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# ABSTRACTS OF RECENT PHD THESES

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## ABSTRACTS

# DEVELOPMENT AND ANALYTICAL CHARACTERIZATION OF NOVEL SYNTHETIC IONOPHORE-BASED ION-SELECTIVE ELECTRODES

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The implementation of the first synthetic ionophore dates back in the 1960s. The tailored design and synthesis of selective complexing agents immediately attracted much attention and extensive research in this area resulted in more than 60 analytes being now assessable with ionophore-based ion-selective electrodes (ISE). However, the application of ionophores is not limited to their potentiometric application and they can be generally used for selective extraction/separation of ions from aqueous solutions. In this respect, the nuclear industry can be considered as one of the application areas with the largest practical and economical impact. Suitable ionophores can provide the selective extraction of radioactive isotopes, such as $^{137}Cs$ from nuclear wastes and by that reducing the problem of nuclear waste storage. Therefore, one of the goals of my doctoral research was the synthesis and testing of novel cesium ionophores [1, 2]. The potentiometric performance characteristics of bis(benzo-18-crown-6)ethers and tiakalix[4]mono-and biscrown ionophores were determined in solvent polymeric membranes. As a conclusion of this work we have found among the tested novel thiacalixcrown compounds possessing $Cs^+$ion selectivity that clearly grade them among the best cesium ionophores ever reported.

While the main asset of the ionophore molecules is their selectivity additional requirements are often formulated by specific application, such as optical activity or attachment to a polymeric backbone for extended lifetime. In this respect I have been involved in the synthesis of potassium selective bis(benzo-15-crown-5)ethers for their application as chromoionophores in direct fluorescent optodes. For the covalent immobilization of potassium ionophores to polymeric backbones I have synthesized a suitable bis(benzo-15-crown-5)ether based ionophore bearing a terminal alkenyl-chain. The compound was attached to both acrylic and vinyl chloride type polymers. The latter compound is the first ionophore ever reported obtained by direct copolymerization of an ionophore and vinyl chloride monomer [3]. Since this compound was the first ionophore grafted on an inert polymeric chain the selectivity, complex stability constants and diffusion properties have been thoroughly studied and determined. All properties were compared with that of the relevant, mobile ionophores [4].

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# ENZYMES FOR IMPROVED HYDROLYSIS OF LIGNOCELLULOSICS

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The considerably low $\beta$-glucosidase activity: FPA ratio of 0.5–0.6 represented by the enzyme complex of *Trichoderma reesei* RUT C30 results in poor hydrolysis potential. To overcome this problem culture conditions were developed to enhance $\beta$-glucosidase production. Mandels' medium supplemented with tris-maleate buffer proved to be efficient for cellulase production with elevated $\beta$-glucosidase activity. $\beta$-Glucosidase activity: FPA ratio of the obtained enzymes were around the optimal on Solka Floc, lactose and glucose carbon sources. Furthermore, there were no considerable changes in maleic acid concentration of cultivations throughout the fermentations, therefore it is tempting to speculate that maleic acid is a kind of $\beta$-glucosidase inductor. In addition, in cultures with tris-maleate buffer pH values varied in a narrow range, thus tris-maleate buffered cultures can be used in shake flask experiments for modelling fermentations running at constant pH.

Tris-maleate buffer system was applied in shake flask experiments to test steam pretreated corn stover, spruce and willow for cellulase production. On steam pretreated corn stover higher cellulase activities could be obtained than on Solka Floc that was used as reference. However, the achieved $\beta$-glucosidase activity was higher on Solka Floc compared to steam pretreated corn stover. On the other two steam pretreated materials lower enzyme activities were reached than on Solka Floc. The produced enzymes and two commercial cellulases (Celluclast 1.5 L and Econase CE) were tested in hydrolysis experiments using the three pretreated materials and Solka Floc as substrates. Generally, the highest yields were obtained using the enzyme produced on steam pretreated corn stover. Moreover, the highest sugar yield was reached on steam pretreated corn stover using the enzyme produced on steam pretreated corn stover. Similar results were obtained in the case of chemically pretreated corn fiber. Significantly higher sugar yields were obtained in the hydrolysis of corn fiber using the enzyme produced on the same substrate *i.e.* on corn fiber than applying commercial cellulases.

It was shown that mannanase and endoglucanase expressed coordinatedly on the examined carbon sources, since a good correlation was observed between the two enzyme activities. This observation might be valuable information to understand the regulation mechanism of hemicellulase genes in *Trichoderma reesei*.

Results of mixed cultivation of *Aspergillus niger* and *Trichoderma reesei* indicate that *Trichoderma* can be used to produce glucose for *Aspergillus* from lignocellulosic wastes, which might be advantageous if cheap raw material is needed for large-scale production of $\beta$-glucosidase by *Aspergillus* species.

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# FRAGMENTATION PROPERTIES OF BRIDGED P-HETEROCYCLES; 7-PHOSPHANORBORNENES, PHOSPHABICYCLOOCTENES AND 1,2-OXAPHOSPHABICYCLOOCTENES

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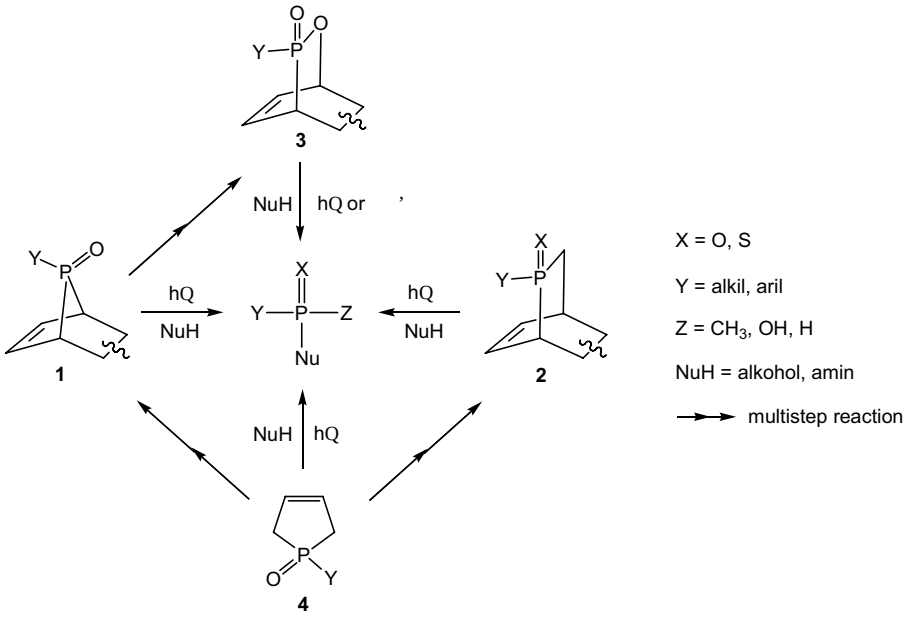
Our aim was to synthesize novel bridged P-heterocycles such as 7-phosphanorbornenes (**1**), phosphabicyclo[2.2.2]octenes (**2**), 1,2-oxaphosphabicyclo[2.2.2]octenes (**3**) and dihydro-1*H*-phosphole oxide derivatives (**4**) to examine their UV light mediated and/or thermoinduced fragmentations. In certain cases 7-phosphanorbornenes could be replaced by the more simple dihydrophosphole oxides (**4**) in the UV-light mediated phosphorylation of methanol, resulting the corresponding H-phosphinates.




Our experimental results suggested that beside the previously proved elimination-addition mechanism, an other, additional-eliminational route might also be involved in the UV-light mediated phosphorylation reaction using phosphabicyclooctenes (**2**) as well as in the thermo-induced fragmentation reaction of 1,2-oxaphosphabicyclooctene derivatives (**3**).

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# DEVELOPMENT OF RECOMBINANT *Pichia pastoris* FERMENTATION

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In spite of the fact that the recombinant *P. pastoris* is capable to grow in a wide temperature and pH range on glycerol, generally 30 °C and pH 5.0 is used for heterologue product formation on methanol carbon source. As a great number of product proteins are sensitive for the degradation by neutral and alcalic vacuolar *Pichia* proteases, lowering the pH of the product formation period seemed to be a desirable strategy to increase product yield. Decreasing the temperature is proven to hinder cell lyses, however it may enhance specific product formation as well. The evaluation of the effect of pH and temperature on the specific growth rate, specific product formation rate, volumetric productivity and product yield was performed by expanding a linear orthogonal design in the range of pH [3.2; 5.2] T [23; 29] °C with a full second order design for pH [5.2; 7.2] and T [17; 23] °C. *P. pastoris* GS115 $Mut^S$ HSA producing strain was used for the experiments. Statistical analysis showed that specific growth rate is practically independent of pH and T, whereas the other variables are significantly influenced by pH and T. These results suggest that the volumetric productivity is determined by the specific product formation rate and not by the specific growth rate in respect of pH and T. By mathematical description of specific product formation rate both itself and the volumetric productivity can be optimized [4, 7]. Two methods were used to characterize specific product formation rate in the function of pH and T: the stepwise decomposition of a full second order model and the application of a formal kinetic description: The formal kinetic model was more adequate in describing the specific product formation rate. The experimental realization of the optimum (pH 5.64 and 20.24 °C) showed the highest specific product formation value (0,379 mg HSA/g CDW/h) in the whole experimental range. The pH and T optima for cell mass production on glycerol and for heterologue protein formation on methanol are different, thus the batch and the fed-batch phase of the *P. pastoris* $Mut^S$ fermentation should be carried out among different circumstances. As the model product human serum albumin was not the target of significant proteolytic degradation, it is assumed that the model and the optimum point clearly characterize the specific product formation rate. In this case the optimum and the normalized model can be used for any extracellular heterologue protein expressed in *P. pastoris* GS115 $Mut^S$, unless the product requires extreme post-translational modifications.

In order to control the methanol concentration in *P. pastoris* fermentations, an $SnO_2$ semi-conductor based system was developed [1, 6]. According to statistical analysis among the parameters which possibly influence the sensor signal, only the surface of mass transfer (lengths of tubing) proved to be significant. The sensor signal was described by a simple mathematical model both in water-methanol system and cell suspension. *P. pastoris* GS115 $Mut^+$ shows classical substrate

inhibition kinetics in the function of methanol concentration. Generally the accumulation of reactive metabolic products of methanol oxidation, e.g. formaldehyde and hydrogen-peroxide are blamed for the decrease of specific growth rate, however the catabolite repression on alcohol-oxidase (AOX) promoters by methanol has been also arisen as a possible reason. In case of *P. pastoris* GS115 $Mut^S$, the specific growth rate was independent of the methanol concentration in the range of [0.45; 8.85] g/L in my experiments. This implies that neither metabolic products have inhibitory effect on specific growth rate, nor methanol has catabolite repression on AOX2 promoter. On the other hand, specific product formation rate was strongly influenced by methanol concentration with maximum measured value at 0.45 g/L. Whereas volumetric productivity is determined both by the specific growth and product formation rate for $Mut^+$ cells, and the optimum is between the maxima of the two specific rates (at 2.1 g/L methanol), only specific product formation determines the maximum of volumetric productivity for $Mut^S$ cells, and thus the two maxima coincide at 0.45 g/L methanol concentration. Specific rates in the optimum points were reproducible in scale-up experiments. The value of maintenance coefficient was determined (0.026 1/h). As the specific growth rate is determined at transcription level through the steady-state concentration of Aox in the cells and no significant metabolic product inhibition is present in $Mut^S$ cells, the decrease of heterologue product formation under the control of AOX1 promoter for the increase of methanol concentration indicates the catabolic repression of AOX1 promoter by methanol. The methanol concentration independence of specific growth rate in $Mut^S$ cells implies that no such catabolic repression is present on AOX2 promoter. This difference in the control of Aox production explains the so far unknown physiological role of the two parallel AOX genes in *P. pastoris* [3, 5, 8].

*Citrobacter freundii* propanediol-oxidoreductase (EC 1.1.1.202) was expressed in active form in *P. pastoris*. The best producing strain was successfully selected by the application of a self-designed and tested quantitative expression selection system. The selected *P. pastoris* SMD1168 strain showed reproducible product formation in spinning test-tube, shaking-flask and stirred bioreactor cultivations, however required complex media components for successful product formation. In optimized fermentation of the selected *P. pastoris* SMD1168/49 strain, we reached the same volumetric productivity as in optimized *Klebsiella pneumoniae* fermentation (10.7 and 10.3 U/L fermentation broth/h, respectively), however the value of specific activity was 15 times higher in case of the recombinant yeast (1540 U/L fermentation broth). The fermentation process of the recombinant strain was scaled-up to pilot scale without decrease in volumetric productivity [2].

It is generally accepted that methanol concentration during fed-batch recombinant *P. pastoris* $Mut^+$ fermentations can be controlled by the change of dissolved oxygen level for periodic methanol addition. In order to investigate the above statement, the model of Zhang and co-workers was completed by an oxygen balance equation. The model treats the assimilatory and dissimilatory methanol pathways separately, using a partition coefficient 'a' to express the share of substrate between the metabolic paths. During the model development and parameter fit process, the

methanol concentration dependence of the oxygen transfer coefficient was experimentally determined and the original value of cell mass/oxygen yield ($Y_{x/MeOH}$) was altered. The most adequate model uses $Y_{x/MeOH} = 0.104$ g CWW/g methanol and a = 0.764 mol $O_2$/mol methanol. The value of the partition coefficient implies the dominancy of the assimilatory pathway and is between the 0.5 value of the model of Ren and the 1.17 value, suggested by Jahic [8]. The mathematical model-based investigation showed that the methanol concentration can not be properly controlled by the dissolved oxygen concentration change for periodic methanol addition. The analysis of variance of the experimental data supplied parallel result with the *in silico* experiments.

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# CHANGES OF BIOLOGICALLY ACTIVE COMPONENTS IN WHEAT SEEDLINGS UNDER CADMIUM STRESS

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Changes of biologically active components in wheat seedlings differing in drought stress tolerance [*Triticum aestivum* L. cv. Chinese Spring (CS; moderately tolerant) and Cappelle Desprez (CD; sensitive)] were studied under cadmium stress conditions. Seedlings were grown in half-strength Hoagland solution under controlled conditions in a growth chamber for 4 weeks, and were exposed to $10^{-7}$ M and $10^{-3}$ M cadmium for 7 days and subsequently cultivated for a 7 day recovery period on Cd-free nutrient solution. Samplings were done at the end of the 7 day stress treatment and the 7 day recovery period. Among growth parameters, the length, the fresh and dry weight and the dry matter content of wheat shoots and roots were measured using standard methods. Chromatography was used for the analysis of the free amino acids and the polyamines, spectrophotometric methods were used for the determination of the guaiacol peroxidase (POD), ascorbate peroxidase (APX) and gluthatione reductase (GR) enzyme activities and the total phenol content, and atomic emission spectroscopy was used for the analysis of the cadmium content. Statistical analyses were carried out using analysis of variances, Duncan test and correlation analysis.

I studied the response of the chosen wheat genotypes under cadmium stress at first. The cadmium exposure caused stunting and chlorosis to the wheat seedlings.

Among the free amino acids, the well-known stress marker proline, among the polyamines, putrescine and spermidine proved to be suitable for distinguishing between the two wheat cultivars differing in drought stress tolerance. CS shoot accumulated 61 times more proline than CD at the $10^{-3}$ M cadmium concentration during the recovery period.

The moderately tolerant cultivar seemed to be much more effective in the ability to eliminate the reactive oxygen species generated during the $10^{-3}$ M Cd stress, due to the induction of the antioxidant defensive system (POD, APX, GR, phenolic compounds), than the sensitive one.

The present findings prove, that the drought-tolerant cultivar tolerated cadmium exposure better than the sensitive one, and the biologically active components play a considerable role beyond this cross-tolerance.

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# INVESTIGATION OF ASYMMETRIC SYNTHESIS ON $\beta$-CARBOLINES

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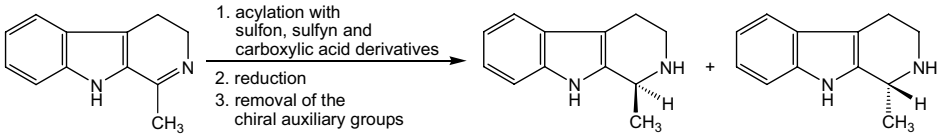
Asymmetric synthesis of 1-substituted $\beta$-carbolines was investigated, using the easily available 1-methyl-3,4-dihydro-$\beta$-carboline (harmalan) as model compound. Acylation of the latter by different chiral sulfonic and sulfinic acid derivatives as well carboxylic acides and chlorides, resulted in substitution at the 2N position or at the methyl group of the harmalan. The new C1 asymmetry center was formed by reduction of the resulting optically active dihydro intermediate. After removal of the chiral auxiliary groups, the enantiomeric excess of the 1*R*- and 1*S*-tetrahydroharman products was studied.




harmalan (1*S*)-tetrahydroharman (1*R*)-tetrahydroharman

In addition the effect of the chiral auxiliary groups, influence of the applied solvent, reagent and catalyst was also examined. For the separation of the intermediate diastereomers, new HPLC and GC methods were developed. The best results (63.8% *de*, 52.4% *ee*) were obtained by reduction of the (1S)-camphanyl derivative.

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# APPLICATION OF X-RAY FLUORESCENCE ANALYTICAL METHODS TO DETERMINE THE COMPOSITION OF ARCHAEOLOGICAL AND ENVIRONMENTAL SAMPLES

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In research fields where non-destructive methods are needed for simultan, multi-element analyses, the X-ray fluorescence spectroscopy is a most-widely applicable analytical method. The quantitative and qualitative analysis of the alloying components in the museum-piece coins and jewellery demands a non-destructive method of measurement where neither the surface nor the images and inscriptions get damaged. All that is ensured by the XRF analytical method.

In the opinion of historians, the possibilities of archaeological research into the early middle ages have, in effect, expired, whereas the investigation of the composition of coins and jewellery may provide new information. Analysing the elements making up the archaeological artefacts makes it possible to compare the objects originating from different ages, and in that way may promote the determination of the place of origin and time of production. Knowing the exact concentration of the main components is generally important, and the identification of trace elements may also help answering archaeological queries.

The first part of Ph. D. dissertation is about the procedures developed for the determination of the concentrations of different metallic components in silver and gold coins. The X-ray fluorescence analysis is an especially matrix-dependent analytical procedure as a result of which almost all kinds of sample require an individual method of quantitative evaluation. In the case of precious metal alloys a strong matrix effect is to be expected because of the high atomic numbers. As the gold and silver pieces have a given shape and structure, preparation of the specimen is not possible: the size and structure of the specimen cannot be chemically adjusted to the given conditions. To eliminate the geometrical differences, various methods were worked out, these methods were compared and the respective advantages and disadvantages were highlighted. To validate the methods, comparative tests were done using prompt-gamma neutron activation analysis, while the accuracy and reliability were checked using gold and silver certified coins and sheets, which were obtained from Hungarian National Bank and from the Institute for Testing and Standardization of Nobel Metals. Identification of the impurities in the silver and gold coins, which are characteristic of the ore mine, was also carried out with this X-ray fluorescence technique.

In the second half of the thesis, a sample preparation process was worked out for the X-ray fluorescence analysis of biological and environmental samples. For the quantitative spectrum analysis of fish, soil and sediment samples, the Canberra AXIL softwer was employed, namely the method of direct comparition of

count rates. To test this method, international reference materials were used (sediment IAEA-SL-1; soil IAEA-SOIL-7, dogfish muscle NRC-DORM-2; dogfish liver NRC-DOLT-2). Comparative studies were carried out with grafit furnace atomic absorption spectometry (GFAAS) and flame atomic absorption spectometry (FAAS) techniques.

With the methods developed for the evaluation of spectra, the compositions of several hundreds of gold and silver pieces as well as that of old jewellery were determined, just as the compositions of different sediment and fish samples. All in all, the result of our work summed up in this dissertation is that our measurement data provide new, valuable information, all practically applicable.

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# SEPARATION OF NON-IDEAL QUATERNARY MIXTURES WITH NOVEL HYBRID PROCESSES BASED ON EXTRACTIVE HETEROGENEOUS-AZEOTROPIC DISTILLATION

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The sustainable development and consumption require the more efficient use of natural resources. The solvent recovery is an important task of such activity to minimize burden upon the environment. Besides the exhaustive use of solvents it reduces also the emissions associated with the incineration of the used solvents. The solvent recovery is usually also an economic solution compared to the case when always fresh solvents are used.

## *New Approach for the Classification of Quaternary Mixtures*

The study of the VLLE of quaternary mixtures is a bit handicapped by the fact that it needs a presentation in the space in a three-dimensional tetrahedral diagram that is in a tetrahedron. This problem can be solved if a quaternary mixture is built up from its ternary sub-mixtures. That would mean that one quaternary mixture consists of four ternary sub-mixtures. Since the ternary mixtures have been already exhaustively investigated and also classified, this way can be followed.

After studying the ten quaternary mixtures that form minimum boiling both homogeneous and heterogeneous azeotropes, several conclusions can be drawn in the change of the character of the nodes if the components are studied in the ternary sub-mixtures or in the quaternary mixture.

## *New Hybrid Separation Processes*

The separation of highly non-ideal mixtures is a complicated problem. It usually needs the hybrid separation technology, which is the combination of different unit operations. These design strategies help for the engineers but due to the complexity of the different separation problems always new design alternatives are needed.

Several industrial case studies show the necessity of the separation of highly non-ideal quaternary mixtures. New separation structures are designed for a more efficient separation of the quaternary highly non-ideal mixtures studied based on the so called extractive heterogeneous azeotropic distillation. This hybrid separation tool is developed to be applied for heterogeneous azeotropes. It combines the advantages of the extractive and the heterogeneous azeotropic distillation. Water is

always present in every quaternary mixture coming form the industry. Since water is usually the heaviest component and form heterogeneous azeotrope with the top products of the distillation it can be used as entrainer in the separation.

The extractive heterogeneous azeotropic distillation units are tested experimentally for each mixture and the agreement of the measured and simulated data gives confidence of the simulation work.

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# THERMOSENSITIVE POLYMER GELS – FROM THEORY TO APPLICATION

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Development of the so-called 'functional materials' was initiated by the needs of new structural materials and rather special industrial expectations and aims. One of the challenging tasks is to manufacture and characterize new multifunctional materials possessing 'intelligence' at the material level. Several scientists focus their attentions on polymer gels.

Polymer gels are cross-linked polymeric networks which swell by imbibing into a high affinity solvent. These gels are unique multifunctional materials for their capability of responding to several environmental stimuli, e.g., temperature, pH, solvent composition or electrical stimuli, etc. Not only the volume of the gel but related properties, like mechanical and optical characteristics may also change as a consequence of the stimulus.

These interesting characteristics of polymer gels may be used in a variety of applications, for instance, in controlled drug release, in molecular separation processes, for tissue culture or as artificial muscles, etc. There are several possible technical applications, like valves, selective absorbers, sensors, actuators, interfaces or large area displays.

The main aim of my PhD work was to modify the volume phase transition temperature of poly(N-isopropylacrylamide)hydrogel (34 °C) and to study the optical properties as a function of temperature. Temperature-sensitive polymer gels and interpenetration networks were synthesized, which show a reduced volume change at their phase transition due to the temperature-dependent interaction between the polymer network and the swelling agent. Alternative polymer gel systems were also prepared. In these systems the phase transition and thus the change of optical properties occur within the swelling agent. The thermal properties of poly(2acrylamido-2-methylpropylsulfonic acid) gels were also studied.

The thermal properties, particularly the temperature induced volume phase transition, of the gels were characterized by cloud point measurements, differential scanning calorimetry (DSC), stress-strain measurements (unidirectional compressing) and swelling degree measurements.

Finally, I succeeded in constructing an intelligent gel-glass that is able to moderate the amount of transmitted light and radiated heat. This environment-sensitive glass, which is composed of a smart hydrogel layer placed between two glass or plastic sheets, becomes opaque when the temperature exceeds a critical value. It becomes transparent again if it is cooled down. The adaptive properties of gel-glasses make them promising materials in protection from strong sunlight and heat radiation. Based on the phase transition of polymer gels, a novel electrically

adjustable window was also developed. These windows substantially reduce glare and thus increase the thermal and visual comfort. Another promising area is their application in greenhouses and hot water supplies for optical and thermal control. These materials are also good candidates for large displays.

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# SUPERCRITICAL FLUID EXTRACTION OF PLANTS AND THE FUNCTIONAL PROPERTIES OF THE EXTRACTS

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Our developed World has a strong demand for creation healthy and less polluted environment using clean technologies and producing solvent residue-free, nutritional foods. These food products must possess natural colour, taste and self-live extensive properties as well as must contain biologically active, health-preventive compounds (e.g. antioxidants, vitamins). Supercritical fluid extraction (SFE) is one of the desirable technologies, which uses carbon dioxide for extraction of essential oils, fatty oils, pigments, and natural waxes from natural sources, mainly from herbs, spices and medicinal plants. The supercritical $CO_2$ extraction is carried out at moderate temperature (mainly between 31–60 °C), therefore thermo-labile compounds can be obtained without any decomposition. The extract is absolutely solvent residual-free as the $CO_2$ is in gaseous state at room temperature.

My goals were applying supercritical $CO_2$ extraction to obtain clean and residual-free plant extracts in which high valued compounds were accumulated. With the aim of further application, the physical-chemical and biological properties of these high valued products were widely mapped. The volatile oil, fatty acid and pigment (carotenoids and cholorphylls) compositions and the antioxidant, antimicrobial properties of the extracts obtained from marjoram (*Origanum majorana* L.), thyme (*Thymus vulgaris* L.), and industrial waste, tomato pomace (*Lycopersicon esculentum* Mill.) were revealed. Traditionally applied extraction methods were compared to the supercritical $CO_2$ extraction. From the three plants the alcoholic extraction resulted the highest amount of extracts, with supercritical $CO_2$ and hexane extractions lower amounts of extracts were obtained. The effects of the process parameters of SFE on the overall yields and on the yields of certain high valued compounds were investigated. Applying a 32 factorial design the experimental results demonstrated that the linear and quadric terms of pressure and the relation between temperature and pressure terms were highly significant on 95% significance level on the yield of marjoram extraction. In the extraction of thyme on the yield of SFE, the linear and quadric terms of pressure, the linear term of temperature and the interactions between these two parameters were significant, while at the extraction of tomato pomace only the effect of temperature was significant on 95% significance level.

The volatile components of marjoram in the extracts were compared. The main components were terpinen-4-ol and ã-terpinene in the marjoram essential oils, in the alcoholic- and in the supercritical extract. The fatty acid compositions of tomato pomace extracts were obtained. The ethanolic and apolaric (*n*-hexane and $scCO_2$) solvent extracts had similar fatty acid compositions, with main components of linoleic- (45.1–51.6%), oleic- (19.1–21.5%) and palmitic acids (16.6–23.5%).

The carotenoid and chlorophyll pigments in the marjoram and tomato pomace extracts were deepen mapped determining carotenoid-rich products. In marjoram the chlorophyll-a and –b and their decomposed compounds such as pheophytin-a and –b green pigments were found in high amount in the ethanolic extracts. Among the carotenoids, marjoram contained only $\beta$-carotene and lutein in higher amount. From tomato pomace high amount of carotenoid-rich extract (34.9 mg carotenoid/100 g d.m. in which the lycopene content is 90.1%) can be achieved applying high pressure and high temperature during SFE.

The antioxidant capacity of marjoram herbs and extracts were obtained and compared in *in vitro* aqueous and lipophilic test systems. The main diterpene and triterpenoid molecules possessing antioxidant activity were quantified in the herbs and extracts of marjoram. The herbs contained ursolic acid in higher amount (708–907 mg/100 g d.m.) and carnosol in smaller amount (56–73 mg/100 g d.m.). Ursolic acid was found mainly in the ethanolic extracts, meanwhile the carnosol was concentrated in the extracts obtained with *n*-hexane and $scCO_2$.

The antimicrobial properties of essential oils and solvent extracts of marjoram and thyme were examined against food-borne and food poisoning fungi and bacteria strains. The antifungal activities and the minimal inhibition concentrations (MICs), at which no fungal growth was observed, were obtained by agar diffusion method against three filamentous fungi *Trichoderma viride*, *Aspergillus niger,* and *Penicillium cyclopium.* The SFE extract of marjoram showed significantly stronger antifungal activities ($MIC_{SFE}$ =0.4–0.5 g extract/100 g medium) than the ethanolic extract ($MIC_{EtOH}$ =5 g extract/100 g medium) against the three tested fungi strains. Among the thyme essential oil and solvent extracts, the essential oil showed the strongest antifungal activity ($MIC_{EO}$ =0.025 g essential oil/100 g medium). The SFE extract at the concentration of 0.04% and the ethanolic extract at the concentration of 1% presented total inhibition against the three food-borne fungi. The antibacterial properties of marjoram and thyme extracts against three health significance and food poisoning bacteria (*Escherichia coli, Pseudomonas fluorescens* and *Bacillus cereus*) were revealed by dilution method following the bacterial turbidity. The antibacterial activity of marjoram ethanolic extract was insufficient, meanwhile the SFE extract at the concentration of 0.4% showed strong antibacterial activities (> 85% inhibition) against the three bacteria. The thyme essential oil at the concentration of 0.1% totally inhibited the three bacteria, while SFE extract at the concentration of 0.1% showed similar inhibition properties except in the presence of *P. fluorescens.* For total inhibition against this species, the SFE extract was used at the concentration of 0.2%. The ethanolic extract showed slight antibacterial activity.

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# EFFECT OF THE MAGNETIC FIELD ON THE ELASTICITY OF COMPOSITE GELS AND ELASTOMERS

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The research in the field of functional materials was stimulated by the expanding use of structural materials and new customer needs. Special attention was paid to polymers which have tunable physico-chemical properties in external electric or magnetic fields. In the Laboratory of Soft Matters at the Department of Physical Chemistry, BME under the leadership of Prof. Miklós Zrínyi magnetic polymergel, a novel composite material has been developed.

This magnetoelastic material contains magnetic micro or nanoparticles in a highly elastic matrix. In a properly chosen external magnetic field this polymer can be elongated, bent, rotated or contracted. The aim of my work in the group was to optimize the influence of the external magnetic field on the elastic modulus of isodimensionally filled poly(dimethylsiloxane) (PDMS) elastomers. Isotropic and anisotropic magnetoelastomers of different crosslink density were synthesized. Carbonyl iron and $Fe_2O_3$ particles were used as fillers. The influence of the external magnetic field on the elastic modulus was systematically investigated in different experimental arrangement to reveal the role of the relative orientation of the magnetic field, the alignement of the particle aggregates and the direction of the deformation.

It was concluded that their magnetic field induced elastic modulus depends on the direction of the deformation and the magnetic field applied, as well as the particle pattern developing in the network. (In case of anisotropic elastomers it depended on the orientation of the particle structure and the direction of the external magnetic field.)

A phenomenological expression was developed to describe the relationship between the elastic modulus on the magnetic induction for the carbonyl-iron and $Fe_3O_4$ (Bayferrox 318M) loaded isotropic and anisotropic elastomers. Within the experimental accuracy the prediction of the phenomenological equation was supported by the experimental data.

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