



May, 2009

1. ACE AFTER TEN YEARS

In 2000 a group of French scientists under the leadership of Eric Lichtfouse started to organize a scientific conference on environmental chemistry. Interestingly, this so-called 1st French Meeting on Environmental Chemistry, held in Nancy, received a high international, in particular European attention, although it was originally designed to be a more national event. Since so many European scientists contributed to the success of the conference it was decided to follow the way of organizing a conference series, now under the name *European Meeting on Environmental Chemistry* EMEC. Additionally, the foundation of an European association was initiated two months prior to the meeting and many scientists from UK, Switzerland, Norway, Germany, Italy, Estonia and agreed to support the French initiative by participating in the Board of this new organization. Hence, this was the hour of birth of the ACE, the *Association of Chemistry and the Environment*.

The organization of annual EMECs remained as one of the most important activities of ACE and, consequently, now in 2009 we can celebrate the 10th anniversary of this conference series, which is now a well established event in the European calendar of scientific meetings. In the past nearly ten years, the meeting visited in total seven countries more or less well distributed all over Europe. In detail EMECs took place in

2000 Nancy, France (2000)
Dijon, France (2001)
Geneva, Switzerland (2002)
Plymouth, UK (2003)
Bari, Italy (2004)
Belgrade, Serbia (2005)
Brno, Czech Republic (2006)
Inverness, UK (2007)
Girona, Spain (2008)

and now in 2009 the EMEC series is coming back to France, Limoges. Nevertheless, many European countries and regions are still left and the *Association of Chemistry and the Environment* invites any interested scientist to get in contact in order to discuss the possibility to organize forthcoming EMECs. Contact information can be found on our homepage at www.europeanace.com (or contact directly me: schwarzbauer@lek.rwth-aachen.de).

Jan SCHWARZBAUER

2. WEBSITE UPDATE

The new ACE website was launched in early 2008 and celebrated its first birthday recently! The website is an integral part of what the ACE is trying to achieve and its functionality has been developed to improve its usefulness to ACE members. The Home Page is continually updated with news of ACE and other relevant facts and events, including conferences, so if you have any information that you would like to publicise then please send it to me at mfitzsimons@plymouth.ac.uk for publication on the webpage. The *Journal* link allows you to preview the latest articles accepted for *Environmental Chemistry Letters* (we have had some problems with the RSS feed lately but this is now resolved). The *Collaboration Network* will shortly be finalised, allowing members to find the scientific interests of other members and make contact. This will be facilitated by the website and I will send details on how to access the data as soon as it becomes available. I am looking forward to being updated with requests to publicise your activities and achievement – don't disappoint me!

Mark FITZSIMONS

3. IMPRESSIONS FROM EMEC9 MEETING IN GIRONA

The scientific programme for EMEC9 was based at Escola Politècnica Superior in the Campus Montilivi of the Universitat de Girona. EMEC9 was held between 3rd and 6th of December and attracted a truly international delegation of around 150 people from 30 countries.

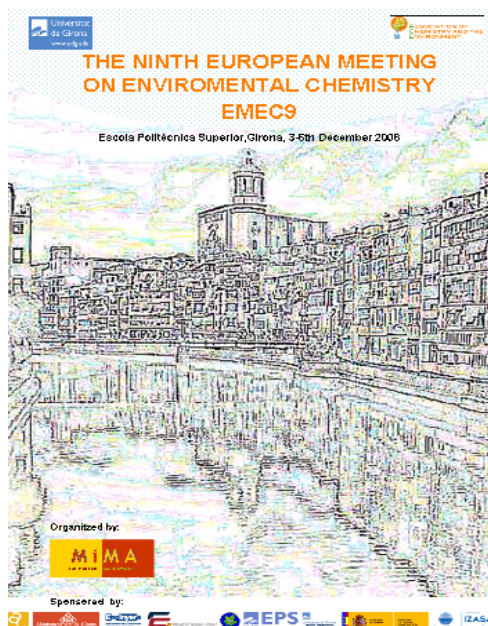


Delegates came from across Europe and countries of further continents including Canada, Australia, South Africa, Morocco,

Saudi Arabia, United Arab Emirates and Egypt.

The aim of the organizing committee was to combine the scientific program and social events that would be of very high scientific level and greatly enjoyable from both professional and personal perspectives. Sessions were dedicated to themes including Ecotoxicology, Emerging Contaminants, Waste treatment and Management, Water treatment and re-use, Analytical Methods for Environmental Science, Clean Technologies and Green Chemistry, Pollutant Chemistry, Soil Chemistry, Soil, Water, Atmospheric Systems and Aquatic and Marine Chemistry. Four plenary lectures given by relevant researchers in the fields of Ecotoxicology, Waste Management, Analytical Methods and Soil Chemistry opened the corresponding sessions. The scientific programme comprised a total of 119 papers from which 54 were oral communications and 65 posters. The high quality of the presentations and their interdisciplinary nature gave the delegates much to learn, discuss, exchange ideas and plan possible collaborations.

From 119 papers, 44 were presented by students and following with the tradition of awarding the best papers presented by young researchers, the EMEC9 prizes awarded by the Escola Politècnica Superior of the Universitat de Girona and ACE were:





The award for the best oral presentation at EMEC9 was given to Malgorzata Piecha for the paper “Cholesterol-lowering skating drugs- an environmental trea?” By, M. Piecha, M. Sarakha, P. Trebse from University of Nova Gorica (Nova Slovenia) and Université Blaise Pascal (France).

Best oral presentation



The award of the best poster presentation at EMEC9 was awarded to Maria del Carmen Hernández-Soriano from the K.U. Leuven (Belgium) and CSIC Granada (Spain), for the poster entitled “Approach to the Chemicals speciation of Cd, Cu, Pb and Zn in an anionic surfactante-soil system with GEOCHEM” by MC. Hernández-Soriano, F. Degryse, E. Smolders, A. Peña, M.D. Mingorance.



Best poster presentation

Accompanying the scientific programme was a full social programme. The welcome reception was the first opportunity to meet delegates who attended previous EMEC meetings. Next, the delegates had many other opportunities to socialize and to have scientific discussions during coffee breaks and lunch time. A guided tour through the Jewish quarter and the narrow streets of the medieval town, allowed the visitors to know part of the culture and history of

Girona. The same day, the social dinner provided the attendants to the meeting a great opportunity to learn and enjoy catalan dancings.



Last day, the farewell lunch held in Golf Girona, with a wonderful landscape was the the best way to close the meeting. We, the organizing committee, were certainly tired but very very satisfied to notice that people had enjoyed their attendance to the meeting and their stay in Girona for few days.

It was a pleasure and a privilege to host all of you and we invite you to participate in EMEC10 in Limoges in December 2009.

Isabel VILLAESCUSA

4. “4th MEETING ON CHEMISTRY AND LIFE 2008”

The **4th Meeting on Chemistry & Life** was organized at the Faculty of Chemistry, Brno University of Technology under the auspices of the rector of the Brno University of Technology, prof. Karel Rais, CSc., MBA., from September 9 to 11, 2008, Similarly as previous meetings it provided a forum for exchange of ideas on recent advances in research and development in chemistry, biotechnology, materials science and environmental technology for people from industry, research and academia, reflecting the specialization of all four departments of the Faculty of Chemistry. In comparison with previous 3rd meeting held in 2005 there was significant increase in the number of participants – 184 from the Czech Republic and 140 from 17 other countries all over the world. In total, 100 lectures and 320 posters have been presented in 7 scientific sessions. It seems that Meetings on Chemistry & Life which

represent one of the activities of the Faculty of Chemistry of the Brno University of Technology, re-established in 1992, found their place in the scientific life of the Czech Republic and their reputation was further improved.

The section of Environmental Chemistry and Technology was probably the most attractive section of the 4th Meeting on Chemistry & Life with greatest number of contributions: 2 plenary lectures, 2 keynote lectures and 12 oral presentations were delivered; poster session consists of almost 90 contributions. It was very hard job for the jury to select the best oral presentation of young scientist and the best poster!

The contribution of European Association of Chemistry and the Environment to the scientific level and to the success of the whole 4th Meeting on Chemistry and Life was significant; two of four plenary lectures at the Meeting were presented by ACE members – Jan Schwarzbauer delivered lecture entitled “Organic anthropogenic contaminants in river systems - complementary environmental approaches” and Branimir Jovančičević read the lecture “Transformation of Petroleum Type Pollutants in the Environment”.

Important part of all scientific events is also social program, which consists of two events. The first one, conference dinner, took the participants to the picturesque South-Moravian village of Mutěnice,



Opening ceremony - from the left: Prof. Jaromír Havlica, dean of the Faculty of Chemistry; prof. Ladislav Omelka, vice-dean for research and science; prof. Karel Rais, rector of the Brno University of Technology; prof. Michal Kotoul, Vice-Rector for Creative Activities, Science and Research

where they spent very pleasant evening in the wine cellar of the Jarošek's family with excursion to wine museum offering the view into the history of wine-making in the Mutěnice region, followed by visit of large wine cellars with wine tasting. The second event was post-conference tour to Moravian Karst, which is the most important karst area in the central Europe, with almost 1100 caverns and gorges, from which only 4 are open to public. Participants enjoyed the view into the Macocha abyss, romantic water cruise on the underground Punkva River and admired unique stalactite and stalagmite decoration in the Pukva cave.



Jan Schwarzbauer - Plenary lecture



Branimir Jovancicevic – Plenary lecture

The 5th Meeting on Chemistry & Life will be organized at the Faculty of Chemistry, Brno University of Technology, in September 2011. All of you are cordially invited to participate at this event!

Josef CASLAVSKY

5. MASS SPECTROMETRY IN XXI CENTURY

If we consider the year 1901, when German physicist W. Kaufmann created the first prototype parabolic mass spectrograph for studying “cathode rays,” as the date of birth of mass spectrometry, this method has recently celebrated its centenary. The 2002 Nobel Prize in chemistry awarded to John B. Fenn and Koichi Tanaka, may be considered as symbolic. It is evident that this award was in no way dated to the jubilee, but was the recognition of the revolutionary changes in the mass spectrometry during the last decade of the 20th century. The most important result of these changes was the onrush of mass spectrometry into studies of thermally labile, nonvolatile, highly polar, and high-molecular-weight compounds. The rapid penetration of mass spectrometry into various life sciences is of particular importance. Now this technique allows studying proteins and peptides, nucleic acids and carbohydrates, even entire microorganisms. These biopolymers were previously practically inaccessible not only to mass spectrometry but to other methods as well. This success was supported by the creation of new unique methods of ionization, ion separation and detection, and the wide introduction of computers. New instruments were developed, so that the basic characteristics of the method (sensitivity, rapidity, resolution, reproducibility, and automation level) were improved. In almost all of the above characteristics, mass spectrometry now surpasses the overwhelming majority of the other methods of analysis. We can hardly find a field of knowledge where mass spectrometry is not used. Nowadays, it is an efficient tool in different branches of physics and particularly chemistry (inorganic, analytical, organic, bioorganic, biochemistry, proteomics, etc.), biophysics, medicine (pharmacology, toxicology, and doping control, diseases diagnostics), geochemistry, petrochemistry, food industry, geology, space research, forensic sciences, environmental studies, hygiene and

sanitary, archeology, control of industrial processes, defense, industrial separation and the investigation of radioactive isotopes, antiterrorist activity, and many other fields. What are the principal general features of the method.

The method allows the determination of the molecular weight of a compound, that is, its important individual characteristic. Knowing the exact molecular weight (high-resolution mass spectrometry), one can determine the elemental composition of compounds even without their isolation from mixtures. The presence of rare chemical elements does not make the task more difficult. The elemental composition may be resolved after just one measurement. This fact significantly distinguishes mass spectrometry in comparison with traditional methods of elemental analysis. Since atomic or molecular mass is a unique characteristic of a substance the method can successfully treat all chemicals, beginning with chemical elements and finishing with the most complex biopolymers. The record measured molecular mass is 110000000 Da [1].

The set of fragment provides information about the structure of the studied substance. Structural elucidation is possible with the computer libraries of mass spectra and "manually", taking into account the known fragmentation laws. Many compounds are now easily identified by their mass spectra using available data bases. The last versions of commercial computer libraries contain several hundred thousands of mass spectra, allowing the identification of the studied compound within several seconds. The NIST/EPA/NIH mass spectral library is most efficiently used in the electron ionization mass spectrometry; the last NIST05 version was issued in 2005. The library contains 190825 spectra for 163198 compounds. In addition, it contains 120786 published and estimated gas-chromatographic indices for 25728 compounds and 5191 MS/MS spectra for 1920 primary ions.

Mass spectrometry is characterized by an extraordinary sensitivity and, in many

cases, can be used as an outstanding tool for the quantitative analysis. Routine instruments require 10^{-12} g or 10^{-14} M of an individual compound. The attained sensitivity records are as low as 10^{-18} g or 10^{-21} M. Fig. 1 proves the detection of 800 yoctomoles (800×10^{-24}) of des-Arg⁹-bradykinin [2] in the sample. Taking into account Avogadro number (6.022×10^{23}) one can realize that mass spectrometry has approached the absolute theoretical limit of a chemical analysis. In the presented case there were only 480 molecules of the peptide in the sample.

Mass spectrometry offers a unique possibility for the direct qualitative and quantitative analysis of the most complex mixtures of organic compounds (to several thousand components) using combinations of a gas or liquid chromatography, capillary electrophoresis, or their multidimensional versions with mass spectrometry in the real-time mode. Methods of tandem mass spectrometry in the analysis of mixtures in some cases do not require the use of additional separation techniques. Fig. 2 represents a GC-GC-MS analysis of a light diesel in water before and after its treatment with sodium hypochlorite [3]. More than 2000 individual compounds were identified and quantified. Each peak represents an individual compound, while its volume on the three-dimensional picture is proportional to the quantity of this compound in the mixture. The results (Fig.2) provide also reliable information on the reaction activity of various classes of hydrocarbons. Thus the levels of inactive alkanes and naphthenes did not change after the aquatic chlorination. Fifty percents of the more reactive alkylbenzenes transformed to the corresponding chlorinated derivatives, while the most reactive alkyl-naphthalenes completely disappeared with formation of the most various chlorination products.

Mass spectrometry provides the highest speed of analysis. For example, time-of-flight (TOF) analyzers with a registration speed of up to 500 full spectra per second ensure the qualitative and quantitative determination of 150 priority organic

pollutants in 8-10 min. Thus, completely automated procedure of environmental monitoring may be realized in 24-hour non-stop regime. Similar approach may be used to detect hundreds of pesticides, by-products or diseases biomarkers in the most various samples.

For a long time a disadvantage of mass spectrometry was related to the necessity of sample preparation, which in some cases may be quite complicated. In 2004, a new method was reported. It deals with bombardment of a surface with a flow of charged electrosprayed solvent drops directly in air [4]. The method was named desorption electrospray ionization (**DESI**). The microdrops hitting the surface desorb ions of different organic compounds (from low-molecular to proteins) (Fig. 3). The resulting gas-phase ions are sucked into the mass spectrometer and analyzed. An advantage of the method is the absence of the sample preparation. Any surface (metal, plastic, paper, soil, animal tissues) can be treated. For example, an experiment on the determination of medical preparations in a human body by directing charged drops of water-ethanol mixture at a human finger was described in [4]. The method opens up new horizons for the use of mass spectrometry in pharmacology, medicine, and ecology, both under stationary and field conditions. Forensic examinations and antiterrorist applications of this method are highly important. Luggage screening at airports for traces of chemical and biological agents or drugs can easily be carried out using stationary devices.

Similar approach using accelerated metastable atoms of inert gases is used in DART method (direct analysis in real time). Again, the absence of sample preparation accompanied by highly reliable analysis of individual chemicals makes this method extremely perspective. Fig.4 represents the detection of drugs on the banknote. The time of analysis is actually 1 second.

Mass spectrometry proved itself as a powerful tool in the taxonomic studies. A lot of work has been done on the fast and reliable detection of microorganisms [5].

For example, Fig.5 represents matrix assisted laser desorption/ionization (MALDI) mass spectra of the closely related *Arthrobacter* bacterial strains. Although classic microbiological distinguishing between these species is quite a challenge, their mass spectrometric identification is simple and obvious [6]. Same approach may be used to study animals. Thus the differences in the peptide profile (skin secretion) of the same species (*Rana ridibunda*) inhabiting Moscow region with moderate climate and Kolkhida region with humid subtropical climate is quite obvious [7].

Imaging mass spectrometry is a unique technique, allowing studying of chemical compounds directly in animal (human) tissues. In one analysis it is possible to establish the spreading of the applied pharmaceutical (in the mouse brain, Fig.6), the spreading of its metabolites and of the peptides developed by the organism in response [8].

References and notes

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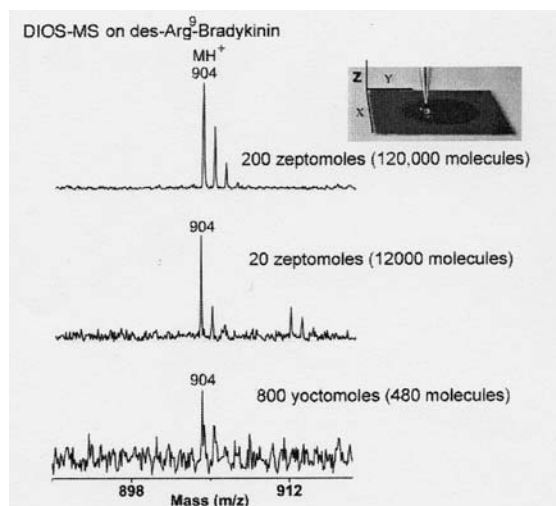


Fig.1. Desorption ionization on organic silicon mass spectra of various quantities of des-Arg⁹-bradykinin.

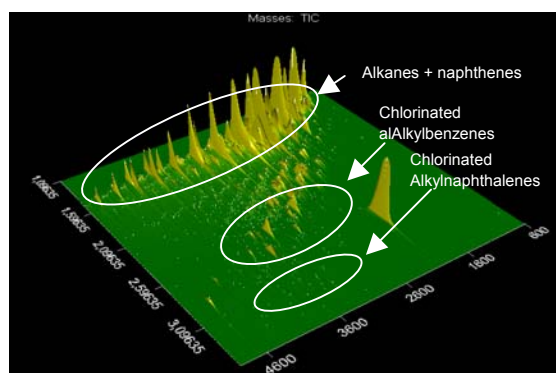
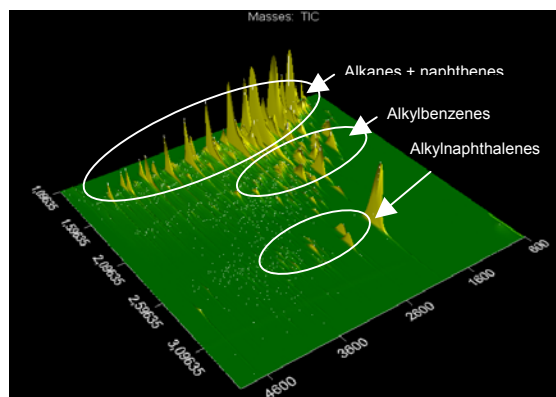


Fig.2. GC-MS analysis of the light diesel in water before (up) and after (down) its treatment with sodium hypochlorite [3].

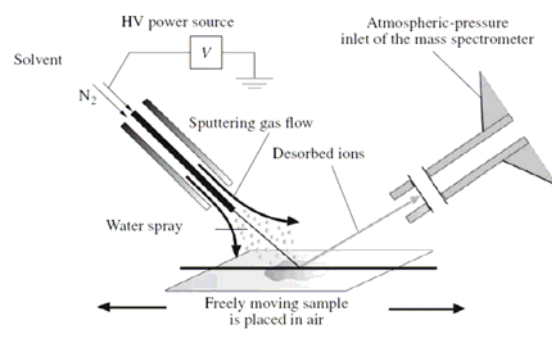


Fig.3. A conceptual sketch of the method of desorption electrospray ionization (DESI).

DART – direct analysis in real time

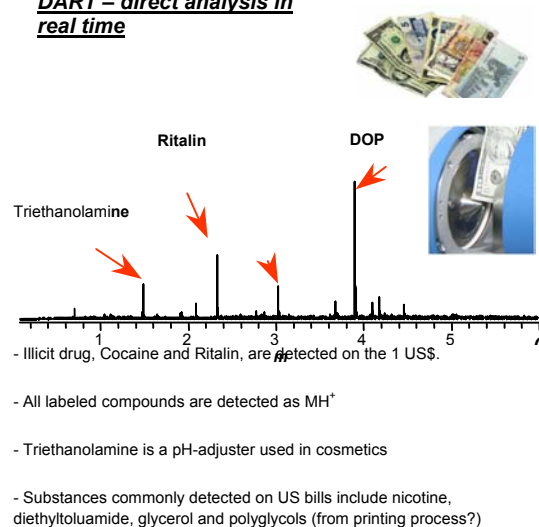


Fig.4 DART analysis of a banknote for the presence of illicit drugs.

Comparative study of 11 strains of *Arthrobacter* family (b)

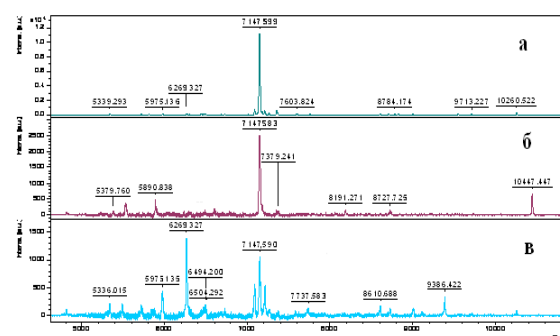


Fig.5. MALDI-profiles of *Arthrobacter* strains on sinapinic acid as a matrix (a – *A. nicotinae*, b – *A. polychromogenes*, B – *A. sp.* KM-4).

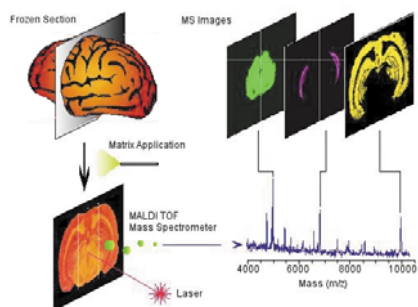


Fig.6. Imaging mass spectrometry. Analysis of compounds of interest in the animal tissues [1].

Albert T. LEBEDEV

6. DEGRADATION PRODUCTS OF SYNTHETIC POLYMERS: POTENTIAL THREAT FOR THE ENVIRONMENT

Josef Čáslavský, Daniela Mácová, Milada Vávrová, Helena Zlámalová Gargošová

Synthetic polymers are widely used due to their excellent properties which can be “tailored” with respect to their planned use. The total amount of synthetic polymers produced and used all over the world is constantly increasing.

At the end of their life cycle great part of the polymer containing products is disposed on the waste dumps, where they remain mostly for very long time, because they are commonly resistant against the natural decomposition processes. Therefore, polymers with increased biodegradability are proposed and synthesized with the perspective of shorter decomposition period after being disposed. On the other hand the production of degradation products is correspondingly higher. From this point of view it would be very useful to evaluate the possible environmental effects of these degradation products.

In our study we focused on polyurethanes, which represent the 6th most abundant polymer and their worldwide production exceeded 10 mil. of tons in 2003 and is constantly increasing. Approximately 1/3

of the world production takes place in the North America, 1/3 in Europe and the rest in the remaining areas. The properties of polyurethane could vary in extremely wide range; very popular are flexible polyurethane foams used in upholstery and rigid foams used as insulation foam, showing density of 6 kg/m³. On the contrary solid polyurethane elastomers with density of 1,200 kg/m³ are used e.g. for the production of print rollers.

The fate of polyurethane based products in Europe was described in 2004 [1]. From the whole production approximately 5 % is recycled and almost the same amount is incinerated. Remaining 90 % is deposited on various landfills.

In our study we focused our attention on the polyurethanes with enhanced biodegradability, which are studied at the Institute of Material Science of our Faculty. The samples were synthesized by the reaction of 2,4-toluene diisocyanate with polyether polyol at the presence of catalyst, surfactant and water. Part of synthetic polyether polyol (from 1 to 30 %, v/v) was substituted by bio-originated and biodegradable polyols: carboxymethylcellulose, cellulose acetate, acetylated potato starch, 2-hydroxyethylcellulose and hydrated wheat protein. PUF without additives was used as the reference. These materials were subjected either to natural degradation under natural conditions, or to accelerated degradation using hydrolysis or photodegradation under UV-light. Resulting degradation products were subjected to ecotoxicological testing using Thamnotoxkit FTM and *Sinapis alba* root growth inhibition toxicity test. Individual degradation products were identified by chromatographic methods connected with mass spectrometry.

In comparison with reference PUF foam the hydrolytic degradation products of model foams showed different ecotoxicity. The PUF containing hydroxyethylcellulose showed the worst effects with mortality twice higher than the reference sample; on the other hand PUF with acetylated starch toxicity was half of the reference PUF. Root growth inhibition toxicity test

showed stimulation in all cases with one exception (addition of 30% of carboxymethylcellulose, 100% concentration of tested solution).

Non-volatile hydrolytic degradation products were identified by HPLC/ESI-MS. In this category various fragments of the polyurethane chain were found, the influence of biodegradable polyol was not important. Volatile photodegradation products were sampled by SPME using polydimethylsiloxane and polyacrylate fibres and analysed by GC/MS. Again, wide range of various degradation products was found; some of them were found independently on the type of biodegradable filler (e.g. methyl-tetradecanoate, 2-ethylhexanoic acid), some were markers of the filler used – e.g. cellulose acetate was characterized by dicyklohexylmethylamine, carboxymethylcellulose by bis(2-ethylhexyl)ester of hexandioic acid. In the case of cellulose based fillers also the presence of highly toxic 2,4-toluene diisocyanate was proved.

In the near future we plan to extend our findings from qualitative to quantitative basis using photodegradation flow-through experiments. We also plan to evaluate other types of biodegradable fillers.

Acknowledgement: This work was supported by the grant MSM 0021630501 from the MSM of the Czech Republic.

References: Ron Zevenhoven, Ph.D. Thesis, Helsinki University of Technology, 2004

7. COOPERATION BETWEEN AMERICAN AND SERBIAN CHEMICAL SOCIETIES IN ENVIRONMENTAL CHEMISTRY

Two years ago, the American Chemical Society invited several younger scientists from Serbia, Croatia and Montenegro to attend a PITCON conference. Accepting the kind invitation, a group of nine chemists from these Balkan countries participated in the Chicago (USA) PITCON Conference held in February 2007. In addition to presenting their papers, they used the occasion to get

acquainted with other participants of this widely known conference as well as with several high officials of the American Chemical Society, and to discuss scientific problems of mutual interest, particularly in the field of environmental chemistry and protection. The discussions resulted in a general initiative aimed at improving scientific cooperation between American and Balkan countries' chemical societies.

The preliminary Chicago contacts were followed by an invitation of the Serbian Chemical Society to Dr. Jurgen H. Exner, chairman of the American Chemical Society Environmental Division, to visit Belgrade, Serbia. Accompanied by his wife, Dr. Exner visited Belgrade in June 2007, and delivered a few lectures at the Department of Chemistry and the Department of Technology and Metallurgy of the University of Belgrade. After the visit to Belgrade, Dr. Exner was joined by Professor George P. Cobb from Texas Tech University and they both attended the Regional Conference on Environmental Chemistry held in Miločer, Herceg Novi, Montenegro. The participants at the same regional conference were also Professor Ivanka Popović, ex-vice president and now the president of the Serbian Chemical Society, and Professor Branimir Jovančičević, chairman of the Environmental Chemistry Section of the Serbian Chemical Society. That was a good occasion to continue talks on ACS-SCS cooperation, which eventually resulted in a suggestion that an agreement on scientific cooperation between the two environmental chemistry divisions should be made.

Finally, on July 2008, an AGREEMENT OF MUTUAL COOPERATION was signed by the chairmen of the corresponding divisions and the presidents of the American and Serbian Chemical Societies. Based on this Agreement, Professor Dionysios Dionysiou from the University of Cincinnati, Professor Mark Nanny from the University of Oklahoma and Dr. Jurgen Exner shall visit Belgrade to participate in a Serbian Chemical Society Seminar entitled „Energy and

Environment“, to be held in Belgrade on June 19, 2009.

On the other hand, Professor Ivanka Popović, Professor Branimir Jovančičević and Dr. Bojan Radak were invited by the American Chemical Society to participate in a Symposium organized by the ACS Division of Environmental Chemistry at the 238th National Meeting of the American Chemical Society, to be held on August 16–20, 2009 in Washington, DC.

It is hoped that the initial cooperation between the two chemical societies will progress to the benefit of environmental chemistry and protection.

Branimir JOVANČIČEVIĆ