbons obtained were characterized by textural studies, determination of pH and the number of surface oxygen groups. The sorption properties of the materials prepared were characterized by iodine, methylene blue and crystalline violet removal at room temperature.

The results obtained in our study have shown that the residue after supercritical extraction of camomile can be used as precursor for production of effective carbonaceous adsorbents. However, further investigation should be aimed at the optimum choice of the temperature of pyrolysis and activation in order to significantly improve the textural parameters of the activated carbons.

Sorption properties of activated carbons prepared from residue after supercritical extraction of hops

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***Keywords**: residue after supercritical extraction, activated carbons, physical activation, H_2S removal*

Development of civilization and industry inevitably brings increasing level of pollution in the natural environment. This forces activities aimed on the one hand at limiting the amount of pollutants introduced into water and air and on the other hand at effective removal of polluting substances already present in the natural environment. One of the effective methods of this aim realization is adsorption on activated carbons. Activated carbons can be produced from different precursors of organic origin including peat, wood and coals. Wider and wider range of their application cause increasing demands for these materials and stimulate the search for new precursors. Attractive precursors of activated carbons can be the waste products left after extraction of plant raw materials with supercritical CO_2.

Therefore, the aim of the study was to obtain the activated carbons by carbonization and physical activation of the waste left after supercritical extraction of hops and application of the adsorbents obtained for removal of H_2S from gas phase.

The starting material was dried and sieved to the grain size of 0.10-0.85 mm. At first the precursor was subjected to carbonization process. The samples were heated from room temperature to the final carbonization temperature of 500, 600 and 700ºC. The sample was kept for 1 hour and then cooled in inert atmosphere. The chars were next subjected to physical activation at 800ºC under a stream of carbon dioxide, for 1 hour.

The activated carbons obtained were tested as adsorbents against hydrogen sulfide. The carbon materials obtained were characterized by elemental analysis, determination of the surface oxygen groups and textural parameters.

The result presented have shown that residue after supercritical extraction of hops can be cheap, easily accessible and promising precursor for activated carbons.

Ultrafiltration membranes with additional adsorber properties for removal of heavy metal ions

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Keywords: *ultrafiltration membranes, click chemistry, star polymers, atom transfer radical polymerization*

Heavy metal ions are one of the most serious environmental problems today. In the last years various methods for heavy metals removal from water and wastewater have been studied. Up to now removal of metal ions from water by ultrafiltration (UF) is only possible after formation of large complexes or micelles. Therefore this project is focused on the development of novel UF membranes with particular adsorber properties. Processes and materials should be developed by which the entire surface of the membrane can be utilized.

In this project, polysulfone (PSU) membranes will be functionalized with linear and star-shaped polymers containing chelating groups via azide-alkyne cycloaddition click chemistry. The clickable polymers are prepared directly via atom transfer radical polymerization (ATRP). The synthesized polymers are characterized by nuclear magnetic resonance spectroscopy (^{1}H-NMR), dynamic light scattering (DLS), rheology, gel permeation chromatography.

PSU functionalisation is performed as reported in published literature. Different membranes with variable degrees of functionalization as well as variable ratios of functionalized to non-functionalized PSU were prepared via non solvent induced phase separation.. The functionalized UF membranes were characterized by scanning electron microscopy, infrared spectroscopy, contact angle, and zeta potential measurements. Membrane performance was initially analyzed by water permeability and batch metal ion binding measurements.

The first step towards membrane characterization was the determination of the azido group activity after casting the membranes. It was necessary to ensure that enough azido groups stayed active after membrane casting to enable the following click reactions. Easily detectable and highly reactive molecules were used to quantify the amount of active azido groups in the membrane, for example with ^{1}H-NMR measurements and elementary analysis.

Removal of drugs from wastewater by adsorption on porous solids

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***Keywords**: drugs, selective adsorption, wastewater treatment, Metal-Organic Framework, mesoporous silica materials*

Poorly water-soluble drugs are affected by insufficient absorption in the gastrointestinal tract. The undissolved drugs cannot be removed completely in sewage treatment plants and originate in the environment. Therefore, there is a need to optimize current technologies used in waste and drinking water treatment plants for elimination of pharmaceutical residues. Removal of pharmaceuticals by adsorption is one of the most promising techniques. In this work, the adsorption capacities of several mesoporous silica materials and Metal-Organic Frameworks (MOFs) for carbamazepine and naproxen as well as their mixture were investigated.

Synthesized materials were characterized by powder X-ray diffraction (PANalytical) and nitrogen sorption measurements (Micromeritics). Adsorption isotherms and kinetics were determined in batch experiments and the dynamics of adsorption and desorption were studied in a fixed-bed adsorber. After defined time intervals, samples were withdrawn from the vessels and analyzed by UV/VIS spectrometer V-650 (Jasco) or in the case of drug mixture after the separation by HPLC (Jasco).

For all chosen materials adsorption equilibrium is reached after a few minutes and regeneration of the adsorbents is possible. Mesoporous silica materials show a low affinity to carbamazepine, but the adsorption capacity can be improved by modification of the surface or the incooperation of hydrophobic groups in the pore system. In the case of MOFs, MIL-100(Fe) has a high affinity to naproxen and low affinity to carbamazepine. CAU-1 leads to a high adsorption capacity of both drugs. The influence of pH and temperature on the adsorption kinetics of drug mixture with CAU-1 and MIL-100(Fe) were investigated. CAU-1 shows comparable adsorption properties to charcoal and MIL-100(Fe) leads to very selective adsorption. By variation of pH between 3 and 9 no change in adsorption kinetics is found for carbamazepine. On the contrary, the adsorption of naproxen on both MOFs increases at a pH of 4.5. Change of Temperatures in the chosen range does not change the adsorption capacity significantly.

Probabilistic simulation of fire scenarios using Monte Carlo analysis

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Keywords: *fire modeling, Monte Carlo, FDS, uncertainty, sensitivity analysis*

Mathematical techniques are integral methods used for fire modeling nowadays. Traditionally, fire models in enclosures and estimation of fire consequences have been performed by means of deterministic models. These can be characterized by a given set of input variables, which always lead to the same prediction – given set of outputs. However, in many cases user can define input variables within a range of values based on common knowledge, generally accepted practices in the field or even may use a best guess. That is why in this paper other approach will be presented – instead of creating a model, in which single point estimates of outputs are produced by single point estimates of inputs, it will be shown that a distribution of output variables can be produced by sampling distributions of input variables.

This probabilistic approach can be achieved by a number of techniques. The most simple one would be to take into account uncertainty and distribution of input variables varying them manually within some allowable range. However, in more complex cases it is needed to use Monte Carlo techniques – a method of performing multiple experiments by means of random sampling of variables within given probability distribution. What is more, when performing Monte Carlo analysis, it is needed to select the most relevant input variables, which should be investigated. This can be done using sensitivity analysis, which allow to analyze whether the output parameters are sensitive to changes in input parameters and to determine which input parameters contribute most to the uncertainty in fire model.

This paper discusses current capabilities of quantifying user uncertainty in fire modeling by means of Monte Carlo analysis. Present state of art in probabilistic Monte Carlo analysis of fire scenarios will be presented – regarding both zone models and FDS simulations. The most relevant results will be discussed – which input variables are the most sensitive and how uncertain is the output data to variations in the input variables. Finally, recommendations for future work will be given.

Stability testing of cosmetic formulations containing vegetable oil

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***Keywords**: meadowfoam seed oil, stability, particle size distribution, zeta potential*

Vegetable oils are commonly used as raw materials in the chemical and cosmetic industry due to their specific properties. Meadowfoam seed oil (MSO) is one of the cold pressed vegetable oils. It is characterized by composition of long chain fatty acids (C20-22), predominantly monoene fatty acids. This property has an influence on the stability of formulations containing MSO.

Two types of cosmetic formulations were prepared in order to carry out the research. The oil phase: 9.80 wt.% of Creagel® EZ 7 (thickener) and 16.70 wt.% of Alphaflow® 20 (lubricant) were mixed. Then, they were dispersed in purified water in the ratio of 1:7 to produce cream I (o/w), i.e. pure base and cream II (o/w) – base containing an active ingredient - 4.50 wt.% of meadowfoam seed oil. The emulsions were stirred to obtain the consistency of a cream. The prepared formulations were stored at 4, 25 and 40°C in order to examine their stability. Selected methods were used to evaluate the physical and chemical parameters of tested emulsions. The viscosity was measured by RC02's Rheotec viscometer, the particle size distribution by laser diffractometry (Malvern Mastersizer 2000E) and the zeta potential by using Malvern Zetasizer Nano Z.

MSO-containing cream had noticeably higher viscosity in comparison to pristine cream I. The difference was particularly evident in the case of creams stored at 4°C. The determination of particle size distribution showed the smaller changes in the particle size for cream II (with MSO), especially at elevated temperature (40°C). The zeta potential for MSO-containing emulsion had significantly bigger values than |±30mV|, indicating a good predicted physical stability.

Meadowfoam seed oil can be successfully used as an effective cosmetic raw material with high stability. Physicochemical methods confirmed the positive influence of MSO on the stability of cosmetic formulations containing it (both at reduced and elevated temperature).

The influence of *Limnanthes alba* seed oil on functional parameters and its effectiveness in cosmetic formulations

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***Keywords**: Limnanthes alba (meadowfoam) seed oil, in vivo tests, skin hydration*

Limnanthes alba (common name: meadowfoam) seed oil (MSO) is obtained from seeds of *Limnanthes alba* by cold pressing. MSO has a characteristic composition of long chain fatty acids, which determines its cosmetic properties and predisposes MSO to use it as an effective cosmetic ingredient.

In vivo tests were preceded with the preparation of two types of cosmetic formulations. 9.80 wt.% of Creagel® EZ 7 and 16.70 wt.% of Alphaflow® 20 were mixed. Then, they were dispersed in purified water in the ratio of 1:7 in order to obtain the consistency of a cream. Additionally, 4.50 wt.% of meadowfoam seed oil was added to cream II as an active ingredient. *In vivo* tests lasted six weeks and they were conducted to evaluate the effectiveness of MSO in formulations and functional parameters of cosmetic formulations containing it. Measurement of selected skin parameters was carried out using the MPA apparatus (*Courage+Khazaka* electronic GmbH), which consisted of Corneometer CM825 and Tewameter TM300. Furthermore, research participants assessed the functional parameters of tested formulations by filling out a questionnaire.

The biophysical skin parameters such as skin hydration and transepidermal water loss (TEWL) were improved as a result of application of MSO-containing cream. The increases of skin hydration level were noticeable and qualified the skin of the most research participants as a sufficiently moisturized skin. The maintenance of a high degree of hydration or eventually its minimal decrease were observed after discontinuation of the usage of tested formulation. The functional parameters of cream II (with MSO) were assessed by research participants with high scores, what proved the beneficial impact of MSO on application of the cream II.

The positive effect of *Limnanthes alba* seed oil on functional parameters and its effectiveness in cosmetic formulations was confirmed. *In vivo* tests have shown a significant improvement of the epidermal barrier function (TEWL values and the skin hydration level) as a consequence of the usage of cream with MSO.

The impact of the synthesis methods on physicochemical properties of SBA-15 materials containing nitrogen or sulfur atoms

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Keywords: *SBA-15, synthesis procedures, surface modification, grafting, co-condensation*

Mesoporous matrix of SBA-15 type is of great scientific and commercial interests due to its attractive physicochemical properties, namely the presence of pores of diameters ranging from 2 to 50 nm, their high ordering and large surface area reaching even 1000 m^2/g. All these features of the ordered mesoporous silicas have potential applications in catalysis or adsorption.

The goal of our study was targeted towards designing the efficient synthesis methods for obtaining ordered mesoporous silicas of SBA-15 type and their equivalents modified with organic compounds containing heteroatoms, such as nitrogen or sulfur.

Mesoporous materials of SBA-15 type were prepared by using tetraethyl orthosilicate (TEOS) as the silica source and triblock copolymer (Pluronic P123) as a template. The surface of the obtained materials was modified with amino groups (from Z-6020 or Z-6032 organosilanes), which gave basic active centers, or with thiol groups (from MPTMS), which gave acidic active centers. The functional groups were introduced onto silica matrix using two different methods: co-condensation and grafting.

Structure and surface properties of the synthesized materials were evaluated by several techniques. X-ray diffraction analysis proved the ordered hexagonal structure of the obtained materials. FT-IR spectroscopy and elemental analysis confirmed the presence of functional groups. Measurements of the low-temperature nitrogen sorption gave the information about the surface area and pore size distribution. Transmission electron microscopy was used as a complementary technique in the evaluation of mesopores ordering. Additionally, selected materials were used in catalytic reactions in order to verify their catalytic properties.

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Catalytic activity of SBA-15 materials modified with organic groups containing sulfur or nitrogen atoms in relation to the synthesis methods

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***Keywords**: SBA-15, surface modification, acid-base catalysts*

Mesoporous silicas of SBA-15 type are high surface area materials that possess a well-developed and highly ordered system of mesopores. Interestingly, surface of the silica matrix can be modified among others by organic groups, which can generate basic or acidic centers. These features of SBA-15 silicas generate a possibility of using them in acid-base catalytic processes.

The purpose of the study was to obtain SBA-15 materials with organic groups containing sulfur or nitrogen atoms and investigate the effect of synthesis method and reaction conditions on their catalytic activity.

Syntheses of SBA-15 materials were performed using tetraethyl orthosilicate (TEOS) and non-ionic surfactant (Pluronic P123). The surface of the obtained materials were functionalized using organosilane compounds containing S atoms (3-mercaptopropyltrimethoxysilane) or N atoms (Z-6020 or Z-6032 amines). This procedure enabled creation of basic and acidic active centers, respectively. Different synthesis conditions were applied with varying aging time and temperature. Additionally, two methods for introducing functional groups were used, namely grafting and co-condensation.

Materials containing amino groups were tested for their catalytic activity in the Knoevenagel condensation, whereas those containing thiol groups were applied in the Friedel-Crafts reaction. The catalytic tests were carried out in different conditions of temperature and time.

Post-reaction mixtures were analyzed by GC-MS and GC methods, showing satisfactory catalytic performance of the obtained mesoporous materials. The use of various reaction conditions and synthesis methods affected their catalytic activity. The obtained results show that SBA-15 materials modified with organic groups containing sulfur or nitrogen atoms can be used in the acidic or basic catalysis.

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Structure, properties and the electrooptical performance of azo-die doped ferro- and anfiferroelectric smectic liquid crystals

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***Keywords**: photoalignment, liquid crystals, spontaneous polarization P_s, switching times $\tau_{10\text{-}90}$, tilt angle θ, electrooptical characteristics I(U), rotational viscosity γ_φ*

The photoalignment of liquid crystal material and the most commonly used rubbing technique are alternative methods of aligning of liquid crystalline structures of displays or photonic devices. Both mentioned techniques are aimed at creating the surface mediated anisotropic properties of the polymer layers (so called ordering layers) present on the boundary surfaces of the thin liquid crystalline slab.

The rubbing method has several disadvantages like generation of the dust and electric charge. The photoalingment of the ordering layers, which is the non-contact process, eliminates drawbacks mentioned above giving uncomparable even structures, however induces a permanent structure of the director within liquid crystalline slab. In case of surface stabilized ferro (FLC)- and antiferroelectric (AFLC) structures (SS(A)FLC) the surface induced alignment is inevitably connected with induction of several structural defects like two domain structure or zig-zag defects.

Towards the manufacture the dynamically oriented SS(A)FLC structures and testing of the potential of a new photoorientation technique for eliminating optical defects the azo-dye doped FLC and ALFC structures have been studied. These parameters have been examined for the following substances: 1% or 5% 4-(4-heptyloxy-phenylazo)-benzonitrile in mixture of FLC W302 and AFLC W1000. The examination of the of the spontaneous polarization P_s, the switching times $\tau_{10\text{-}90}$, the tilt angle θ and the rotational viscosity γ_φ of the azo-dye doped FLC and AFLC mixtures has been done. The SS(A)FLC have been prepared and the observation of textures as well as the electrooptical characteristics I(U) have been studied. The results have been discussed in the context of the application of the azo-dye doped SS(A)FLC structures for photonic applications.

Application of component number analysis methods on Raman maps

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***Keywords**: pharmaceutics, chemometrics, variable clustering, sum of ranking differences, single angle mapper*

In field of pharmaceutics it can be avoided that the chemical compositions of some products are unknown for the analyst. Drug counterfeiting or generic drug development can be led to partly or entirely lack of information about the samples. The microscopic Raman technique has many advantages. One of the best characters is that a component can be detected even in small concentration assuming it has a heterogeneous distribution. If there is a spectral library with plenty of possible Raman spectra the Boiret's iterative approach can be used for pure compound identification. This approach cannot lead to proper results if there are no enough pure reference spectra. In this case the multivariate curve resolution methods such as MCR-ALS, PMF or SIMPLISMA can be applied for pure component spectra determination. For these methods the component number is needed to determine as a parameter. In our experiments the variable clustering method has been used for this purpose.

Two different multicomponent systems were investigated. The one of studied samples was an in-the-house developed tablet consisting of six components with low-concentrated Mg-stearate and aerosil. The other sample was a complex powder for mammalian cell culture broth containing glucose, amino acids and many other partly known components. The former sample was measured in 41×41 points, the latter Raman map contain 22×22 spectra.

Each component of tablet was detected by Boiret's orthogonal projecting method and variable clustering has determined the four major components as well. The complex powder cannot be examined properly by orthogonal projecting method in the absence of reference spectra. The variable clustering supposed 11 clusters. It has found more unknown components. The clustering method was validated by SRD as a non-parametric method using for comparing and connecting a cluster to a reference.

Flow chemistry in macrocyclization of crown ethers

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***Keywords**: flow chemistry, crown ether, solid base, Williamson ether synthesis*

Optically active crown ethers have attracted a great deal of attention due to their chiral recognition abilities. Their derivatives have been widely used in the resolution of various chiral compounds containing a protonated primary amino group. Synthesis of pyridino-18-crown-6 ethers is traditionally a long linear synthesis with a crucial ring closure step. In batch conditions this reaction takes several hours long using NaH as a base and usually provides poor yields.

Our aim was to optimize this reaction step with the help of continuous-flow chemistry. Modification of a starting material and optimization of the parameters provide higher yields and shorter reaction times. In these conditions the deprotonation of a primary or a secondary alcohol occurs with KOH instead of a strong base such as NaH.

The used experimental setup is shown below. The syringe pump loaded with THF stock solution of the starting materials is able to pump the fluid through the solid base containing column. The flow rate was properly adjusted to have a 30 min reaction time.

The setup presented here is suitable for the preparation of ethers with *Williamson* synthesis in continuous-flow.

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Effect of addition of fly ash on properties of light ceramic proppants

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Keywords: *light ceramic proppants, fly ash, clays,*

Light ceramic proppants are defined as a chemically inert, non-combustible and mono dimensional solid granules that supplied by a liquid during hydraulic fracturing to a gas or oil deposits. Their main task is to keep shale open for the entire time of extraction from the rock gas and / or oil. These materials should be characterized by a high strength, suitable porosity and spherical shape which allow to better flowing of the hydrocarbons in the extraction of shale. In this research the feasibility of recycle fly ash from the combustion of biomass to manufacture light ceramic proppants were studied. The microstructure and phase composition of specimens were investigated. The influence of firing parameters on the densification, mechanical properties and the pore distribution of light proppants were tested.

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Application of spectroscopic methods in studying novel materials: black glasses

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***Keywords**: black glass, sol-gel, dip-coating, MAS NMR, MIR*

Black glasses are modern materials based on the silicon oxycarbide. The structure of this amorphous material can be compared to amorphous silica SiO_2 with part of oxygen atoms removed and replaced with carbon atoms, causing the shrinkage of the structure. The results of the structure change are high hardness, stability and resistibility at elevated temperatures and in aggressive chemical environment. These interesting and attractive properties from the point of view of material engineering make black glasses a perfect material for protective layers on various substrates in applications such as biomaterials and fuel cells.

Obtaining this kind of glass is impossible in the way of classical melting because of the silicon carbide crystallization. Researchers decided to use one of the *soft chemistry* methods – sol-gel method. From this approach preceramic polymers – oligo- and pilisilsesquioxanes – were obtained on the path of hydrolysis and polycondensation of alcoxysilanes with at least one of the silicon-carbon bond preserved. The use of such a component lets the Si-C bond stay unchanged throughout the synthesis path, coating and then thermal treatment. Obtained sols were deposited on the metal substrates by using the dip-coating apparatus, which enabled to create thin layers. After that the materials were processed at high temperature treatment in the argon protective atmosphere to prevent the oxidation of carbon and it loosening from the structure.

Obtained materials were examined on the every step of the preparation as well as its final result. Various techniques of analysis were applied. Starting from the techniques such as XRD (DSH powder method and GID), SEM and focusing on the middle-infrared vibrational spectroscopy technique (MIR), magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR), X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDS). Because in this particular case researchers were examining novel material, for which standards are not available, it was necessary to provide molecular modeling of the reference spectra.

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Bioactive properties of the silicon oxycarbide amorphous coatings on the titanium substrates

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***Keywords**: bioactivity, black glass, sol-gel, MIR, Raman*

Bioactivity is the ability of the surface or the coating of the implant to adhere directly to the soft tissue or osseous tissue, without the creation of an intermediate layer constructed from the modified tissue. Metallic materials are most commonly used in the bone surgery, prosthodontics and cardio surgery as products for long-term usage. Their biggest disadvantage is irresistibility against corrosion or, which is the case of titanium, the uncontrolled creation of passive layer, which is not necessarily biocompatible. That is the reason of why it is indispensable to cover the surface of this materials with the protective inert layers or bioactive materials, bioceramic – glass coatings or glass-ceramics. Among all the methods that can be used, for example CVD, PVD, EPD, the one which deserves special attention is sol-gel method, which provides the obtaining of thin layers on the implants without restrictions about shape of the implant or conductivity of the substrate material.

As it was mentioned before, the coating layer needs to be characterize by the high resistibility on corrosive and tribological wear and moreover excellent adhesion to the implant surface. Those abilities draw attention to the amorphous silicon oxycarbide. So called black glasses are excellent coating materials of high performance which is the result of the dense structure. If we compare their structure to the amorphous silica SiO_2, it can be said that part of oxygen atoms were removed and replaced with the carbon atoms, provided that two atoms of oxygen are replaced by one carbon atom. Good adhesion is secured by the application of sol-gel method and deposition using dip-coating. Use of sol-gel method, which is based on the hydrolysis and polycondensation of di- and trialcoxysilanes, enables to obtain preceramic polymers, which can easily cover substrates with the use of dip-coating method for the creation of permanent thin layers after heat treatment. Bioactivity of the obtained materials were confirmed by *in vitro* tests. During the research vibrational spectroscopy techniques, MIR and Raman spectroscopy, together with microscopic techniques: SEM (coupled with EDX) and AFM were used.

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The stability studies of macroemulsions containing phenylalanine derivative

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***Keywords**: stability, amino acid derivative, active substance, undecylenoyl phenylalanine*

The stability of formulations is a fundamental parameter, without which it is not possible to introduce the product to the market. The development of a stable formulation is not an easy task. The manufacturer has to declare the shelf life of the product. During that period the formulation should remain stable. Stability studies are based on an assessment of changes in formulations stored at different conditions at appropriate intervals. Stability tests are carried out either by a simple centrifuge test or by multiple light scattering method using Turbiscan Lab Expert apparatus. The second technique provides information about the instability types such as flocculation, coalescence, creaming or sedimentation. The changes are visible on the entire height of the sample. The advantage of this method is the relatively short time of analysis in comparison with conventional methods. Operation of the device is based on measuring the intensity of the transmitted and/or backscattered light from the sample, so it is possible to observe the phenomenon associated with migration and changes in particle size.

In this study the macroemulsions containing undecylenoyl phenylalanine as the active compound were obtained. This substance is used in dermatology, especially in skin problems associated with hyperpigmentation. The aim of this study was to prepare macroemulsions with an active compound and monitor their stability at different storage conditions (at 4°C, 25°C and 37°C, relative humidity 80%) during two months. Two oil-in-water emulsions were obtained by different methods. The results showed that composition of formulations and storage conditions had influence on stability. In all of the emulsions stored at three different temperature conditions only the changes in the backscattering intensity along the whole sample height were observed that could be corresponded to the slight particle size variation such as flocculation. The biggest changes were observed in the case of emulsions subjected to the accelerated test, which may be associated with high humidity (80%).

Physicochemical properties of macro- and microemulsions containing undecylenoyl phenylalanine

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***Keywords**: undecylenoyl phenylalanine, amino acid derivative, active substance, release, stability*

The determination of physicochemical properties is very important during the development of new formulations. Each novel product has to meet the appropriate requirements to be placed on the market. The basic studies include examination of viscosity, stability and pH of the formulation. Viscosity can be determined by a rotational viscometer, while stability studies can be assessed by centrifuge test or by multiple light scattering. The last method allows to track changes in sample during the storage period without its dilution. In order to estimate the efficiency of the active ingredient, the release tests are carried out.

In this study the undecylenoyl phenylalanine was used as the active compound of differente formulations. The phenylalanine derivative is applied in dermatology to treat melasma, a skin problem associated with the occurrence of brown spots around the face and neck.

The aim of this study was to prepare cosmetic formulations such as macro- and microemulsions containing undecylenoyl phenylalanine, study their physicochemical properties and stability. Additionally, the release kinetics of phenylalanine derivative from formulations obtained through different membranes was monitored.

The obtained results proved that macroemulsions have higher viscosity and are less stable than microemulsions. The storage conditions and preparation method had influence on the stability of macroemulsions. The higher release rate of undecylenoyl phenylalanine from microemulsions through the membrane was associated with the greater hydrophilicity of this formulation. Futhermore, the results proved that the thickness and pore size of the membrane influence the permeation ability of the active compound.

Synthesis and mesomorphic properties of 4'-[(4'-pentylbiphenyl-4-yl)ethynyl]biphenyl-4-carbonitrile derivatives – four ring Liquid Crystalline materials with high melting points.

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***Keywords**: liquid crystal, nematic, biphenyl, acetylene, organic cyanides*

Liquid crystalline mixtures contain components of different types, one of the role played by some dopants is to increase the clearing point and the order parameter. Additionally dielectrically positive long core molecules exhibit low values of molecular rotation frequency along short axis, which is desirable property for designing of dual frequency liquid crystal materials.

The aim of this research was to synthesize compounds with long highly polarizable core. We assumed that 4'-[(4'-pentylbiphenyl-4-yl)ethynyl]biphenyl-4-carbonitrile is the molecular core which will be functionalized in different places in the lateral position. Based on our experience in synthesis of liquid crystals and their purification process we decided on the following strategy. Firstly we synthesized 4-iodo-4'-pentylbiphenyl derivatives. Secondly we synthesized 4'-ethynylbiphenyl-4-carbonitrile derivatives. Prepared intermediates have been cross-coupled in last step to the final product, which could be isolated with purity above 99,5%.

Due to the fact that the research is still in progress the final results and conclusions will be presented on the conference poster. However, preliminary results show that the received compounds have high clearing point (above 320^{o}C). In addition, we plan to present the influence of type, position and number of lateral substituents on mesomorphic properties, phase transition temperatures and enthalpies of compounds.

Influence of synthesis methods on catalytic properties of MCM-41 mesoporous materials modified with basic or acidic functionalities

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***Keywords**: MCM-41, basic and acidic functionalities, Friedel-Crafts alkylation, Knoevenagel condensation*

Ordered mesoporous silicas, such as MCM-41 containing basic or acidic functionalities are very interesting materials due to the possibility of their use, e.g. in catalysis. Introduction of amino or sulfonic groups onto siliceous matrix generates basic or acidic properties, respectively that in consequence enables the use of those materials in acid-base catalytic reactions. Therefore, the aim of this study was to investigate the catalytic properties of MCM-41 materials modified with basic or acidic functionalities and obtained by different synthesis methods.

In order to examine the catalytic activity of the obtained mesoporous materials two different reactions were applied, namely Knoevenagel condensation between benzaldehyde and ethyl acetoacetate (for MCM-41 materials containing amino groups) as well as Friedel-Crafts alkylation of anisole with benzyl alcohol (for MCM-41 materials containing sulfonic groups).

MCM-41 materials were synthesized with tetraethyl orthosilicate (TEOS) as a silica source and cetyltrimethylammonium bromide (CTABr) as a template. As a source of amino groups two aminoorganosilanes were used, whereas 3-mercaptopropyltrimethoxysilane (MPTMS) was applied as a source of thiol groups. Thiol-modified MCM-41 materials were oxidized by H_2O_2, because Friedel-Crafts alkylation performs preferably on sulfonic functional groups. Two different synthetic procedures were involved during our studies, i.e., co-condensation and grafting. Both techniques were applied with varying time of reagents mixing and functional groups addition.

Different synthesis methods enabled obtaining the materials dedicated to acidic or basic catalytic reactions. Performed catalytic tests showed, that synthesized amino-modified MCM-41 materials may be used as selective catalysts in Knoevenagel condensation, while oxidized thiol-modified MCM-41 silicas may be applied as an efficient catalyst in Friedel-Crafts alkylation.

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Synthetic approach to mesoporous silicas of MCM-41 type modified with amino or thiol moieties

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Keywords: *ordered mesoporous silicas, MCM-41, surface modification,grafting, co-condensation*

First synthesis of ordered mesoporous materials of MCM-41 type performed in 1992 has initiated intensive research activities. This kind of silica materials are characterized by ordered structure, presence of tunable mesopores, well-developed surface area and other specific textural features. The surface of these materials can be modified by introducing organic groups (e.g. vinyl) or groups containing heteroatoms (e.g. amino or thiol groups). Modified ordered mesoporous silicas of MCM-41 type have a broad range of potential applications, e.g. in catalysis.

The main purpose of the presented studies was focused on the development of efficient methods for obtaining ordered mesoporous silicas of MCM-41 type and their modification with organosilanes containing nitrogen or sulfur atoms.

In the first stage of the study, ordered mesoporous materials of MCM-41 type were synthesized in basic conditions with tetraethyl orthosilicate (TEOS) as a silica source and cetyltrimethylammonium bromide (CTAB) as a template. Materials containing functional groups were prepared using two different aminoorganosilanes as a source of amino groups or with mercaptoorganosilane as a source of thiol groups. All syntheses were carried out with two different procedures: direct synthesis, namely co-condensation and with post-synthetic functionalization ("grafting").

In the next stage of the study, all synthesized materials were evaluated regarding their structural/textural properties. The samples were characterized by small-angle X-ray diffraction (XRD), low-temperature N_2 sorption and FT-IR spectroscopy. Selected materials were analyzed by transmission electron microscopy (TEM) and elemental analysis as well as applied in preliminary catalytic tests involving acid-base catalytic reactions.

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Rational-by-design strategy of ZnO nanocrystals and their antibacterial activity

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***Keywords**: zinc oxide nanoparticles, organometallic synthesis, antibacterial*

The unique physicochemical properties of zinc oxide nanocrystals (ZnO NCs) are dependent on various factors, including chemical composition, crystallinity, purity, size-dispersion, shape, hydrodynamic diameter, aggregation or agglomeration, surface character and surface ligand organization. All these factors are largely determined by the synthetic procedures, however the comprehensive toxicological impact posed by the character of ZnO NCs is the subject of a continuous debate and still remains unclear. Recent studies on eukaryotic and prokaryotic cells revealed that biological activity of ZnO could be correlated both with intrinsic and extrinsic NCs' properties. Such knowledge opens the door for the rational-by-design strategy of ZnO NCs for further bioapplications. Moreover, there is a growing need for reducing bacteria's activity due to constantly unresolved problem of increasing infections, and thus ZnO NCs are considered to be a promising and effective antimicrobial agents.

In the reported work, we have focused on the synthesis of bare and organic ligand coated ZnO NCs using an organometallic approach, and then, determined their antibacterial properties. As a control, ZnO NCs synthesized by an inorganic method were applied. The resulting ZnO NCs were fully characterized in terms of ZnO NCs inorganic-organic interface (crucial factor, which creates the opportunity to influence the interactions with biological material) using a wide library of analytical techniques. The ZnO NCs-induced toxicity was tested with Gram-negative Escherichia coli and Gram-positive Staphylococcus aureus strains. The results demonstrate that, when fully optimized, our organometallic approach could be a highly promising method for obtaining homogenous, stable ZnO NCs with antibacterial properties as a safe alternative to commonly used antibiotics.

The characteristic of graphene

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Keywords*: graphene, history, synthesis, properties, applications*

Graphene is a two dimensional monoatomic one atom thick system and one of the carbon allotrope. This is an individual layer of graphite looking like a honeycomb lattice made of carbon atoms.

The graphene's history starts in 1859 when British chemist Benjamin Brodie obtained what he called 'carbonic acid' by exposing graphite to strong acids. Brodie believed that he discovered 'graphon', being a new form of carbon with a molecular weight of 33. Today we know that he observed a suspension of tiny crystals of graphene oxide in water, that are graphene sheets densely covered with hydroxyl and epoxide groups. Over the next decades while studies on graphene were in progressive, a lot events has happened. For example: reduced graphene oxide was prepared by the chemical and thermal reduction of graphite oxide, van Bommel and co-workers prepare monolayer graphite by subliming silicon from silicon carbide, Boehm and co-workers recommend that the term 'graphene' could be used to describe single layers of graphite-like carbon and eleven years later IUPAC accept this term. Finally, after so many unsuccessful attempts, in 2004 two scientists Andre Geim and Konstantin Novoselov rediscovered, isolated and characterized graphene by using only piece of graphite and scotch tape. They are also the Nobel Prize in Physics for 2010 awarders and their topic was 'for groundbreaking experiments regarding the two-dimensional material graphene'. Since that time graphene has attracted great interest in physics, chemistry and material science for its unusual electrical, magnetic and other properties that it possesses.

The aim of this review are various synthesis processes of graphene and also thermal, optical, electrical and other properties with their potential applications.

This one atom thin nanomaterial has a very high mechanical stiffness, antibacterial and extraordinary thermal transport properties and many others. Since the seminal work of Geim and coworkers on freestanding graphene material in 2004, various forms of graphene sheets have been actively explored with novel applications such as transistors, solar cells and gas sensors.

The physicochemistry methods used in criminalistics

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***Keywords**: criminalistics, criminalistics traces, analytical chemistry*

Criminalistics is a lawful education which was created in the late nineteenth century. The father of this education is Hans Gross, an Austrian criminal jurist. In 1893, he release the book titled ‘Handbook for Coroners, police officials, military policemen, et cetera’ (original German title is ‘Handbuch für Untersuchungsrichter, Polizeibeamte, Gendarmen, u.s.w.’). Of course the crime and ways of catching criminals were known much earlier, however this event is believed to be the beginning of criminalistics.

Despite the fact that this form of an education is very young, it has so many definitions. Nowadays, criminalistics can be defined as a practical education, on the basis of which it is possible to recognize, detect, prove and prevent the crime. It also divides on technique, tactic, strategy, methodology and theory of criminalistics.

Criminalistics uses many methods to work against the crime events. The most often used are the physicochemistry methods. The object of interest which is analyzed by the physicochemistry methods is called a criminalistics trace. This is a residue after some incident and it has to be revealed, collected and protected before an analysis. Glass, alcohol, fiber, lacquer, soil, clothes, all biological traces which contain DNA, explosives, drugs and many other subjects can contain the criminalistics traces. The police laboratories use many methods to analyze the criminalistics traces. There are spectroscopy, chromatography, electrophoresis or microscopy methods.

In this account, we made an attempt to review selected groups of the criminalistics traces, mentioned above. We also review some analytical methods, viz., microscopy, spectroscopy, chromatography, electrophoresis.

The characterized methods enable to analyze inorganic and organic substances, and it is possible to know about a composition of mixture and an quantity each substance. Moreover, the result of analysis is objective and precise. Full automation of analysis give us the result in very short time.

The use of jasmonates in pharmaceutical and cosmetic industry

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***Keywords**: jasmonates, plant hormones, antiinflammatory and anticancer agents*

In pharmacology and cosmetic industry there is a growing interest in replacing synthetic compounds with plant-derived molecules, e.g. plant hormones. Jasmonic acid and its derivatives, collectively called as jasmonates, are linolenic acid derivatives that are structural analogues of cyclopentanone. Jasmonates occur ubiquitously and exclusively in plants, where play a significant role in e.g. growing process, metabolism and stress response.

LR2412 (sodium tetrahydrojasmonate) has been used to combat visible signs of skin ageing by reducing wrinkles and discolorations and promoting epidermis desquamation. It was also suggested to use jasmonates in oily skin therapy as well as in scalp and hair treatment. These plant hormones may be also used in tumour therapy. According to result of studies, jasmonates are able to supress proliferation and induce the apoptosis of tumour cells in diseases such as leukaemia, melanoma, neuroblastoma, and lung, colon, prostate and breast cancers. It is also believed, that jasmonates have anti-inflammatory activity. The results of *in vivo* studies of activity of methyl jasmonate derived from the red alga *Gracilaria verrucosa* showed, that MeJA anti-inflammatory potential is similar or even more effective than prostaglandin-like compounds. Moreover, jasmonates showed antiparasitis activity against *Trichomonas vaginalis*, protozoan parasite and the causative agent of trichomoniasis, by inducing both time- and dose-dependent reduction in the number of living organisms.

The oral use of these phytohormones has not been studied sufficiently yet, however according to the results of toxicity studies, application of methyl jasmonate (doses ranging from 100 to 500 mg kg^{-1}) administered intraperitoneally was well tolerated by mice and did not cause acute toxic symptoms or the animals death. To sum up, jasmonates may be used as an active substances in both cosmetic and pharmaceutical industry.

The use of laser diffraction (LD) technique in detection the instability of emulsions containing jasmonates

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***Keywords**: jasmonates, laser diffraction, emulsion stability*

Jasmonates are phytohormones that are responsible for growth regulation and development of plants. Especially they affect the storage of protein in seeds and root growth, thus these compounds may be an interesting issue for both pharmacology and cosmetology. It is believed, that jasmonates may be used in tumor therapy and skin disorders associated with inflammatory. They may be also used as cosmetic active ingredients to improve appearance of the skin and thus combat visible signs of ageing.

To enable the topical application of an active substance, it has to be first mixed with cosmetic/pharmaceutical base. The base must be safe and stable in a certain period of time and under storage conditions. It is also important to determine, if an active substance does not cause the instability of formulation. Aggregation of dispersed droplets of the inner phase of the emulsion is one of the most typical phenomenon for emulsion destabilization. This phenomenon can be analyzed using a laser diffraction (Mastersizer 2000, Malvern, UK). Using this technique, the change of particle size distribution of formulations in time can be measured. To study the stability of formulations containing jasmonates, emulsion o/w and w/o prepared at 70^{0}C as well as emulsion o/w prepared at 25^{0}C and gel were used. All these formulations contained jasmonic acid (JA), methyl jasmonate (MeJA) or methyl dihydrojasmoate (MeDiJA) and were stored in different temperature conditions (4, 25 and 45^0 C). The measurement was performed at the day of preparation and after 70 days. It was observed, that the most stable were formulations stored at 4^{0}C, whereas the less stable were those stored at 45^{0}C. Moreover, it was concluded, that the addition of jasmonates to the cosmetic base did not cause significant difference in formulation stability, so jasmonates may be an active substance of stable cosmetic/pharmaceutical formulations.

The carbon material modified with a low-temperature plasma iodine as electrodes of the electrochemical capacitor

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Keywords: *supercapacitor, plasma treatment, carbon materials*

Electrochemical capacitors are interesting energy storage systems. Their performance bases on the formation of an electric double layer, i.e. electrostatic attraction of ions at an electrode/electrolyte interface. A great enhancement of capacitance can be obtained by additional pseudocapacitance effects due to the presence of faradaic reactions assigned to various redox couples.

The aim of the presented study was to demonstrate influence of low-temperature plasma iodine treatment on carbon tissue that can be used as electrode material in electrochemical capacitors.

In presented study a scanning electron microscope was used to investigate the structure of the materials. The BET specific surface area was determined from N_2 adsorption/desorption at 77 K. The XPS technique was applied in order to determined surface functional groups.

The electrochemical studies were used in order to estimate the performance of the supercapacitor based on the modified and unmodified carbon tissue. From two-electrode cell measurements it can be found that the obtained capacitance of supercapacitor based on the modified material is higher than that of the untreated one. Iodides which are presented in the structure of carbon are responsible for the pseudocapacitative properties of the active material.

All obtained results indicate that the low-temperature plasma iodine treatment of carbon tissue is a very attractive method to increase the capacitance of electrochemical supercapacitors.

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Electrochemical properties of bisulfate ionic liquids

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Keywords: *ionic liquid, lead-acid battery*

Lead- acid batteries are most common secondary batteries in the world. The most important recipient of lead- acid batteries is automotive industry, for its purpose SLI (starting, lighting, ignition) battery is produced. Other important applications of lead-acid batteries are backup energy devices or electric vehicles.

Despite of the fact that lead- acid cells were invented over hundred fifty years ago, they constantly under research to improve operating and electrical properties. Main problems are corrosion of current collectors and connection between active mass and current collectors.

Ionic liquids are one of the most promising chemical compounds. The most important attribute of them is ability of varying the chemical properties by changing structure of cation and selection of appropriate anion. Ionic liquids due to low toxicity, high ionic conductivity and thermal stability found application as electrolytes in devices for energy storage and conversion.

In this work influence of addition of bisulfate ionic liquids on electrochemical properties of lead/lead(IV) oxide cell was presented. Electrochemical properties were examined by measurement of conductivity, using potentiodynamic method and by electrochemical impedance spectroscopy.

It has been shown that ionic liquids influence on the electrochemical properties of electrolyte and corrosion of current collectors. Extending the electrochemical stability of electrolyte can partially prevent problem of gas evolution on surface of electrodes during charging of cell. It can be effective way for extending life of battery and as a result positively influence on environment.

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Functionalized activated carbon as electrode material in electrochemical capacitor

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Keywords: *electrochemical capacitor, activated carbon, surface modification*

Electrochemical capacitors, also known as supercapacitors had received grown attention due to high specific power, long cyclic stability, use of safe and nontoxic materials. Unfortunately they suffer from low energy density, usually around 2-4 Wh kg^{-1}.

Functionalization (introducing heteroatoms in structure) of activated carbon is one of main approaches, next to utilization of metal oxide or electroconducting polymers, to increase capacitance of material. Heteroatoms in functional groups are able to enhance capacitance due to appearance of fast faradic reaction, called psudocapacitance effect. Most studied heteroatoms are oxygen, nitrogen and sulphur.

In presented study activated carbon was functionalized by reaction with ammonium persulfate, widely used radical oxidant. Specific surface area of synthesized material was studied by BET method, amount of oxygen was estimated using elementary analysis, additionally material was studied using Raman spectroscopy. Electrochemical studies, to estimate change of capacitance of material, were performed by using cyclic voltammetry, galvanostatic charge/ discharge and electrochemical impedance spectroscopy.

Simple modification of activated carbon allowed increase the amount of oxygen containing functional groups on the surface of activated carbon which enhanced specific capacitance of it.

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Antibacterial properties study of surface modified PDMS

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***Keywords**: antibacterial properties, infections, medical devices*

Nosocomial infections are still a big problem both for patients and hospitals. One of the major source of infection is the use of medical devices, mainly including bladder and central venous catheters. Effective methods of prevention of the bacterial biofilm formation on the surfaces of these medical devices are still sought.

In the present work, two types of antimicrobial coatings for polydimethylsiloxane (PDMS) were developed. PDMS material is widely used in the production of many types of medical devices. The effectiveness of the coatings in contact with the bacteria (*Micrococcus luteus*, *Escherichia coli* and *Proteus rettgeri*) using bridge model test and confocal laser scanning microscopy (CLSM) were studied.

Bridge model test showed that our coatings are able to resist bacteria migration along the surface of the sample better than uncoated material as well as commercially available coating containing silver. Microscopic observations allowed us to notice, that our coatings prevent or substantially reduce the adhesion of bacteria cells to the material surface for at least 48 hours of samples incubation under optimal conditions for the microorganisms growth.

The results suggest that developed coatings may be used for the production of silicone medical devices resistant to the adhesion of certain bacteria. This may reduce the amount of nosocomial infections in the future.

A screening method of surfactants and their mixtures for chemical enhanced oil recovery

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***Keywords**: surfactants, screening method, method development, CEOR*

After the application of primary and secondary recovery methods, the need for CEOR (Chemical Enhanced Oil Recovery) techniques to recover a higher proportion of crude oil has become essential in the last decade. The polymer-surfactant flooding is one of the tertiary techniques that can improve the oil production where flow modifier polymer and a mixture of surfactants are incorporated. It allows to control the mobility and to increase the efficiency of the oil production. Our researches focus on the evaluation of various surfactants by several test methods in order to develop effective surfactants or their mixtures and to characterize the most important surfactant properties.

Previously the CE complex evaluation method was created to select the surfactants. A weak correlation between the data of laboratory tests was detected by using the CE complex evaluation method thus further developments were needed to contribute significantly to the selection of the new experimental non-ionic surfactants and their mixtures for EOR applications. A new solubility property was incorporated to the complex method to improve the correlation. Then the method was extended to characterize other own-developed surfactants. By this method the cost and the time required of the applied laboratory screening method could be reduced.

The usage of the reaction calorimeter for studying the kinetics of chemical reactions

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***Keywords**: reaction calorimeter, kinetics, reaction rate*

Kinetics of chemical reactions enables finding mathematic model, which shows dependence of the reaction rate on operating conditions, such as: concentration of reactants, temperature or application of the catalyst during reaction.

The method based on usage of the calorimetric reactor is able to allow studying the kinetics of different reactions. Theoretical aspects mass and heat transfer phenomena will be analysed as well as principles of operation of the calorimetric reactor and calculations methods will be given.

The results of carried out experiments will be presented. The hydrolysis of acetic anhydride as the tested reaction has been chosen. This reaction is very fast even at room temperature and without addition of the catalyst. Moreover, there a significant heat effect is noticed. Thanks to these facts, it was possible to study kinetics of those reactions with RC1 reaction calorimeter.

The experiments were carried out at isothermal conditions, following the periodic operating mode. In every experiment the initial concentrations of reactants were the same and the reaction temperature was only changed. In result, it was possible to find the dependence of reaction rate constant on the temperature (the Arrhenius model was used). In addition to that, the reaction rate and the reactants concentration at each moment of the reaction run, the degree of reactants conversion, the reaction enthalpy were determined.

AAS analysis of *Agaricus bisporus* biomass to artificial gastric juice after optimization their culture *in vitro*

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Keywords: *bioelements, in vitro cultures, gastric juices, analysis, AAS*

Agaricus bisporus (J. E. Lange) Imbach is one of the most popular edible mushrooms. Pro-health qualities and the natural ability of mushrooms to accumulate the valuable bioelements for human body from environmental were the reason for choosing in actually research. In experiment five enriched and optimized *in vitro* cultures of *A. bisporus* were obtained. Those *A bisporus* biomass were characterized by high and reproducible increase of biomass. After liophilization biomass from *in vitro* cultures were extracted in a solution of artificial saliva, and then for 15, 60 and 120 minutes in artificial gastric juice and intestinal juice in order to mimic the natural conditions in gastrointestinal tract of humans. The material under study was *A. bisporus* biomass from *in vitro* cultures. The optimal *in vitro* cultures conditions were obtained by using a modified liquid Oddoux medium with addition of salts of Mg, Fe, Cu, Zn in various combinations of concentrations (0.01 g-1 g). Next, the biomass was subjected to extraction in artificial saliva, gastric and intestinal juices prepared according to the specified procedure. The incubation process was conducted in human body temperature (37°C) in the apparatus Gastroel-2014 (Department of Inorganic and Analytical Chemistry UJ CM). Extracts were analyzed by the Flame Atomic Absorption Spectrometry. The results of extractions to artificial digestive juices showed that the amount of released element depends on the time of incubation in gastric juice and of metal. The highest concentrations of elements were obtained after incubation in times of 60 and 120 minutes. The lowest level of concentration of elements was after 15 minutes of incubation. The results presented stated that *A. bisporus* has a natural ability for accumulation of bioelements and may be a natural source of them in the human diet.

Analysis of kinetics elements changes in *Agaricus bisporus* optimized medium for *in vitro* culture

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***Keywords**: kinetics, sterile conditions, bio elements, in vitro cultures, analysis*

The optimization of culture conditions allowed providing the *in vitro* culture of mushrooms in conditions which allowed to high bioaccumulation of selected elements in biomass. So the aim of work was to obtain the enriched in bioactive elements the medium for *Agaricus bispor*us *in vitro* culture.

Because of edible mushrooms possibility for accumulations of elements they can be a natural ingredient of human diet. Therefore valid aspect was that research into the use of *A. bisporus* as a medium for accumulation of micronutrients. An important issue arising from the need to maintain sterile conditions, were the monitoring mechanism of the accumulation elements in *in vitro* cultures and changes in the composition of the medium during the culture. To this end, the attempt was made to construct equipment allowing analysis. For the study, five optimal *in vitro* cultures enriched for selected elements were chosen. Then, over a period of three weeks the culture medium was monitored by analyzing quantities of 2 ml with the method of ASA (flame technique). The procedure of collecting medium was carried out in two ways. Some the culture was carried out in special flasks, with a hole, which allowed the direct collection of the sample. The rest of the culture was performed in flasks with immersed specially prepared permeable membrane installed in tubes. The obtained results led to the conclusion that accumulation of elements, in which the medium was enriched, does not occur for the full duration of the culture. Furthermore, the proposed solution and equipment made it possible to monitor the composition of the culture medium without exposure to the infection.

The fruiting bodies of edible mushrooms as a source of selected macro- and microelements

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Keywords: *mushrooms, bioelements, analysis, gastric juices, AAS*

The fruiting bodies of edible mushrooms–are a good source of macro- and microelements (Cu, Zn, Mg, Fe, Ca, Na, K) and organic compounds (phenolic acids, indole compounds). In actually research the content of selected microelements were analyzed in twenty edible mushrooms. The freeze-dried fruiting bodies of mushrooms were extracted in artificial saliva, gastric and intestinal juices. This procedure was designed to mimic conditions occurring in the human digestive tract. Furthermore, the relationship between the amount of the extracted individual elements of artificial juices and species of mushroom, the construction and the time of incubation in the gastric juice (incubation time was: 15min., 60 min., 120 min.) was studied. The obtained material – extracts of mushroom materials in artificial digestive juice was analyzed by using atomic absorption spectrophotometry (flame technique). The results of analysis showed that the methodology is accurate and reliable as demonstrated reproducibility of results obtained for independent measurements. In addition, the minimum incubation time of 15 min. in the gastric juice is not sufficient for effective extraction to the mushroom material. For the most of elements (Cu, Zn, Mg, Fe, Na, Ca), the optimal extraction time was 60 minutes. In case of K the optimal incubation time was 120 min. What was interesting, the amount of Ca released into the saliva was on the same level in all species of analyzed fruiting bodies of mushrooms (272.90-367.83 mg/100 dry weight). It was demonstrated for the first time that mushrooms release and are a good source of macro- and microelements to artificial digestive juices imitating conditions in the human digestive tract.

Sorption properties of polymeric membranes obtained from cellulose acetate

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***Keywords**: polymer membranes, dyes removal, separation*

Water contains dyes from paper, food, cosmetic and textile industries is a huge problem for environmental. Inherency of azo dyes in water is dangerous both humans and organisms live in water. It’s important to reduce amount of these pollutants in wastewater. For their removal technics like adsorption, coagulation, flocculation, oxidation and membrane separation have been proposed.

Membrane filtration is one of the popular method used in environmental protection. It is used to remove different pollutions from liquid phase such as dyes, heavy metals or organic compounds. For wastewater purification there are commonly used polymer membranes. They can be used in micro-, ultra- or nanofiltration and reverse osmosis. They are usually made from cellulose acetate (CA), polysulfone (PS) or polyethersulfone (PES) by phase inversion method. This method consists of immersing the mixture of compounds in a coagulation bath after evaporating the solvent. By this method the porous membranes can be prepared. Membranes can be modified by polyvinylpyrrolidone as a pore generating agent or activated carbons.

The purpose of this work was to obtain cellulose acetate membranes with polivinylpyrrolidone and to characterize their sorption properties of dyes from liquid phase.

The experiments were performed using compressed nitrogen gas and dyes solutions. Final concentrations of testing solutions after experiments were analyzed using an UV-Vis spectrophotometer (Varian Cary 100 Bio).

Moreover, we determined porosity, equilibrium water content, contact angle, content of surface oxygen groups, water flux and membrane resistances.

Conditions of dead zone forming in porous catalyst pellet.

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Keywords: *critical Thiele modulus, conditions of dead zone forming*

The great part of chemical production processes is run by applying solid state catalysts. If diffusion of reagents into pellet of such catalyst is slower than chemical reaction inside them (large Thiele modulus Φ), concentration of reagents inside pellet decreases and effectiveness of catalyst utilization also decreases. For some kinetic equations and for Thiele modulus greater than critical value concentration in the pellet center can even drop down to zero. In this case in central part of catalyst appears zone where reaction does not occur (so called: dead zone). So that, for optimal utilization and designing of catalyst (e. g. correct active sites distribution), it is important to analyze influence of diffusional limitations on catalyst work. In presented work authors focused on conditions of dead zone forming.

Firstly by applying some basic mathematics on mass balance equation it was checked for which types of kinetic equations and for which value ranges of their parameters dead zone occur in slab catalyst pellet. These conditions state for sufficient conditions of dead zone forming in pellet of such geometry. Secondly it was shown that for cylindrical or spherical pellet sufficient conditions are the same as for slab pellet. Next critical Thiele modulus values were calculated for two often used in practice kinetic equations to obtain necessary conditions of dead zone forming. Langmuir – Hinshelwood kinetic and non-isothermal power kinetic were these two examined kinetics.

Obtained results shown that only kinetic terms of kinetic equations have influence on sufficient conditions of dead zone forming. Neither geometry of pellet or adsorption/Arrhenius terms of kinetic equations have not such influence. They can only modify critical Thiele modulus value and in this way induce that sometimes in practice dead zone does not occur. Also it was clearly shown what is an influence of parameter values of both examined kinetics on critical Thiele modulus value.

The influence of molecular weight of polymer on a degradation rate of polylactide membranes for tissue engineering

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***Keywords**: tissue engineering, scaffolds, polylacide, biodegradable polymers, cell cultures*

Three-dimensional cells scaffolds are structures used for tissue cultures. They are generally in form of semi-permeable membranes, which provides delivery of nutrients to the cells and evacuation of metabolites outside the scaffold. The most popular material for the preparation of scaffolds are synthetic biodegradable polyesters such as a polylactide (PLA), poly-ε-caprolactone (PCL), polyglycolide (PGA) or their copolymers. They are characterised by biocompatibility and biodegradability and are well-tolerated by organisms. Moreover, these compounds and their degradation products are non-toxic to the organism cells. In organisms, polyesters are subject to hydrolytic decomposition, first to the building monomers and in the end to CO_2 and water. These products are easily excreted from the organism.

Polyesters differ in the time of hydrolytic degradation. The longest time (in organism, pH 7,2) has poly-ε-caprolactone (more than 2 years), the shortes – polyglycolide (few months). Time of hydrolysis of polylacitde is middle compering to PCL or PGA, around 2 years. This time, for a given polymer, increases with the length of carbon chain. This feature has influence on the degradation time of the whole scaffold and functional properties. It is very important feature for application of scaffolds in the therapy of damaged tissues.

Experimental results of the preparation of semi-permeable membranes for cell cultures were presented. The effect of molecular weight of polylacitde on the morphology of the membranes and functional properties was studied. Membranes were obtained by inversion phase method. Morphology membranes was analyzed using Scanning Electron Microscopy. Degradation rate was analyzed by Gel Permeation Chromatography.

The influence of molecular weight of polymer on a morphology of polylactide membranes for tissue engineering

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***Keywords**: tissue engineering, scaffolds, polylacide, biodegradable polymers, cell cultures*

Cell cultures are important aspect of tissue engineering (TE). TE is a field whose main aim is to support regeneration of damaged, difficult to regeneration tissues. The scaffolds are the main and the latest issue of this science. Scaffolds are medium for cell culture characterized by a highly developed, three-dimensional spatial structure. One forms of scaffolds are semi-permeable membranes. The structure of the membrane provides delivery of nutrients to the cells and evacuation of metabolites outside the scaffold.

Scaffolds are usually made form a biodegradable polymers. One of the most popular polymers in TE is polylactide (PLA). PLA is easily processed and characterized by biocompatibility and biodegradability and are well-tolerated by organisms. Moreover, this compound and their degradation products are non-toxic to the organism cells. In organisms polyesters are subject to hydrolytic degradation, first to the building monomers and in the end to CO_2 and water. These products are easily removed from the organism.

Polylactides differ in degradation time. This time increases with the length of carbon chain. This feature has influence on the degradation time of the whole scaffold and functional properties. For this reason, depending on the type of tissue to be regenerated it is necessary to select a polymer with adequate molecular weight.

Experimental results of the preparation of semi-permeable membranes for cell cultures were presented. The effect of molecular weight of polylacitde on the morphology of the membranes and functional properties was studied. Membranes were obtained by inversion phase method. Morphology membranes was analyzed using Scanning Electron Microscopy.

Hydrogen storage in Ti, V and their oxides- based thin films

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***Keywords**: thin films, hydrogenation, RBS, XRD, XRR*

We are interested in characterization of the film structure and properties of Ti, V and their oxides- based thin films, in particular the interlayer properties and the influence of hydrogen intake on the microstructure and electronic structure of the films.

A series of Ti-TiO_2 and VO_x-TiO_2 thin films with different layer structures, geometries and thicknesses have been prepared by the sputtering technique on Si(111), silica SiO_2 and C-foil substrates. For the selected film, an additional Pd layer was deposited on the film surface by MBE technique The film chemical composition, depth profile, layer thickness and structure were determined by combined analysis of x-ray diffraction (XRD), x-ray reflectometry (XRR), Rutherford back-scattering (RBS) and optical spectrophotometry. The hydrogen depth profile was determined by means of a secondary ion mass spectroscopy (SIMS) and N-15 Nuclear Reaction Analysis (^{15}N-NRA method).

Our analysis indicates that for the Ti-TiO_2-Ti films, hydrogen can be stored up to 50% in the Ti layers and palladium could act as a good catalyst for hydrogen diffusion into the films. A large hydrogen absorption can be also obtained in the thin films of VO_x-TiO_2 system if the surface layer is V_2O_5 layer.

Interdiffusion and ion beam mixing effect in single layer and bi- layer magnetite films on the MgO(001) substrate

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Keywords: *magnetite, thin films, interdiffusion, IBMM, RBS*

Magnetite has attracted much attention due to its interesting electronic and magnetic properties. It has a high potential for technological applications and it is viewed as a promising material for the spintronic applications at room temperature. We are interested in controlling and modeling of interfaces of magnetite thin film systems with optimal structures and desired properties.

A series of single Fe_3O_4/MgO(001) and bilayer Fe_3O_4/Fe/MgO(001) thin films have been prepared by Molecular Beam Epitaxy (MBE) technique. Film structure and properties have been investigated by Rutherford backscattering spectrometry and X-ray reflectometry in the three different states: 1) as grown, 2) after a post- annealing treatment and 3) after being modified by 1Mev Ar^+ and Kr^+ ion beam (with different ion influences in the range of 10^{15}- 10^{17} ions/cm^2). For the data evaluation, the computer code SIMNRA was employed.

Our analysis of the effect from post-annealing indicates that Mg and Fe diffusion during film growth forming interface. The most important findings of our investigations is that pure magnetite layer in the bi-layer films is well preserved upon an ion irradiation with small doses. It indicates a high stability of the stoichiometric Fe_3O_4 layer of the magnetite-on-Fe films.

Synthesis of enantiopure cinchona alkaloid derivates for organic solvent nanofiltration recycling purposes and their application in asymmetric synthesis

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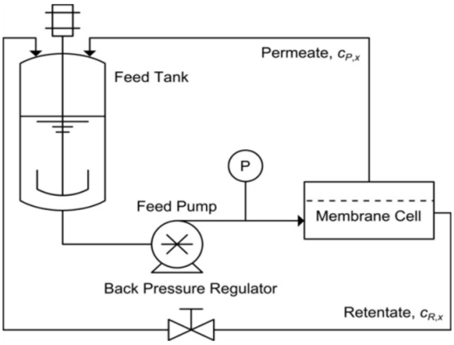
***Keywords**: organic solvent nanofiltration, organocatalysis, cinchona alkaloids, immobilization, catalyst recovery*

Organic solvent nanofiltration (OSN) is a relatively new membrane separation technique, capable of distinguish between molecules with size from 50 to 2000 Da, by only applying a pressure gradient. It is located between the membrane processes ultrafiltration (generally used to separate molecules and colloidal material) and reversed osmosis (typically used in water desalination). The name OSN refers to membrane processes running in organic solvents.

Our aim was to synthesise new enlarged cinchona alkaloid catalysts using an effective organocatalyst from the literature as a building block. The catalysts were planned to be tested in an asymmetric *Michael* addition. Being valuable catalysts they were intended to be recycled by the relatively new technique, the OSN. Furthermore, our objective included the filtration of two commercially available cinchona alkaloid catalysts for setting up the filtration system, screening different membranes and compare rejection values at different pressures. The setup presented here is suitable for nanofiltration in cross-flow configuration with recirculation.

Financial support of the Hungarian Scientific Research Fund (OTKA No. PD 108462) is gratefully acknowledged.



3,5-Dinitrosalycylic Acid (DNS) sensor for in-situ measurement of sugar derived from starch biomass using α-amylase-immobilized on stainless-steel membrane

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Keywords*:* *Starch biomass, α-amylase, immobilization, stainless stain membrane, zeolite Beta, 3,5-dinitrosalicylic acid (DNS)*

Biomass is one of the renewable energy sources which consists of plant material, vegetation, animal and agricultural waste. The conversion of biomass to bioenergy has recently gained increasing importance. This can be achieved by a number of different pathways leading to biofuels, heat and power, and biogas. Starch is one of the non-woody biomasses which has been used in many industrial fields. Although, starch-containing products can be directly used as a source of food, it has been exploited for production of glucose, fructose, maltose and dextrin via enzymatic catalysis. α-amylase has been mostly preferred for degradation of starch molecules instead of conventional chemical processes due to the mild reaction conditions. However, catalysis with free enzymes experiences several difficulties in operational stability, recovery and recycling. These challenges can be overcome by immobilization of enzymes on a wide variety of different supports. Recently, inorganic porous materials have been explored as enzyme carriers due to their beneficial mechanical properties. Macroporous stainless steel discs have emerged as interesting supports which have to be modified in order to prevent leaching of the enzyme.

In this project, a novel DNS sensor was discovered to determine the α- amylase activity using a stainless steel membrane as an enzyme host. The determination method is based on in-situ UV-Vis spectrophotometric measurement of glucose and maltose produced by starch hydrolysis using DNS color reagent. The working wavelength was determined to be 554 nm at 90 °C. In this work, immobilization by physical adsorption and cross-linking were investigated for the non-coated and zeolite-beta coated stainless steel membranes. It was observed that cross-linking with glutaraldehyde using non- coated stainless steel membrane showed the highest volumetric activity of

75.5% with respect to free enzyme, while the zeolite-beta coated membrane

where α-amylase is immobilized without cross-linking.

Interferometric fibre sensor for monitoring the torsional effects in engineering constructions

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Keywords: *torsional effects, interferometer, sensor, engineering construction, rotation*

Numerical analysis of a buildings' dynamic response to ground vibrations, generated by an earthquake or induced by human activities, assumes the occurrence of an uniform impact. However, it is a considerable simplification in case of large-size constructions. In practice, a rapidly developing engineering technology and access to innovative materials give opportunity to design and construct high, irregular and complex engineering structures. In these constructions a strong wind, tectonic movements or traffic generate horizontal components which have a direct influence on torsion effects and inter-storey drifts. Thus, registration and continuous monitoring of these phenomena are significant due to the fact that commonly applied analytical and numerical methods give a limited information about the complex buildings' response to ground vibrations, as well as these methods have a high level of an estimated uncertainty.

The main objective of this work is to characterize the performance of an interferometric fibre sensor which has been designed in order to register rotational phenomena, both in seismological observatories and in engineering constructions. It bases on the well-known Sagnac effect which enables to detect a rate of rotation in a direct way and without any reference system. It is significant during an earthquake when everything is destabilized. The presented device Fibre-Optic System for Rotational Events & Phenomena Monitoring (FOSREM) allows to measure a component of rotation in a wide range of a signal amplitude form 10^{-8} rad/s to 10 rad/s, as well as a frequency from 0 Hz to the upper frequency between 2.56 Hz to 328.12 Hz. The laboratory investigation of our system indicated that it keeps the theoretical sensitivity equal to $2\cdot10^{-8}$ rad/s/Hz$^{1/2}$ and the accuracy no less than $6\cdot10^{-9}$ to $5\cdot10^{-5}$ rad/s in the above mentioned frequency band. Moreover, the system size that equals 36x36x16 cm and the opportunity to remotely control the system via Internet by special Server make FOSREM mobile and autonomous device.

Small diameters vascular graft manufacturing method development

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***Keywords**: polyurethane, graft, cardiovascular implants*

Cardiovascular diseases are major cause of death worldwide. In many cases it is necessary to replace the damaged organ or blood vessel with artificial implant which has suitable properties. Nowadays doctors use many types of implants, but despite their usefulness they require their properties improvement. The current aim of cardiovascular engineering is to obtain the coatings that would not induce negative replies from the body, so it would reduce the need of use the anticoagulants and the risk of thrombosis. The most promising approach may be creating a hybrid implant - a polymeric material coated with human endothelial cells. Such modification would increase material biocompatibility and hemocompatibility. Thus, would significantly reduce the negative response of the organism.

The purpose of this study was to produce small diameter grafts using phase inversion, and their physicochemical and mechanical properties examination. The main material used for the graft production was the medical grade polyurethane, which is one of the most commonly used polymers in cardiac implants. Anti-solvent concentration, incubation time and plasticizer addition was studied.

Graft’s surface topography was examined using SEM, which has enabled to choose variants with the most favorable porosity. Pore size, their density and localization on the surface was evaluated. Also the wettability was examined and it was confirmed that pure and modified with plasticizers polyurethane has hydrophilic properties.

The microstructure of the black glass layers on the titanium substrate

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***Keywords**: black glass, microstructure.*

Black glasses are materials of amorphous silica structure, in which two O^{2-} ions are substituted by one C^{4-} anion. That type of substitution leads to a local increase in the density of bonds and therefor to a significant strengthening of the network. This results in increase of mechanical strength, thermal stability, electrical, oxidation and chemical resistance of the glass.

The first attempts to introduce carbon into the structure of silica glass, were done mostly by classical melting of dry raw mix. However, obtaining black glasses in this way is very difficult due to the loss of carbon and the decomposition of the material to crystalline SiC and SiO_2. The simplest and most effective way of obtaining the black glasses is to use the sol-gel method with appropriate polymeric precursors which contain Si-C bonds. These bonds are characterized by high durability and are retained in both the xerogel and in the glass obtained on the basis of pyrolysis process.

Layers of black glass on the titanium substrate have been received by dip-coating technique. The resulting layers were annealing in an argon atmosphere at a temperature of 500 to 800 ° C. As a result of annealing we got layers of black glasses.

In order to determine the microstructure of the layers we conducted a detailed study on the scanning, confocal and atomic force microscope.

The study revealed that we received a tight layers of black glasses on a titanium substrate. The comparison of test results obtained for layers of different temperatures suggests that this parameter is of vital importance from the point of view of the quality of the layers.

Acknowledgments

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Willemite glass-ceramic glazes

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***Keywords**: crystalline glazes; ZnO; willemite, microstructure.*

This paper is focused on glass-ceramic glazes from the SiO_2-Al_2O_3-CaO-MgO-K_2O-Na_2O system with ZnO additions (2.5, 5, 10, 15, 15, 20 and 25 wt%).

Zinc ion-containing glass-ceramic glazes are one of the most difficult and time-consuming techniques of decorating ceramics. The main problem is that the glaze ingredients should be selected in such a way that zinc silicate - willemite crystals (Zn_2SiO_4) are formed in a long and quite complicated process of firing. Such glazes, due to their various shapes, sizes and the possibility of dying willemite crystals form very effective coating on ceramic products.

To obtain more information on the chemical composition of fired glazes, wavelength dispersion X-ray fluorescence (WDXRF) analysis was used. The phase composition of the resulting glazes was determined by X-ray diffraction method. Information on the phase composition of the designed glazes was obtained also via FTIR and Raman spectroscopy.

Zinc oxide (ZnO) addition to the chemical composition of glazes of SiO_2-Al_2O_3-K_2O-Na_2O-CaO-MgO system significantly influences glaze microstructure. Presence of 2.5% ZnO by weight in a glaze structure changes the morphology of diopside $CaMg(Si_2O_6)$ crystals. A gradual increase in zinc oxide content up to 20% by weight results in a purely amorphous material. Addition of 25% ZnO by weight to the base glaze enhances crystallization of zinc silicate - willemite.

Acknowledgements

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Phase composition and microstructure of stabilized and partially stabilized zirconia ceramics

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Keywords: *zirconium oxide, tetragonal zirconia, cubic zirconia, uniaxial pressing*

Zirconia ceramics is one of the most important ceramic material. Unusual combination of properties like strength, low thermal conductivity and fracture toughness allows the use of many applications. Zirconia has three polymorphs: monoclinic, tetragonal and cubic. Naturally form of zirconium oxide is monoclinic, which is stable form under normal atmospheric conditions. For stable cubic and tetragonal forms at lower temperature necessary is the additions of alloying elements such as yttrium or cerium. Tetragonal phase can still transform to monoclinic phase under extremal loading or due to crack propagation in surrounding regions. Tetragonal and cubic form of zirconia have better properties than monoclinic form, so the possible applications for these form can be wider.

For this work the samples were prepared from the nano-size ZrO_2 powder stabilized by 3 mol% Y_2O_3 and nano-size ZrO_2 stabilized by 8 mol% Y_2O_3. The samples were formed by uniaxial pressing and sintering at temperature 1450°C. The physical properties of prepared samples were measuring by Archimedes method. The phase composition and microstructure of the zirconia ceramic were characterized by X-Ray diffraction and SEM.

Acklowledgements

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Ceramic nanopowders-modified glassy carbon electrode for cyclic voltammetry detection of hydrochinon

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Keywords: *Voltammetry, ceramic nanopowder, glassy carbon electrode, hydroquinone.*

For many years ceramic materials constitute an interesting material used in numerous "high-tech" applications like fuel cells, gas sensors, high temperature superconductors, optoelectronic elements and so on. Simultaneously, the nanopowders' properties and parameters can be changed (influenced) by means of substrates doping (especially with transitions metals). Considering electrodes modifications the occurrence of active centers enabling catalytic reactions as well as analyte adsorption, is of high importance. Both phenomena allow achieving high sensitivity, selectivity and low detection limit.

The determined substance is hydroquinone - the organic compound from the group of phenols having two hydroxyl groups attached to the benzene ring in para position. The other two isomers – catechol (ortho position) is electroactive whereas resorcinol (meta position) is not electroactive. The traditional name of compound results from the fact that hydroquinone is most commonly produced by reduction of paraquinone.

Voltammetric methods, due to its numerous advantages are a tool often used by the modern scientists. The research technique used is cyclic voltammetry.

The analysis was performed on a glassy carbon electrode, an electrode modified with PEDOT and an electrode modified with a ceramic nanopowder P25(TiO_2). The comparison between various fabricated sensors was performed under the same measurement conditions and with the same analyte concentrations. On the basis of calibration and analysis of the received signals the influence of modification on analytical parameters have been established.

Acknowledgement

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The role of the rhamnolipid in the water treatment

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Keywords: *biosurfactants, rhamnolipids, biodegradability, bioremediation*

Rhamnolipids are surface active agents of natural origin. They are produced as a mixture by gram-negative bacteria - *Pseudomonas aeruginosa*. Rhamnolipids are very interesting surfactants both from the ecological and the technological point of view. They show very high biodegradability, low toxicity, low values of critical micelle concentration, high efficiency and effectivity of adsorption as well as high surface activity. In comparison to classical (synthetic) surfactants their use is environmentally safe. Moreover, rhamnolipids, like other biosurfactants, can be used in the processes of hydrocarbons degradation, metals remediation, bioremediation and water treatment because various kinds of pollutants (organic or inorganic) can be removed through physicochemical or biological processes in which biosurfactants are involved.

To understand the practical application of rhamnolipids in the processes of water treatment the knowledge of their tendency to adsorb and to aggregate in the bulk phase is very helpful. Therefore, I have made thermodynamic analysis of the processes of rhamnolipid adsorption and micellization on the basis of the data obtained from the measurements of the surface tension, density, viscosity and conductivity of aqueous solutions of this biosurfactant at natural pH in a broad range of its concentration.

The obtained results indicate that rhamnolipids have very high surface activity and high tendency to adsorb at the water-air interface and to form micelles. I used these results to clarify the role of rhamnolipids in the water treatment e.g. their function in membrane based systems, which are general used for water purification. As well as to describe a cooperation between this biosurfactant and the bacteria in the removal of hydrophobic, organic contaminants from the aquatic environment.

Study of Sunset Yellow FCF adsorption from aqueous solution onto mesoporous carbons functionalized by ammonium persulfate

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***Keywords**: mesoporous carbon, adsorption, Sunset Yellow FCF, functionalization, ammonium persulfate*

Synthetic colorants are a very important class of food additives that are widely used in food and therefore they are given high priority by the food industry. However, some of these colorants pose a potential risk to human health, especially if they are consumed in excess. Because of their high organic matter concentrations and their intense colors, the effluents discarded by the food industry are an important source of pollution for water bodies. Consequently, their removal from such industrial effluents is challenging requirement to produce a safe and clean environment. Sunset yellow FCF (SY) is a pyrazolone dye used in common food products such as beverages, candies, dairy products, pharmaceuticals and bakery products. The presence and content of SY must be controlled since the related industries often release large amount of this dye into effluents. Many technologies, including flocculation, coagulation, precipitation, biosorption, membrane filtration, electrochemical techniques and adsorption have been used for the removal of dyes from industrial effluent.

The aim of our study was the preparation of the mesoporous carbons functionalized by chemical oxidation and their application in the Sunset Yellow FCF adsorption process.

Mesoporous carbon was prepared by soft template method with triblock copolymer Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) as the soft-template matrix and resorcinol together with formaldehyde as carbon precursors. In the next step, the material was treated with 1 M ammonium persulfate solution. Different durations (6, 12, 24 h) and temperatures (30, 60, 100°C) were adopted to achieve different levels of texture and surface modification as well as to determine the oxidation resistance of the carbon.

The results show that surface modification of relatively inert pristine mesoporous carbon via wet oxidation introduce oxygen-containing functional groups onto its surface. The surface area and porosity deteriorate considerably compared to the pristine carbon after the oxidation treatment, and the micropores/small mesopores are the major contribution to the deterioration. All mesoporous carbons functionalized with ammonium persulfate are promising adsorbents of Sunset Yellow FCF with high capacities and excellent binding capabilities.

Synthesis of polysaccharide nanoparticles for targeted drug delivery system

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Keywords: polyaldehydedextran (PAD), nanoparticles (NPs), folic acid (FA), targeted drug delivery

Cancer treatments are one of the most challenging issues in contemporary medicine. Many problems are associated with side effects caused by drugs used in chemotherapy and hormonal therapy. For this reason new strategies are still developed. Nanocarries for targeted drug delivery system are one of possibilities to overcome limits of conventional drug treatment used nowadays. In this area introducing of target ligands on nanocarriers surface is an important problem for efficient the drug delivery systems.

This work describes preparation and characterization of dextran NPs decorated with folic acid as targeting ligand. Synthesis was begin from introduction of aldehyde group in dextran (70 kDa) chains using sodium periodate oxidation method. Next PAD was modified by reaction with ethylene diamine in aqueous solution (pH 9 or 11, time of reaction 2 or 24h). After purification and lyophilization amine-containing dextrane chains were conjugated with folic acid using *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride. Reaction was carried out in PBS for 2h. During synthesis all vessels with FA were protected from light. FA modified dextran was used for the synthesis of self-assembled NPs. NPs were formed due to introduction of hydrophobic domains in dextran chains. In other variant of experiment, first NPs were formed and then were modified with target ligand of FA. NPs diameter was determined using NanoSight instrument and cytotoxicity was measured using MTT test. Observation of drug containing NPs cells uptake was carried out with confocal microscopy.

The size of obtained NPs is in the range of 55 to 130 nm. Size depends on parameters of reaction (pH, time). Microscopic observation confirmed that received NPs with targeting agent faster reached cells nucleus than NPs without FA. The therapeutic response in cytotoxicity test depended on reaction conditions and FA concentration. For receiving drug toxic effect it is important to find an optimal proportion between anticancer drug and folic acid to obtain maximal therapeutic effect. Based on the results, we conclude that nanocarries for targeted drug transport are promising idea, but it requires further development.

The impact of materials forming the cladding on propagation in biconical optical fiber taper

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***Keywords**: tapered optical fiber, temperature sensor, taper technology*

In this paper is present an analysis of a theoretical and experimental beam propagation in a taper fiber with variable external conditions. That was dictated by the possibility of creating low-cost sensor system based on the ability to control beam propagating in an optical fiber.

Simulations were performed by using MODE Solutions software by Lumerical for selected structures. There are changes of a beam propagation in fibers with different dimensions of the core and cladding with variables external conditions (different reflective index of an environment). The results confirm that tapering of an optic fiber make sensitive area which we can used as a sensor.

Theoretical simulations were the basis for the preparation of an experiment which used a taper fiber and materials: pentadecane, heptadecane and wax. Tapered optical fiber was manufactured on FOTET (Fiber Optic Element Technology) with parameters diameter of taper 6,5 ± 0,5 μm and loss 0,18 ± 0,02 dB. Research was carried on system consist of: climatic chamber Votsch VCL 7010, optical spectrum analyzer AQ6319, power meter PM 300 and lasers. It was used two sources of light: laser 3FC1550 - DFB Benchtop Laser Source, 1550 nm, 1.5 mW, FC/PC which received hysteresis of temperature sensor and spectral characteristics of supercontinuum source SC450-4-AOTF.

An analysis confirm that there is possibility to manufacture the whole scale temperature sensors using a different types of materials. This kind of sensor have a lot of advantages: low-cost, low lost technology, smart sensor working as an in-line element and work range of white spectrum.

Use of organic compounds in solar cells

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***Keywords**: organic photovoltaics, solar cells , P3HT*

The growth of the world's population and the emergence of India, China, and Brazil on the global market have created millions of new consumers of electronic gadgets, mobiles, tablets etc., and due to this the need for energy is increasing every year. Governments subsidize the search for cheaper forms of energy. One of the possibilities for cheaper energy is gaining electricity from the power of the sun. Inorganic solar panels are expensive to manufacture because of the needs for high temperature and high pressure, but since 2015 when a 15% efficient solar cell based on organic material was made, researchers' efforts are being put on searching for a proper material which could have the potential to show ideal photovoltaic properties.

This paper presents the preliminary investigations of the activity of few organic low molecular weight compounds in organic solar cells. The photovoltaic properties of those compounds as an active layer in organic solar cells at the configuration ITO/PEDOT:PSS/active layer/Al under an illumination of 1.3 mW/cm^2 were studied. Seven kinds of devices which differ in the composition of their active layers were fabricated. As a hole transporting material PEDOT:PSS was used. As an anode ITO was used, whereas as a cathode aluminum was used.

Thin films were made by dissolving all substances in chloroform, making desirable mixtures and spin-coating (at various amounts of rotations per minute) the mixtures on ITO-covered glass. Layers were also heated in a vacuum heater. In order to evaporate aluminum electrodes the samples were introduced to a high vacuum chamber.

Introducing various compounds to the mixture obtained a quantum yield of chips of 0.3 %. The study shows that the structures shown in the work exhibit the photovoltaic effect, but it does not lend directly to commercial applications, and requires further research. In order for these structures to show greater efficiency the thickness of the layers and the weight ratios of the individual components need to be changed, and one more component of appropriate energy levels HOMO and LUMO need to be added.

Hot-stage microscopy in determining the suitability of selected clay rocks to manufacture lightweight aggregates

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Keywords: *Hot-stage microscopy, LECA, Smectitic clays*

The author tested the suitability of some clay raw materials from Poland to manufacture lightweight expanded clay aggregates (*LECA*). The samples represented the claystones and clays with elevated smectite contents from Wielgomłyny, Bełchatów and Dylągówka. Hot-stage microscopy (HSM) combined with the image processing analyses was an important part of the methods, including also X-ray diffraction, smectite content determinations and grain size analyses. The HSM procedures introduced by the authors involved the continuous (frame-after frame mode) recording of the firing process and a dedicated image digitalization technique developed with the Matlab software. The highest volume increase, equal to *ca* 200%, reveal the claystones from the upper and lower parts of the Dylągówka deposit and sample from Wielgomłyny. Their expansion coefficient *S* is considerable higher than that of the clays in north Poland currently used to produce *LECA*. Such a favourable *S* value results from elevated contents of clay minerals (particularly of smectite) and hematite in the rocks. Clay raw materials from Dylągówka have also a wide interval of thermal expansion (the *I* coefficients reach 150ºC), being mainly an effect of higher opal amounts. Such features open possibilities of a modification of the clay- and opal-rich charge into the process by introducing various technological additives. In turn, the presence of feldspars in the charge considerably lowers the firing interval as it generates the formation of an undesired liquid phase with low viscosity at the temperatures not exceeding 1100ºC.

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The impact of modifications of the Krakowiec clays on their thermal expansion ability

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***Keywords**: Hot-stage microscopy, Smectite modiffications, Krakowiec clays*

The effects of modifications of the clay rocks containing smectite on their thermal expansion have been studied at the example of the Krakowiec clays from Wola Rzędzińska, Hadykówka and Łukowa (south-eastern Poland). Hot-stage microscopy (HSM) was employed combining a dedicated procedure of digital image analysis. The chemical modification of three rock types (which differ in the mineral composition) included the treating with an soda addition and acid activation. The investigations of thermal expansion have shown that the clays can be acid activated with a slight improvement their expansion in comparison with such an ability of natural rock equivalents. It is a result of the induction of a reducing atmosphere inside fired pellets connected with form gypsum by reaction of sulfuric acid with calcite. The liquid phase (the melt) with a high viscosity may form a cover on the surface of granules of the product being fired and prevents the expulsion of gases into the ambience. The introduction of a reducing atmosphere promotes the release of oxygen during conversion associated with the change of the iron oxidation degree. An soda addition is favourable as it considerably lowers the firing temperature of the expanded product.

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The influence of ZrO_2 on the surface parameters

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Keywords: *glaze, porcelain, zirconium oxide, whiteness*

The production of ceramic porcelain glazes is strongly dependent on the chemical composition of the glaze. In production process it is very important to obtain an appropriate surface parameters. Addition of some oxides can significantly change the parameters.

This researches were carried on the influence of adding the zirconium oxides on the surface parameters, for firing temperature 1220-1240°C. The examined glazes had a constant of molar ratio of $SiO_2/Al_2O_3 = 3$ and $Na_2O/K_2O = 1$ and variable of a molar ratio of CaO/MgO and amount of added of zirconium oxide (1,5%, 3% and 6%). During this research some parameters such as: whiteness in CIE L*a*b* in system, gloss and roughness of the surface were measured. The obtained results show that the addition of zirconium oxide and variable of molar ratio of the alkaline earth oxides in an interesting way affects on the appearance and parameters of the surface of glaze.

The influence of ZrO_2 on the technological parameters

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Keywords: *glaze, porcelain, zirconium oxide*

Ceramic glazes are coatings which are applied to a ceramic body to improve its parameters. The proper modification of glazes with use some oxides or chemical compounds causes the changes of technological parameters of glazes. One of the oxides which are added to glazes is zirconium oxide.

The research focused on the influence of addition of zirconium oxide on some technological parameters of porcelain ceramic glazes, which were created to fire in temperature 1220-1240^{o}C. The examined glazes had a constant molar ratio of SiO_2/Al_2O_3 =3 and Na_2O/K_2O=1. The variables were a molar ratio of CaO/MgO and amount of added of zirconium oxide (1,5%, 3% and 6%). As the result of examination some parameters were obtained such as: characteristic temperatures, coefficient of thermal expansion by dilatometric method and the viscosity of glaze as a function of temperature. The obtained results indicate on a lot of important dependences, which were caused by the changing molar ratio of the alkaline earth oxides and the addition of zirconium oxides to the glazes.

Adsorption of acidic dyes onto modified carbon xerogels

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Keywords: *carbon xerogels, removal of acidic dyes, adsorption, modification*

Carbon gels are porous materials with a reticular structure. They are synthesized through the carbonization of an organic gels obtained from the polycondensation of hydroxylated benzenes (e.g., resorcinol, phenol, catechol) with aldehydes (e.g., formaldehyde, furfural). The textural and structural properties of carbon gels can be controlled and tailored to fit specific applications by modifying the process conditions. Well-developed pore texture of these materials is a great advantage in the fields of adsorption, energy storage and catalysis. Their applications as adsorbents are recently increasing and present promising results for the removal of dyes (such as acid blue 113, reactive red 241, methylene blue, chromotrope 2R or rhodamine B) and Cu(II) ions.

The main purpose of our study was the application of carbon xerogels modified with amine groups and $CuCl_2 \cdot 2H_2O$ in adsorption process of acidic dyes.

Carbon xerogel (CX) was prepared by the conventional sol-gel approach using formaldehyde and resorcinol. The gelation step was allowed to proceed at 85°C for 3 days. After this period gels were crushed and dried in an oven during 4 days at 60, 80, 100 and 120°C. In the next step, samples were carbonized under nitrogen flow (100 ml/min) in a tubular furnace at 900°C. Surface of CX was oxidized with ammonium persulfate and functionalized with amine groups. Additionally, materials have been modified with $CuCl_2 \cdot 2H_2O$. Structure and surface properties of carbon xerogels were characterized in detail by low-temperature nitrogen sorption, X-ray diffraction and infrared spectroscopy. The content of the surface oxygen functional groups, both acidic and basic, was determined in accordance with Boehm method. All materials obtained were tested in the adsorption of acidic dyes (tartrazine, methyl orange).

The results show that the modified samples have lower surface areas and smaller pore volumes than pure CX. The impregnation of carbon xerogel with copper(II) chloride leads to an increase in the content of surface functional groups, both basic and acidic. It was observed that adsorption capacities of the materials examined towards dyes increased with increasing of initial dyes concentrations. The most effective adsorbent of acidic dyes is a sample modified with amine groups and copper(II) chloride dihydrate.

The removal of herbicide from various aqueous systems by EAOPs combined with biological methods

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***Key words**: Electrochemical Advanced Oxidation Processes, biodegradation, herbicides*

The environmental contamination dramatically increased with the developed of industry. It is also connected with invent new synthetic substances, that not exist in the nature, like drugs, pesticides and others. Most of them are used in the agriculture it cause that those compounds easily get to the aqueous and soil systems, for example the herbicides are spread on large scale to improve the effective and quality of harvests. Further, they have the significant negative influent on the biosphere and destabilize ecosystems.

It is very important to find the efficient methods to eliminate those synthetic compounds. The biological methods are the previous and most common choice. They are mostly effective and very cheap for the readily biodegradable compounds, compared to chemical and physical treatments require less energy and chemicals. Although, they have disadvantages, one of them is a long acclimation period is often necessary to degrade persistent pollutions. Next, the substances as pharmaceutics, herbicides and others can be toxic for bacteria.

The new concept is used various Electrochemical Advanced Oxidation Processes (EAOPs) as support for biological methods. The studies showed that the electrochemical pretreatment allows for reduction toxicity and increasing the biodegradability of persistent compounds. On contrary, it was also noticed that in the same case the organic compounds after electrochemical oxidation can be more toxic than previous substances. It is mentioned that the chloride ions included in electrolyte increase the efficiency of oxidation process but it can generate the halogenated derivatives (more toxic) and chloride radicals that have disinfection properties. However, it was very preliminary studies and this topic demand detail studies.

The aim of these studies was investigate the influence of electrochemical pretreatment of 4-chloro-2-methylphenoxyacetic acid (MCPA) in different support electrolytes on environmental bacterial consortia. It was evaluated by using toxicity and biodegradation tests, but also the analytical methods were applied to estimation the changes of MCPA concentration. Additionally, the kinetics parameters of electrochemical oxidation were determined.

The electrochemical studies showed the difference between electrochemical oxidation conducted in the various support electrolytes, and further it has influence on the toxicity and biodegradation.

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The removal of sulfonamides from aqueous systems by electrochemical oxidation process combined with biological methods

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***Key words**: Electrochemical Advanced Oxidation Processes, biodegradation, sulphonamides*

One of the most difficult environmental problems is the utilization of bioactive compounds. Among these substances, we can distinguish: pesticides, drugs and other. Every day, the large numbers of small doses of these compounds land into water by different ways and are accumulated in reservoirs, wastewater, soils, and even in living organisms. So far, it has been tested various remediation methods of highly contaminated areas by these persistent substances. The results showed that the conventional methods are ineffective, so great hopes are associated with Advanced Oxidations Processes (AOPs) and the hybrid processes (combination of the AOPs with biological methods). The electrochemical oxidation is example of AOPs, which is recognized as promising technique of elimination persistence organic pollutions but used of them is expensive. The solution for reduction of cost will be combination with the biodegradation.

The sulfonamides are the oldest group of synthetic antibiotics currently used on the large scale in the agriculture. It caused that increased their quantity detected in the aqueous systems, what cause fear and force to make an intensive studies under the highly competitive water treatment technology for the removal of those pollutants.

The aim of studies was evaluate the possibility of used the electrochemical oxidation combined with biological method to remove the selected sulfonamides: sulfomethazine, sulfamerazine and sulfadiazine from aqueous systems. The electrochemical oxidation processes are conducted in three electrode cell. The carbon material was used as the working electrode. It is cheap and eco-friendly solution. The electrochemical methods were used to determinate kinetics parameters and to evaluate the change of electrode material. The influence of electrochemical pretreatment on biodegradation of selected sulfonamides was measured. The changes of sulfonamides concentration was evaluated by analytical methods.

The positive effect of electrochemical pretreatment on biodegradation of selected compounds causes in consequence that this hybrid technology is promising solution. Moreover, it is important to evaluate the factors influence on process kinetics, efficiency and bacterial adaptation for further optimization of the complex process.

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Potassium-selective electrodes modified with superhydrophobic polymer/carbon black nanocomposite

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Keywords: *carbon black, superhydrophobic polymer, solid contact*

In recent years nanomaterials have been widely used in many various areas. Nanostructured materials possess important properties such as good conductivity, high mechanical strength, high reactivity and easiness of dispersion. Lately, nanomaterials were also introduced into potentiometric sensors for example as solid contacts. A solid contact between an ion-selective membrane and an electronic conductor is the weighty element for preparing a solid-state ion-selective electrodes with excellent analytical parameters. A good hydrophobicity and high surface area of different carbon-based materials, for example nanotubes, fullerenes or graphene, used as intermediate layers improves the potential stability of ion-selective electrodes.

Carbon black can be also successfully applied in potentiometric sensors and moreover, characterized by low cost. There is also a possibility of using nanocomposite of carbon black with superhydrophobic polymer as the solid contact layer. Due to the high hydrophobicity of such combination of materials it has not been observed undesirable aqueous water layer between the solid contact and polyvinyl chloride-based ion-selective membrane. Developed sensors modified with fluorinated acrylic copolymer/carbon black nanocomposite were sensitive to potassium ions.

The morphology and static water contact angle of proposed solid-contact layers were examined. The values of the double layer capacitance of glassy carbon disc electrodes coated with materials mentioned above were determined using various electrochemical method. The stability of the electrical potential of potassium sensors with intermediate layer made of carbon black-fluoropolymer composite was studied during chronopotentiometric measurements. Potential stability and capacitance of electrodes was higher than these for sensors with non-modified carbon materials. Moreover, solid-state ion-selective electrodes exhibited a good slope of calibration curves, low detection limit and showed excellent a long-term potential stability.

Obtained results indicated that the application of superhydrophobic carbon materials as solid-contact improves analytical parameters of ion-selective electrodes.

Tetrathiafulvalene modified ion-selective electrodes for the determination of nitrate

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***Keywords**: ion-selective electrode, tetrathiafulvalene, nitrate*

Widespread usage of nitrates in various application fields, including explosives, drugs and fertilizers causes different environmental pollution. The content of nitrates in drinking water, and also in surface and ground water should be continuously verified. Therefore, there is a requirement for the monitoring the concentrations of nitrates with the use of fast, inexpensive and above all selective method. Voltammetry, amperometry, chromatography or spectrophotometry could be applied for the nitrate determination but most of these analytical methods need expensive equipment. Moreover, such analysis are complicated and time-consuming. Potentiometric measurements are inexpensive, insensitive to the physical or chemical properties of the sample and procedure is simple and fast.

In our research we proposed the application of tetrathiafulvalene (TTF) or its nitrate salt (TTF(NO_3)) for the nitrate-selective electrodes. TTF and its salts may exhibit conductive and superconductive properties. Therefore they can be used in solid-state ion-selective electrodes as an intermediate layer between the electrical conductor and the ionophore-doped solvent polymeric membrane. Studied electrodes were obtained basing on the drop casting method. The morphology of TTF and TTF(NO_3) layers were tested by scanning electron microscopy. The parameters of fabricated electrodes and possibility of their analytical application were examined using potentiometry, chronopotentiometry and electrochemical impedance spectroscopy measurements.

Proposed nitrate-selective electrodes showed a Nernsitan slope in a wide range of linearity, low detection limit, short time of response and repeatable and reproducible values of standard potential. Application of the TTF or TTF(NO_3) as an intermediate layer reduces the membrane resistance and improves stability of the potential compared to electrodes without such layers. Moreover, the selectivity of TTF- or TTF(NO_3)-modified electrodes was significantly improved compared to other nitrate sensors.

Thus, the developed electrodes exhibited better analytical parameters than non-modified electrode and were successfully applied for the nitrate determination in water samples.

Wide range of applications of ANOVA with regard to the problems of mineral processing

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***Keywords**: mineral processing, flotation, ANOVA, type I and II errors, multidimensional analysis*

The variability is a property that characterizes all scientific measurements and observations of various phenomena. For each experiment is affected by controlled and uncontrolled factors that are responsible for the divergence of results. A significant number of random factors (errors) which occur during the experiment can disturb the measurements. Thus, the more complex the phenomenon is analyzed the higher the likelihood of variability of results. Fisher faced the problem of his analysis of variance. It is a statistical method that minimizes the impact of uncontrolled factors on the result of experiment..

The paper presents the scheme of conducting ANOVA, which is the basis for the analysis of various complex phenomena in various fields of science. It can be implemented in different fields such as: medicine, psychology, chemistry, agriculture and others. More and more often this analysis is used in various industries to solve complex technological problems and optimize production processes.

The article is mainly focused on the presentation of different areas of application analysis of variance to the problems of mineral engineering. Mineral resources are characterized by different physical, chemical or mechanical properties. This fact determines their complex nature, which, from a scientific point of view, is described by a multidimensional vector of grain property set. Therefore, using the analysis of variance for the study of the properties of mineral resources and optimization of processing procedures are fully justified and they are shown in the text.

Lecithin coatings on stainless steel 316L obtained with the use of electrodeposition process

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Keywords: *stainless steel, lecithin, electrodeposition, coatings*

Evolution of medicine and reconstruction techniques allows repairing damaged tissues. This is possible because of using suitable type of implant or biomaterial. The success of the reconstruction depends on biocompatibility. Stainless steel 316L is a material widely used in implantology, but it is poorly compatible with human body. For that reason it is necessary to create coatings to increase its biocompatibility. In this study the surface of stainless steel was modified by layer of lecithin applied by electrodeposition. Lecithin is a natural mixture of phospholipids (e.g. phosphaditylcholine, phosphaditylethanolamine), which is derived from egg yolk, soya, rapeseed or flax. Our work was focused on the selection of conditions for electrodeposition and characterization of obtained materials. We ~~have~~ studied process parameters including the composition of the electrolyte solution, its pH, concentration of lecithin, addition of salt to ensure bigger conductivity, the addition of the substance to ensure better adhesion of lecithin to the steel. The quality of obtained materials was tested by using techniques such as infrared spectroscopy, scanning electron microscopy and profilometry. As a result, it was found that the best conditions for the process include lecithin solution with a concentration of 0.5% and a pH 4 and a time 30 min. and a current density of $6.49 \cdot 10^{-3}$ and $26 \cdot 10^{-3}$ mA / mm^2. During our work the influence of the materials on live cells L929 mouse fibroblasts cultured in vitro has been also examined. We incubated the cells with extracts prepared from coated materials and characterized their viability. The results indicate a positive effect of a coating of lecithin on a steel surface. In all cases the viability of cells was higher than after incubation with extracts derived from uncoated steel. So there is a possibility that lecithin increases biocompatibility of steel. Electrodeposition of lecithin on the steel surface is innovative method which is uncomplicated and can be used on a large scale for coating different workpieces. Moreover, it is not required to use toxic, organic solvents. In particular this method can be useful for the modification of stents due to the mild processing conditions. There is thus a possibility to create a new biomaterial which finds an application in medicine.

In vitro studies of PLA-chlorphenesin hybrid nanospheres

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***Keywords**: polymeric DDS, release profile, nanospheres*

Modern drug research focuses not only on seeking new active substances (*Active Pharmaceutical Ingredient*, API), but also on finding new, more effective and safer ways to deliver them. Increasing number of patients suffering from chronic conditions led to manufacturing of Drug Delivery Systems (DDSs). Two of many DDS types are nano- and microspheres and macromolecule prodrugs. The fusion of them give hybrid polymeric spheres, double drug delivery system. The matrix is made of prodrugs from biodegradable polymers, such as polylactide (PLA).

In my research hybrid spheres containing both: free and bonded chlorphenesin were prepared via emulsification-solvent evaporation method. Prodrug of PLA and chlorphenesin was used as a matrix. Chlorphenesin (3-(4-chlorophenoxy)propane-1,2-diol) is bacterio- and fungistatic API, approved to use in cosmetics as preservative in a concentration below $0{,}3\%_{\mathrm{mass}}$. Release profile was established using UV-vis spectroscopy.

In vitro studies were performed to find out whether hybrid spheres still are active towards microorganisms. Antifungal activity preserved, although antibacterial activity do not. It is worth noting that chlorphenesin is used commercially mainly as antifungal. Release profile of chlorphenesin out of DDS spheres was also conducted: first two hours API liberates quickly, then liberating rate decreases. Also additional increase of API release occured after 26 h. The conclusion is that hybrid PLA-chlorphenesin nanospheres can be used as drug delivery systems. They release API in a proper way and its antifungal activity is not affected.

Optimisation of PLA-chlophenesin hybrid nanospheres production through DOE

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***Keywords**: DOE, polymeric DDS, nanospheres*

Design of experiments (DOE) are mathematical operations that aim to find the most effective conditions to get the best results. DOE gives outcome that can hypothetically predict result of experiment conducted under specific conditions. The hypothesis is then statistically and experimentally tested to be true. Those experiments advance knowledge in science. They give more insight about optimized process.

Modern drug research focuses not only on seeking new active substances (*Active Pharmaceutical Ingredient*, API), but also on finding new, more effective and safer ways to deliver them. Increasing number of patients suffering from chronic conditions led to manufacturing of Drug Delivery Systems (DDSs). Two of many DDS types are nano- and microspheres and macromolecule prodrugs. The fusion of them give hybrid polymeric spheres, double drug delivery system. The matrix is made of prodrugs from biodegradable polymers, such as polylactide (PLA).

In my research hybrid spheres containing both free and bonded chlorphenesin were prepared via emulsification-solvent evaporation method. Prodrug of PLA and chlorphenesin was used as a matrix. Chlorphenesin (3-(4-chlorophenoxy)propane-1,2-diol) is bacterio- and fungistatic API, approved to use in cosmetics as preservative in a concentration below $0,3\%_{\text{mass}}$. Diameter of spheres were discovered via dynamic light scattering (DLS) method.

First influence of process parameters on size of obtained spheres were studied. Based on that results variables were selected and process of spheres' preparation was optimized. Optimization was conducted via mathematical methods of design of experiments (DOE). Specifically factorial plan 2^3 was used. An adequate regression equation was found, that will lead to preparation of hybrid spheres with required size.

Alkanes-filled Photonic Crystal Fibers as sensor transducers

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Keywords: *photonic crystal fiber, optical fiber filling technology, sensor transducers, thermo-optic properties, higher alkanes, multistage temperature threshold sensor*

In this paper we propose alkanes-filled PCFs as the new class of transducers for optical fiber sensors. We investigated experimentally thermo-optic properties of a commercially available LMA 10 partially filled with different alkanes with a higher number of carbon atoms. A partially filled PCF spliced with standard SMFs constitutes one of the newest types of transducers. We have selected a group of eight alkanes which have melting points in different temperatures. An analysis of temperature spectral characteristics of these samples will allow to design an optical fiber sensor with different temperature thresholds at specific wavelengths.

As filling materials we have tested special selected eight alkanes with a high number of hydrocarbon atoms. We have selected them according to their melting points (MP) between (9–47 ^{0}C) and their refractive indices between (1.431–1.450). For all substances it was possible to fill the LMA 10, except for tetracosane (MP 49-52 ^{0}C) and octacosane (MP 57-62 ^{0}C). For nonadecane (MP 28-30^{0}C) and docosane (MP 42-45 ^{0}C) - they can be filled into the PCF, however, their refractive indices are too close to silica. Thus, we do not observe transmission in any interesting temperature. Finally, four compounds: pentadecane (MP 9-10 ^{0}C), hexadecane (MP 18 ^{0}C), heptadecane (MP 20-22 ^{0}C), and octadecane (MP 26-29 ^{0}C) have been selected to be used as transducers which are useful for our experiment. By analyzing their thermo-optic properties, we observed that for all samples the melting points are close to product information. For all samples we have had hysteresis between melting and crystallization points which makes us believe that a high purity grade of the used materials and a small number of crystallization centers are the major problems in this case. Summarizing, from authors' point of view this class of materials is a very good candidate for manufacturing a multistage temperature threshold sensor.

Thermal properties of Photonic Crystal Fiber transducers with ferromagnetic nanoparticles

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Keywords: *photonic crystal fiber, Fe_3O_4 NPs, ferromagnetic nanoparticles, optical fiber sensor, thermo-optic effect in optical fiber*

In this work we propose ferromagnetic nanoparticles' filled photonic crystal fibers (PCFs) as the class of transducers for optical-temperature fiber sensors. Research began with the preparation and characterization of a ferromagnetic colloid, followed by examination of the effect of synthesized structures, the propagation of an electromagnetic wave over wavelengths range from 900 nm to 2400 nm, in a variable temperatures and external magnetic field.

The first step of the study was to synthetize a ferromagnetic colloid, with nanostructures having a predetermined size (85±20) nm and characteristics of them obtained by using the dynamic light scattering (DLS) and atomic force microscopy (AFM). Synthetized specific colloid with Fe_3O_4 NPs was introduced to specialty fibers (LMA 10 and PM 1550), which were spliced with a single mode optical fiber (SMF 28e) to form a patch cord terminated with FC/PC connectors. These patch cords were tested in the variable temperatures and in an external magnetic field. So it was possible to apply this type of transducer based on a photonic crystal fiber filled with ferromagnetic colloid as a sensor of temperature changes.

During these tests was found an absorption band around the wavelength of 1450 nm which is closely related to the optical properties of colloid filled fiber and, additionally, for the wavelengths of 1310 nm and 1600 nm we were shown dependences of optical losses as a function of temperature, which were linear, but trends of the losses were to the contrary.

The temperature measurements of the prepared patch cords have shown that optical transmission is not changed. Now, we are carrying out a further research to find optimal composition of the ferrofluid in order to have a minimum light - absorption and to measure influence of magnetic field significant to the transducer.

Effective polymer connection between polymer and silica optical fibers

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Keywords: *polymer optical fibers, polymer microbridges, connecting optical fibers, photopolymerization*

In the current state of telecommunication technology, silica optical fibers play a major role. However, from the economical point of view, the aim is to replace them by the polymer optical fibers (POF's). In practice, it requires the development of technology for manufacturing low loss and mechanically stable connection, especially for POF's. Standard methods of splicing optical fibers, due to high temperature used in these methods which destroy POF's, cannot be applied. Thus, other methods for connecting POF's with silica fibers are sought, including gluing and the use of specific intermediate microstructures. In this case, a suitable method for producing microstructures on optical fibers, seems to be a process of free radical photopolymerization. In this paper, we present the polymer structure manufactured in the process of photopolymerization, combining glass fiber with the polymer one.

Three-component photopolymerizable mixture consists of photoinitiating system and multifunctional triacrylate. Photopolymerization is carried out using a laser with generated wavelength of 532 nm, and the growth of polymer microbridge is controlled by the beam parameters – the optical power and the time of exposure of mixture to the light.

Polymer microbridge grows as the extension of the fibers' cores of both optical fibers, thanks to "self-guiding" effect of the light beam in the photopolymerizable mixture. Such structure works as the waveguide with the proper refractive index distribution – higher inside the structure (core region) and lower outside (cladding region). For the optimized geometry of the polymer microbridge (the initial optical power $P = 20\ \mu W$, time of the exposition the photopolymerizable mixture to the light 60 s and the length of the microbridge around 45 μm) the optical losses are 0,15 ± 0,03 dB.

In authors opinion, the possibility of using polymer microbridges as junctions for polymer and silica optical fibers seems to the ideal method for connecting such different geometrical and material optical fibers.

Synthesis of 4-(alkyl-1-yn-1-yl)-bromobenzenes – useful intermediates for highly birefrigent Liquid Crystals

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***Keywords**: liquid crystal, nematic, optical anisotropy, terminal acetylene*

Liquid Crystalline material became important class of electronic functional materials for display and photonic applications. Special attention has been paid recently for increasing optical anisotropy of nematic liquid crystals. Optical anisotropy is in simple approximation the parameter related to the maximal modulation of light by the LC medium reoriented in certain geometry. Hence some applications require high values of birefringence (optical anisotropy in the case of nematic medium), which can be ensured by mesomorphic molecules having high anisotropy of electronic polarizability $\Delta\alpha$. In the case of calamitic LC molecules, designing molecules with long conjugated π electronic systems can generate such polarizability anizotropy. One of the molecular design approaches is based on 4-(alkyl-1-yn-1-yl)-phenyl-4-yl unit as a nonpolar terminal endcap of the molecule.

The synthesis of 4-(alkyl-1-yn-1-yl)-bromobenzenes with longer alkyl part (for alkyl longer than four) can be synthesized via direct Sonogashira cross-coupling of terminal alkyn with 1-bromo-4-iodobenzene. The reactivity difference of bromine vs. iodine, in the case of Sonogashira reaction, is sufficient to ensure efficient mono-functionalization from the iodo-side. The situation becomes more complicated for shorter homologues since the terminal alkynes are gases at normal conditions and direct protocol cannot be employed.

In our work we developed methodology of synthesizing 4-(alkyl-1-yn-1-yl)-bromobenzenes, either short and longer chained systems. The intermediates can be used directly in further Suzuki coupling or can be converted into boronic acids before coupling reactions. Some examples of LC molecules synthesis will be given and other possibility will be discussed.

Novel voltammetric procedure for Bisphenol A determination in real samples using glassy carbon electrode modified with Carbon Black nanoparticles

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Keywords: *Bishpenol A, Voltammetry, Carbon Black, Glassy Carbon Electrode*

Bisphenol A (BPA) is mainly known for its use as monomer in the production processes of polycarbonate plastics, epoxy resin linings for food and beverage containers and polyacrylate dental materials. Recently, BPA has gained significant public attention as an environmental pollutant and because of side effect for human health. Consequences for BPA exposure are endometrial hyperplasia, decrease of humans sperm quality,abnormal karyotype, polycystic ovarian syndrome, ovarian and testicular cancers.

Determination of Bisfenol A was performed using different pulse voltammetry and standard addition procedure in phosphate buffer (pH=7.0) using glassy carbon electrode modified with carbon black nanoparticles. Several samples which could contain BPA were analyzed. One group of samples consists of milk and orange juice carton, bottle water and rice bag and in second group were thermal paper samples like receipts, tickets. First group checked if the bisphenol can pass from the packaging to the beverages and second one had to define how much BPA is in the samples. It also examined whether BPA from thermal paper passes to the human skin.

None of the samples from the first group contain Bisfenol A. The highest amount of Bisphenol A were determined in the receipt from the ATM (12.32 mg/g) and the lowest in receipt from currency exchange (3.43 mg/g) - which could be caused by high weight. Acceptable recovery from 94-114% indicates that methods could be used for BPA determination in beverages and thermal paper samples. Unfortunately, results confirmed the fact that keeping receipts particularly greasy hand cause faster migration of BPA to the skin.

Development of method for determination of this harmful substance to human health is very important. Proposed procedure allows sensitive and fast determination of Bisfenol A in real samples.

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Simple and high sensitive voltammetric sensor for quetiapine fumarate determination

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Keywords: *Voltammetry, Carbon Black, Quetapine fumarate, drugs*

Quetiapine fumarate (QTF) is a dibenzothiapine derivative with chemical name: Bis[2-(2-[4-(dibenzo[b,f][1,4]-thiazepin-11-yl)piperazin-1-yl] ethoxy) ethanol] fumarate. Quetiapine is an “atypical” antipsychotic drug. It is used in the treatment of schizophrenia and of mania associated with bipolar disorders. It is also used to treat other disorders, such as post-traumatic stress disorder, alcoholism, obsessive compulsive disorder, anxiety disorders. Various methods have been reported for QTF determination so far such as HPLC with UV detection, chemiluminescence spectrometry, spectrophotometry, capillary electrophoresis, flow injection titration, X-ray powder diffraction and voltammetry.

Quantitative measurements of quetiapine fumarate were performed using differential pulse voltammetry (DP) and the standard addition procedure using a multipurpose Electrochemical Analyzer M161 with the electrode stand M164. Working electrode was glassy carbon electrode modified with carbon black nanoparticles. Voltammograms were recorded in the potential range of 400 mV to 130 mV in phosphate buffer (pH=6.0). The effects of several factors like preconcentration potential and time, amount of carbon black, step potential, pulse height, and electrolyte composition were optimized. The detection limit, linear range and possible interferential substances were also studied. In order to validate methods, determination of quetiapine fumarate in drugs (Ketapinor, Ketilept) was performed.

Electrode modified with carbon black nanoparticles caused 20-fold increase in the peak current compared to the bare electrode. The repeatability of the methods was also acceptable.

Simple and high sensitive voltammetric sensor has been developed for determination of quetiapine fumarate. Sensor was successfully validated by studying the recovery of QTF in drugs.

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Hydrophobic polymer/silica films deposited on the glass surface

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Keywords: *hydrophobic film, contact angle, surface free energy*

Intensive technological development has caused huge changes in the production and processing of glass. Recently, glass coatings with specific properties became very popular. The coatings with hydrophobic properties result in water repellency and leads to prevention from the water spreading on the surface. These properties are attractive for many applications such as anti–sticking of snow for antennas or water proof coatings for electrical devices and power electronics. According to many studies introducing silica particles into polymer solution can improve some properties of created hydrophobic coatings, such as mechanical and adhesive properties, UV protection or scratch resistance.

The purpose of our studies was surface properties investigation of polymer/silica films composed from poly(methyl methacrylate) (PMMA) and silanized silica with different surface fraction coverage deposited on glass support. To improve adhesion between support and film, plasma treatment of glass surface with air plasma was used. For the surface properties determination of obtained coatings contact angle measurements by sessile drop method were performed and next, the total surface free energy was calculated from contact angle hysteresis (CAH) approach. Scanning electron–ion microscopy (SEM) was used for morphology investigation.

The performed studies shown, that air plasma treatment influence on glass surface and leads to adhesion improvement. From the other hand, values of the measured contact angles and surface free energy confirm that obtained films are hydrophobic. Images obtained using SEM technique show that silanized silica is homogenously dispersed in PMMA solution and do not create aggregates.

Retrieval of water quality algorithms from airborne HySpex camera for oxbow lakes in north-eastern Poland

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Keywords*: oxbow lakes, remote sensing, Biebrza National Park, HySpex, water quality, empirical formulas*

The aim of this study was to retrieve empirical formulas for water quality of oxbow lakes in Lower Biebrza Basin (river located in NE Poland) using HySpex airborne imaging spectrometer.

Biebrza River it is one of the biggest wetland in Europe. It is characterised by low contamination level and small human influence. Because of those characteristics Biebrza River can be treated as a reference area for other floodplains and fen ecosystem in Europe. Oxbow lakes are important part of Lower Biebrza Basin due to their retention and habitat function.

Hyperspectral remote sensing data were acquired by the HySpex sensor (which covers the range of 400-2500 nm) on 01-02.08.2015 with the ground measurements campaign conducted 03-04.08.2015. The ground measurements consisted of two parts. First part included spectral reflectance sampling with spectroradiometer ASD FieldSpec 3, which covered the wavelength range of 350-2500 nm at ~1 nm intervals. In situ data were collected both for water and for specific objects within the area. Second part of the campaign included water parameters such as Secchi disc depth (SDD), electric conductivity (EC), pH, temperature and phytoplankton.

Measured reflectance enabled empirical line atmospheric correction which was conducted for the HySpex data. Our results indicated that proper atmospheric correction was very important for further data analysis. The empirical formulas for our water parameters were retrieved based on reflecatance data. This study confirmed applicability of HySpex camera to retrieve water quality.

High sensitive determination of levothyroxine on mercury film silver based electrode

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***Keywords**: Levothyroxine sodium, voltammetry, mercury film silver based electrode, hormone determination*

Thyroid hormones are one of the most important signaling molecules in human body. One of the most important is thyroid hormone thyroxine, that plays a crucial role in organism development since the very beginning of life. Keeping appropriate amount of thyroid hormones level is necessary in order to provide optimal functioning of all biological systems. However, affecting the balance of thyroid hormones excretion may cause diseases connected with necessity of using their synthetic analogs or antagonists in order to keep homeostasis. Most common synthetic hormone used in hypothyroidism therapies is levothyroxine sodium, which structure and properties are almost identical as thyroxine. Undeniable importance of thyroxine measurements causing development of high sensitive methods of its determination, including HPLC, mass spectrometry or enzyme immunoassay techniques. Most of these methods are time consuming and requires multi step pre-treatment of sample. Stripping voltammetry allows to reduce amount of waste and provide fast and accurate method of T4 detection.

A multipurpose Electrochemical Analyzer M161 with the electrode stand M164 (both MTM-ANKO, Poland) were used for all voltammetric measurements. Homemade silver based mercury film electrode (Hg(Ag)FE) was used for sensitive levothyroxine sodium determination in drugs. Instrumental parameters of proposed method, such as pulse of amplitude, potential step, preconcentration time and composition of supporting electrolyte were optimized. Repeatability of measurements was determined as RSD (%). The proposed method was validated using recovery parameter.

In this work electrochemical behavior of levothyroxine sodium at a mercury film electrode (Hg(Ag)FE) was presented and a differential pulse adsorptive stripping voltammetric method (DPAdSV) was developed for determination of this hormone. New procedure was successfully applied for its sensitive determination in different pharmaceutical products.

Acknowledgement

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Voltammetric determination of estradiol on carbon black modified glassy carbon electrode

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Keywords: *Estradiol, voltammetry, carbon black, hormone determination*

Estrogens are primary endogenous female sex hormones, responsible for development and regulation of the numerous physiological actions and secondary sex characteristics. Estradiol (17β-estradiol) is a steroid estrogen hormone, essential for the development and maintenance of female reproductive system. In women, its main functions include control of ovulation, cyclical preparation of the reproductive system for fertilization and implantation, and control over mineral, carbohydrate, protein, and lipid metabolism. Estrogens also have important actions in males, including effects on bone development, spermatogenesis, and behavior. Due to increasing popularity of using estradiol in contraceptives and menopausal hormone therapy and considering importance of its precise dose in pharmaceutical products, high sensitive methods of estradiol determination are desired. Most of the papers propose determination of estradiol in body fluids and pharmaceutical preparations by high performance liquid chromatography (HPLC) and radio immunoassay techniques (RIA). Despite high sensitivity of these methods, they still require expensive equipment and time consuming preparation of sample. In order to eliminate these inconveniences, Differential Pulse Voltammetry was proposed.

Carbon black modified glassy carbon electrode was used for sensitive determination of estradiol. Instrumental parameters of DPAdSV method, such as pulse of amplitude, potential step, preconcentration time and composition of supporting electrolyte were optimized. Repeatability of measurements was determined as RSD (%). Validation of proposed method was using recovery parameter.

In this work electrochemical behavior of estradiol at a carbon black modified glassy carbon electrode was presented and a differential pulse adsorptive stripping voltammetric method (DPAdSV) was developed for determination of this hormone. New procedure was successfully applied for its sensitive determination in different pharmaceutical products.

Acknowledgement

The work was supported by Ministry of Education and Science (AGH UST University Project No. 11.11.160.799).

The study of voltammetric determination of phenolic acids with the application of different electrodes

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***Keywords**: antioxidants, voltammetry, phenolic acids, glassy carbon electrode, carbon fibre microelectrode*

During the process of ATP generation, which is necessary for the aerobic organisms, the reduction of oxygen overlaps partially. As the effect the formation of endogenous reactive oxygen species (ROS) can be observed. Moreover, the exposure to cigarette smoke, ionizing radiation are the sources of exogenous ROS. Their accumulation leads to the disorder of homeostasis, which is known as the oxidative stress. It is considered as s a source of aging, cell destruction and finally leading to cancer, neurodegenerative diseases such as Alzheimer or cardiovascular disorders. However, some organic compounds exhibit the minimizing properties of negative effect of the large number of ROS. They are called antioxidants and play significant role in the defense mechanism against the oxidative stress. One of the most strongest antioxidants are polyphenolic acids, that can be found in fruits and vegetables.

The electrochemical determination of polypenolic acids: caffeic, vanillic, ferulic and syringic acids, which can be easily found in wines, was the subject of this studies. The experiments were conducted with the use of voltammetric technique DPV (differential pulse voltammetry) in a three-electrode quartz cell. Three types of working electrode were applied. Two of them (commercialy bought) were GCE (glassy carbon electrode) with the diameter of 3 mm, CFME (carbon fibre microelectrode) with the diameter of 7 μm. The third electrode was the home-made glassy carbon electrode with the untypical diameter of 1 mm. The reference electrode was double-junction Ag|AgCl|KCl electrode and the counter electrode - platinum wire.

In case of the measurement with the use of CFME the important part of the measuring system was a Faraday cage, which allows the elimination of noise coming from network disruptions. Additionally, during the measurement, the system worked on an internal battery, which accounted for an additional eliminating AC interference. The equipment allowed the registration of current at the impressive pA level.

Voltammetric techniques in the distinction of the absinthe origin

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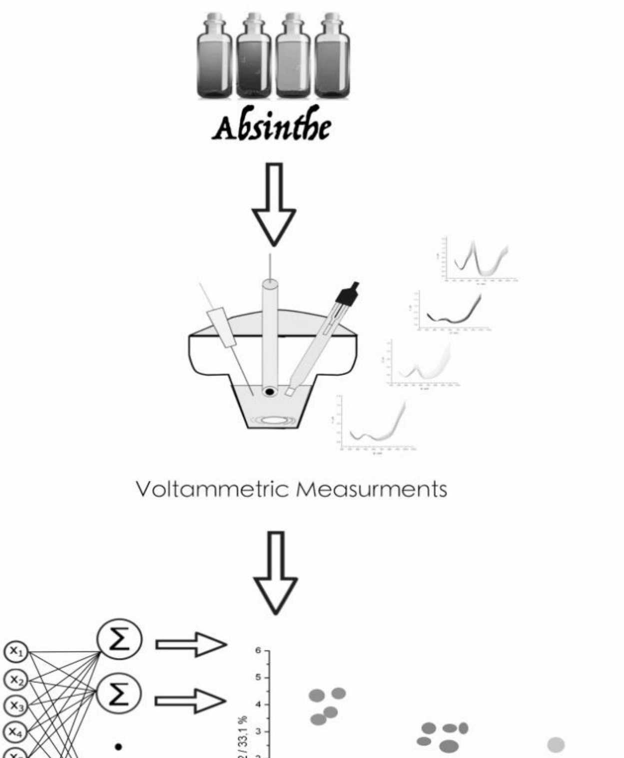
***Keywords**: absinthe, voltammetry, boron-doped diamond electrode, chemometrics*



Absinthe is a popular alcoholic beverage often associated with the green fairy. It is manufactured in many countries nowadays. The connoisseurs of the absinthe can distinguish them. Herds came the question, if there is any possibility to observe the differences between bottles of absinthe based on voltammetric signals. DPV (differential pulse voltammetry) was used in this investigation to distinguish absinthe from different countries. The sensor was the BDD (boron-doped diamond electrode) being also a working electrode. The registered voltammograms and application of chemometric methods were the great tool to distinguish these beverages.

Analysis of predictive methods to calculate heat transfer coefficient during flow boiling of NH_3

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***Keywords**: ammonia, heat transfer, predictive methods, boiling*

Due to European Union regulations common used in refrigeration and air-conditioning systems refrigerants from HCFC group are or will be forbidden. Because of that scientist are looking for other refrigerants as a replacement. There are two groups of refrigerant proposed to use: new synthetic refrigerants and natural refrigerants. In the second group can be mentioned carbon dioxide, propane, isobutene and ammonia.

Designers of refrigeration systems need to use calculation methods to predict heat transfer coefficient. In literature can be found a lot of calculation methods to predict heat transfer coefficient, but most of them are prepared for synthetic refrigerants. In order to verify possibility of using those methods the paper present analysis of some existing methods to calculate heat transfer coefficient during flow boiling of ammonia. For analysis Guerrieri and Talty, Mumm, Liu and Wintertone, Kenning and Cooper and Kutateladze methods were used. Methods were analyzed by use of mean absolute error, average deviation and number of data within ±50%.

Enhancement in properties of the fly ash-epoxy resin composite by investigation of filler size and silane treatment

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Keywords: *Fly Ash, Filler Size, Silanization, Mechanical properties, Thermal Conductivity*

The epoxy resin is a commonly used insulation material for electrical and electrotechnical devices. In order to fulfill its role, that type of material should exhibits suitable mechanical properties and high thermal conductivity. A good method to enhance both of features is incorporation of filler into the epoxy matrix. The low expensive fly ash was found as a filler, which can successfully replace the most popular filler in the epoxy system – silica flour. However, it must be noticed that grain size distribution of the fly ash is much different from that of the silica flour and compatibility of the fly ash to the epoxy resin is low.

The trials to solve these two problems of the fly ash (Greenbet) were undertaken by means of two processes. In the first step the fly ash was sieved, and five various fillers fractions were obtained with size of particles as follows: <25µm, <56µm, <75µm, <100µm and original size. Composites based on the epoxy (Huntsman) and filled with these fillers were examined in relation to tensile strength, Young modulus, fracture toughness and thermal conductivity. After that measurements, fraction of particles form the composite with the best properties was selected for the second part of experiment, where the fly ash was covered with the [3-(2-Aminoethylamino)propyl]trimethoxysilane (Sigma Aldrich). Silane coupling agent provide improvement in connection between inorganic filler and polymeric matrix. Presence of the silane layer on the fly ash surface was confirmed with use of Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM). Finally, the epoxy resin composite filled with the silanized fly ash was examined in the same way as the composites in the first part, and the results were compared.

Presented studies allow to confirm that the size of the filler, as well as coupling to the matrix are crucial for the final properties of the composites and the influence of these two factors were examined. Moreover, the presented procedure provide method to obtain a useful filler for the epoxy resin system from a waste material.

Silanization proccess of fly ash as an effective way to obtain useful filler from a waste material

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Keywords: *Fly Ash, Silanization, Fourier Transform Infrared Spectroscopy, Thermogravimetric Analysis, Scanning Electron Microscopy*

Silanes are well-known coupling agents, which consist of two different types of groups. First of them are hydrolysable groups, which provides possibility to couple silanes with inorganic materials reach in OH groups. The organic groups are the second one, and they are compatible with polymers. As final, silanes have ability to couple inorganic filler with polymeric matrix. The fly ash is inexpensive waste material, which can be successfully used as a filler for the epoxy resin system. However, compatibility of these two materials is relative low and covering the fly ash with the silane was found to be a proper way to bond it with the epoxy.

Silzanization process of the fly ash (Greenbet) was carried with [3(2Aminoethylamino)propyl]trimethoxysilane (Sigma Aldrich) in eight different ways. During the experiment amount of the silane, time and temperature of the reaction were changed. In order to confirm presence of the silane on the fly ash surface, three complementary research methods were used, namely: Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM).

All used combinations of amount of the silane, time and temperature of reaction result in successfully covering the fly ash with the silane layer. Moreover, slightly differences are observed in obtained layers in relation to used parameters, especially with FTIR method. Obtained results confirm possibility to create the silane layer on the fly ash surface. For this reason, the silanized fly ash can be a useful filler for the epoxy resin system, with enhanced compatibility to the matrix.

Fluorescence quenching of pyrene in surfactant solutions

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Keywords: *surfactant, pyrene, quenching, fluorescence*

Pyrene is the most commonly used fluorescent probe in the emission spectrum. It has five characteristic peaks. The ratio of the intensity of first and third peaks (I_1/I_3) depends on the type and concentration of the substance in the solution. This parameter determined on the basis of this spectrum is especially important properties in the analysis of the surface active agent.

Surfactants have two distinct regions in their chemical structure, one of which is water-liking or hydrophilic and the other of which is water-hating or hydrophobic. They have unique properties, i.e. the ability of adsorption at various interfaces and formation of aggregates called micelles. Surfactants changes interfacial properties and due to their capacity of the micelles formation in the bulk phase after crossing a CMC (the critical micelle concentration) of the solution. The surfactants have wide application in many industrial sectors and in everyday life, because of their ability to change the interfacial properties. One way of determining the CMC of the surfactant is drawing the dependence of I_1/I_3 of pyrene in the function of surfactant concentration in the solution. Very important is to determine the number of aggregation of the surfactant for example by the pyrene fluorescence quenching method. The fluorescence quenching involves reducing the intensity of the fluorescent substance by the action of the quencher substance.

The aim of this study was to record the emission spectra of pyrene in solution of the Triton X-114 at different temperatures and in the presence of CPC (cetylpyridinium chloride).

The analysis of the emission spectra of pyrene in the solutions of Triton X-114 and in the presence of the CPC shows that the mechanism of quenching the fluorescence of pyrene in the surfactant solutions depends on its concentration and the temperatures.

Surfactant-based extraction of plant origin compound

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Keywords: *surfactant, micellar extraction, flavonoid*

The surface active agents (surfactants) are substances that lower the surface tension of a liquid, allowing easier spreading, and can lower the interfacial tension between two liquids. Surfactants are usually organic compounds and they are amphiphilic. They are built of hydrophilic (“tail”) and hydrophobic (“head”) groups. These compounds are soluble in both organic solvents and water. At low surfactant concentration in the solution the surfactant molecules arrange on surface. The addition of the surfactant molecules will lead to formation of micelles. Critical Micelle Concentration (CMC) is the concentration above which micelles are formed. One of the latest application is the use of micellar solution of surfactants for the extraction of plant origin compound such as quercetin, rutin.

Quercetin is a representative of flavonoids (3,5,7,3’,4’-pentahydroxyflovonol) and it is also one of the widely used pharmaceutical flavonoids compound. Quercetin is commonly found in fruits and vegetables, especially in onions, citrus and apples. It has many properties, which have positive effect on humans health. Quercetin acts like antihistamine and an anti-inflammatory. It can help protect against heart disease and cancer.

The purpose of the presented studies was to determine the interactions between the non-ionic surfactant, Triton X-114 (TX114) micelles and quercetin by the spectroscopic methods.

The presented results are expected to contribute to understanding interactions of natural flavonoids with interfaces modelled by non-ionic surfactant systems and to interpreting reactions with free radicals in microheterogeneous environments present in a wide range of foods, cosmetics and pharmaceuticals.

Characterization of the magnesium-containing bioactive silico-phosphate glasses

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***Keywords**: glass structure and microstructure, FTIR spectroscopy, bioactivity.*

In many cases of trauma and injuries to the skeletal system, the particular need for biomaterials with superior properties is required. One of the most attractive materials are bioactive glasses, which have the ability to form strong chemical bonds with living tissue. Mg-doped silico-phosphate glasses and glass-ceramics have been shown to be bioactive. Moreover, magnesium ions have fundamental role in cellular processes and human metabolism.

Application of glasses as biomaterials is limited mainly due to their very low strength and chemical stability. One of the best way to improve the mechanical properties of the glasses is to carry out their partial devitrification that allows to obtain glass-crystalline materials. However, this process needs to be controlled in order to not lose the bioactivity of the glassy precursor.

Several compositions of glasses from $NaXPO_4$-SiO_2 system (where X = Ca or/and Mg) were obtained by melt-derived method. The morphology and composition of the glasses were analyzed by scanning electron microscopy equipped with energy dispersive spectroscopy. The occurrence of phase separation was seen in the obtained materials. The structure of glasses and the corresponding crystalline phases was characterized by X-ray diffraction and IR spectroscopy showing that complete substitution of calcium ions by magnesium ions causes glasses structure homogenization. However, partial substitution of calcium ions by magnesium ions decrease the homogenizing influence of magnesium ions on the silico-phosphate glasses structure. Moreover, thermal analysis using differential scanning calorimetry was performed to check the thermal properties of the glasses, including devitrification temperature. The crystallization of all studied glasses is multistage; the matrix and inclusions crystallize separately. This study shows that it is possible to obtain glass-crystalline materials by direct crystallization process.

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Differences in bioactivity of silico-phosphate glasses containing antibacterial ions

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***Keywords**: bioactivity, silico-phosphate glasses, antibacterial properties.*

The main aim of this study was to obtain silico-phosphate glassy materials from the $NaCaPO_4$-SiO_2 system containing different antibacterial ions and to compare their bioactive properties. Glasses from this system are one of the most attractive bioactive materials due to their ability to form a layer of hydroxycarbonate apatite on their surface when they are in contact with biological fluids. Silico-phosphate glasses can also offer antibacterial properties due to the pH rise caused by cations release, but it is more advantageous to modify bioactive glasses by introducing antibacterial ions in the glass network such as (e.g. silver, copper, zinc, cerium, titanium, gallium and gold). These ions can reduce the amount of microbes on an implant surface and kill bacteria or inhibit their growth. It is difficult to determine if antibacterial ions improves glass bioactivity because studies have not been carried out on one glass composition and they have been obtained various methods.

This work focuses on one melt-derived silico-phosphate glass composition doped with either zinc, copper or cerium. In order to check bioactivity, the glasses were soaked in a simulated body fluid (SBF) at 37^{o}C for 30 days (SBF was changed every 7 days). The morphology and composition of the glass surfaces were analyzed by scanning electron microscopy equipped with energy dispersive spectroscopy (EDS). The structure of the glasses and their surface phases were characterized by Raman and IR spectroscopy. Moreover thermal analysis differential scanning calorimetry (DSC) was carried out to examine the thermal properties of the glasses, including devitrification temperature (T_D). This work shows that it is possible to create bioactive glass materials with antibacterial ions.

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Interatomic and intermolecular interactions of graphene oxide and reduced grapheme oxide

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Keywords: *Graphene, Graphene oxide, Reduced grapheme oxide, Lennard-Jones potential function*

Graphene was obtained for the first time in 2004 by Andre Geim and Konstantin Novoselov. Aforementioned scientists received the Nobel Prize in physics in 2010 for this achievement. Graphene structure is made from atoms of carbon, which forms a single layer. For this reason it is sometime called “two dimensional graphite”. The first obtainment was the result of mechanical separation of graphite layers.

Graphene oxide (GO) and reduced graphene oxide (rGO) are the materials which are similar to graphene in structure and acceptor-donor properties. GO is amorphous, chemically modified graphene sheet containing reactive functional groups such as epoxide, hydroxyl and carboxyl groups. Product of reduction of GO is rGO which composition and properties depends on the method of reduction.

The chemical properties and different types of intermolecular interactions of graphene and its derivatives are discussed and described in the paper. The selected potential functions describing the aforesaid interactions are characterized. The analyzed potential functions characterized of the parameters of distance and potential for interactions of graphene oxide and reduced graphene oxide with the selected substances are calculated. The mutual comparsion of them is also done. The results, which are obtained in the aforementioned manners are the basis to formulate the conclusions.

All of calculated functions are similar to each other in their courses. The interactions of heavier molecules with graphene-like materials are characterized by a greater degree of potential well. The deepest potential wells are created by GO structures, which is caused by high number of heteroatoms in its structure.

Application of bismuth bulk electrodes with electrochemical activation system to determination of Fe(III) trace

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***Keywords**: Bismuth bulk electrode, Stripping voltammetry, Iron, Mercury-free electroanalysis*

Of the many different reports, only a few studies have concerned the application of bismuth bulk electrodes (BiBEs) in stripping voltammetry (SV). In our work, we present a renewable bismuth bulk annular band working electrode (RBiABE), which central element is a ring made of metallic bismuth. Working with the solid-state electrodes requires mechanical or electrochemical treatment, therefore, also outer cell activation was used in order to remove reaction products of the surface electrode.

The application of the RBiABE and optimization procedure for determination of iron traces by differential pulse adsorptive stripping voltammetry (DP AdSV) is presented in this work. The procedure is based on the pretreatment and electrochemical activation working electrode before each measurement at a potential of -1.9 V for a 20 seconds. The next, Fe(III)-triethanolamine (TEA) complex is cathodic reduction to Fe(II) at a potential -0.96 V (versus Ag/AgCl/3 mol L^{-1} KCl) in an alkaline supporting electrolyte consisting of 29.1 mmol L^{-1} sodium hydroxide and 4.9 mmol L^{-1} triethanolamine. The reduction current of complex Fe(III)-(TEA) is catalytically enhanced by the addition of 4.9 mmol L^{-1} bromate ($KBrO_3$). The dependence of the Fe peak current on the concentration of Fe was found to be linear in the range from $1.8 \cdot 10^{-9}$ to $1.5 \cdot 10^{-5}$ mol L^{-1}, with detection limit $2.2 \cdot 10^{-10}$ mol L^{-1}, obtained without any preconcentration procedure. Finally, the RBiABE was applied to the determination of cobalt in certified reference material and water samples with satisfying results.

Determination of Zn(II) trace in water samples by anodic striping voltammetry at a bismuth bulk electrode

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***Keywords**: Bismuth bulk electrode, Water analysis, Zinc, Mercury-free electroanalysis*

The methods used most often by researchers to determine Zn(II) are spectroscopic and voltammetric techniques with the two basic electrode systems, the mercury-film electrode (MFE) and hanging mercury drop electrode (HMDE), have gained wide acceptance in the development of stripping voltammetry. The toxicity of Hg and strict environmental regulations have prompted the search for new alternative electrode materials with a similar performances are highly desired, particularly for meeting the growing demands for on-site environmental monitoring of trace metals and decentralized clinical testing of toxic metals. As an alternative to mercury electrodes, the environmentally friendly bismuth electrode can be used.

In our work, we present a bismuth bulk annular band electrode (BiABE) to determination of Zn(II) by differential pulse anodic stripping voltammetry (DP ASV) in a relatively fast, simple and cheaper method. The procedure is based on the preconcentration of the Zn(II) ions at testing electrode held at -1.5 V (versus Ag/AgCl/3 mol L^{-1} KCl) in a supporting electrolyte consisting of 19.6 mmol L^{-1} sodium acetate buffer (pH=5.8). Finally, the BiABE was tested by analyzing tap water and river water samples; the latter were collected at two different sites on the outskirts of (Kraków, Poland).

Corrosion-protective coating based on triethoxyoctylsilane

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Keywords: *corrosion, linear polarization, organosilicon coating, stainless steel*

Until recently, corrosion protection was mainly based on the introduction of heavy metals (as the corrosion process inhibitors) to metalworking and coatings. Promising candidates that could take their place in the anti-corrosive branched of the market seems to be organofunctional silanes. Due to their structure, they are organic-inorganic hybrids that combine features of both organic and inorganic compounds, which makes them capable of forming covalent bonds with inorganic substrates such as glass or metal, and with organic polymers.

In this study we present a new approach to silane coatings deposited on the surface of stainless steel 304. The deposition was performed in different solutions with a variety of pH values. Three types of aforementioned solutions were prepared i.e. neutral, containing only methanol with triethoxyoctylsilane and two acidic consist of methanol, triethoxyoctylsilane, tetraethoxysilane and hydrochloric acid which was used to establish pH values equal to 1 and 3.5. Anti-corrosive properties of triethoxyoctylsilane $CH_3(CH_2)_7Si(OC_2H_5)_3$ and tetraethoxysilane $Si(OC_2H_5)_4$ were examined using surface analysis as well as, electrochemical and spectroscopic methods.

It was observed that the silane coating effectively inhibits corrosion on the surface of stainless steel 304. The values of the equilibrium potential (corrosion potential) of the test samples are more positive than the corrosion potential of bare stainless steel 304. Moreover, the values of the cathode and anode current densities of these samples are much lower compared to bare steel.

Due to the presence of oxide passive film on the steel surface, metal-O-Si bonds are formed, thus creating an intermediate layer between the oxide passive layer and the outermost siloxane layer (Si-O-Si). Furthermore, presence of long aliphatic chain of triethoxyoctylsilane compound increases steel surface hydrophobicity.

This work was supported by funds from the National Science Centre (Poland) granted on the basis of decisions number DEC-2013/10/E/ST5/00719 and DEC-2013/09/D/ST5/03845.

Characterization of ZnO-based nanomaterials using Analytical Ultracentrifugation

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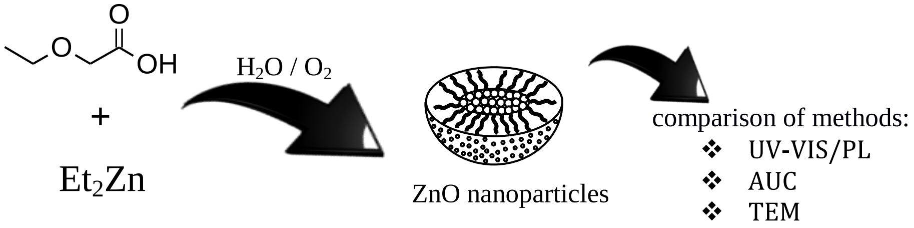
Keywords: *zinc oxide, nanoparticle, analytical ultracentrifugation*

Quantum dots (QDs), due to their unique properties (broad light absorption spectrum, narrow light emission spectrum and long term stability) might find application in many areas of human life. Moreover the possibility of surface modification increase the potential of QDs related with their utility in biomedical studies including both *in vitro* and *in vivo* bioapplications.

In the reported study we describe a novel, non-external-surfactant-assisted, wet-chemical processing method that yields monodisperse, high-quality ZnO QDs coated by organic ligand. The key feature of our strategy is the use of easy-to-prepare RZn(X)-type precursors (X ≡ monoionic organic carboxylate ligand, R ≡ Et), which act as a self-supporting system. Resulting ZnO NCs were characterized using a wide library of analytical method including High-Resolution Transmission Electron Microscopy (HRTEM), UV-Vis absorption and photoluminescence (PL) spectroscopy and Analytical Ultracentrifugation (AUC). Particularly relevant to the present work is the AUC method, which was used to characterize both size distribution and surface chemistry of ZnO-QDs. Additionally, the stability of the resulting nanoparticles in organic solvents and water as well as their potential application in cell labeling have been investigated.



Scheme 1. Schematic representation of the synthesis of bio-compatible QDs-ZnO.

Synthesis, structure and reactivity of alkylzinc carboxylates

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Keywords*: alkylzinc carboxylates, zinc oxide, nanoparticle*

Alkylzinc carboxylates are of great interest due to their fundamental role in biochemical systems, catalysis and material science. For instance, alkylzinc complexes stabilized by carboxylate ligands play an important role as catalysts for the copolymerization of carbon dioxide with epoxides as well as a secondary building blocks for porous materials like metal‒organic frameworks (MOFs). Moreover, alkylzinc carboxylates appear to be a very promising organometallic precursors, which lead to formation of ZnO-based nanomaterials.

In this work, we report on the synthesis and structural characterization of alkylzinc complexes with various supporting carboxylate ligands. All of the as-prepared alkylzinc complexes $[R'OCH_2C(O)OZnR]_n$ (where R, R' ≡ Me, Et, n = 6) were analyzed using Single-Crystal X-ray Diffraction Study, ^{1}H NMR and IR spectroscopy. Furthermore, all of studied complexes appear to be a very promising precursors toward ZnO nanocrystals (NCs) of controlled size and shape under mild conditions using a bottom-up approach from organometallic precursor.

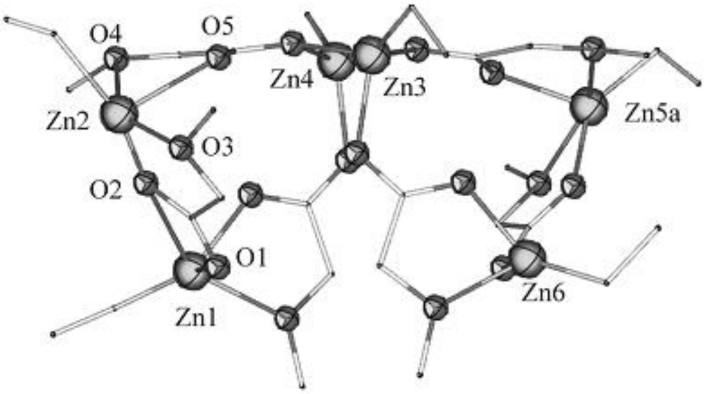

Figure 1. Molecular structure of $[CH_3OCH_2C(O)OZnEt]_6$.

A comparative analysis of selected mills and grinding media used in them to achieve a certain degree of particle size.

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Keywords*: milling, grinding media, electromagnetic mill*

The article presents the characteristics of four types of mills with regard to the selection of grinding media. Milling is a process depending on many factors related both to the construction of the grinding plant and the nature of the material to be fragmented. Properly selected device parameters affect the effectiveness of its work both technologically and economically. The mills are devices used in the processing of raw materials.

Selection of the mill and its technical parameters determines the products' degree of fineness. A very important role to play in the grinding process is the proper selection of grinding media parameters such as the diameter and material.

Selection of appropriate grinding media allows to improve energy efficiency and to increase the efficiency of the process. Electromagnetic mill stands out in this ranking. Shredding system in the device with the control unit, allows the grinding of dry or wet raw materials in a closed cycle, with the possibility of a very wide selection of speed of movement of the grinding media with different frequencies. The ability to control the size of the dosing feed and grinding media, ongoing analysis of particle size and the operating status of the mill and the flow of recycle will allow the full and far more effective activation of the mechanical properties of the grains with specific physical and mechanical parameters (size, shape, area and energy surface, surface properties), and also significantly increase the grinding capacity and reduce energy consumption.

The influence of climatic and mechanical changes on glued connection between GI- POF and MMF

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Keywords: *optical fiber mechanical splice, optical fiber glued connection, polymer optical fiber, thermal properties of optical fiber connectors,*

Telecommunication systems based on optical fibers have worked in different temperature and humidity conditions. One of the most important parts of such system are connectors and splices. Until these connections are made between silica optical fibers mentioned above, climatic parameters changes do not influence telecommunication system. Hybrid telecommunication systems require to develop a new type of connections. In this paper we present the influence of climatic conditions for an adhesive-based mechanical splice between GI- POF (Graded Index Polymer Optical Fiber) and a silica-based MMF (Multimode Optical Fiber) and a pair of GI - POFs. We have tested the prepared connection under simultaneous temperature and humidity changes and tensile strength, as well.

The experiment was carried out on glued connections by using the method we had previously developed. In order to create appropriate conditions we use a climatic chamber (Vötsch Industrietechnik) which allows to manipulate the temperature and humidity. As light sources we have used a supercontinuum generator (Fianium) and a laser at λ= 1310 nm (Yenista). Measurement of output optical power we have calculated optical connector losses as a function of temperature which was changed within the range of -40^{o}C - 80^{o}C. We have investigated the influence of relative humidity for some of temperatures from the above range. We have concluded that SOF-POF connections can work within the range of -40^{o}C + 60^{o}C and humidity does not affect optical loss of the splice. However, connections POF- POF are unstable with regard to temperature and humidity changes. The only restriction for the glued connection is vibration associated with the work of the climatic chamber.

Tensile strength of glued connection was investigated by using a proof tester which is intended for stretch the fusion splice. We have monitored transmitted optical power during connection stretching. Mechanical splice of MMF- POF has strength within the range of 12- 16kpsi, whereas the POF-POF joint is unable to perform this test due to a longitudinal extension of the POF.

Numerical inversion of Laplace transforms: a useful technique for solve a mathematical model of gas flow

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Keywords: *Laplace transform, numerical Laplace inversion methods, numerical accuracy, gas flow model, Maple®program*

Laplace transform is a powerful technique that plays a significant role for solving and analyzing of linear differential and linear integral equations in varied fields of physics, mechanics, mathematics, and computational sciences. Using of Laplace transform greatly simplifies the solution of models representing physical systems [e.g Kocabas I., Application of iterated Laplace transformation to tracer transients in heterogeneous porous media, *Journal of the Franklin Institute*, 2011, 348, 1339-1362]. The inverse transform can be made by employing tables of Laplace transform as well as Computer Algebra Systems (e.g Maple). Sometimes, an analytical inversion is difficult or even impossible to obtain, then one of numerous numerical methods of inverse Laplace transform can be used. According to literature reports [e.g Hassanzadeh H., Pooladi-Darvish M., Comparison of different numerical Laplace inversion methods for engineering applications, *Applied Mathematics and Computation*, 2007, 189, 1966-1981] numerical methods have their own applications and any problem under consideration a suitable method should be chosen.

For this reason, in this paper, we have undertaken an attempt to find most effective numerical method of inverse Laplace transform to solve a mathematical model of gas flow. The measurement unit, its application as well as its model were described in details in this work [Wójcik M., Szukiewicz M., Kowalik P., The application of the Laplace transform for modeling of gas flow using Maple®, *The Journal of Applied Computer Science Methods*, 2014, 6, 43-53]. We examined three methods for the numerical inversion: the Gaver-Stehfest method (it is based on the sequence of Gaver functions), the Durbin method and the Koizumi method (both methods are variants of the Fourier series method, and are based ona Fourier series expansion method using of the Poisson summation formula). We concluded that all algorithms could be used to solve this problem. All the methods were precise but the Gaver-Stehfest method was the most effective. The model was solved using the computer algebra system Maple®. Implementation of the methods were done by authors.

Methyl formate hydrolysis performed in fixed-bed chromatographic reactor. Simulation and experimental results

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Keywords: *chromatographic reactor, parameter estimation, gPROMS simulation*

Presented work is focused on modeling process of reactive chromatography, which combines chemical reaction with simultaneous chromatographic separation. In general, different affinity of reagents to fixed adsorptive bed is used to instantaneously separate products. Therefore, high yield is achieved and high purity products leave the chromatographic column one after another. This type of reactor is applied in petrochemical synthesis, pharmacy, optically active ingredients and esters industriesy, especially when standard separation techniques are inefficient or difficult to implement.

The hydrolysis reaction of methyl formate catalysed by Dowex 50WX8-200 ion exchange resin was carried out periodically in a fixed bed chromatographic reactor. Several experiments were conducted with different flow rates and temperatures. A number of parameters were calculated with statistical moments method. Based on experiments with non-adsorbing, non-reactive tracers KCl and MgCl2 bed porosity was calculated. Experimental data for adsorption processes with methanol and formic acid were used to evaluate adsorption coefficients for both products of methyl formate hydrolysis.

Mathematical model of chromatographic reaction process was presented and implemented in commercial software "gPROMS Model Builder". For PDE calculations solver SRADAU was chosen. Implemented model was used to estimate all unknown parameters in the process. Bed porosity obtained from simulations was slightly lower in comparison with experimental data. Apparent dispersion coefficient was estimated based on simulations. Simulation carried out for pure methanol and pure formic acid resulted in acquiring adsorption coefficients. Apart from chromatographic process characteristic, reaction parameters were estimated with implemented mathematical model. Arrhenius equation was chosen as model of temperature influence.

Conclusion was that the presented mathematical model with good likelihood can simulate process of methyl formate hydrolysis in fixed-bed chromatographic reactor and can be recommended for obtaining process parameters.

Marula oil as a successor of argan oil

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Keywords: *fatty acids, argan oil, marula oil, UV-Vis, fluorescence.*

Commonly known argan oil (*Argania spinosa kernel oil*), containing over 100 active substances, supports regeneration of the skin and limits transepidermal water loss as well as additionally moisturises and smoothes the epidermis. Marula oil (*Sclerocarya birrea seed oil),* much less widespread, has very similar composition and properties as the argan oil. Marula oil is rich in essential fatty acids omega-9 (oleic acid) and omega-6 (linoleic acid) that deeply hydrates and reduces redness of the skin and possesses anti-inflammatory properties, moreover nourishes, heals, moisturises and improves skin elasticity. In our study, we characterized the presence of fatty acids contained in the argan oil and the marula oil by using ultraviolet-visible (UV-Vis) and emission (fluorescence) spectroscopy. We also investigated the skin care properties of formulation contained these oils.

The measurement of the absorption spectra in the visible (Vis) region was made by using a spectrophotometer Genesys™6 (Milton Roy). Synchronous fluorescence spectrum was done by using a Fluorolog spectrofluorimeter 3-11 (Jobin Yvon-Spex). For the investigation of the physical and chemical stabilities, formulations containing marula oil were stored at 4, 25 and 40 °C. The viscosity was measured with RC02's Rheotec viscometer, the formulation stability was examined by using Formulaction Turbiscan™LAB (multiple light scattering technique), the zeta potential with photon correlation spectroscopy (Malvern Zetasizer Nano Z) and the mean particle size distributions using laser diffractometry (Malvern Mastersizer 2000E).

The spectra obtained by using a variety of spectroscopic techniques provided information about the chemical components in both oils. Bandwidth in the range of UV-Vis was attributed to the absorption of carotenoid pigments and chlorophyll. On the other hand, the fluorescence spectra of oils were regarded as due to the presence of compounds from the group of tocopherols, chlorophylls, phenols and other fluorescent components.

Sacha inchi oil for the production of vitamin E loaded nanostructured lipid carriers in cosmetic formulations

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Keywords: *sacha inchi oil, vitamin E, tocopherol, nanostructure lipid carriers, NLC, cosmetic formulations*

Natural oils are gaining increasingly popularity in the cosmetic industry due to their natural origin and the content of valuable lipids. Sacha inchi oil, cold pressed from seeds shrub of Inchi (*Plukenetia Volubilis*), has the highest content of omega-3 (~60 wt.%) and omega-6 (~40 wt.%) fatty acids among all natural oils. It can soften the *stratum corneum* of epidermis, forms the occlusion film, provides protection against UV radiation, inhibits the transepidermal water loss (TEWL) or supports the synthesis of lipids. In our study, we produced vitamin E (tocopherol) loaded nanostructured lipid carriers (NLC) contained sacha inchi oil instead of its semi-synthetic substitute.

Rotor stator dispersion (Ultra-Turrax T25, Jahnke and Kunkel) was combined with high pressure homogenization (Micron LAB 40, APV) to produce two formulations of vitamin E loaded NLC suspensions (Compritol 888 ATO, Miglyol 812 / Sacha inchi oil, Miranol Ultra C32). For the investigation of the physical and chemical stabilities, the prepared suspensions were stored at 4, 25 and 40°C. Chemical stability of tocopherol was assessed with high performance liquid chromatography. The viscosity of cosmetic formulations contained vitamin E loaded NLC was measured with RC02's Rheotec viscometer, the stability was examined using Formulaction Turbiscan^{TM} LAB (multiple light scattering technique) and the mean particle sizes and size distributions were analyzed with photon correlation spectroscopy (Malvern Zetasizer Nano Z) and laser diffractometry (Malvern Mastersizer 2000E).

As a result, natural vitamin E loaded NLC formulation contained sacha inchi oil was successfully developed with a similar physical and chemical stability as semi-synthetic liquid lipid. Moreover, conducted research proved a high stability of sacha inchi oil and thus can be applied in a wide range of cosmetic formulations.

A possibility to obtain an Al_2O_3-Ni composite by centrifugal slip casting

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***Keywords**: centrifugal slip casting, composites Al_2O_3-Ni, functional graded material (FGM)*

This work presents the results of studies concerning the production and characterization of Al_2O_3-Ni composite materials with a gradient concentration of metal particles. The centrifugal slip casting technique (CSC) was applied for the purpose of producing these materials. The final product of the applied process was the hollow cylinder sample with graded distribution of Ni particles.

Centrifugal slip casting was performed at centrifugal acceleration equal 1.42 G. The α-Al_2O_3 powder with 99.99% purity and average particle size of 133nm and Ni powder with 99.99% purity and a medial diameter of 8.5µm were used as the starting materials. Water based slurries with 50 vol.% content of solid phase containing α-Al_2O_3 and Ni powder were study. Citric acid (CA) and diammonium citrate (DAC) were used as the deflocculates.

Sintered Al_2O_3-Ni composite samples were subjected to XRD analysis. The microstructures of the sintered ceramics were studied by means of scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS). Quantitative description of the microstructure of the Al_2O_3-Ni composites was made on the basis of micrographs using computer image analysis.

Application of the CSC method allows for the graded distribution of metal particles in the Al_2O_3-Ni composite. All obtained result support the gradient distribution of nickel particles in the composites material.

Acknowledgements

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