

**BAŽANT**  
**POSTGRADUATE CONFERENCE**

**2014**



**INSTITUTE OF CHEMICAL PROCESS FUNDAMENTALS OF THE ASCR**

Editor © Magdalena Bendová and Zdeněk Wagner, 2014

Institute of Chemical Process Fundamentals AS CR, v. v. i.  
Prague 2014

## CONTENTS

Mikroreaktorové systémy pro fotooxidační procesy <i>Ing. Ondřej Beneš</i> . . . . .	5
Cílená příprava fotokatalyzátorů pro studium fotooxidačních procesů <i>Ing. Pavlína Dragounová</i> . . . . .	7
Odstraňování fenolových látek z odpadních vod pomocí sorpčních technik <i>Ing. Martina Matějková</i> . . . . .	8
Synthesis of [ <i>n</i> ]Phenacenes for Optoelectronics <i>Ing. Pavel Jakubík</i> . . . . .	9
Structure of Ionic Liquids and their Mixtures with Molecular Solvents <i>Ing. Jan Rotrekl</i> . . . . .	10
An Experimental Assessment of the Evaporation of Ammonium Nitrate Aerosol <i>Nicholas Talbot, MSc.</i> . . . . .	12
Photocatalytic and Photolytic Degradation of 4-Nonylphenol in Two Types of Batch Reactors <i>Ing. Lucie Spáčilová</i> . . . . .	14
Degradation of 4-Chlorophenol in a Photo Microreactor—Comparison with a Batch Reactor <i>Ing. Magdalena Drhová</i> . . . . .	16
Homogeneously Catalyzed Transfer Hydrogenation in Microfluidic Flow Reactor <i>Ing. Jana Pavlorková</i> . . . . .	17
Chiral Stationary Phases Based on Silica Modified by Helicenes <i>Ing. Martin Bernard</i> . . . . .	19
Supercritical Fractionation of Volatiles from Geranium ( <i>Pelargonium graveolens</i> L.) <i>Ing. Martin Topiař</i> . . . . .	21
Extraction of Phytoecdysteroid from <i>Leuzea carthamoides</i> Using High-Pressure Methods <i>Ing. Zdeňka Machalová</i> . . . . .	23
Preparation of Thin Layers of Ferromagnetic Semiconductors <i>Ing. Martin Koštejn</i> . . . . .	25
Physicochemical Characterization of Chiral Ionic Liquids, Their Applications and Environmental Impact <i>Ing. Adéla Andresová</i> . . . . .	26

Wintertime Aerosol Source Apportionment in Prague <i>Ing. Otakar Makeš</i> . . . . .	28
Comparison of Summer and Winter Submicron Aerosol Composition Studied by the Aerosol Mass Spectrometer at an Urban Background Site in Prague <i>Ing. Lucie Kubelová</i> . . . . .	30
Urban and Suburban Intermodal Fraction of Atmospheric Aerosol in Winter 2014 <i>Mgr. Jana Kozáková</i> . . . . .	32
Optical Sensors for Biotechnology and Food Industry <i>Mgr. Lucie Maixnerová</i> . . . . .	34
Novel Apparatus for the Study of Gushing in Beer <i>Ing. Michaela Poštulková</i> . . . . .	36
Combustion of Coal in a Bubbling Fluidized Bed <i>Ing. Tomáš Durda</i> . . . . .	37

# Mikroreaktorové systémy pro fotooxidační procesy

*Doktorand: Ing. Ondřej Beneš  
Školitel: Ing. Olga Šolcová, DSc.*

Mikroreaktorové technologie jsou trendem poslední doby pro výrobu chemických specialit, zejména pro léčiva, kde je důraz kladen na vysokou čistotu a kvalitu produktů. Typický rozměr pro mikroreaktor je pod 1 mm. Díky malému vnitřnímu objemu a vysokému poměru povrchu ku objemu nabízejí tyto technologie mnoho možností a výhod. V mikroreaktorových systémech lze snadněji určit kinetiku, neboť je zde zaručen výborný přenos a kontrola reakčního tepla, hmoty a hybnosti. Přesná kontrola reakčních podmínek je nezbytná nejen pro bezpečný provoz chemických zařízení, ale také pro ekonomiku procesu. Reakce prováděné v mikroreaktorových systémech vykazují velmi vysokou konverzi a selektivitu, což snižuje například náklady na separaci a čištění produktů. Díky nízké době zdržení reaktantů vykazují mikroreaktory vysoký výkon vzhledem k času a objemu, proto jsou tyto systémy ideální pro rychlé a tepelně zabarvené reakce jako například oxidace, hydrogenace či nitrace. Naopak pro pomalu probíhající reakce a příliš viskózní směsi jsou mikroreaktory nevhodné. V neposlední řadě je tato technologie šetrná k životnímu prostředí. V dnešní době se v chemickém průmyslu vyrábějí chemické speciality ve velkých vsádkových reaktorech. To by se však v budoucnu mohlo změnit použitím mikroreaktorových systémů a kontinualizací procesů. Jelikož použitím mikroreaktorů lze získat mnohonásobně menší objem produktů, je snaha o takzvaný numbering up, tzn. o kombinaci několika mikroaparátů, které pracují paralelně ve velkém počtu. Další výhodou by byl ušetřený čas a finance na vývoj a výzkum nových reakcí a tím i jednodušší přenos z laboratorního do výrobního měřítka. Mikro-fotoreaktorový systém Ehrfeld Mikrotechnik BTS byl sestaven pro studium oxidačních a fotooxidačních reakcí. Jako modelová reakce byla zvolena parciální oxidace benzaldehydu na kyselinu benzoovou.

### *Literatura*

1. Fuse, S.; Tanabe, N.; Yoshida, M.; Yoshida, H.; Doi, T.; Takahashi, T.; Continuous-flow synthesis of vitamin D-3. *Chem. Commun.* **2010**, 46, 8722–8724.
2. Kockmann, N.; Roberge, D. M. Harsh Reaction Conditions in Continuous-Flow Microreactors for Pharmaceutical Production *Chem. Eng. Technol.* **2009**, 32(11), 1682–1694.
3. Hanika, J.; Mikroreaktory a vývoj nových technologií. *Chem. Listy* **2010**, 724–725.

# Cílená příprava fotokatalyzátorů pro studium fotooxidačních procesů

Doktorand: Ing. Pavlína Dragounová  
Školitel: Ing. Olga Šolcová, DSc.

Tenké vrstvy oxidu titaničitého a dopovaného oxidu titaničitého byly připraveny nanášením tekutého solu na skleněný substrát. Sol byl připraven sol-gel metodou s použitím reverzních micel jako molekulárních vzorů. Sol-gelové čisté, železem a cerem dopované vrstvy oxidu titaničitého byly nanášeny na skleněný substrát pomocí potahovací, tzv. „dip-coating“, techniky.

Čistý sol oxidu titaničitého byl připraven z neionogenního tenzidu (Triton X-102), cyklohexanu, destilované vody a prekursoru kovu (titanium (IV) isopropoxid TiOP). Pro přípravu dopovaného oxidu titaničitého byl místo destilované vody použit roztok obsahující ionty železa a ceru. K přípravě roztoku pro dopování železem byly použity dva jeho zdroje, a to dusičnan železitý a síran železnatý. Zdrojem ceru byl dusičnan ceritý.

Opakovaným potahováním byly postupně naneseny tři vrstvy oxidu titaničitého na skleněný substrát. Potažená skla schla na vzduchu, organický podíl byl odstraněn během kalcinace. Kalcinace trvala čtyři hodiny při teplotě 450 °C. Strukturní vlastnosti takto připravených tenkých vrstev byly popsány několika charakterizačními metodami, a to Ramanovo spektroskopii, UV-Vis spektrofotometrií a SEM.

## Literatura

1. Kim N. J., La H. Y., Im H. S., Ryu B. K.: *Thin Solid Films* **2010**, 518, 156.
2. Matějová L., Valeš V., Fajgar R., Matěj Z., Holý V., Šolcová O.: *J. Solid State Chem.*, **2013**, 198, 485.
3. Naceur J. B., Mechiakh R., Bousbih F., Chtourou R.: *Appl. Surf. Sci.*, **2011**, 257, 10699.
4. Kuang S., Yang L., Luo S., Cai Q.: *Appl. Surf. Sci.*, **2009**, 255, 7385.
5. Patil S. R., Hameed B.H., Skapin S. A., Stangar U. L.: *Chem. Eng. J.*, **2011**, 174, 190.

# Odstraňování fenolových látek z odpadních vod pomocí sorpčních technik

*Doktorand: Ing. Martina Matějková*

*Školitel: Ing. Olga Šolcová, DSc.*

Možný zdroj kontaminantů představují odpadní vody vznikající in-situ při podzemním zplyňování uhlí (UCG – Underground coal gasification) [1, 2]. Technologie UCG je dobře použitelná u obtížně dostupných loží uhlí, nebo např. u velmi hlubokých loží. Při zplyňování uhlí dochází ke vzniku odpadní vody, ve které představuje významnou skupinu organických kontaminantů skupina fenolů [3]. Tato práce je zaměřena na dekontaminaci simulovaných i reálných odpadních vod po UCG procesu pomocí sorpční techniky.

K odstranění fenolů z kontaminovaných vod byly použity sorbenty na bázi přírodních zeolitů (Bentonit Braňany, Montmorillonit), aktivních uhlí (Supersorbon, Norit) a nanoželezo (Nanofer). Texturní vlastnosti jednotlivých sorbentů byly získány pomocí heliové pyknometrie, rtuťové porozimetrie a fyzikální adsorpci dusíku.

Sorpční experimenty probíhaly nejen v laboratorním, ale i ve čtvrtprovozním měřítku, kde byly sorbenty použity jako sorpční bariéra. Sorpční bariéry byly umístěny ve speciálním průtočném kanálu, který byl pro tyto účely vyvinut. Účinnost sorbentů a jejich sorpční kapacita byla stanovena sorpcí modelových roztoků fenolu o různých koncentracích a to v laboratorním měřítku. Experimenty v průtočném sorpčním kanálu byly prováděny s reálnou odpadní vodou z podzemního zplyňování uhlí. V rámci práce byl také zkoumán vliv různých forem použitých sorbentů na jejich sorpční účinnost.

## *Literatura*

1. Liu S., Li J., Mei M., Dong D.: *Groundwater Pollution from Underground Coal Gasification*, J. China Univ. Mining and Technology, 17 (2007), 467–472.
2. Bhutto A. W., Bazmi A. A., Zahedi G.: *Underground coal gasification: From fundamentals to applications*, Prog. Eng. Combust. Sci., 39 (2013), 189–214.
3. Kapusta K., Stańczyk K., Wiatowski M., Chečko J.: *Environmental aspects of a field-scale underground coal gasification trial in a shallow coal seam at the Experimental Mine Barbara in Poland*, Fuel 113(2013), 196–208.

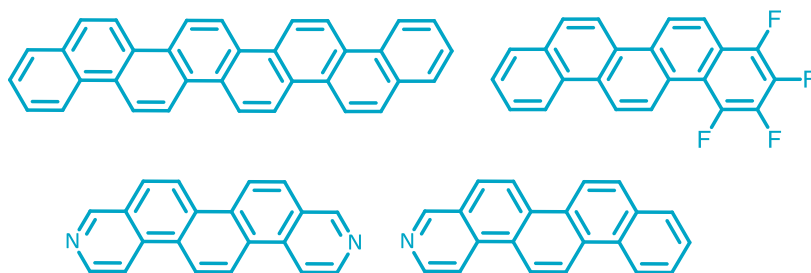


# Synthesis of $[n]$ Phenacenes for Optoelectronics

*Student: Ing. Pavel Jakubík*  
*Supervisor: Ing. Jan Storch, Ph. D.*

$[n]$ Phenacenes are a group of polycyclic aromatic hydrocarbons, which are isomeric forms of linear  $[n]$ acenes. Thanks to their conjugated  $\pi$ -electron system, both of these groups are suitable for usage in optoelectronics (OLED, OFET). But unlike  $[n]$ acenes, attributes of  $[n]$ phenacenes are more promising in practical use. Due to higher stability and preferable semiconductive characteristics in both N-type and P-type semiconductors,  $[n]$ phenacenes can potentially find practical utilization in optoelectronics over  $[n]$ acenes.

The goal of this work was to develop a multigram scale photochemical synthesis of  $[n]$ phenacenes and their derivatives from stilbene precursors. In the past, vast efforts were made to examine  $[n]$ phenacenes-based organic P-type semiconductors, but this work is focused on introduction of electron-acceptor substituents (fluorine, nitrogen, oxygen) into or onto phenacene system (Scheme 1). These substitutions lead to a shift of semiconductivity from P-type to N-type and with their proper choice, semiconductive properties of  $[n]$ phenacenes could be modulated and their use in practical applications can be predetermined.



Scheme 1. Examples of  $[n]$ phenacenes

# Structure of Ionic Liquids and their Mixtures with Molecular Solvents

*Student: Ing. Jan Rotrekl*

*Supervisor: Ing. Magdalena Bendová, Ph. D.*

Even after three decades of intensive research the properties and behaviour of ionic liquids (ILs) are still not described exhaustively. From the variability of ILs structure originates the idea of task-specific ionic liquids (TSILs); by modifying their chemical structure, the properties of ILs can be tailored to a concrete application [1, 2, 3]. The rational design of TSILs requires to have a sufficiently comprehensive thermodynamic description of pure substances and industrially important mixtures. In this way, a starting point and a benchmark for the theoretical description of the studied systems and the base for group contribution method development is provided [4]. Consequently, the theoretical and group contribution methods will enable us to predict properties of new ILs from their chemical structure.

This work addresses an experimental study of novel imidazolium-based ILs synthesized with the aim to expand the knowledge on physico-chemical properties of ILs. Three isomeric ILs, 1-alkyl-3-butylimidazolium bis((trifluoromethyl)sulfonyl)imide (abbrev. [C<sub>4</sub>yC<sub>5</sub>im][Tf<sub>2</sub>N]), where alkyl stands for pentyl, isopentyl, and cyclopentyl, are studied. Density, viscosity and electrical conductivity of these ILs as function of temperature was already measured in previous work [5]. In this work, isobaric heat capacities from 293.15 K to 348.15 K and the temperatures of decomposition of these ILs were acquired.

In addition to the basic thermodynamic characterization of pure compounds, emphasis is placed on the description of mixtures. Due to its environmental importance, the solubility of ILs in water is measured. Because of the hydrophobicity of the [Tf<sub>2</sub>N]<sup>-</sup> the solubilities of the studied ILs in water are low, typically between 10<sup>-4</sup> and 10<sup>-5</sup> in mole fraction. By measuring the properties of homogeneous mixtures it is possible to obtain the excess thermodynamic quantities, i. e. the deviations from ideal behaviour of the mixture as defined by the Amagat law. Excess thermodynamic quantities as function of composition are of a fundamental importance, as they can provide information about

the behaviour of the mixture at the molecular level [6]. For this reason, the excess molar volume and excess isobaric heat capacity will be measured with methanol and acetonitrile.

#### *Acknowledgement*

The author would like to acknowledge the financial support of the Ministry of Education, Youth, and Sports of the Czech Republic (Grant No. LD14090).

#### *References*

1. Plechkova, N. V.; Seddon, K. R. Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev.* **2008**, *37*, 123–150.
2. Davis Jr., J. H. Task-Specific Ionic Liquids. *Chem. Lett.* **2004**, *33* (9), 1072–1077.
3. Ranu, B. C.; Banerjee, S. Ionic Liquid as Catalyst and Reaction Medium. The Dramatic Influence of a Task-Specific Ionic Liquid, [bmIm]OH, in Michael Addition of Active Methylene Compounds to Conjugated Ketones, Carboxylic Esters, and Nitriles. *Org. Lett.* **2005**, *7* (14), 3049–3052.
4. Lei, Z.; Zhang, J.; Li, Q.; Chem, B. UNIFAC Model for Ionic Liquids. *Ind. Eng. Chem. Res.* **2009**, *48*, 2697–2704.
5. Andresová, A.; Storch, J.; Traïkia, M.; Wagner, Z.; Bendová, M.; Husson, P. Branched and cyclic alkyl groups in imidazolium-based ionic liquids: Molecular organization and physico-chemical properties. *Fluid Phase Equilib.* **2014**, *371*, 41–49.
6. García-Miaja, G.; Trocoso, J.; Romani, L. Excess properties for binary systems ionic liquid + ethanol: Experimental results and theoretical description using the ERAS model. *Fluid Phase Equilib.* **2008**, *274*, 59–67.

# An Experimental Assessment of the Evaporation of Ammonium Nitrate Aerosol

*Student: Nicholas Talbot, MSc.*

*Supervisor: Ing. Vladimír Ždímal, Dr.*

*Supervisor–specialist: Ing. Jakub Ondráček, Ph.D.*

The dissociation of ammonium nitrate was investigated under laboratory conditions using a tandem differential mobility analyzer/scanning mobility particle sizer technique. Changes to aerosol size and mass were recorded before and after transportation through a temperature controlled, 2-meter laminar flow reactor. The resultant changes to particle size and mass were then used to determine the dissociation rate, whilst ammonia gas concentrations were also measured simultaneously, on-line.

Four temperature settings were chosen as representative of typical indoor temperatures, whilst three aerosol sizes investigated typifying those of outdoor ammonium nitrate. Flow rates were also altered to allow for different residence times within the reactor, which can then be used as a proxy for outdoor ammonium nitrate penetrating indoors (Fischer et al., 2003, Lunden et al., 2003).

Results show dissociation rates are strongly linked to temperature, as suggested by previous literature, with increasing temperature rapidly increasing rates of dissociation of ammonium nitrate (Dassios and Pandis, 1998). Residence time within the reactor also changes the degree of dissociation, with the increased time spent in the reactor accelerating the rate of dissociation through all temperature regimes. A corresponding increase in ammonia was also observed with accelerated increase in concentration correlating to increasing temperature.

These results have important implications for measurements where ammonium nitrate volatility provides an unwanted positive artifact, possible new particle formation indoors, as well as for preservation research.

## *Acknowledgement*

The financial support of this work by EC through project HEXACOMM (FP7-PEOPLE-2012-ITN, project No. 315760) is gratefully appreciated.

### References

1. Fischer M L, Littlejohn D, Lunden M, and Brown L, (2003), Automated Measurements of Ammonia and Nitric Acid in Indoor and Outdoor Air, *Env. Sci. Technol.*, **37**, 2114–2119.
2. Dassios K.G, Pandis S.N, (1999) The mass accommodation coefficient of ammonium nitrate aerosol, *Atmos. Environ.*, **33**, 2993–3003.
3. Lunden M M, Revzan K L, Fischer M L, Thatcher T L, Littlejohn D, Hering S V, Brown N J, (2003), The transformation of outdoor ammonium nitrate aerosols in the indoor environment, *Atmos. Environ.*, **37**, 5633–5644.

# Photocatalytic and Photolytic Degradation of 4-Nonylphenol in Two Types of Batch Reactors

*Student: Ing. Lucie Spáčilová*  
*Supervisor: Ing. Olga Šolcová, DSc.*

4-nonylphenol belongs to the group of the environmental estrogens that act as the hormonal system of the body. It is present in waste water and sewage treatment plants fail to decrease the content of this compound.

The degradation of 4-nonylphenol was measured in two types of batch reactors: Beaker with  $\text{TiO}_2$  bed (Fig. 1) and Erlenmeyer flask with  $\text{TiO}_2$  on glass beads in suspension (Fig. 2). The initial concentration of 4-nonylphenol was ranged between 8 to 12 ppm.

$\text{TiO}_2$  thin layers were prepared by the sol-gel process controlled in a reverse micellar environment.  $\text{TiO}_2$  was synthesized by the addition of Titanium (IV) isopropoxide into formed inverse micellar solution made of cyclohexane, nonionic surfactant Triton X-114 and distilled water. The molar ratio of cyclohexane/Triton X-114/water/ $\text{Ti}(\text{OC}_3\text{H}_7)_4$  was kept at 11/1/1/1 (volume ratio TX-114/cyclohexane = 0.49). Prepared solution was stirred intensively for homogenization and formation of inverse micelles. Then liquid Titanium (IV) isopropoxide was regularly dropped to the micellar solution during the vigorous stirring.  $\text{TiO}_2$  films were deposited by the four cycles of the dip-coating method. Among the single dip-coating cycles the samples were thermally treated by calcination at 400 °C for 4 hours with the temperature

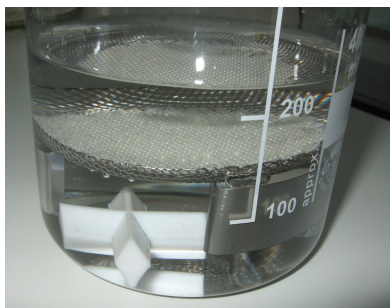


Figure 1. Batch reactor – Beaker with  $\text{TiO}_2$  bed



Figure 2. Batch reactor – Erlenmeyer flask

ramp 1 °C/min in the air flow in a muffle furnace. TiO<sub>2</sub> photocatalyst in the anatase crystalline form possesses surface area 70 m<sup>2</sup>/g with the small content of micropores ( $V_{micro} = 15 \text{ mm}^3/\text{g}$ ) and the layer thickness 340 nm. For photocatalyst activation the medium pressure mercury lamp was used.

Experimental data show involvement of two degradation processes; photocatalysis together with photolysis. Photolytic process generates intermediates with high toxicity and estrogenic activity and therefore is desirable to minimize it. For suppressing of the photolysis process the special glass filter was applied to eliminate UV C and 80% of UV B radiation. The endocrine disruptor degradation activity was compared together with selectivity for both arrangements with respect to the possible applications.

# Degradation of 4-Chlorophenol in a Photo Microreactor—Comparison with a Batch Reactor

*Student: Ing. Magdalena Drhová*  
*Supervisor: Prof. Ing. Jiří Hanika, DrSc.*  
*Supervisor–specialist: Ing. Jiří Křišťál, PhD.*

Application of photocatalyzed reactions in the continuous microreactors successfully combines the advantages of microreactor technology with the light as the clean and traceless reagent. Thin layers in the microreactor allow effective and uniform penetration of light throughout the whole reaction volume (as expressed in the Lambert-Beer law).

Degradation of 4-chlorophenol at presence of sensitizer sulphonated zinc phthalocyanine was tested in the photo microreactor and then compared with batch reactor. The experiments were carried out in the calibrated optical bench. Therefore, both systems had the identical conditions as light source (100 W high pressure lamp), light irradiance, wavelength, pH, and temperature. The continuous photo microreactor had reaction space located between exchangeable 270  $\mu\text{m}$  perfluoroalkoxy spacer and the quartz cover window. The batch reactor represented quartz glass cuvette with the internal dimensions 36  $\times$  20  $\times$  52 mm.

The influence of the different reactions conditions was measured and compared for microreactor and batch reactor. The batch reactor had 74 times longer light path length than the photo microreactor. Thus, the whole reaction volume in the batch reactor could not be uniformly irradiated as in case of microreactor. This fact confirmed experiments with different concentration of sensitizer. In case of microreactor higher concentration of sensitizer had positive effect on reaction rate of 4-chlorophenol degradation. But in batch reactor there was no positive effect at higher concentration of sensitizer on reaction rate.

The performance of both reactors was compared. The comparison was based on the modified reaction ratio  $k^*$  between the photo microreactor and the batch reactor. The value of the  $k^*$  showed approximately 5 times better performance of photo microreactor for polychromatic tests and 2 times for monochromatic tests.



# Homogeneously Catalyzed Transfer Hydrogenation in Microfluidic Flow Reactor

*Student: Ing. Jana Pavlorková*  
*Supervisor: Doc. Dr. Ing. Petr Klusoň*  
*Supervisor–specialist: Ing. Jiří Křišťál, Ph. D.*

Nowadays, microreactor technology is both highly advanced and safe technology offering an accurate control of reaction conditions. High heat, mass, and momentum transfer are ensured by the high active surface to reaction volume ratio. These necessary characteristics are absolutely required by pharmaceutical and fine-chemical industries. The benefits of microreactor technology seem to be profitable for the homogeneously catalysed asymmetric transfer hydrogenations of functionalized  $\beta$ -keto esters. And so we focused our attention to this challenge. As the model reaction the homogeneously catalysed transfer hydrogenation of methyl acetoacetate to methyl hydroxybutyrate was selected. In transfer hydrogenation, the organic molecules (e. g. 2-propanol) are used as the hydrogen donors in the presence of a transition-metal catalyst such as Ru-BINAP complexes as one of the most active and selective catalytic structures.

The application of accurately controlled microreactors to highly sensitive reaction will provide tailored reaction conditions resulting in better process performance, improved utilization of the homogeneous catalyst and increased selectivity.

For the purpose of model reaction, the glass microcapillary reactor was selected. First of all, the microreactor system had to be designed and fully optimized. The microreactor system contains the microfluidic chip that serves as an ideal mixing unit with the integrated staggered oriented ridge mixing elements. The chip is connected to the microcapillary wrapped on the heating cartridge extending the reaction zone of the microreactor system. The whole assembly is closed into the glove-box with nitrogen atmosphere for the prevention of the catalyst contamination due to the sensitivity of Ru-BINAP to oxygen, CO<sub>2</sub> and moisture. For chemical analysis the GC was calibrated and the analytical method established.

Experimental microreactor system is ready for the optimization of the reaction conditions for the model reaction with racemic Ru-BINAP catalyst.

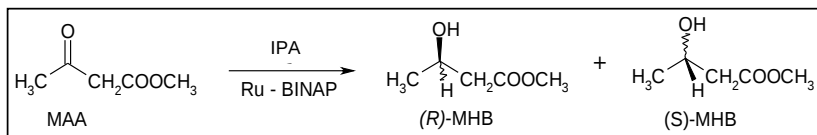
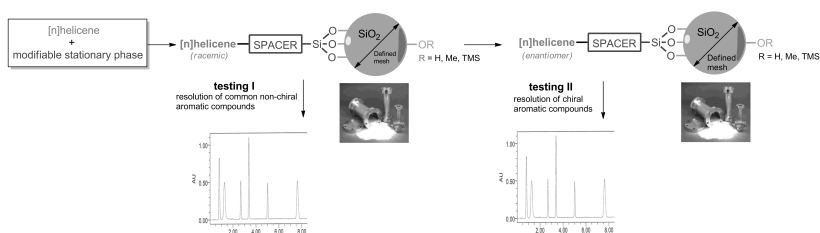


Fig. 1: Simple reaction schema

# Chiral Stationary Phases Based on Silica Modified by Helicenes

Student: Ing. Martin Bernard  
Supervisor: Ing. Jan Sýkora Ph. D.  
Supervisor–specialist: Ing. Jan Storch Ph. D.

Helicenes are inherently chiral *o*-condensed polyaromatic compounds with various potential applications such as chiral selectors in separation techniques. We have developed a multigram-scale synthesis of various helicenes [1] based on photocyclization, some of them purposely derivatized [2] for anchoring on proper matrices via covalent bond. There are commercially available spherical stationary phases of defined parameters, possibly SiO<sub>2</sub> surface is covered by appropriate reactive species enabling diverse approaches to further modifications. Recently, we have prepared silica-based phases modified by various racemic helicenes used for preliminary testing of their general properties (except the studies of *chiral* activity). Both proper stationary phase and helicene are connected together with variable spacer forming the preferred material (suitable for use in non-chiral HPLC). Further, considering the target *chiral* activity of our prepared materials, the most ambitious stationary phase was prepared in the form containing just one enantiomer of helicene. This material is subjected to testing in chiral HPLC and results should show us the way of further optimizing—potential final imperfections of our materials (e.g. spacer length, helicene substitution) are tunable. *Scheme* describing the chronological stages of the process is shown below, current state of knowledge will be discussed.



*Scheme*

### *Acknowledgement*

We appreciate the financial support from the Technology Agency of the Czech Republic (Grant No. TA01010646).

### *References*

1. Storch J., Círka V., Bernard M., Vokál J., Pat. No. 303997/PV 2012–245, applied: 12.04.11.
2. Žádný J., Velíšek P., Jakubec M., Sýkora J., Círka V., Storch J., Tetrahedron 2013, 69 (30), 6213–6218.

# Supercritical Fractionation of Volatiles from Geranium (*Pelargonium graveolens* L.)

*Student: Ing. Martin Topiař*

*Supervisor: Ing. Helena Sovová, CSc.*

*Supervisor–specialist: Ing. Marie Sajfrtová, Ph. D.*

Many green plants contain biologically active substances that are or could be used in pharmaceutical or food processing industry. Rose geranium (*Pelargonium graveolens* L.), an evergreen shrub, is a source of an essential oil used in aromatherapy, skin care, and as a food flavour. In addition to that, several studies also indicated antioxidant and insecticidal activity of geranium extracts [1, 2].

Supercritical fluid extraction (SFE) using carbon dioxide is an innovative green technology for obtaining valuable botanical substances without traces of organic solvents. In contrary to traditional separation techniques, such as hydrodistillation or organic solvent extraction, SFE allows separation of the isolate into several fraction during the extraction.

Focus of this work was on using SFE combined with the different fractionation techniques (additional separator, sorption on silica gel in one step with extraction) in the range of pressures and temperatures (9–30 MPa, 40–50 °C) for enhancement of volatiles in extracts from geranium aerial parts. The efficiency of SFE in terms of composition and yield was compared with hydrodistillation. The composition of volatiles in the isolates was determined using GC-MS and GC-FID.

Major compounds analyzed in SFE isolates were citronellol (17.7% w/w), geraniol (16.9% w/w) and citronellyl formate (8.8% w/w). The extraction yields obtained by SFE at conditions 30 MPa, 40 °C (10 mg/g) and 12 MPa, 40 °C (9.9 mg/g) were comparable with the yield of essential oil (10.1 mg/g) obtained by hydrodistillation, although the concentrations of volatiles in the SFE extracts were lower. Use of additional separator under conditions of 9 MPa and 0 °C led to separation of cuticular waxes and other high molecular substances from the volatile fraction. The fractionation using silica gel as sorbent was effective in terms of separation of citronellol and geraniol within the second fraction, which was obtained by extract desorption with pure CO<sub>2</sub> at 30 MPa and 40 °C.

The validity of using SFE combined with different fractionation techniques as a method for enhancement of extract volatiles' concentration was demonstrated, as well as its advantages over simple extraction. Future work will be focused on optimization of adsorption and desorption conditions during SFE fractionation with several types of sorbents.

#### *References*

1. Mnif, W.; Dhifi, W.; Jelali, N.; Baaziz, H.; Hadded, A.; Hamdi, N.: *J. Essent. Oil-Bear. Plants*, 761–769, 14 (2011).
2. S. Niculau, E.; Alves, P. B.; Nogueira, C. P.; Moraes, R. V.; Matos, A. P.; Bernardo, A. R.; Volante, A. C.; Fernandes, J. B.; Silva, M. F. G. F.; Correa, A. G.; Blank, A. F.; Silva, A.; Ribeiro, L.: *Quim. Nova*, 1391–1394, 36 (2013).

# Extraction of Phytoecdysteroid from *Leuzea carthamoides* Using High-Pressure Methods

Student: Ing. Zdeňka Machalová

Supervisor: Ing. Helena Sovová, CSc.

Supervisor–specialist: Ing. Marie Sajfřtová, Ph.D.

Plant material is a rich source of biologically active compounds. Conventional extraction methods, which are still widely used for isolation of these compounds, have some disadvantages such as a long extraction time and use of a large amount of organic solvent. Therefore, interest in high-pressure extraction methods with minimal consumption of organic solvent to isolate these compounds has increased. Pressurized solvent extraction (PSE) and supercritical fluid extraction with CO<sub>2</sub> as a solvent (SFE) represent two of these methods.

The PSE uses elevated temperature and pressure, which facilitate better penetration of solvent to the matrix pores and offers advantages with regard to extraction time, yields and consumption of solvent. In spite of the high temperature above the normal boiling point of solvent, thermo-labile substances are mostly preserved because of the short extraction time (5–20 min). The elevated pressure is mainly used to keep the solvent liquid.

Contrary to PSE, the SFE is carried out at low temperatures and is mostly used for the extraction of nonpolar compounds, but it is also suitable for the extraction of polar compounds by adding a small amount of organic solvent into the system (as modifier). The SFE is more selective and provides extract of higher purity than conventional methods and also allows isolation of thermo-labile compounds due to the use of low temperature.

A combination of these methods can increase the concentration of polar compounds in the final extract. Firstly, SFE removes the nonpolar compounds, and then PSE should provide a more concentrated extract using the same material.

Phytoecdysteroids are polar compounds located in various plant parts. The most famous ecdysteroid is 20-hydroxyecdysone (20-HE), which is the most abundant ecdysteroid in the adaptogenic plant *Leuzea carthamoides* [1]. The 20-HE is known for its anabolic and tonic effects on mammals and is used as dietary supplement. Moreover, 20-HE

is a steroid hormone responsible for insect moulting and metamorphosis. Therefore, it could be applied to control the harmful insect population in agriculture [2].

This work is focused on the extraction of 20-HE from roots of *Leuzea carthamoides* using SFE, PLE, and Soxhlet extraction. The SFE and PSE conditions (pressure, temperature, concentration of solvent and extraction time) were optimized to improve the extraction yields and concentrations of 20-HE in extracts. These methods were compared with a conventional Soxhlet-type extraction. The SFE experiments were carried out at temperature 40 °C, pressure 30 MPa and with addition of 5–20 % of co-solvent (ethanol). PSE was made at temperatures from 80 °C to 120 °C, pressures from 10 to 30 MPa and static extraction time from 5 to 15 min. Soxhlet extraction with ethanol was used to evaluate the total content of 20-HE in roots. The concentration of 20-HE in extracts was determined by HPLC coupled with mass spectrometry.

In case of PSE, the concentration of 20-HE in extract and total yield of extract were significantly influenced by temperature and extraction time. In the contrary to that, the concentration of 20-HE in the CO<sub>2</sub> extracts and yield of the CO<sub>2</sub> extracts were dependent on the concentration of ethanol in CO<sub>2</sub>.

#### *References*

1. L. Kokoska and D. Janovska, *Phytochemistry* 2009, 70, 842–855.
2. L. Dinan, *Phytochemistry* 2001, 57, 325–339.



# Preparation of Thin Layers of Ferromagnetic Semiconductors

*Student: Ing. Martin Koštejn*

*Supervisor: RNDr. Radek Fajgar, CSc.*

*Supervisor–specialist: Prof. Ing. Pavel Fiala, CSc.*

Recently there is a big demand for finding new materials usable in computing devices for improving performance and power consumption. One group of such materials is called ferromagnetic semiconductors (FMS).

Nowadays there are no industrially produced FMS materials. For using of the spin polarized current it is necessary to add ferromagnetic properties into semiconductor materials. One proposed way is an incorporation of metal atoms (manganese) in a semiconductor from group IV A (silicon or germanium). The incorporated metal should have a half-filled outermost electron shell, which brings the best magnetic moment of an atom.

Highly non-equilibrium conditions are applied for a preparation of Si/Mn or Ge/Mn amorphous materials by a reactive excimer laser ablation. A manganese target is ablated under a low pressure of silane ( $\text{SiH}_4$ ) or germane ( $\text{GeH}_4$ ) by a focused ArF laser beam. The ablated manganese atoms interact with  $\text{SiH}_4$  or  $\text{GeH}_4$  molecules in the gas phase. As a result, thin amorphous silicon or germanium layers with the incorporated manganese atoms (with concentrations up to 50 %) are deposited. The deposited layers are analysed by electron microscopy (both scanning and transmission), X-ray photoelectron spectroscopy and SQUID (superconducting quantum interference device) techniques. An electron diffraction is used for identification of nano-crystallites formed by annealing of the deposit at temperatures up to 1100 °C.

## *References*

1. E. S. Demidov, et al., High-temperature ferromagnetism in laser-deposited layers of silicon and germanium doped with manganese or iron impurities. *J. Magn. Magn. Mat.* 321 (2009) 690–694
2. L. Ottaviano, et al., Room-temperature ferromagnetism in Mn-implanted amorphous Ge. *Phys. Rev. B* 83, (2011) 134426

# Physicochemical Characterization of Chiral Ionic Liquids, Their Applications and Environmental Impact

*Student: Ing. Adéla Andresová*

*Supervisor: Ing. Magdalena Bendová, Ph. D.*

The steady interest in ionic liquids (ILs), salts with melting points typically around room temperature and always below 100 °C, comes from their remarkable physicochemical properties, such as a negligible vapor pressure, high thermal stability, high ionic conductivity, non-flammability, wide electrochemical window, task-specificity, and simpler recycling.

Chiral ionic liquids (CILs) are a subclass of ionic liquids; they are prepared from naturally existing building blocks such as amino acids, hydroxyl acids, sugars, alkaloids and other precursors obtained from the chiral pool. CILs provide an essential alternative to transition-metal catalysts in heterogeneous catalysis, especially the stereoselective hydrogenation [1]. To design and optimize efficient applications of CILs [2], the research of properties of these pure substances as well as their mixtures is necessary. Theoretical chemistry provides another way for understanding the relations between the macroscopic properties and the molecular structure. However, the development and prediction of models and computational simulations is not possible without knowledge of basic experimental data [3]. Moreover, the impact of ionic liquids on the environment is becoming increasingly important. Although ILs have a nearly negligible volatility, the potential hazard to the environment is not. A key indicator in the assessment of environmental risk is partition coefficient 1-octanol/water  $K_{OW}$ .

This study aims to characterize the thermodynamic properties of a homologous series of 1-[(1*R*, 2*S*, 5*R*)-(-)-menthoxyethyl]-3-alkylimidazolium salts with the bis(trifluoromethyl)sulfonylimide anion where the alkyl chain length ranges from methylene to dodecyl. The present range of CILs has an application potential mainly as reaction media and sources of chirality in asymmetric catalysis, but also as antielectrostatic and antibacterial agents. Basic thermophysical and thermodynamic properties of pure ionic liquids, such as their heat capacity, density, and refractive index are studied for determination of influence of the structure and the length of the alkyl chain on their

properties. To evaluate their hydrophobicity and/or lipophilicity, liquid-liquid equilibria in binary systems CIL + water, CIL + 1-octanol, and their partition coefficient 1-octanol/water  $K_{OW}$  are investigated. These parameters may be used as a departure point for the assessment of toxicity, biodegradability and tendency to bioaccumulation [3, 4].

Heat capacities are measured on Setaram  $\mu$ DSCIIIevo microcalorimeter from 293.15 K to 348.5 K. The results show that the heat capacities of CILs increases both with growing temperature and with the length of the alkyl chain. The liquid-liquid equilibrium in binary system CIL + water is determined by a direct analytical method with spectrophotometer detection. The solubility of studied ionic liquids in water is about  $10^{-5}$  mole fraction units.

#### *Acknowledgement*

The author would like to acknowledge the financial support of the Ministry of Education, Youth, and Sports of the Czech Republic (Grant No. 7AMB14PL005).

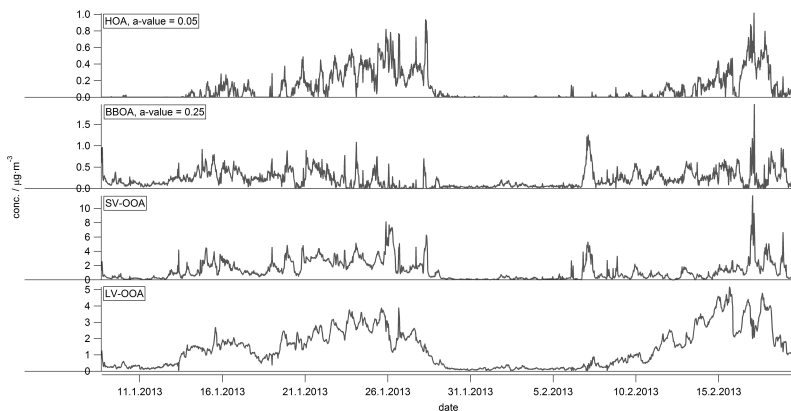
#### *References*

1. Ni B., Zhang Q., Headley A.D. *Tetrahedron Letters* 49 (2008) 1249–1252.
2. Payagala T., Armstrong D.W. *Chirality* 24 (2012) 17–53.
3. Lee B.S., Lin S.T. *Fluid Phase Equilibria* 363 (2014) 233–238.
4. Deng Y., Bess-Hoggan P., Sancelme M., Delort A.-M., Husson P., Costa Gomes M. *Journal of Hazardous Materials* 198 (2011) 165–174.

# Wintertime Aerosol Source Apportionment in Prague

*Student: Ing. Otakar Makeš*  
*Supervisor: Ing. Jaroslav Schwarz, CSc.*

Organic aerosol (OA) is the most abundant but still poorly characterized component of airborne particulate matter. This situation is even more complicated in large cities where many anthropogenic sources of primary organic aerosol (POA) are situated. In recent years, aerosol mass spectrometry has been increasingly applied to obtaining highly time-resolved chemical composition of ambient aerosol. This is considerably important for clarification of organic aerosol life cycles and sources. During six weeks in January and February 2012 the measuring campaign was performed at suburban site Prague – Suchdol. Aerosol data were measured by Aerodyne compact time-of-flight aerosol mass spectrometer (AMS) which is able to characterize chemical and size composition of submicron ( $PM_{1}$ ) fraction.



Organic aerosol data were averaged to 30 min. intervals and analyzed by receptor modelling based on positive matrix factorization. Multi-linear engine (ME-2) (Paatero, 1999) firstly identified set of factors by unconstrained technique. These factors correspond both to primary organic aerosol sources and secondary organic aerosol (SOA). Primary sources include hydrocarbon-like organic aerosol (HOA) from

traffic and OA emitted by coal and biomass burning (BBOA) in local heating. POA portion was ranging from 10% to 30% of organic aerosol. SOA consists of two types of oxygenated organic aerosol differing in volatility. Semi-volatile oxygenated organic aerosol (SV-OOA) shows maximal concentration during the night and minima in the afternoon. Low-volatile oxygenated organic aerosol (LV-OOA) has an opposite daily pattern and is more oxidized than SV-OOA. Retrieved factors were then specified by ME-2 partially constrained technique: a-value approach (Canonaco, 2013).

#### *Acknowledgement*

The financial support by the Czech Science Foundation (CSF P209/11/1342) is gratefully appreciated.

#### *References*

1. Canonaco, F., Crippa, M., Slowik, J. G., Baltensperger, U., and Prévôt, A. S. H.: Atmos. Meas. Tech., 6, 3649–3661, 2013.
2. Paatero, P.: J. Comput. Graph. Stat. 8, 854–888, 1999.

# Comparison of Summer and Winter Submicron Aerosol Composition Studied by the Aerosol Mass Spectrometer at an Urban Background Site in Prague

*Student: Ing. Lucie Kubelová*

*Supervisor: Ing. Vladimír Ždímal, Dr.*

*Supervisor–specialist: Ing. Jaroslav Schwarz, CSc.*

Aerosol particles are proven to affect climate change, visibility and human health. To gain a better understanding of their origin and behavior, it is necessary to describe their chemical composition and number size distribution with high resolution. In the Czech Republic or any of its neighboring countries except Germany, no results have been published from such measurement yet.

This abstract summarizes the results of two measurement campaigns conducted at a Prague background station Suchdol with focus on data from the compact-Time of Flight-Aerosol Mass Spectrometer (c-ToF-AMS). The c-ToF-AMS provides time resolved chemical composition and size distribution.

In order to obtain reasonable mass concentration measured by the AMS, it is necessary to set correct Collection Efficiency (CE), i.e. the fraction of particles that are detected by the instrument from all particles introduced to the system. The probability of particle detection depends mainly on its phase. The main factors influencing the particle phase in the AMS are relative humidity in the sampling line, acidity/neutralization of the sulfate content, and ammonium nitrate content [1].

It was shown that for most ambient environments it is possible to reach reasonable agreement with other measurements by using the CE of 0.5. In order to determine whether this applies for our measurement we compared AMS data with results from Ion Chromatography (IC). We found that for our summer and winter campaign the appropriate CE's were 0.294 and 0.352, respectively. This result was justified by further comparison of AMS data with measurement from Scanning Mobility Particle Sizer (SMPS, TSI) and Organic Carbon/Elemental Carbon Analyzer (OC/EC field instrument, Sunset).

We also applied the Chemical Dependent Collection Efficiency (CDCE) that accounts for the increased concentration of ammonium nitrate and high acidity of the sulfate content. However, the CDCE correction did not lead to a significant change in the agreement between the AMS and IC results.

#### *Acknowledgement*

The authors of this work gratefully appreciate financial support by the Czech Science Foundation under project No. CSF P209/11/1342.

#### *References*

1. Middlebrook, A. M., Bahreini, R., Jimenez, J. L. and Canagaratna, M. R. (2012). Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data. *Aerosol Science and Technology* 46:258–271.

# Urban and Suburban Intermodal Fraction of Atmospheric Aerosol in Winter 2014

*Student: Mgr. Jana Kozáková*  
*Supervisor: Ing. Jaroslav Schwarz, CSc.*

Fine ( $PM_1$ ) and coarse ( $PM_{10-2.5}$ ) aerosols differ not only in size but also in chemical composition, health effects, type of sources, and others. A dividing line between fine and coarse aerosol is not clearly defined. These fractions overlap in the aerodynamic particle size range 1-2.5  $\mu\text{m}$ , also called the intermodal fraction. Sources of both coarse and fine aerosols contribute to the intermodal fraction to a different extent relating to different meteorological conditions and types of locations. According to several studies, the intermodal fraction highly correlated with coarse aerosol in dry areas during high wind speed episodes [1, 2]. In contrast, other studies have shown higher or comparable correlation with fine aerosol [e.g. 3]. The aim of this study is to characterize the intermodal fraction in urban and suburban localities and estimate to what extent fine/coarse aerosol sources contribute to this fraction.

The measuring campaign took place from 5.2.–7.3.2014 at an urban (Radvanice) and a suburban (Plesná) site situated in Ostrava city, Czech Republic. At both sites, aerosol size distributions from 0.5–20 micrometers (5 min resolution) were determined, and daily samples of size resolved aerosol particles were sampled by Personal Cascade Impactor Sampler (PCIS) and Berner Low Pressure Impactor (BLPI).

The results from PCIS showed that the intermodal fraction represented mass range 3–31% of the total  $PM_{10}$  in both locations with higher mass range in the suburban locality. The Table 1 summarizes the statistic characterization of 24 hours concentrations from PCIS.

Table 1: The statistic characterization of 24 h concentrations from PCIS

	Radvanice			Plesná		
	$PM_1$	$PM_{2.5-1}$	$PM_{10-2.5}$	$PM_1$	$PM_{2.5-1}$	$PM_{10-2.5}$
Average ( $\mu\text{g}/\text{m}^3$ )	40.4	3.5	5.1	31.9	3.8	2.4
Median ( $\mu\text{g}/\text{m}^3$ )	38.5	3.0	4.1	27.7	2.8	2.1
Min ( $\mu\text{g}/\text{m}^3$ )	14.3	1.7	2.2	9.1	0.7	0.6
Max ( $\mu\text{g}/\text{m}^3$ )	89.6	10.8	12.2	61.1	22.4	11.3



In-depth aerosol source identification of the intermodal fraction will be conducted with the help of ion chromatography (IC), inductively coupled plasma mass spectrometry (ICP-MS), and transmission electron microscopy (TEM) applied to aerosol samples.

#### *Acknowledgement*

The project is supported by the Czech Grant Agency (P503/12/G147) and the Charles University Grant Agency (274213).

#### *References*

1. Kegler, S.R., Wilson, W. E. and Marcus, A.H.  $PM_{10}$ , intermodal ( $PM_{2.5-10}$ ) mass, and the soil component of  $PM_{2.5}$  in Phoenix, AZ, 1995–1996, *Aerosol Sci. Technol.*, 35 (2001), 914–920.
2. Claiborn, C.S., Finn, D., Larson, T.V. and Koenig, J.Q. Windblown dust contributes to high  $PM_{2.5}$  concentrations, *J. Air Waste Manage. Assoc.*, 50 (2011), 1440–1445.
3. Geller, G.D., Fine, P.M. and Sioutas, C. The Relationship between real-time and time-integrated coarse (2.5–10  $\mu\text{m}$ ), intermodal (1–2.5  $\mu\text{m}$ ), and fine (<2.5  $\mu\text{m}$ ) particulate matter in the Los Angeles basin, *J. Air Waste Manage. Assoc.*, 54 (2012), 1029–1039.

# Optical Sensors for Biotechnology and Food Industry

*Student: Mgr. Lucie Maixnerová*  
*Supervisor: Ing. Gabriela Kuncová, CSc.*

A surveillance of quality and freshness of food as well as regulation of biotechnological process require cheap and fast, online monitoring techniques for a determination of biologically active substances such as biogenic amines, glucose, cholesterol, alcohols, etc.

A biosensor is an analytical device, used for the detection of an analyte that combines a biological component with a physicochemical detector [1].

In my work I focus on optimization of preparation, mathematical description and determination of long-term stability of a sensitive layer (SL) of the enzymatic sensor with optical oxygen transducer for a determination of biogenic amines and glucose.

The biological part of the SL was the immobilized diamine oxidase. This enzyme catalyzes oxidative deamination of biogenic amines, resp. glucose oxidase, which catalyzes the oxidation of glucose. The optical transducer was a ruthenium complex. Fluorescence of this complex is quenched proportionally with oxygen concentration. Sacharose was added as a porogen all components were encapsulated in a UV-curable inorganic-organic polymer Ormocer®. Various SLs were prepared differing in composition and UV-curing time.

The analytical characteristics of SL for the detection of biogenic amine, putrescine, were dependent on oxygen concentration. Sensitivity (S) varied from 0.70 to 6.87  $\mu\text{s.l.mmol}^{-1}$ , the limit of detection (LD) varied from 0.01 to 0.43  $\text{mmol.l}^{-1}$ , the limit of quantification (LQ) varied from 0.04 to 1.43  $\text{mmol.l}^{-1}$  and linear dynamic range (LDR) varied from 0–0.10 to 0–1.75  $\text{mmol}^{-1}$ .

Glucose SL performed S varied from 0.19 to 0.41  $\mu\text{s.l.mmol}^{-1}$ , LD varied from 0.15 to 0.30  $\text{mmol.l}^{-1}$ , LQ varied from 0.50 to 1.00  $\text{mmol.l}^{-1}$  and LDR varied from 0–1.50 to 0–3.50  $\text{mmol.l}^{-1}$ . The analytical characteristics were dependent on SL thickness and UV-curing.

A mathematical model of reaction-transport processes inside the SL was proposed, which revealed qualitative dependencies of the biosensor behavior (S, LD, LQ, LDR and response time) on the thickness of

the SL, concentrations of substrates in the solution, enzyme activity and SL permeability.

Analytical characteristics of SL, both glucose and putrescine, were repeatedly checked during two years (putrescine) and three month (glucose). Within this periods S, LD, LQ, and LDR fluctuated with a relative standard deviation in the range from 5% to 9%.

#### *References*

1. Turner, Anthony; Wilson, George and Kaube, Isao (1987). *Biosensors: Fundamentals and Applications*. Oxford, UK: Oxford University Press. p. 770. ISBN 0198547242.

# Novel Apparatus for the Study of Gushing in Beer

*Student: Ing. Michaela Poštulková*

*Supervisor: Doc. Ing. Tomáš Brányik, Ph. D.*

*Supervisor–specialist: Doc. Ing. Marek Růžička, CSc.*

Gushing is a negative phenomenon when a foam spontaneously gush out when a bottle or can is opened. Despite a long-term research the gushing still has not been fully explained. The problem of gushing is its seasonal variability, depending on the raw materials and processing technology. In addition, gushing intensity may change over the years. Furthermore, gushing also related to the fact that there is no simple and inexpensive method for measuring. The aim of this work was to find a suitable gushing matrix which could be helpful to study gushing in a new experimental pressure equipment. Simple and inexpensive apparatus was built for the study of overfoaming beer. The valve system (placed on the pressure equipment) control outlet/inlet gas and liquid phase. The pressure and temperature sensors can be also connected to the equipment. It is also possible to regulate the rate of decrease gas pressure above the liquid—the sudden reduction ideally simulates the classic opening beer bottles.

# Combustion of Coal in a Bubbling Fluidized Bed

*Student: Ing. Tomáš Durda*

*Supervisor: Prof. Ing. Václav Janda, CSc.*

*Supervisor–specialist: Ing. Michael Pohořelý, Ph. D.*

The greenhouse effect is caused by the so-called greenhouse gases; e. g.,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ . Their concentrations in the atmosphere have recently significantly increased and therefore, in order to stop this increase, the general aim is to limit their sources. The emissions of  $\text{CO}_2$  are produced the most by conventional coal combustion. In terms of the European policy concerning climate changes and energy, the main goal is to reduce the emissions of  $\text{CO}_2$  coming from coal combustion.

For this purpose, it is possible to use one of the following technologies of  $\text{CO}_2$  capture: (1) post-combustion capture, (2) pre-combustion capture or (3) oxy-fuel combustion capture. The technology of **post-combustion capture** is especially suitable for completion of the existing coal-burning facilities. This  $\text{CO}_2$  capture technology is based on the chemical absorption of  $\text{CO}_2$  in an appropriate solvent from the flue gas. **Pre-combustion capture** technology can be used in the Integrated Gasification Combined Cycle (IGCC). Coal is gasified and a so-called producer gas is formed; then,  $\text{CO}$  is converted into  $\text{CO}_2$  during the homogeneous water gas reaction together with the conversion of  $\text{H}_2\text{O}$  to  $\text{H}_2$ . Physical absorption follows in order to separate  $\text{CO}_2$  from the producer gas before its combustion and its use in a gas turbine. This approach benefits from lower volumes of producer gas compared to the resulting flue gasses. The third technology allowing a seizure of  $\text{CO}_2$  is the so-called **oxy-fuel combustion process**. Oxy-fuel combustion is characterized by the utilization of a mixture of pure  $\text{O}_2$  and  $\text{CO}_2$ -rich gas (from the flue gas recycle). The temperature of combustion process is regulated by  $\text{CO}_2$ -rich recycle flue gas instead of being modulated by  $\text{N}_2$  from the air. The  $\text{CO}_2$ -rich recycle flue gas ensures the process of fluidization in the case of the fluidized bed technology. Oxygen is separated from air using the established cryogenic methods.

The presented work deals with oxy-coal combustion process and in addition, with enriched-air-coal combustion. This enriched air is available in industrial practice as a by-product of nitrogen separation from the air. Nitrogen can be obtained from air using vacuum swing adsorp-

tion (VSA) or pressure swing adsorption (PSA) or vacuum pressure swing adsorption (VPSA). Enriched air could be used as combustion gas for the combustion with the heat output of 5–50 MWt.

This work is specifically focused on the comparison of the efficiency of the combustion process and the emission of pollutants under different combustion atmospheres (air, enriched air, pure oxygen). Concerning the efficiency of the combustion process and the emission of pollutants, the best results were achieved when coal was burnt in enriched air atmosphere (30 vol. % of  $O_2$  and 70 vol. % of  $N_2$ ). The oxy-fuel combustion process (with 21 vol. % of  $O_2$  and 79 vol. % of  $CO_2$ ) was evaluated as the least effective process. Coal combustion by air (21 vol. % of  $O_2$  in 79 vol. % of  $N_2$ ) led to better results than oxy-fuel combustion (with 21 vol. % of  $O_2$  and 79 vol. % of  $CO_2$ ), but worse results than the oxy-fuel combustion (with 30 vol. % of  $O_2$  and 70 vol. % of  $CO_2$ ) and of course worse results than the combustion with enriched air.

# Bažant Postgraduate Conference 2014

Proceedings of abstracts

Magdalena Bendová and Zdeněk Wagner (editors)

Layout: Magdalena Bendová and Zdeněk Wagner

Typesetting: Zdeněk Wagner

Published in 2014 by

Institute of Chemical Process Fundamentals AS CR, v. v. i.

Rozvojová 1/135

165 02 Prague 6

[www.icpf.cas.cz](http://www.icpf.cas.cz)