

Book of Abstracts

COST action D32 Mid Term Evaluation Meeting

Book of Abstracts: COST action D32 Mid Term Evaluation Meeting

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Welcome

COST ACTION D32
Chemistry in High-Energy Microenviron-
ments

Hamburg, JUNE 7th - 8th 2006

Mid Term Evaluation Workshop

Satellite Event to 10th Meeting of the
European Society of Sonochemistry

Organisers

Local Organisers:

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Support

The meeting is Supported by COST :

European Cooperation in the Field of Scientific and Techno-
logical Research

In the domain of **Chemistry and Molecular Sciences and**
Technologies

within the Action D32

Frame Programme

Wednesday 7th June 2006

Afternoon: arrival and social events with ESS, putting up of posters, evening meal

Thursday 8th June 2006

8.30 am Putting-up of remaining posters (posters are available for inspection throughout proceedings)

9 am Introductions:

COST Science Officer - Hannelore Roemich

Chair D32 - David J. Walton

Local Organiser - Uve Neis

9.30 am Oral reviews- Working Groups

WG 2: Andreas Thiem

WG 3: Cristina Leonelli

10.30 am Coffee and posters

11.00 am Oral reviews - Working Groups

WG 4: Joze Gonzalez-Garcia

WG 5: Antonio Canals

WG 6: Giancarlo Cravotto

12.30 Lunch and posters

13.30 Oral reviews - Working Groups

WG 7: David H. Bremner

WG 8: Thimoty J. Masson,

WG 9: Robert Mettin

15.00 Tea and Posters

15.30 Oral reviews -Working Groups

WG 10: Dariusz Bogdal

WG 11: Andrea Zille

16.30 Conclusions

Chair, Science Officer, Assessors, TC Rapporteur

17.15 Management Committee Meeting and parallel poster session

20.00 Evening Meal

Friday 9th June 2006

Departure

Programme

Thursday, 8 June

Introductions

COST Science Officer - H.Roemich

Thursday morning, 8 June, 9:00

Oral reviews - Working Groups

Thursday morning, 8 June, 9:30

9:30

Oral

High-energy micro-environments in biotechnology: year 2006 update

Andreas Tiehm

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Non-traditional techniques creating high-energy micro-environments represent novel options for hazardous waste treatment, pollutant degradation, water purification, conversion of biomass, and disinfection. These techniques can be applied as stand-alone measures or as novel components of multi-disciplinary approaches. In particular in combination with microbiological approaches, there is a high potential to improve economical and technological efficiency. A sufficient understanding of the specific chemical reaction mechanisms including possible side reactions and of the interactions with microorganisms and enzymes is a pre-requisite for optimized integrated approaches. The working group focusses mainly on ultrasound and electrochemistry in environmental biotechnology and bioengineering. The activity of microorganisms and enzymes are studied in the presence of ultrasound and electric fields, and after pre-treatment of dissolved pollutants or solid waste.

In recent years, significant progress has been achieved in the following areas:

- Disintegration of sewage sludge: new ultrasonic reactors and treatment concepts resulting in a significantly reduced energy consumption
- Application of ultrasound in combined disinfection processes: demonstration of efficient removal of algae and bacteria; reduced requirements for chlorine
- Pollutant removal: new insights in ultrasonic reaction mechanisms; demonstration of reduced biotoxicity after

ultrasonic pre-treatment

- Application of electrodes in biochemical synthesis: increased product yield by the integration of electrokinetic processes
- Electrodes in environmental remediation and waste water treatment: reduction of energy consumption in electrochemical pollutant degradation; feasibility demonstration of bio-electro-remediation of contaminated sites

The presentation will summarize COST D32 "working group 2" activities and highlight some recent findings.

10:00

Oral

Ultrasonic and Microwave Assisted Synthesis of Nanometric Particles

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Coffe break and posters

Thursday morning, 8 June, 10:30

Oral reviews - Working Groups

Thursday morning, 8 June, 11:00

11:00

Oral

Electrochemistry with ultrasound: Report on WG4 activity

Jose Gonzalez-Garcia

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The research of the Working Group "Electrochemistry with ultrasound" concerns the application of ultrasound to electrochemical systems. It builds upon earlier collaborations in the field to now address significant practical issues, while at the same time maintaining the important level of mechanistic underpinning necessary to best benefit the widest range of practical applications.

Electrochemical processes of considerable socio-economic importance include electrosynthesis, electroanalysis, electrocatalysis, electrodeposition, electrodisolution and corrosion and there are applications in synthesis, environmental science, biotechnology, catalysis, sensor science, polymers and other major industries and technologies. A particular environmental benefit is that electrochemistry is a clean technology that allows waste minimisation, sustainability and pollut-

ant degradation.

The laboratories in the Working Group offer a range of different electrochemical methodologies, from microscale analytical studies in real-life media, through to scale-up of synthetic processes, in all of which we notice effects due to ultrasound. In this presentation the achievements from the research groups are presented.

11:30 Oral

Microwaves and Ultrasound Activation in Chemical Analysis

Antonio Canals

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An itemized description of activities of the working group D32/0005/04 ("Microwaves and Ultrasound Activation in Chemical Analysis"), which will address the overall science of the working group, will be presented.

12:00 Oral

Ultrasound and Microwave in the Synthesis of Fine Chemicals: A "Relay Race" or a "Tandem"?

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The production of fine chemicals requires efficient synthetic protocols characterized by high regio-, chemo- and stereoselectivity, the activation of poorly reactive substrates and side products formation to be kept to a minimum. A reduction of catalyst loading is also mandatory to avoid the risk of metal or ligand contamination in the final product. A way to achieve this goal is to resort to heterogeneous catalysis using solid or supported catalysts (1), and so minimize the amounts of transition metal that are present in solution. To this end high-intensity ultrasound (US) can play a fundamental role owing to its ability to activate catalysts and disperse them in the system. In the last few years the development of synthetic protocols employing microwave (MW) (2) and US (3) has determined an epoch-making change in organic synthesis. These techniques can dramatically speed up organic reactions and activate poorly reactive substrates. Both are providing new answers to the stringent imperative to decrease the output of industrial waste and to develop clean technologies, e.g. the possibility of carrying out reactions without solvents under MW or in heterogeneous systems under US (4). In these ways

they can greatly contribute to a program of sustainable chemistry through the use of less toxic solvents and reagents, the gains in selectivity and energy savings. This program overlaps the application domain of the most versatile among green solvents, namely the room-temperature ionic liquids (RTILs), whose synthesis itself can be efficiently promoted under US (5) and/or MW irradiation (6). Combined irradiation with US and MW is a very promising innovation. Especially in heterogeneous catalysis, additional effects are to be expected when the large amount of energy released by cavitation collapse (causing particle fragmentation and molecular excitation) is associated with MW dielectric volumetric heating. This combination of energy sources can promote or improve a number of chemical processes such as synthetic reactions, extraction of natural matrices and sample preparation for chemical analysis. Because of technical hurdles it has not been systematically investigated as yet (7). In the synthesis of fine chemicals we can exploit US or MW alone in "relay race", choosing the appropriate technique for each single step; or use both of them in "tandem" in combined reactors (Fig 1). Results, type of collaboration and synergy within the working group will be discussed.

References

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Lunch and posters

Thursday afternoon, 8 June, 12:30

Oral reviews - Working Groups

Thursday afternoon, 8 June, 13:30

13:30 Oral

Report by the Cavemen (WG007)

David H. Bremner

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This talk will describe the work carried out so far by the WG007 (Cavemen) regarding papers published, meetings at-

tended, collaborations, STSMs hosted and other matters relating to COST D32. WG007 has been expanded to seven members all of whom are involved in the use of ultrasound for wastewater remediation.

There were seven objectives in the original work plan and these have largely been achieved:

1. Establishment of a database and website for references to ultrasound/ cavitation/AOP: **The former has been started although the website has not been established.**
2. Examination of the effects of different wavelengths of ultrasound on the degradation of real polluted waters: **Some progress has been made.**
1. An investigation into the use of acoustic and hydrodynamic effects, both separately and together, for the degradation of organic compounds: **Considerable work has been done on the former and the latter is about to begin.**
2. Study ultrasound/cavitation techniques in conjunction with added reagents such as hydrogen peroxide/ozone/singlet oxygen on the degradation of organic pollutants: **Most of the work done in the group has concentrated on this area.**
1. Investigate cavitation techniques in conjunction with UV and/or electrochemistry: **As yet little work has been done on this objective.**
1. Examination of ultrasonic/cavitation techniques for use in continuous catalytic oxidation of pollutants: **Much work has been reported in this area.**
1. Organisation of a conference relating to cavitation/AOP/water treatment: **Planning has begun.**

Since 2004, members of WG007 have published 24 peer reviewed journal papers and patents and presented talks at 15 conferences. There has been one STSM (Stefano Di Carlo from Torino to Dundee) and joint publications with (a) Christian Petrier and Nilsun Ince and (b) David Bremner and Giancarlo Cravoto (WG006). As a direct result of COST D32 meeting in Alicante Spain David Bremner acquired a large grant from EPSC (UK) for 0.5m Euros.

14:00

Oral

Sonochemistry and the Environment - providing a "green" link between chemistry, physics and engineering

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The tenth meeting of ESS provides an ideal opportunity to trace the development and possible future prospects for the uses of sonochemistry in environmental protection and general green technologies. A search of the older texts on power ultrasound reveals ideas on some applications of ultrasonics which have lain dormant for many years but have re-emerged, albeit in slightly different guises, as viable possibilities using modern technologies. Consider for example the removal of smoke or the atomisation of materials and the treatment of disease.

In the early days of ESS the majority of research projects were linked to improved methods of synthesis as evidenced by the proceedings of the first meeting of ESS at Autrans in 1990. However even in those days it was clear that sonication provided faster and cleaner methodologies and linked well with an emerging interest in "Green Chemistry".

The increasing international regulation on pollution has helped to promote the uses of sonochemistry in environmental protection. This has developed not only into improved methodologies for emission control i.e. end of pipe treatment but also to the removal of existing pollution e.g. the purification of water (chemical and biological), the decontamination of the atmosphere and soil remediation.

So what are the prospects for sonochemistry in a green future for mankind ? On a small scale the costs are quite reasonable but there has always been a question about the economics of scale-up. Nowadays academics, equipment designers and manufacturers are actively engaged in planning for larger scale sonochemical processing. Without any question this will be an essential component in the final exploitation of green sonochemistry.

14:30

Oral

Fundamentals in cavitation, sonochemistry and sonoluminescence: Report on WG9 activity

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Results and ongoing work of the members of Working Group 9 are presented. The topics include experiments and calculations of aspherical bubble collapse, laser induced bubble dynamics and sonoluminescence, molecular dynamics calculations of the bubble interior, interaction of sound field and cavitation bubble structures, and others.

Tea and posters

Thursday afternoon, 8 June, 15:00

Oral reviews - Working Groups

Thursday afternoon, 8 June, 15:30

15:30

Oral

Diversity oriented synthesis under (highly efficient) microwave conditions. Report on WG10 activity.

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The work that has been performed since the beginning of the Action D32 by the members of working group WG10 "Diversity oriented synthesis under (highly efficient) microwave conditions" related to the joint papers, proceedings, presentations, visits, student exchange, STSM, and other joint grant applications will be presented.

16:00

Oral

High-Energy Micro-Environments Applications in Textiles (HEMEAT)

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Non-traditional techniques creating high-energy micro-environments could represent novel processing routes for the

textile industry. The use of high-energy micro-environments (particularly ultrasound and microwaves) could enhance mass transport in wet processes from bulk of the industrial liquors to textile structured materials. Those techniques could also be applied in the treatment of dye-house effluents providing better solutions to the decrease of pollution content. These techniques can be applied as stand-alone measures or as novel components of multi-disciplinary approaches. Recent in the area of high-energy micro-environments have shown potential to apply these techniques in the production of novel textile finishing effects and products, like coated and glued textile materials. In this presentation the last developments from all partners with the WG will be presented and discussed.

Conclusions

Thursday afternoon, 8 June, 16:30

Management Committee Meeting and parallel poster session

Posters are listed here in alphabetic order.

Thursday afternoon, 8 June, 17:15

17:15

Poster

1

Multicomponent Reactions in Microreactor Technology: Imidazole Synthesis via a Four-Component Reaction

Davy R. Acke¹, Romano V. Orru², Christian V. Stevens¹

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In this study, the CYTOS[®] College System, a microreactor produced by CPC-Cellular Process Chemistry Systems GmbH [1], was used to produce imidazoles in a continuous way.

The imidazole core is an important unit in heterocyclic chemistry. It occurs in different natural products and in a variety of synthetic compounds. Some examples of imidazole-containing compounds in living organisms are the essential amino acid histidine and histamine. A lot of imidazoles show biological activities [2]. Known imidazole based drugs are ketoconazole, which has antifungal properties and losartan, a drug against hypertension. More recently, interest in imidazoles is still increasing due to applications as green solvents by means of ionic liquids [3] and in organometallic chemistry as N-

heterocyclic carbenes [4].

Many procedures have been developed to generate a broad range of differently substituted imidazoles [5]. Although there is a wide variety of synthetic routes towards imidazoles, only a few studies exist for the synthesis of 1,2,4,5-tetrasubstituted imidazoles which are mostly performed via multistep routes or via a trisubstituted 1*H*-imidazole in which the nitrogen is substituted in the final step.

Using the modified Radziszewski reaction [6] (Figure 1), a procedure has been optimized for the generation of tri- and tetrasubstituted imidazoles via microreactor technology. Optimization included the search for a suitable solvent mixture, temperature and reaction time. Finally, the generality of the optimized reaction was tested using different starting materials.

It was possible to create a variety of tri- and tetrasubstituted imidazoles in moderate to good yields (up to 1.6 g/h) via a continuous procedure [7].

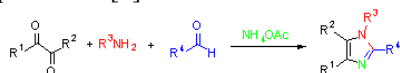


Figure 1: Imidazole formation through a 4-CR

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17:15

Poster

2

Sono-enzymatic coloration of wool

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Laccase from *Trametes villosa* was tested in combination with ultrasound to improve coloration of wool by "in situ" radical polymerization of catechol. Catechol and catechol/laccase solutions, in presence of wool, were treated at 30 and 50 °C without and with ultrasound at 20 kHz at different power intensities (3, 10, 20, 35 and 42 W). The results were analyzed by spectrophotometric and HPLC analyses. No coloration was observed in the sonicated catechol system due to the formation of hydroxyl radicals that attack the phenol molecules in solution or in the collapsed cavitation bubbles interface.

Catechol in this condition does not polymerize and degrades in biodegradable and colorless products such as carboxylic acids. However, in the sonicated laccase/catechol system a large polymerization was observed even more than the laccase/catechol stirring system. The degree of enzymatic coloration of wool fabrics, measured by spectrophotometric analysis, has showed a linear correlation at 50 °C between the absorbance and the ultrasound power intensity in a direct correlation. The HPLC (High Performance Liquid Chromatographie) analyses of the sonicated system have confirmed the formation of a larger quantity of polymer in respect to the stirred system as well as the production of polymers with higher molecular weight. In presence of laccase, the direct ultrasound catechol degradation showed lower kinetic than the ultrasonic enhanced catechol polymerization due to the indirect physical and chemical ultrasound effects on the enzyme.

This study have demonstrated that the ultrasonic waves improve the diffusion processes and may also have positive effect on the laccase active center structure. Moreover the hydroxyl radicals produced by ultrasound can react with the intermediate molecules produced by the enzyme, enhancing the enzymatic catechol polymerization.

17:15 Poster 3

Determination of total, labile and inert lead in coastal seawater by chelex-100 titration-ETAAS following ultrasound-assisted desorption

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Enhancement of desorption with ultrasound has recently been reported by several workers and exploited for fast regeneration of adsorbent resins in industrial applications (Breitbach and Bathen, 2001; Breitbach et al., 2003). In this work, application of focused ultrasound transmitted from a probe for desorption of metals from Chelex-100 was attempted. The aim is to investigate also the possible degradation of the resin due to the application of high intensity ultrasound. A t test was applied to these data and showed that there were no significant differences between elution procedures (Ultrasound and magnetic stirring). After a number of sorption/desorption cycles it could be observed that no significant differences between results obtained by repetitive usage of the same batch occurred, meaning that the resin did not become damaged and kept its complexing properties. The performance of ultrasound-assisted elution was also tested for other divalent metal ions such as Cu²⁺, Ni²⁺ and Cd²⁺. Like Pb, these metals could be eluted in a short time (1 min) by applying ultrasound with good performance. Therefore, not only the elution time is considerably reduced (from an hour with magnetic stirring to a minute with the ultrasounds probe) but the necessary acid volume is also reduced (only with 1 mL), so higher preconcentration factors can be achieved. A speciation method based on Chelex-100 titration and ultrasound-assisted elution has been developed to study the distribution of Pb among different fractions in seawater. Complexation mechanisms of Pb were investigated from the sorption curves of Pb on Chelex-100 according to the Gibbs-Donnan model. Three complexes were formed. Assuming that inorganic species are quantitatively retained by the resin, it was possible to distinguish between labile inorganic species (completely retained) and labile organic species. The variation of the labile Pb fraction (inorganic+organic) with pH was obtained from the difference between Pb concentration retained on the resin and free ion concentration. Likewise, variation of inert Pb fraction with pH was obtained by subtraction of the Pb concentration retained on the resin from the total Pb concentration. The method has been applied to seawater samples from Ria de Vigo (Galicia, Spain). References [1] Breitbach, M. and Bathen, D., 2001. Influence of ultrasound on adsorption processes. *Ultrason. Sonochem.*, 8:277-283. [2] Breitbach, M.,

Bathen, D. and Schmidt-Traub, H., 2003. Effect of Ultrasound on Adsorption and Desorption Processes. *Ind. Eng. Chem. Res.*, 42:5635-5646.

17:15 Poster 4

Ultrasound Assisted Enzymatic Hydrolysis of PET Fibers

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Alkaline hydrolysis of PET is well known method for improving the hydrophilicity and the handle of polyester textile materials. Reaction conditions lead to obtaining of water soluble products (sodium terephthalate and ethylene glycol). As a result the textile surface has a good contact with the reaction media during the treatment time.

In our experiments with some lipases and pectinases we found out that the pectinase (*Aspergillusniger*, EC.3.2.1.15 - Biovet Joint Stock Company, Peshtera, BG) can hydrolyze PET fibers. The enzyme was tested on polyester textile in pH range 5-9 and temperatures from 25 °C to 55°C. Treated polyester textile material has higher hydrophilicity as well as the weight losses after the enzymatic treatments. That changes were explained with the hydrolysis of PET fibers. Highest values of these characteristics were found at temperature 55° and pH 6. Obviously at that conditions the hydrolysis could stop at a very early stage because of water insoluble (PET oligomers or terephthalic acid) reaction products.

The aim of the work is to study the possibility of applying ultrasound treatment during the enzymatic hydrolysis of PET fibers for accelerating the removal of reaction products from the textile surface.

Experimental results about the weight loss and hydrophilicity showed that the ultrasound treatment can considerably increase the effect of enzymatic treatment with the pectinase EC.3.2.1.15 on PET fibers containing textiles.

17:15 Poster 5

Mechanism And Efficiency Of Atrazine Degradation Under Combined Oxidation Processes

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The mechanism of atrazine degradation in the aqueous phase was investigated under sonolysis at 20 kHz, ozonation, photolysis at 254 nm and photocatalysis on TiO_2 under irradiation in the 315 - 400 nm wavelength range, employed either separately or in combination (1). Aim of the work was to compare the efficiency of such different advanced oxidation techniques in inducing not only atrazine degradation in water, but also its overall detoxification. Particular attention was focused on the influence of the irradiation wavelength in photoinduced water treatments and on the existence of possible synergies in the combined use of the investigated oxidation techniques, especially for achieving water detoxification. Information on the mechanism and efficiency of atrazine degradation under the different experimental conditions was obtained from the concentration profiles of the main degradation intermediates.

Ozonation and photocatalysis, both proceeding mainly through $\cdot\text{OH}$ radical attack, induced atrazine de-alkylation, followed by slower de-chlorination, while direct photolysis at 254 nm produced very efficient de-chlorination, through the homolytic cleavage of the C-Cl bond occurring from the electronically excited state of atrazine. Simultaneous sonolysis had beneficial effects on ozonation and photocatalysis, especially by increasing the rate of $\cdot\text{OH}$ radical initiated de-alkylation, and no effect on the unimolecular photolytic de-chlorination of atrazine. Thus, synergistic effects induced by sonolysis simultaneous to photocatalysis and ozonation, which have been observed in the degradation of different pollutants (2-4), in the case of atrazine degradation can mainly be attributed to the ultrasound-induced enhancement of mass transport phenomena and possibly to an increase of photocatalyst dispersion. An effectively higher concentration of reactive radical species produced by cavitation effects should be excluded by the fact that under sono-photocatalysis and sono-ozonation the same set of intermediate species was produced as under photocatalysis and ozonation, with ultrasound apparently inducing an increase of the rate constants of all degradation steps.

Complete atrazine mineralization, as monitored by TOC analysis, did not proceed beyond ca. 65%, corresponding to the removal of 5 out of the 8 carbon atoms originally present in the molecule. This confirms the well recognized stability of the s-triazine ring toward conventional oxidation (5), atrazine oxidative degradation proceeding only up to cyanuric acid formation. However, atrazine degradation and overall detoxification, as related to the disappearance of chlorinated by-products, proceeded at the highest rate when photolysis at 254 nm was combined with ozonation.

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17:15	Poster	6
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Potential of Ultrasound in Combined Disinfection Processes

Torben Blume, Uwe Neis

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Low-frequency high-power ultrasound is an effective method for the separation of bacteria cells because of its strong mechanical shear stresses. Low doses of energy produce here at first a de-agglomeration; with high intensities and long exposure times the cell wall of the bacteria can also be so damaged that it causes their death. Since the required energy input is very high in the latter case, the disinfection of wastewater only with ultrasound does not yet seem economically viable.

In this work, it was investigated whether the efficiency of UV can be improved by a combined application of ultrasound and UV. Even in lab-scale tests with well clarified wastewater samples (TSS: 14 mg/L) a strong tailing effect could be observed after exposure to UV irradiation. However, preceding sonication for just 5 s resulted in a dispersion of bacteria/suspended matter and hence in a notable increase of bacteria's vulnerability to UV: Efficiency was improved by up to 1 log unit. Pilot-scale tests at a municipal sewage treatment plant (volumetric flow: 2 - 4 m³/h) showed similar effects, although less pronounced. At higher concentrations of suspended matter ultrasonic pre-treatment had a more definite effect on the improvement of UV efficiency.

Furthermore, the application of chlorine was examined to find out whether a combination of ultrasound with smaller chlorine concentrations can be as efficient as what would only be possible with higher dosing of the environmentally harmful chlorine. For combined sonication/chlorination an efficiency gain up to 2.5 folds is possible, especially at very low chlorine concentrations (see figure 1). Consequently, lower dosing of the environmentally harmful chlorine is possible to obtain a specific disinfection rate, and the formation of by-products is correspondingly reduced.

Since the efficiency gain of the disinfection in our experiments was explicitly higher during the simultaneous sonication than as pre-treatment, ultrasound is not only effective

with respect to the declumping of agglomerates but also on the temporary perforation of bacteria's cell walls.

17:15	Poster	7
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Monitoring the oxidation of vegetable oil by ultrasound-assisted-ATR-FTIR spectroscopy

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The degradation process of vegetable oil in storage and usage involves oxidation, cis-trans isomerization and free fatty acids production. Several approaches have been developed in order to measure the oxidative stability of oils, inducing the degradation by conventional heating, microwave¹ and ultrasound energy². The commonest methods for establishing the oxidative stability of oils are the active oxygen method (AOM) and the Rancimat method, based upon conventional heating. However, these methods are time consuming and afford only information on a specific change in the oil. Aging oils by ultrasound energy has been proved more effective and reduces over 100-fold experimental time³.

On the other hand, Fourier Transform Infrared Spectrometry (FTIR) affords a lot of structural information in order to evaluate the degree of unsaturation of edible oils and assesses the quality of the final product. Moreover, specific spectral changes are shown in aged oils, which can be unambiguously due to compositional changes as cis-trans isomerization, hydroperoxides and carbonyl compound formation^{3,4}. Furthermore, Attenuated Total Reflectance (ATR) avoids the use of organic solvent, and then reduces waste production.

In this work, the changes in the (ATR-FTIR) spectra of eighteen edible vegetable oils during oxidation were measured to explore if the oxidation process (induced by ultrasound energy) follows the same pattern in the different types of oil under study. The aim of this study was to monitor the oxidation process in the different samples and to characterize the spectral changes occurring lipid oxidation processes. Thus, it highlights the capability of Fourier Transform Infrared Spectrometry (FTIR) to provide information about the chemical processes taking place during lipid oxidation in a rapid and experimentally simple way.

Keywords: oil, ultrasound, ATR-FTIR Spectroscopy

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Sonochemical synthesis of bismuth oxide

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Synthesis of Bi_2O_3 in ultrasound field of 750-1000W intensity was studied. α phase of Bi_2O_3 was formed in the following three steps: 1. formation of $\text{Bi}(\text{OH})_3$ by precipitation reaction of bismuth nitrate and ammonium hydroxide; 2. condensation of Bi-OH groups and formation of Bi-O-Bi bonds and 3. hydroxide was transformed through oxid-hydroxide semiproduct into crystalline α - Bi_2O_3 .

The crystallization speed increased with time and ultrasound intensity. Ultrasound field speeded up Bi-OH condensation, α - Bi_2O_3 crystallization and α - Bi_2O_3 crystal growth.

Particle size of sonochemically prepared α - Bi_2O_3 was in range of 0,05-5mm, which corresponded to specific surface area of 0,5-17m²/g. The influence of polyethyleneglycol as a chelating agent on particle size is shown.

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Multivariate optimization of a microwave assisted extraction procedure for the determination of flame retardants in dust

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A rapid and simple method for the analysis of PBDEs in

house dust is proposed. An "on batch" cleanup procedure was used for dust extracts treatment, which allowed to increase the speed of analysis. Experimental design analysis allowed obtaining the optimal conditions for microwave assisted solvent extraction process. Quantitative recoveries were obtained for all compounds and method precision was satisfactory. LODs (S/N=3) were lower than 0.15 ng/g dry mass for all compounds. Concentrations of total BDEs in house dust samples were lower than 200 ng/g, which is in agreement with the reported concentrations in samples from other EU countries. Dominant congeners in most of dust samples were those associated with pentaBDE commercial mixture.

17:15	Poster	10
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Development of a hollow-fibre liquid-phase micro-extraction method used for monitoring the sonochemical degradation of Triclosan in water

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The occurrence of pharmaceuticals and personal care products in the aquatic environment has been a worldwide concern over the past two decades. Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) is an antimicrobial agent, listed by the 76/768/EEC European Commission council directive as a preservative for cosmetic products. It has a bacteriostatic efficacy against a broad spectrum of microorganisms as well as a favourable human safety profile. However, previous investigations concluded that the same types of mechanisms involved in antibiotic resistance also account for the observed cross-resistance with antibiotics in laboratory isolates. Hence, there is a link between triclosan and antibiotics, and it is generally believed that the extensive use of products containing triclosan may promote the development of microbial resistance. The presence of triclosan in wastewater, surface water, seawater and sediments has been frequently reported in Europe and the United States. This is of concern, given the fact that under certain conditions (such as sunlight radiation) it can be readily converted into various by-products including amongst others polychlorinated dibenzop-dioxins. Accordingly, current research efforts are directed towards the development of simple and sensitive analytical methods, capable of accurately monitoring the safe removal of trace quantities of triclosan by using innovative treatment technologies.

The ability of hollow-fibre liquid-phase microextraction coupled to gas-chromatography mass-spectrometry to determine trace amounts of triclosan, an antimicrobial agent, in water samples is investigated. The LPME conditions such as extraction solvent, hollow-fibre length, sample volume, ionic strength, pH, agitation rate and sampling time, were investigated. Overall, 13 cm hollow-fibre segments containing 3 µl of toluene were exposed for 10 min to 5 ml aqueous samples stirred at 1000 rpm. The calibration curve for triclosan is linear yielding a 0.9986 correlation coefficient and under the single ion monitoring mass-spectrometry mode the detection limit was found 0.031 µg/l. The repeatability of the proposed method was found to be good and the analysis of spiked wastewater samples revealed that matrix had little effect on extraction. The developed analytical protocol was then used to successfully monitor the sonochemical degradation of a spiked aqueous solution containing 50 µg/l of triclosan subject to pulsed ultrasonic irradiation (80 kHz ultrasonic frequency) at a constant electric power output of 150 W and a 21 °C constant water bath temperature. Triclosan degradation was quantitative in 270 min of reaction.

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Activation of Cycloaddition Reactions: Improvements under Microwaves and Ultrasound

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Some cycloadditions are thermally allowed, especially Diels-Alder reactions, which are often key steps in synthetic organic chemistry. As a result, both ultrasound and microwave irradiations, particularly the latter, by virtue of their thermal effects, have been extensively applied in the search for further improvements. Our research group has recently embarked on an exploration of synthetically useful cycloadditions, where a combination of either microwaves or ultrasound in neoteric reaction media (e.g. ionic liquids) has proven to be of substantial benefit.

Thus, reactions of cyclopentadiene with electronically poor dienophiles conducted in a conventional ionic liquid, [HMI][BF₄], are greatly accelerated (in some cases from 1 h to 5 min). Moreover, the ionic solvent could be recycled for five times without loss of efficiency. These cycloadditions have also been improved with ultrasound in terms of higher yields and shorter reaction times when compared to the corresponding silent reactions. Although the origin of this activation remains uncertain, Lewis acid catalysis caused by

thermal decomposition of the ionic liquid could be ruled out.

Finally, reactions of enaminoesters with chlorosulfonyl isocyanate were significantly accelerated under microwaves. The process is relevant as it leads to a straightforward synthesis of isoorotic acid derivatives. Starting from carbohydrate-based enaminoesters, a series of isoorotate nucleosides could easily be prepared. The process is believed to occur by a sequential process via polar intermediates. The role of microwaves is discussed.

The authors would like to express their gratitude to the Ministry of Education and Science (Grants BQU2003-05946 and BQU2005-07676) and the EU Program Interreg-III (Project Labtrans/SP4E44) for financial support.

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Poster

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Transition Metal-Mediated Cross-Coupling of 2(1H)-Pyrazinones Facilitated by Microwave Irradiation with Simultaneous Cooling

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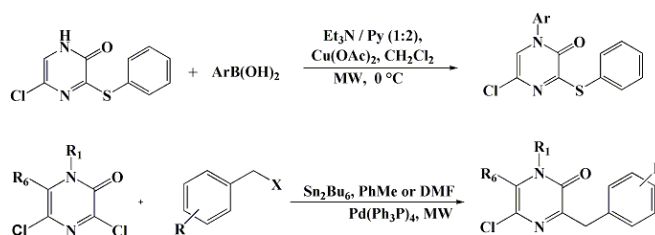
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In the course of the last two decades our laboratory explored 3,5-dichloro-2(1H)-pyrazinones as interesting starting materials for a gateway to the elaboration of different types of biologically active compounds. This valuable scaffold allows an easy introduction of a wide range of pharmacologically active groups with the ability to address the diverse set of biological targets. Some of the recently developed 2(1H)-pyrazinone-derived molecules show very promising activities as non-nucleoside HIV-1 reverse transcriptase inhibitors (NNRTIs) [1], μ -opioid receptor agonists and selective tissue factor VIIa inhibitors.

Recently, our group has developed the microwave-assisted, transition metal-mediated decoration of the 2(1H)-pyrazinone scaffold in solution phase and on solid-support [2].

Here, we want to discuss the application of microwave-assisted transition metal-mediated cross couplings of the 2(1H)-pyrazinone scaffold. We will demonstrate that these reactions³ resulted in significantly improved yields and rates when performed under microwave irradiation with simultaneous cooling. The Cu (II)-mediated Chan-Lam cross coupling and a one-pot Stille reaction will be discussed.



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Poster

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Electrochemical measurements of a flow induced by low frequencies ultrasound. Influence of horn diameter and cell design

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Low frequency power ultrasound (20 kHz to 1 MHz) is more and more used in chemical or electrochemical applications. The main effect of ultrasound is due to the increase of mass transfer nearby the electrode. The major effects are observed when the electrode is positioned in the axis of the transducer, for distances lower than 3 cm. However, the intense cavitation which occurs in this zone as well as the presence of the electrode are at the origin of a extremely perturbed hydrodynamics behavior which it is indispensable to characterize to optimize the sonoelectrochemical processes into develop-

ment. The purpose of this study is to measure the speed of the hydrodynamics flow generated by ultrasound according to the distance between the electrode and the transducer, in various geometrical configurations (horn diameters and cell designs). In the same time, visualizations and speed determinations are carried out by optical techniques (laser tomography and Particle Image Velocimetry). Results are compared with those obtained by electrochemical techniques which consist in measuring the mass transfer coefficient of the reversible couple $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ at a millimeter-length platinum electrode surface. Mass transfer coefficients are converted in a equivalent upward flow speed, according to the Levich model hypothesis, to allow a direct comparison with the velocity vector measures obtained by PIV. Two kinds of reactors with a comparable internal diameter (60 mm) were characterized. The first one is the Compton Cell, a small cylindrical reactor (90 mm height) which allows adapting transducers of diameter 6 and 12 mm. The second is the cylindrical reactor, developed in our laboratory with a higher height (190 mm) and which allows to work with a wider range of transducers (6, 12 and 25 mm in diameter) by a different system of fixation from that of the Compton Cell. The flow velocities measurements turn out very different from a reactor to the other one. In the Compton Cell we observe a strong attenuation of the velocities with the horn-electrode distance. For example, the velocity measured at 1 mm away from the transducer is of the order of 10 ms^{-1} , varying slightly with the ultrasound power for the 6 mm diameter horn. It is divided by 10 for only a distance of 15 mm. Curves can be easily simulated by a simple attenuation law. The increase of the transducer diameter (12 mm) leads to an increase of the flow velocity by a 3 times factor. In the cylindrical reactor, the order of magnitude of the velocities is quite similar, but the variations do not follow a simple attenuation law. A sinusoidal phenomenon is observed, which makes more complex the modelling and leads to less control of the stirring conditions.

Keywords: low frequency ultrasound - sonoelectrochemistry - velocity determination

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Poster

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Ultrasound-assisted mild and efficient one-pot synthesis of room-temperature ionic liquids

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Replacing common molecular organic solvent by room temperature ionic liquids is a topic of great interest in term of eco-chemistry in both academia and industry. Their negligible vapor pressure, their large liquid range and their tunable physical properties make them very interesting in many chemical reactions. During the last decade, their different applications have followed an exponential curve in various domains of chemistry such as electrochemistry, extraction or organic chemistry.

Thus, the huge number of expected possible ionic liquids (10¹⁸) together with their tunable remarkable physical-chemical properties confer on them a high potential for the R&D, opening widely new opportunities for the chemistry science, whatever the topic. However, the lack of thermodynamics data, their toxicity and their preparation prevent their widespread use. The synthesis of ionic liquids has been widely visited and revisited and the necessary reaction time has dramatically been decreased from a few days to a few hours, notably by the emergence of non-conventional activation methods such as microwave and ultrasound irradiations. Even so, almost all published methods deal with a two-step synthesis including the synthesis of the halogenated precursor ionic liquid followed by the metathesis of the anion leading to a second generation ionic liquid with even more remarkable physical chemical properties.

We present here the preliminary results of the first one-pot synthesis assisted by ultrasonic irradiation to access to a large variety of ionic moieties incorporating different cations and anions. Ultrasound can, on one hand enhance radical pathways through chemical effects and on the second hand enhance heterogeneous systems through physical effects such as mass transport, reduction of particles size and micro-emulsion. As the formation of ionic liquids occurs through an ionic pathway, chemical effects are not looked for but on the contrary, physical effects are favoured to overcome the hetero-

geneity of the systems and also overcome the relatively high and natural viscosity of ionic liquids.

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Textile coating assisted by Ultrasound

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Coating processes are widely used to enhance and alter the physical properties and appearance of a fabric. Coating and lamination have bridged across virtually every product group in the textile industry, including composites, where their potential is especially wide.

In this study a 20 kHz US apparatus - realised by Tecnotessile in collaboration with the University of Turin and able to work at different electrical powers (maximum power: 500 W) - was used to investigate the effects of ultrasound in the chemical and physical properties of a water polymer dispersion.

Analyses carried out on the sonicated polymer showed that no significant changes in the chemical composition of tested samples were obtained; in fact, variations of electrical conductivity and pH values were not recorded. Only a slight change in the polymer particle distribution and particle size was recorded, since cavitation promotes fragmentation of the polymer particles by means of a radical depolymerisation reaction.

The most interesting results were obtained in terms of superficial properties of the coating film applied on a textile surface after sonication. Atomic Force Microscopy (AFM) analyses carried out on samples coated with sonicated water polymer dispersions showed that sonication is able to reduce the roughness of coated films.

Preliminary results seem to suggest that superficial changes do not depend on the applied power, but that only frequency affects these properties.

The European Commission is acknowledged for financial support to the ULTRATEC project (Sixth Framework Programme), within which this study was realised.

Keywords: coating, ultrasound, water polymer dispersion, AFM.

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Microwave-assisted Capillary Electrophoresis with Electrochemical Detection

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Microwave-assisted Capillary Electrophoresis with Electrochemical Detection Sascha Förster, Frank-Michael Matysik, Mohamed Ghanem, Frank Marken a) Institute of Analytical Chemistry, University of Leipzig, Germany b) Department of Chemistry, University of Bath, UK Capillary electrophoresis (CE) is one of the most efficient separation methods in analytical chemistry. It is associated with several advantages like automation, high efficiency and miniaturization. The CE technique has a broad potential of analytical applications ranging from small ions up to whole cells. CE measurements require only small quantities of chemicals and small sample volumes. Particularly, the combination of CE with electrochemical detection (ED) makes it possible to analyze species which do not show UV absorption. Microwave radiation (MW) offers an activation of electrochemical processes by self-focusing at the electrode surface. It produces a stable local increase in temperature and serves for the localised acceleration of chemical reactions and the increase of signals in conjunction with analytical voltammetry. Additionally, the convective effects of the buffer solution close to the electrode surface can lead to a focusing of the liquid flow outside of the capillary to the working electrode and consequently to a further increase of analytical signals. The aim of this work was to demonstrate for the first time the combination of CE with microwave-assisted electrochemical detection. A new detection cell was constructed to allow an accurate positioning of the working electrode and the separation capillary in the microwave field. A cooling of the capillary and an optimal irradiation and focusing of the microwave radiation must be realized. Investigations concerning the influence of the microwaves on the detection performance and the stability of the electrode surface have been carried out. A calibration of temperature, mass transport, and kinetic effects of the microwave radiation on the model system $K_4[Fe(CN)_6] / K_3[Fe(CN)_6]$ were measured. The influence of the MWs during the electrophoretic separation on the signal height, the peak symmetry and migration time were determined for a cationic ferrocene derivative, methanol, and for ascorbic acid. A clear increase in temperature was observed and consequently a change of the equilibrium potentials and an increase of the steady-state current of

the cyclic voltammetric characterization of the electrochemical systems were found. Thermal effects and associated convective movements were not measurable because of the small distance of only 50 μm between the working electrode and the separation capillary. However, the kinetic effects on signal magnitude were clearly proven by using ascorbic acid as a model compound. A significant enhancement of sensitivity could be exploited for CE-ED measurements of ascorbic acid in presence of MW radiation.

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Poster

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Microwave accelerated aza-Claisen rearrangement. Synthesis of branched-chain nucleosides

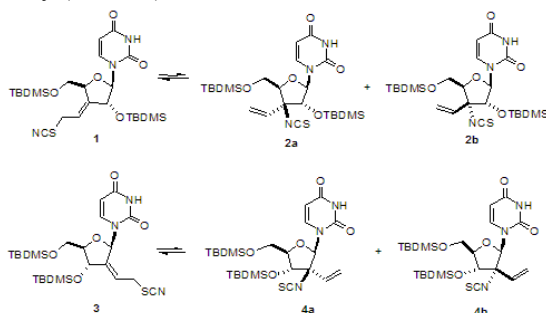
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Considerable attention has been focused on branched-chain sugar nucleosides because of their biological importance. They have shown broad spectrum of biological activities such as antitumor, antiviral or antibiotic. The most representative examples of this group are AZT,¹ ECyD,² CNDAC,³ TSAO and its derivatives.⁴ In our previous communications^{5,6} we published the stereoselective synthesis of the branched-chain sugar 3(*S*)-isothiocyanato-3-deoxy-3-C-vinyl glucose as a suitable precursor for the synthesis of natural compounds and where 1,2-*O*-isopropylidene group is a decisive factor for the stereocontrol in the aza-Claisen rearrangement of allylic thiocyanates.

We report here the study of stereoselectivity of [3,3]-sigmatropic rearrangement of protected uridine allylic thiocyanates **1** and **3**. The key step in the synthesis of branched-chain nucleosides is the stereocontrolled formation of a new C-N. The thermal rearrangement of **1** and **3** was carried out at 70-90°C in various solvents under N₂ for 24 h to give the isothiocyanates **2a-b** and **4a-b** with a relatively low selectivity (Scheme).



The microwave induced rearrangements of **1** and **3** afforded isothiocyanates **2a-b** and **4a-b** in good yields within 20-60 min. The reactions were performed in closed vessels in a focused microwave reactor (CEM Discover), with control of power and temperature by an infrared sensor. We have found that the [3,3]-sigmatropic rearrangement of the uridine thiocyanates is strongly accelerated in microwaves conditions with enhanced stereoselectivities of the reactions. Very interesting was result of rearrangement of **1** under microwave condition without solvent. Reaction take place with high conversion and stereoselectivity to afford isothiocyanate **2b**.

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17:15

Poster

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Interfacing a Microchip Based Electrophoresis System with a Microwave Induced Plasma (MIP) Optical Emission Spectrometer (OES).

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The microwave induced plasma MIP is a small low power plasma that is excellent for the analysis of halogens. The technique of MIP atomic emission spectrometry would be excellent for the speciation of halogens however due to the small size and low thermal temperature of the plasma (compared to its high excitation capability) it cannot be easily interfaced to liquid separation techniques such as HPLC or CE. This problem could be overcome by using lab on a chip technology for the separation as this provides rapid separation with nanolitre volumes of liquid.

The aim of this work is to investigate halogen species which are particularly sensitive in MIP atomic emission spectrometry

The first step is to develop the Interface between the μCE chip and the MIP, in doing this it is important to have an op-

timally designed micronebuliser. The liquid and gas flows then have to be optimised to obtain maximum sensitivity. Once this is achieved a suitable sample injection strategy is required to ensure good reproducibility. Then a high voltage can be applied across the chip to achieve separation of different species.

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Analytical applications of ultrasound to enhance chemiluminescence detection

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Analytical applications of ultrasound with chemiluminescence will be discussed for flow systems with luminol and at liquid interfaces with electrogenerated chemiluminescence. A novel ultrasonic flow injection chemiluminescence (FI-CL) manifold for determining hydrogen peroxide (H_2O_2) was designed and evaluated. Chemiluminescence obtained from the luminol- H_2O_2 -cobalt (II) reaction was enhanced by applying 120 W of ultrasound for a period of 4 s to the reaction coil in the FI-CL system and this enhancement was verified by comparison with an identical manifold without ultrasound. A calibration curve was obtained with a linear portion over the range of 10 - 200 nmol L⁻¹ H_2O_2 (correlation coefficient 0.9945). The detection limit (3σ) was found to be 1×10^{-9} and the relative standard deviation was 1.37 % for 2×10^{-7} mol L⁻¹ H_2O_2 ($n=10$)[1]. The method was applied to the determination of trace amounts of H_2O_2 in purified water and natural water samples without any special pre-treatments.

1. Gillian M. Greenway^{a*}, Tapparath Leelasattarakul^b, Saisunee Liawruangrath^b, R.Alan Wheatley^a, Napaporn Youngvises.^c 2006 Analyst, 131, 501-508

17:15	Poster	20
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Improvement of Sludge Handling in Pulp and Paper Industry Using Ultrasound

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"Improvement of sludge handling in pulp and paper industry

using ultrasound" -project (SONOBIO) is focused on studying the release of water and nutrients from bio-sludge (waste activated sludge) in pulp and paper industry using power ultrasound technology.

The whole project consists of the following main tasks:

1. Review of the ultrasound assisted sludge handling today and actual problems in wastewater and sludge treatment in pulp and paper industry.
2. Solubilisation of bio-sludge substances using power ultrasound and the effects of recycling of disintegrated sludge in aerobic wastewater treatment in laboratory scale.
3. Changes in dewaterability of bio-sludge using power ultrasound:
 - Effects of disintegration parameters (e.g. power level, time, sludge concentration, temperature) on sludge structure e.g. release of EPS and water from sludge flocs.
 - Release of different substances from biomass.
 - Effects of released components on sludge flocculation and dewaterability.
 - Floc strength in pressing experiments.

The project is part of the COST D32 network "High Energy Micro-Environments in Biotechnology". It is financed by VTT, Tekes and companies (Kemira, DWT Engineering, Finnsonic, Botnia). The total budget is 221 000 €. The co-operation between VTT and TUHH includes a period of exchange researcher, planning of US assisted PDU-scale WAS-plant connected to a real WAS plant at a pulp & paper mill in Finland, workshops to analyse the results obtained, to guide the experimental work and publish joint articles.

The project will be carried out during December 2005 and November 2007. If the results are promising the project will be continued with pilot-experiments.

Acknowledgements: COST D32 has made possible to start up this study and intensified exchange of US info between the European US research groups.

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Ultrasonic revelation of hydrophobic interactions.

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The hydrophobic interaction (HI) is the tendency of apolar species to aggregate in aqueous solutions, in order to minim-

ize unfavourable interactions with water. HI is the principal force determining the structures of proteins and nucleic acids, and the binding of substrates to enzymes.¹

HI in aqueous solutions has been paid much attention recently. Reaction rates are frequently determined by HI between the reactants and water or with a cosolute. HI can stabilize the reactants thus diminishing the reaction rate. Accordingly, stabilization of encounter complexes of the reagents by HI brings about a rate enhancement.¹

We have shown that ultrasonication (US) can cause changes in the translational energy of species, thus leading to a solvent structure break or to a shift of solvation equilibria, HI included.² In aqueous ethanol solutions, at ethanol content 40 - 50 wt % hydrophobic reagents can be hidden in the clusters formed of ethanol molecules and thus made inaccessible for the reaction. Ethyl, n-propyl, and n-butyl acetates were used as probes of the inclusion of a reagent in the clusters. Indeed, the US effect on rates of the acid-catalyzed hydrolysis of esters correlated with the order of hydrophobicity of the esters. Butyl acetate should be the most powerfully held by clusters, and US was the least efficient in this case.

A logical inference was an unfavourable effect of US upon the reactions promoted by HI, e.g. Diels-Alder reaction, the benzoin condensation, etc.¹ Indeed, we observed slowing down of the benzoin condensation reaction of benzaldehyde by US in water and in water-ethanol solutions.³

In conclusion, if breaking down the stabilization of encounter complexes between the reagents, US suppresses the reaction rate, while perturbation of the solvent-stabilisation of the reagents by US accelerates the reaction. Thus, US is a useful tool for detection of hydrophobic interactions in solutions.

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Poster

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Microwave-assisted Suzuki-Miyaura reaction catalyzed by a new palladium complex

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Here we want to report the synthesis of a new air and moisture stable palladium complex with a thiosemicarbazone ligand and its catalytic effect in the Suzuki-Miyaura cross-coupling reaction of aryl halides with phenylboronic acid under microwave irradiation. In contrast to other palladium complexes with thiosemicarbazones, this complex was inactive towards the Suzuki-Miyaura coupling under aerobic conditions, by conventional heating. On the other hand, microwave irradiation promoted the effective catalytic activity of the complex for the coupling of aryl bromides and chlorides with phenylboronic acid in DMF/H₂O, under aerobic conditions.

These results lead us to propose that specific microwave effects rather than thermal effects are responsible for the acceleration of this reaction. These specific microwave effects are evidently connected to the involvement of highly polar species and intermediates. The microwave-promoted cross-coupling reaction by palladium complexes with thiosemicarbazones provides a convenient approach relative to existing methods that require an inert atmosphere due to the air-sensitive nature of other catalysts

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Effect of low frequency ultrasound irradiation on room temperature ionic liquid deshydration

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Application of Ultrasound in the Wafer Fabrication: 1) Development of an Ozone Detector and 2) Degasification of Process Water

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Ozone is widely used in the etching technology of wafers and other microelectronic components and in water treatment, too. For both applications a ruggedly designed ozone detector owning high metering precision is necessary. In the ozone detector ultrasound is used to degrade the dissolved ozone to enable the calibration of the zero point of the measuring equipment. The degassing and deoxygenation are key steps during the water circulating process in the fabrication of wafers and microelectronic components. Ultrasound enables a high effective degassing of process and waste water.

Ozone detector

The ozone detector can be widely used in water analytic. The measurement of ozone concentration in water is a part of process control system for example in microelectronic industry and in ozonization of drinking and waste water. Water is taken in a bypass of a technical circulating water system continuously. In the detector the UV absorption of ozone at 254 nm is measured to determine the concentration in a light pipe directly. If the water contains organic compounds the measuring signal increases because of the organics absorb in the same wave length range. By this reason a correction of the signal is necessary. To get the "zero"-value the ozone is degraded by ultrasound periodically. This measured signal is used to make a correction of the ozone concentration.

The first laboratory test equipment was build up with a traditional 24 kHz ultra-sonic system and an ozone detector.

Afterwards the analytical equipment has been optimized (measuring range, frequency of ultrasound, response time in the ultrasonic cell, influence of water parameters and organic

compounds dissolved in the water, robustness etc.).

For a mobile application a scale-down of the ultrasonic system and the ozone measuring cell has been done.

Degasification of process and waste water

The degassing process is applied in treatment of process water of wafer fabrication, in the air sparkling of contaminated ground water, in the biogas plants etc. In the ozone elimination process of the wafer fabrication the ultrasound has to be applied at high flow rates of water and short contact times. To increase the efficiency the ultrasound parameters (power, frequency etc.), process parameters and the reactor geometry were optimised.

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Conventional thermal process versus microwave hydrothermal synthesis of sodalite material

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Several studies have been published on microwave techniques for moisture measurement of bulk materials, such as coal, soil and agricultural products. However, little research work has been carried out on the treatment of wet solids and water slurries at atmospheric pressure using microwave techniques. The microwave-assisted synthesis of inorganic materials at atmospheric pressure using hydrothermal route is still developing.

In the present study, a feasibility study on the synthesis of sodalite ($\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$) from kaolinite ($\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$), metakaolinite (dehydroxylated kaolinite), NaOH and NaCl using a microwave process has been carried out by comparing the heating time and reaction temperature with the same factors under conventional thermal process.

Experiments have been conducted using the hydrothermal method at atmospheric pressure. Microwave power has been kept low (100W) in order to: i) maintain the same temperature as with conventional heating (80°C) and evaluate the real effect of microwave irradiation relative to conventional heating, ii) avoid the thermal runaway phenomenon [1] already observed with zeolite materials after only few minutes under microwave irradiation, iii) study the reaction evolution in time. At 80°C, when the heating time is below 30 min, the XRD analyses of conventional heating (CH) or microwaves (MW)-heated samples have revealed that all resulting products are amorphous. While a prolonged conventional heating (from 30 to 90 min) leads to an amorphous product, microwaves heating (100W) leads to the forming of crystal-

line products. When the heating time was increased up to 180 minutes, the XRD patterns of the resulting product mostly indicate the presence of natural sodalite together with some traces of Zeolite A. A higher reaction time of 6 hours was needed to achieve a complete transformation of kaolinite into sodalite when using conventional heating.

The efficiency of microwave irradiation over conventional thermal process was evidenced by the yield of sodalite in time. The different sodalite yields obtained at 80°C using two different heating modes (conventional and microwave irradiation) can be explained in terms of difference of activation energy for heat treatment or chemical reaction. A remarkable feature of the microwave heating process is related to the athermal-non-Arrhenius effects which are defined as a reduction of activation energy for the heat treatment or chemical reactions in the microwave heating process [2]. It is noted that some chemical reactions under microwave irradiation follow a quite different mechanism route which requires lower activation energy than that needed in the conventional method.

It is noteworthy that MW heat quickly and uniformly leading to the forming of sodalite under soft operating conditions with energy saving and short processing time.

Thermal decomposition of $\text{Na}(\text{AlSiO}_6)\text{Cl}_2$ sodalite occurred at high temperature (1200°C/6h heating) and led to nepheline $\text{NaAlSi}_3\text{O}_8$ formation. Both the good thermal stability and water insolubility of the synthesised sodalites were considered to be essential properties for confinement of nuclear wastes (based-halide salts).

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Conventional thermal process versus microwave hydrothermal accelerated synthesis route of lanthanum manganites perovskites used in methane combustion

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Perovskite type manganese oxides are widely used as catalysts in environmental chemistry that deal with the conversion of carbon monoxide and hydrocarbons. These oxide catalysts possess both high thermal stability and activity and are useful in the combustion of fuels in automobiles and in power

plants. However, the major obstacles to the successful application of these materials in a large scale are both their low resistance to sulphur poisoning and also their scarce BET surface area which is often linked to the catalytic activity.

In the present study, a study on the synthesis of the precursor of $\text{La}_{1-x}\text{Ag}_x\text{MnO}_{3+d}$ ($x = 0; 0.2$) using a microwave process (MWhyd) has been carried out by comparing the heating time and reaction temperature with the same factors under conventional thermal process (CHhyd). Experiments have been conducted using the hydrothermal method at medium pressure ($T = 210^\circ\text{C}$, $P = 22 \text{ atm}$) followed by a thermal treatment at 600°C for 10 h.

Structural and physico-chemical properties of the catalysts were investigated using X ray diffraction, BET-sorption, temperature programmed reduction-, and desorption-mass spectrometry, (TPR-MS and TPD-MS) and X-ray photoelectron spectroscopy (XPS). Permittivity measurements of the obtained powders in the range 0.5-3 GHz have been performed using an Agilent 85070E dielectric probe kit, varying the compaction degree.

While CHhyd and MWhyd powder catalysts exhibited the same XRD patterns indexed as pure perovskite structure, their surface physico-chemical properties were found to be strongly influenced by the preparation procedure. The influence of the nature of oxygen species, their amount and mobility, evidenced by temperature programmed experiments, on the catalytic properties in catalytic combustion of methane in the presence and in the absence H_2S has been studied.

The MWhyd prepared catalysts were found to exhibit a much higher resistance to sulphur poisoning than those prepared using CHhyd preparative procedure. MWhyd $\text{La}_{1-x}\text{Ag}_x\text{MnO}_{3+d}$ was the most active catalyst in methane combustion. These results were considered to be due to the nature, amount and mobility of the oxygen species of the solids.

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Optimisation of sonochemical and/or sonoelectrochemical cell with the help of numerical simulation of ultrasonic intensity distribution

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The all important sonochemical and sonoelectrochemical effects, such as mass transfer enhancement, surface activation

of reactant, catalyst or electrode, change of (electro)chemical mechanism and/or the initiation of novel coupled chemical reactions, are connected with cavitation [1-4]. The presence of cavitation is thus the necessary condition for expression of these effects. The cavitation can take place only if the intensity of ultrasound is higher than cavitation threshold. That is why an intensity of ultrasonic power is the most significant parameter characterizing an ultrasonic field.

Whereas in the case of low intensity ultrasound the measurement of intensity and its distribution is well solved [5], in the case of high intensity (when cavitation takes place) the measurement is much more complicated. That is why the prediction of distribution of ultrasound within the cell based on theory is desirable.

This poster will show how numerical solution of the wave equation can predict the distribution of intensity within the reactor [6].

The calculations together with experimental verification have shown that the whole reactor behaves like a resonator and the energy distribution depends strongly on its shape. Therefore, the simulation of the intensity distribution has been used for optimization of the shape of ultrasonic reactor. The optimal geometry resulted in a strong increase in intensity along a large part of the cell.

The advantages of such optimised geometry are:

- the ultrasonic power necessary for obtaining cavitation is low, consequently, the erosion of the transducer face is minimized;
- low power delivered to the system results in only weak heating, consequently, no cooling is necessary;
- the "active volume" is large, i.e. the fraction of the reactor volume with high intensity is large and is not limited to a vicinity close to the horn tip.

For sonoelectrochemistry two main advantages are evident:

- it is not necessary to place the electrodes into a small area near the horn surface but anywhere in the cell where the intensity is high;
- an electrochemical cell can be simply immersed into the ultrasonic bath. The electrode system is electrically isolated from the horn by the walls of the cell. Consequently, the metallic horn cannot work like an electrode and a four-electrode potentiostat (which is necessary in the case of non-isolated immersed horn) is not required.

This work was financially supported by COST (D32/004/04), the Ministry of Education of the Czech Republic (grant number 1P05OC074) and Generalidad Valenciana (Project GV05/104).

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Poster

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Microwave-Assisted Cloud Point Extraction of Rh, Pd and Pt as preconcentration procedure for ICP-MS

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A new approach of microwave stimulation for cloud point extraction of rhodium, palladium and platinum has been developed. The procedure was applied for preconcentration of trace amounts of platinum group elements followed by inductively-coupled plasma mass spectrometry determination. 2-mercaptobenzothiazole and Triton X-100 were selected as hydrophobic ligand and non-ionic surfactant, respectively. The extraction was carried out with model solutions of platinum group metals in hydrochloric media where they present as chloro-complexes. The exchange of chloride ligands with 2-mercaptobenzothiazole was found to be kinetically inert - especially for Rh and Pt. The following special kinetic features are proved: the velocity of extraction of platinum depends on its oxidation degree - for Pt (II) the process proceeds faster than Pt (IV). The presence of Pd in the system accelerates the extraction of Pt in both oxidation states but it has no significant effect on Rh extraction.

One possible way to promote the complex formation processes is to heat the system which fits well with the need of elevated temperature in order to occur the critical phenomenon of cloud point typical for non-ionic surfactants. The parameters for cloud point extraction process carried out in water bath (conventional heating on hot plate) were varied in respect to the recoveries degree. Working under optimal conditions: acidity of 1M HCl; 1000-fold mass excess of ligand; incubation at 95 °C quantitative extraction of Pt (IV) was achieved at least for 120 min. but under the same conditions the degree of extraction for Rh was found to be only 20%. Pd is extracted completely in less than 30 min.

Microwave irradiation increases the efficiency of the preconcentration procedure reducing the time needed to obtain quantitative extraction in comparison to the conventional heating. The whole cloud point procedure was successively completed in microwave system for less than 20 min and the extraction of Pd and Pt (IV) was shortened by time factor of 3 and 6, respectively. Unfortunately even with the use of microwave stimulated extraction the recovery of Rh still remained lower than 40%.

The complex formation processes for Pt and Rh was successfully accelerated by adding of reducing agents such as KI and SnCl_2 . It was proved that the presence of each reagent leads to equalization of the behavior of both initial oxidation states of platinum. In the case of Rh only SnCl_2 is an efficient promoter of the extraction process. A comparison between conventional heating and microwave irradiation at these conditions was also done. A quantitative microwave-assisted cloud point extraction of platinum and rhodium is obtained in only 10 min (compared to 30 min. for Pt (IV) and 90 min. for Rh, respectively, if conventional heating is used).

Acknowledgements: This work has been undertaken as part of the EU sponsored COST programme (Action D32, working group D32/005/04, "Microwaves and Ultrasound Activation in Chemical Analysis").

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A method for procedural standardisation for preparing and processing nanopowders using microwaves

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In order to establish the work output from a laboratory is of high scientific quality, it is imperative that a well defined procedure is used. The advantages of using a standard procedure are great when comparing the work and results obtained in the same laboratory by many different researchers. It allows immediate verification by the project leader that the data is either of high quality for publication or that it might be necessary to repeat the experiments because data from separate researches are inconsistent. The mechanism of this verification is referred to as TRACEABILITY. The project leader can trace back through the procedures used and determine where the difference or inconsistency may have arisen. If the researchers and their team have followed the defined procedure(s) for that work, then errors or inconsistencies are very

quickly found. Traceability ensures Quality Assurance.

The use of such standard procedures becomes very critical and indispensable when a group of laboratories form consortium and cross check each others work or may undertake different stages of one large project that is clearly too big to be done by one laboratory. This is evident if one looks at the mechanisms used for projects that are multinational where groups of laboratories in each nation are given a set of tasks for the final successful conclusion of a large project.

To illustrate this, the authors present as an example a procedure that was developed for the preparation and processing of nanopowders using microwaves.

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Doping of ZnO nanopowders with Mn and Cr in an ultrasound and microwave driven hydrothermal reaction

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Nano-sized powders of Mn^{+2} doped ZnO and Cr^{+3} doped ZnO have been synthesized in a sonochemical reactor and in a microwave domestic oven. The sonochemical reaction was carried out at 20 KHz frequency, with Power density 100 W/cm², under a pressure of 0.15 MPa of argon for 3 hours. The average temperature of the process did not exceed 70°C. The process was carried out in water and ethylene glycol. The reaction yield was 15 to 55% depending on synthesis conditions. Better results have been obtained for ethylene glycol. The microwave driven hydrothermal reaction has been carried out at 150°C and 280°C for 40 min. and the yield was over 50%. The reaction substrates were a mixture of zinc acetate, Mn^{2+} acetate or Cr^{3+} acetate in the corresponding solvent.

The density, grain size, and lattice constants of the samples have been investigated. The lattice constant increases with Mn content, but the rate of increase decreases above 8% of Mn content. This result speaks for a substitution of Zn ions by Mn ions, however for a limited solubility of Mn.

A phase analysis of the powders obtained shows that although only XRD peaks corresponding to ZnO have been observed

for 10% Mn concentration, for the other elements at 10% initial concentration a peak corresponding to of their oxides appears, indicating a lower solubility limit in the ZnO lattice than in the Mn case. The grain size of the powders obtained is in the range of 20 - 40 nm.

Besides the structure investigations, also optical and magnetic properties of the samples were measured.

The results obtained indicate that both the ultrasound driven and microwave driven reactions are suitable for doping ZnO with transition metals ions. However, the microwave reaction was more efficient, most likely because of the higher average temperature comparing to the ultrasound driven one.

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Investigations of phase composition and grain size distribution in Pr doped ZrO₂

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A high pressure microwave reactor, i.e., a reactor where microwave energy is used to heat the fluids inside the high pressure cell was used to study the hydrothermal synthesis of zirconia doped with praseodymium (Pr content 1 mol%) in temperature range was from 210 to 305 °C. Nanopowders with average grain size in the range of 10 nm were obtained.

A mixture of nanoparticles with tetragonal and monoclinic phase structure was obtained. A new method to determine the grain size distribution, which is based on analysis of the fine structure of the X-ray diffraction line profiles, was applied. It was found that the content of the monoclinic phase decreased with increasing synthesis pressure up to 8 MPa due to dissolution or transformation of grains of smaller diameter than about 12 nm.

Keywords: Hydrothermal synthesis; Microwave; High Pressure; Zirconia; Praseodymium; Grain Size Distribution

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Sonochemical degradation of Reactive Black 5 using low and high frequency ultrasound

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Unconsumed dyes in wastewaters still impose serious aesthetic and environmental problems because of their colour and their high chemical oxygen demand. Especially reactive azo dyes have poor biodegradation under aerobic conditions. Aromatic amines formation under anaerobic conditions is well documented as well. Recent studies indicate that ultrasound as advanced oxidation process might be an alternative for the destruction of many organic compounds including textile dyes [1-3].

The decolouration and degradation of C.I Reactive Black 5, a worldwide used azo dye, by low (20 kHz) and high frequency (279 kHz/817 kHz) ultrasonic irradiation, without the addition of any oxidant was studied. Characterization of the used ultrasound systems was performed using calorimetric measurements and oxidative species monitoring using Fricke and iodine dosimeter in order to find the best experimental conditions - a compromise between acoustic efficiency and radical formation. Emphasis was given to the effect of different operating conditions on radical formation rate, decolouration and degradation efficiency, as well as on the toxicity profile of such treatment.

Sonochemical decolouration was substantially depressed by the addition of *tert-butanol* as a radical scavenger that suggests radical-induced reactions in the solution. Acute toxicity to marine bacteria *Vibrio fischeri* was measured before and after ultrasound irradiation. Degradation efficiency was estimated by TOC measurements.

Degradation products determination was performed using ion chromatography, HPLC and LC-MS-MS at Institute of Chemical Process Engineering and Plant Design in Cologne. The authors are very grateful to prof. Astrid Rehorek for providing these measurements and for useful discussions.

Keywords: Ultrasound, Reactive Black 5, Degradation, *Vibrio fischeri*

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Translation of bubbles subject to weak acoustic forcing and error in decoupling from volume oscillations

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A microbubble in a sound wave oscillates in volume and translates unsteadily. The two motions are coupled. In large-scale simulations of the structure of bubble clouds driven by acoustic fields, it has been of significant convenience to decouple volume oscillations and translation, as an approximation. The errors of this decoupling approximation were considered in an earlier publication (A. J. Reddy and A. J. Szeri, *Journal of the Acoustical Society of America*, 2002), in the parameter range of interest in medical ultrasound. In this work, the approximation is reexamined for a much broader range of driving frequencies and bubble sizes. Solving the equation of motion for linearly oscillating bubbles, it is found that even for weak acoustic forcing, the translation speed obtained with the decoupling approximation can be in error as much as 30% relative to the translation speed in the full equations. The error depends on the

bubble size, the driving frequency, and the liquid properties. The results are presented in a form convenient for applications. The principal utility of the analysis is for bubbles in microgravity, or in normal gravity driven by a soundfield with a horizontal wavenumber vector.

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Chemical evolution of laser-produced bubbles in water

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By focusing a short laser pulse in a liquid a single bubble can be generated at a well-defined position and time by optical breakdown. This method has been utilized extensively to study bubble dynamics at different conditions, but is also used, e.g. in laser-induced breakdown spectroscopy for elemental analysis or in laser ophthalmology. In this work the coupled hydrodynamic and chemical evolution in a laser-generated bubble in water are investigated numerically by means of molecular dynamics simulations. Two different situations are considered: (i) a transient bubble that decays after a few afterbounces, and (ii) a bubble seeded in an ultrasonic field, that transforms into a stably oscillating bubble. The spatial and temporal evolution of temperature, pressure and species concentrations in the collapsing bubble are given for a number of cases with different laser energy and acoustic driving levels. Particular attention is paid to the thermodynamics and chemodynamics during the first bubble collapse and the associated chemical yields. For case (ii), the chemical evolution of the bubble over several cycles is considered.

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Carbon Nanotube Synthesis from Transition Element Doped Mesoporous Silica Using Sonification Techniques

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Carbon nanotubes (CNT), first discovered by Iijima [1] in 1991, have led to a revolution in material science. CNT's have many interesting mechanical properties which have led to some researchers making remarkable predictions about their possible uses from nanoscale machines to earthquake-resistant buildings. Their primary use is likely to be in electronics as interconnects and/or devices. This will however mean that they will have to be controllably placed at very precise locations or grown *insitu* at temperatures low enough to be compatible with CMOS circuitry.

Thus, for on-chip requirements it is necessary to develop: 1) a simple method for processing CNTs at low temperatures; 2) a method which allows nanotubes to be produced non-destructively in a controlled manner 3) have a process whereby the position of nanotubes can be simply pre-determined. At UCC we have shown that CNTs can be prepared in a similar manner to that of Park *et al.* using heterogeneous rather than homogeneous catalyst sources [2]. Here, pre-doped (Zr/Co/Fe) mesoporous silicas were used as catalysts. Sonification in chloroform leads to the synthesis of both MWNTs and SWNT bundles. The product shows a strong dependence on sonification power. TEM shows that the CNTs grow *via* a tip growth mechanism. Raman spectroscopy showed that good quality CNTs were produced. The UCC work shows that it is possible to use a heterogeneous catalyst compared to a homogeneous phase (i.e. liquid ferrocene) suggesting that the reaction may be modified to allow surface processing.

The catalytic activity is primarily due to their novel physiochemical properties and in particular their very high surface areas [3]. We have also pioneered methods of tailoring pore sizes to between 2 and 11 nm [4] diameter and the in-situ modification of mesoporous silicas with the transition element additives. All of the modified mesoporous silicas were characterized using the analytical techniques of x-ray diffraction, BET/BJH surface analysis, x-ray fluorescence

spectroscopy, transmission electron microscopy and x-ray photoelectron spectroscopy.

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Keywords: Carbon nanotubes, sonification, low temperature, mesoporous silica

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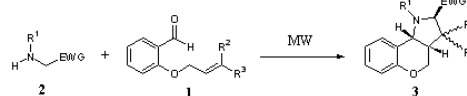
Pericyclic Reactions Initiated by Microwaves

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In the literature one can find many 1,3-dipolar cycloaddition reactions proceeding by an intermolecular process where 1,3-dipole generated by different methods is taking part in a reaction with a dipolarophile under formation of five-membered ring.¹ Only some of them are microwave initiated.² Reactions of the intramolecular type are in the literature even less frequent and represent a source for synthesis of fused heterocyclic systems. Microwaves on azomethine ylides were used only ones.³ Besides reactions with azomethine ylides we tried also to generate *in situ* nitrones for the subsequent intramolecular reaction. In our work we concentrated on preparation of fused hexahydrochromeno[4,3-*b*]pyroles **3** (Scheme 1).



Scheme 1.

Such a structural motive was found in several naturally occurring alkaloids⁴⁻⁶ and even hexahydrochromeno[4,3-*b*]pyroles show interesting biological properties.⁷ The reaction was carried out as "one pot" process under solvent free conditions when the 1,3-dipole was generated *in situ* by the reaction of *o*-allyloxybenzaldehyde **1** (sometimes *w*-substituted with substituents R², R³) with a secondary amine **2** containing electron-withdrawing group. Influence of the substitution at the side chain double bond as well as the substitution R¹ at the nitrogen atom and the electron-withdrawing groups (EWG) upon the yield and stereochemistry of products were searched.⁸ The reaction was attempted also with *o*-

propargyloxybenzaldehyde but there we have not any success. Reactions ended with formation of tar products. Always the reactions were compared with the same reactions under classical heating. It has been proved rather high sensitivity of the chemical reaction on the bulkiness of substituents bound at nitrogen atom of amine. The reactions with unsubstituted allyloxy group proceed with excellent stereoselectivity when only one stereoisomer is formed. The same stereoselectivity was observed when dipolarophiles in *cis*-configuration at double bond bound in side chain of aromatic ring playing dipolarophile role were used (only one stereoisomer was formed). When the configuration on double bond was *trans* two stereoisomers were isolated in different ratio depending on the substitution R^2 , R^3 . Nevertheless, the generated ylide always in the reaction possessed *anti* conformation. We suppose the transition state and its sterical demands influence the stereochemistry of the product formed. The developed method on systems without side chain enabled application for preparation of substituted imidazolidin-4-ones⁹ - versatile synthon for syntheses of α -amino acids and di- or tripeptides. Finally lot of effort was devoted to the application already developed method for *in situ* nitron generation and its intramolecular cyclization to fused isoxazoles. Nevertheless the best achieved yield when the conditions of the reaction were many times varied was about 16% only.

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Decolourization of dyes from a leather factory by sonoelectrolysis treatment

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The discharge of highly coloured wastewater into the ecosystem involves environmental problems. It is detected a widespread contamination of soil as well as ground and surface water by synthetic dyes used for textile dyeing/finishing and also in food, paper and cosmetic industries. Most of these compounds are toxic, mutagenic or at least cause an aesthetic problem in receiving water and soil [1]. Approximately 15% of total world production of wastewater, or 150 tons per day, is estimated to be released into the environment without proper treatment [2].

Several methods are being used to decolourize dye wastewater. Each method has advantages and disadvantages. Biological processes show a limited colour removal due to the toxic nature of some dyes and the high salt concentration. Adsorption in activated carbon, membrane filtration, coagulation-flocculation and chemical oxidation with ozone have a considerable cost. Thus, there is a great need to develop an economic and effective way of removing synthetic dyes from wastewater at the level of the industry itself in the face of the ever-increasing production activities.

In the recent years, there has been a large interest in the use of electrooxidation process. Among them, sonoelectrolysis treatment is an attractive method. In this treatment, electrolysis and sonolysis are combined. In this work, in order to test the feasibility of the method purposed, a comparative study was carried out on the decolourization of dyes from a leather factory using electrolysis treatment alone and sonoelectrolysis.

For this study, electrolysis of several dyes (Trupocor Red, Reactive Black 5, Lissamine Green, Methyl Orange and Acid Black 24) was carried out in an electrochemical cell of 40ml working volume in absence or presence of ultrasound. All experiments were conducted at constant voltage drop (5 V) applied through a couple of graphite electrodes. The equipment used for experiments with ultrasound was Sonoplus HD2070 (20 kHz cycle 10%, power 60%). The effect of ultrasound on the dye degradation was study by immersion of the microtip into the electrochemical cell. Samples of the reaction solutions were removed from the electrochemical cell and were

analysed for pH and dye concentration. Residual dye concentration was measured spectrophotometrically at the maximum visible wavelength of each dye. The decolourization was determined following the decrease in the absorbance at the same wavelength and expressed in terms of percentage [3].

According to the results obtained in the present work, the superiority of sonoelectrolysis treatment over electrolysis has been demonstrated. The application of ultrasound in electrochemistry process permits the degassing and continuous activation of the electrode surface. Moreover, the addition of electrolytes such as Na_2SO_4 improved the efficiency of the sonoelectrolysis process (Figure 1). All experimental results indicate the suitability of sonoelectrolysis process for its application to dye degradation.

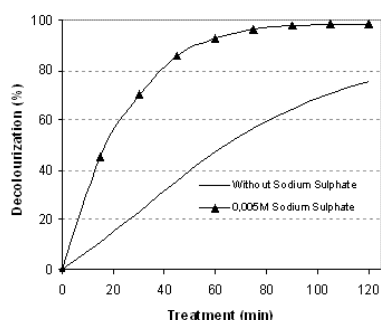


Figure 1. Lissamine Green decolourization by sonoelectrolysis

Acknowledgements

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Non-Linear Oscillations and Collapse of Elongated Bubbles - Simulations of Laser Induced Bubbles

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The details of nonlinear oscillations and collapse of elongated bubbles, subject to large internal overpressure, are studied by a boundary integral method. Weak viscous effects on the liquid side are accounted for by integrating the equations of motion across the boundary layer that is formed adjacent to the interface¹.

For large internal overpressures and moderate elongations there is a critical value of the Ohnesorge number, $Oh = \mu / (\sigma R_p)^{1/2}$, below which the bubble collapses via two jets that enter the bubble through its two poles, propagate in the opposite direction along the axis of symmetry and eventually coalesce in a centered fashion at the equatorial plane. In this process a tiny microbubble is formed, occupying the center of the original bubble, that is surrounded by a larger toroidal bubble. Above this critical value of Ohnesorge the bubble eventually returns to its equilibrium spherical shape. For large overpressures, very large initial elongations and below the critical Ohnesorge number the jet walls are deflected and collapse in an off-centered fashion at the bubble walls, forming two smaller toroidal bubbles and a large one occupying the center of the original bubble. Above the critical Ohnesorge the centered collapse mode with the tiny microbubble at the center is recovered. In all cases of bubble collapse the time from collapse scaled with the $3/2$ power of the minimum distance between the pinching parts of the interface. As the bubble size increases the bubble is destabilized and the above break-up mechanisms are observed for smaller initial elongations. In this case, for very large internal overpressures and small elongations the Rayleigh-Taylor instability appears and the bubble collapses via coalescence of two jets that propagate in opposite directions along the equator.

Simulations of experiments with LASER induced nanosecond² bubbles, initial radius on the order of one mm, exhibit a similar collapse mode. The severity of jet impact during collapse of such bubbles is pointed out. Simulations of experiments with laser induced femto-second² bubbles indicate asymmetric collapse and smaller jet velocities.

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Sonochemical degradation of bisphenol A in natural water

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Bisphenol A (BPA), an organic compound largely used in plastic industry as a monomer for production of epoxy resins and polycarbonate, disturb the behaviour of the aquatic life by its endocrine disrupting effect at low concentration [1]. This xenobiotic compound, can be released in the environment from bottles, packaging, landfill leachates paper and plastic plants [2-4].

In recent years, considerable interest has been shown on the application of ultrasound as an advanced oxidation process (AOP) for the treatment of hazardous contaminants in water. Ultrasonic irradiation of aqueous solutions induces acoustic cavitation, which can be defined as the cyclic formation, growth and collapse of microbubbles. Implosion of the cavities occurs adiabatically in extremely small intervals of time and releases large quantities of energy over a small location. During the collapse, thermal dissociation of water (sonolysis) yields OH radicals, which are reactive species able to oxidize the most part of the organic molecules. On the other hand, hydrophobic and volatile substrates can be destroyed predominantly by direct pyrolytic decomposition inside the cavitation bubbles.

Natural waters are usually complex systems that contain significant amount of inorganic species, which may affect the efficiency of the AOP [5]. In this work, we demonstrate that the sonochemical treatment (300 kHz / 80 W) is a very promising alternative for the BPA removal in natural waters, even at low concentration of BPA (0.034 mg L⁻¹) and high concentration of Cl⁻, SO₄²⁻ and HCO₃⁻ (10, 1182 and 402 mg L⁻¹ respectively).

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Preparation of 4-(4-fluorophenyl)-1-methyl-3-methylenepiperidine by Microwave-assisted Elimination Reaction

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Paroxetine **1** is a selective serotonin-reuptake inhibitor (Paxil, Seroxat) used in the treatment of depression¹ and Parkinson's disease². Its industrial synthesis³ proceeds *via* racemic

trans-4-(4-fluorophenyl)-3-hydroxymethyl-1-methylpiperidine which undergoes optical resolution to provide a desirable (3*S*,4*R*)-enantiomer **2a** and its antipode **2b** whose enantiomeric purity can be improved by a reverse enrichment procedure.⁴

Transformations of **2b** proceeding through 'temporary destruction' of asymmetric centres is challenging particularly in respect to the possibility of converting the unwanted (3*R*,4*S*)-enantiomer into the desirable one with the opposite absolute configuration.

The more accessible of the two chiral centers in **2b** appears to be that on C-3. It can be readily attacked by a strong base in an elimination reaction to furnish (4*S*)-4-(4-fluorophenyl)-3-methylene-1-methylpiperidine **7b** which can be further transformed into an achiral intermediate **8** (Fig. 1).

In an attempt to improve the yields of elimination we decided to employ a supported solvent-free microwave methodology.⁶ Dehydration of **2b** was attempted on acidic clays (KSF, K-10) and calcined alumina, on basic alumina, basic alumina impregnated with KF, neutral alumina and neutral alumina/KF under microwave irradiation.

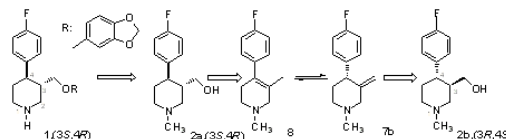


Figure 1.

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Sonochemical Radical Production in Aqueous Systems

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This process has implications for using ultrasound for the destruction of contaminants in water, sonochemical synthesis e.g. of colloidal or precious metal species and in medical uses of ultrasound. The sonochemistry of aqueous systems is dominated by the production of hydrogen and hydroxyl radicals from the sonolysis of water. Further reaction products arise from combination or reaction with other dissolved species.

A number of methods employing radical traps and product analysis have been used to measure the rates of radical production in water and a range of solutions used in industrial processes, including biphasic systems such as emulsions. We have also applied the methods to a number of medical and dental ultrasound instruments.

In conjunction with groups at the University of Melbourne in Australia and the UK's National Physical Laboratory, we have been investigating how the experimental conditions affect changes in sonoluminescence and in acoustic emission from cavitating systems. We have been able to show that these correlate reasonably well with the observed chemical changes. In addition, some unexpected effects were noticed when using ultrasound with two different frequencies, 20 kHz and 515 kHz. A possible model to explain some of these results will be discussed. However, there remain a number of unanswered questions, particularly in regard to the detailed mechanism of some reactions and these will also be posed during the presentation.

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Microwave-Enhanced Synthesis of Vegetable Oil-based Polyols for Polyurethane Applications

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Vegetable oils are an excellent renewable source of raw materials for manufacturing polyurethane components with hydroxyl groups. The transformations of the double bonds of triglycerides to hydroxyls and their application in polyurethanes have been the subject of many studies [1-8]. Taking into

account that European countries have a vast potential regarding cultivation of oil plants, these investigations may result in a significant source of modern, sustainable, more ecological polymers. The real commercial development of natural-oil-derived polyols (NOPs) in polyurethanes is still on a small scale but ever growing number of users is expected. Vegetable oils are triglycerides, esters of different fatty acids and glycerol. The composition of the fatty acids contained in the vegetable oils determines the further use of the oils. The types of unsaturated fatty acids in triglycerides determine the distribution of hydroxyl groups in oil-based polyols. The number of hydroxyl group depends on the type of unsaturated fatty acids and then agent used for oxirane ring opening. oils such as linseed or rapeseed and soybean can also be useful in polyurethane formulation but first, they need to be transformed. There are several methods of converting them into the raw materials contained the hydroxyl group capable of forming new polyurethanes. Through the epoxidation, the double bonds of the triglycerides are transformed into oxirane rings. In the second step, the epoxidized oil can be converted into the polyols by ring opening reaction with alcohols i.e., methanol, ethylene glycol, propylene glycol, glycerol etc. A two-step process was applied for the preparation of rapeseed and linseed oil-based polyols. In the first step, the double bonds of the triglycerides were transformed into oxirane rings through the epoxidation with acetate peroxyacid. In the second step, the epoxidized oils were converted into the polyols using monoethylene glycol (MEG) or diethylene glycol (DEG). In the case of the polyol based on rapeseed and linseed oil and the glycols both steps of the process (epoxidation and oxirane ring opening) were carried out under microwave irradiation. It allowed reducing the reaction time of the epoxidation step ca. 60 % and hydroxylation step ca. 75 % in comparison to the same process carried out under conventional thermal conventions. References [1] Guo A., Jani J., Petrovic Z.: Journal of Applied Polymer Science, 77/2 (2000) 467. [2] Prociak A.: Rigid polyurethane foams modified with vegetable oil-based polyols. UTECH 2006 Conference Papers on CD, Maastricht, The Netherlands. [3] Höfer R.: Oleochemical polyols - New raw materials for polyurethane applications, Proceedings European Coatings Conference, Berlin 1999. [4] Hong Hu Y., Gao Y., Wang D. N., Hu C. P., Zu S., Vanoverloop L., Randall D.: Journal of Applied Polymer Science, 84 (2002) 591. [5] Chian K. S., Gan L. H.: Journal of Applied Polymer Science, 68 (1998) 509. [6] Badri K. H., Ahmad S. H., Zakaria S.: Journal of Applied Polymer Science, 81 (2001) 384. [7] Kozłowski R., Pielichowski J., Prociak A., Marek M., Bujnowicz K.: Raw materials based on linseed oils for polyurethane synthesis. Textiles for sustainable development, International Conference, The Boardwalk, Port Elizabeth, South Africa, 2005, Conference Papers CD, 384. [8] Zlatanovic A., Lava C., Zhang W., Petrovic Z.: Journal of Polymer Science, Part B: Polymer Physics, 42 (2004) 809.

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Improvement of the Degradation of C.I. Reactive Orange 107 by Ultrasound

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The azo dye C.I. Reactive Orange 107 (RO107) is one of the three most important components of "Marine Blue", a dye mixture used worldwide for dyeing of textiles [1]. Dye production and textile dyeing processes are the source for waste water that has to be decolourized by degradation of its pollutants. Even in our days this is still a problem not completely solved for many countries and companies.

The objective of the presented studies is to evaluate the improvement of microbiological azo dye RO107 degradation by ultrasound. As earlier studies have shown, ultrasound can be used as a single procedure to study kinetic and mechanistic aspects of the degradation or, as an additional process engineering step, to improve biodegradability of azo dyes [2]. In order to study both aspects, sonochemical experiments have been performed at different initial dye concentrations and reactor volumes. Ultrasound treatment was carried out at different frequencies and energy input of ultrasound to find optimal radical formation rates.

Dye degradation and formation of intermediates, ions and radicals have been monitored directly or indirectly by HPLC-DAD, LC-MS/MS and ion chromatography [3]. Results are presented that allow insight into the reaction mechanism. The sonolysis has also been carried out in the presence of *tert*-butyl alcohol.

The combination of ultrasound with anaerobic and aerobic microbiological treatments has been studied. The effect of sonochemical treatment prior to anaerobic microbiological treatment, between anaerobic and aerobic treatment and after aerobic treatment has been studied. The best combination and sequence of these treatments with respect to optimal efficiency of sustained decolourization and degradation will be discussed.

Keywords: Ultrasound, Sonochemistry, On-line LC-MS/MS, Marine Blue, C.I. RO 107

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Modification of enzymatic reaction kinetics by sonication of biomass

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Since sludge treatment and disposal in industrialised countries nowadays is a highly problematic issue any method that impacts on the enzyme driven process of biological degradation of organic substrates which eventually results in less surplus bio-mass production is of great practical value. Ultrasound is capable of destroying biological cells and we have found that it might be promising to use ultrasound to disintegrate part of the recycled active biomass in order to achieve a sustainable reduction of filamentous bacteria and to minimize the production of waste activated sludge/biomass in the biological waste water treatment system.

Although it is known that disintegration increases the fraction of soluble substances in a sonicated sample of waste activated sludge, the biodegradability of these released substances is unknown. In preliminary tests in our laboratory we sonicated waste activated sludge with different ultrasound frequencies and a variety of energy inputs and sonication times. The impact of sludge disintegration with ultrasound on the biodegradability of biomass can easily be shown.

The aim of our ongoing work is to proof that the enzymatic reaction kinetics in a continuous activated sludge lab scale plant are modified by sonication of recycled sludge.

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Research in the group "New Technological Development in Electrochemistry: Sonoelectrochemistry and Bioelectrochemistry" Alicante University

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One of the research lines of the group "New Technological Development in Electrochemistry: Sonoelectrochemistry and Bioelectrochemistry" at Alicante University is Sonoelectrochemistry, it means, the study of chemical processes under electrical and ultrasound fields. In this research we are developing not only the design and characterization of sonoelectrochemical reactors but also general aspects of the sonoelectrochemical processes from a fundamental and applied point of view. It is very important to characterize the behaviour of sono(electrochemical)reactors in order to identify accurately the actives zones, especially those related to the cavitation events. Different chemical dosimeters, such as Fricke reaction and iodide oxidation, have been used in order to determined the global generation of hydroxyl radicals developed during the water sonolysis. A new electrochemical probe (lead dioxide electrodeposition) has been proposed for the local hydroxyl radical level. Theoretical characterization by means of numerical simulations have been also carried out in order to characterize the ultrasonic field propagation and to obtain the spatial distribution of the mechanical effect derived from it. The results are in agreement with those obtained with different classical physical methods (calorimetry method, aluminium foil erosion, thermal probes and an electrochemical probe based on $\text{Fe}(\text{CN})_6^{3-}$ anion reduction). Processes like the lead dioxide electrocrystallization have been studied from a mechanistic point of view, and it has been observed that the kinetic parameters are strongly modified by ultrasound. Applied studies have been also carried out analyzing the effect of an ultrasound field in the electrochemical degradation of aqueous solutions of chlorinated organic compounds, such as perchloroethylene, a solvent widely used in the industry. Different collaborations have been also carried out inside of COST D32 action: -Electrochemical nitration and chlorination of bioactive species (enzymes, protein redox and antibodies,) with Dr. John Heptinstall (Coventry University). - Perchloroethylene degradation at high frequency, with Prof David Walton (Coventry University). -Sonoreactor characterization, with Dr. J. Klima (J. Heyrovsky Institute of Physical Chemistry. Czech Republic) -Electrosynthesis of hydrogen

peroxide assisted with ultrasound, with Prof Richard Compton (Oxford University). The authors would like to thank the COST D32 and Generalidad Valenciana for its financial support (Project GV05/104). J.I. gratefully acknowledges the Spanish Programme Ramon y Cajal.

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Effect of ultrasound on hydrolysis of 4-nitrophenyl acetate. A kinetic anomaly associated with the use of titanium horns.

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We recently reported the effects of ultrasound on acid-catalyzed hydrolysis of alkyl esters in EtOH - H₂O mixtures.¹ We speculated that the observed sonochemical acceleration might be related to changes in the molecular structure of the binary solvent, i.e. to a perturbation of hydrophobic solute-solvent interactions.

To gain a better insight in the matter, we extended our kinetic investigation to a mechanistically complementary reaction, the base-catalyzed hydrolysis of 4-nitrophenyl acetate (4-NPA).² The kinetics was studied in H₂O-EtOH mixtures under ultrasound (US) and without it. The effect of US was investigated over the 0-50 wt % range of EtOH concentration and over the 7.5-9 pH range.

A specific feature of our work consisted in the comparative use of two different immersion horns a quartz (21.1 kHz) and a Ti horn (22 kHz). With the quartz probe the well-known problems arising from the erosion of titanium horns did not arise, and it was unnecessary to filter the samples for spectrophotometric measurements. These were carried out with and without sonication successively on the same reaction system.

Experiments with the immersed Ti horn (in H₂O at pH 7.5) revealed a catalytic action of materials formed from dispersed Ti metal and degradation products of 4-NPA. In fact, sonication experiments with a Ti horn on alkyl esters did not exhibit any catalytic phenomena.¹

Experiments with a quartz horn were carried out in H₂O at pH 7.5, 8.0 and 9.0, as well as in aqueous EtOH over the range of 0.8-50 wt% at pH 8.0 and 9.0. Remarkably, no catalytic effect was observed. In H₂O or in the presence of about 1 wt% EtOH the sonication effect did not exceed 10%. With a further increase of the EtOH content the ultrasonic acceleration

increased rapidly, reaching a maximum at $X_{\text{EtOH}} \gg 0.08$; thereafter it dwindled gradually to become almost negligible at $X_{\text{EtOH}} \gg 0.25$.²

Surprisingly, the plots of sonochemical acceleration ($k_{\text{son}}/k_{\text{non}}$) vs. X_{EtOH} for 4-NPA were found to be mirror images of that previously obtained for acid-catalyzed hydrolysis of ethyl acetate¹. Their extremes lie at the same EtOH mole fractions.

The present results led us to relate ultrasonic acceleration of ester hydrolysis in H₂O and in EtOH-H₂O mixtures to a perturbation of solute-solvent interactions by power US. In fact the sonication effect varied inversely with the strength of substrate interactions with the solvent structure. This conclusion, that apparently applies to both acid-catalyzed and base-catalyzed hydrolysis, can be helpful in rationalizing the influence of solvent-solute interactions on these reactions.

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Catalytical and Heating Behaviour of Nanoscaled Perovskites under Microwave Radiation

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Perovskite powders of the type La_{0.5}Ca_{0.5}AlyM₁-yO_{3-δ} (y = 0.25 to 0.5), M = Fe, Cr, Mn, Co, were prepared via sol-gel route according to modified Pechini method. Calcination of the resins at 350 °C in air was performed before final sintering at temperature 1000 °C for 6 hours. La, Ca, Fe, Al, Cr, Mn and Co contents in the solid were determined by microprobe attached to the electron microscope. The phase composition of the products was established by X-ray diffraction analysis and the lattice parameters were calculated using the Rietveld analysis. The shape and size of particles were determined via scanning electron microscopy. The specific surface of powder perovskites was established by the BET method. Perovskites with Co and Cr content (y= 0.75) crystallized in rhomboedric structure with R3cH space group, perovskites with a medium Fe and Mn content in orthorhombic structure with Pbnm spatial group, and the perovskite with the lowest Fe content (y=0.5) in cubic structure with Pm3m space group.

The primary particles were about 200 nm in size and formed agglomerates larger than 1.0 µm. For catalytical investigations we used the experimental set up which was published in ??? The catalytic performance was measured in the most cases at atmospheric pressure with 3 g of catalyst. The partial pressure of propane was 0.4 kPa with air as the carrier gas in all runs. Flow rates were controlled by electronic mass flow controllers (Tylan[®], FC□260□2s). The flow rate was 0.4 L h⁻¹ for propane, 100 L h⁻¹ for air.

First results show a strong dependency of catalytical and heating behavior on the nature of B-atom.

Conclusions and outlook

Nanoscaled perovskites of the type La_{0.5}Ca_{0.5}AlyM₁-yO_{3-δ} (y = 0.25 to 0.5), M = Fe, Cr, Mn, Co are interesting materials for microwave-assisted heterogeneous gas phase catalysis. We could found a strong dependency between the catalytical and the heating behaviour of the materials and the nature of B atom. Correlation between TPD and oxidation behavior of the materials has to be done in the next future

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Shape stability and violent collapse of micro-bubbles in acoustic travelling waves

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Acoustically driven bubbles can develop shape instabilities. If forced sufficiently hard, the bubbles distort greatly and break up. Perturbation theory provides some insight as to how these nonspherical shape modes grow initially but loses validity for large deformations. To validate the perturbation theory, we use a numerical model capable of simulating nonspherical, axisymmetric bubbles subject to acoustic driving. The results show that the perturbation theory compares well with numerical simulations in predicting bubble breakup and stability. Thereafter, we compare the peak temperatures and pressures of spherical to nonspherical bubble collapses by forcing them with standing waves and traveling waves, respectively. This comparison is made in parameter ranges of relevance to both single bubble sonoluminescence (SBSL) and multi-bubble

sonoluminescence (MBSL) or sonochemistry. At moderate forcing, spherical and nonspherical collapses achieve similar peak temperatures and pressures but, as the forcing is increased, spherical collapses become much more intense. The reduced temperatures of nonspherical collapses at high forcing are due to residual kinetic energy of the liquid jet that pierces the bubble near the time of minimum volume. This is clarified by a calculation of the (gas) thermal equivalent of this liquid kinetic energy.

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Integration Between Electrochemical and Biochemical Methods for Industrial Wastewater Treatment

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Previous studies of the Group evidenced that the kinetics of the removal of pollutants from industrial wastewater by electrolysis is a function of the anode material and of the applied electrochemical parameters. These factors govern the type of electrode reactions, including an eventual direct discharge of pollutants and the relative contribution of direct and mediated electro-oxidation. On the basis of the experimental results two anode materials: Ti/Pt-Ir and Ti/PdO-Co₃O₄ can be indicated as appropriate for electrochemical treatment of those wastewaters, in which removal of pollutants is to be achieved by an indirect, Cl₂ mediated oxidation. These two materials proved to be excellent catalysts for the chlorine evolution reaction. Under certain conditions, participation of other mediators, apart of active chlorine, as e.g. hydrogen peroxide or hydroxyl radicals, was also proved possible. Generally, the depletion of pollutants was well described by a pseudo-first order kinetics. For example the kinetic rate constant equal to 0.75 min⁻¹ was achieved for N-NH₃ removal from tannery wastewater using the Ti/PdO-Co₃O₄ anode. In case the organic load is efficiently removed by a conventional biological process, electrochemical oxidation can be applied as a post-treatment step to remove residual N-NH₃ with low energy consumption (0.4 kWh/m³), offering a valid alternative to biological nitrification/denitrification. Experimental results proved also the feasibility of application of electro-oxidation for the destruction of the pollutants present in dyeing baths containing partially soluble disperse dyes. Electrochemical oxidation, which led to substantial decolorisation, is a promising tool for treatment of this kind of wastewater. The efficiency of the treatment depended on the nature of the supporting electrolyte and the bulk pH in the reactor and, to a lesser degree, on the type of the anode material. The best res-

ults were obtained in a chloride-rich medium under acidic pH using the Ti/Pt-Ir anode. Since a cyclic voltammetry study showed no direct discharge of pollutants at the Ti/Pt-Ir anode, it was concluded that the process was mediated by chlorine-hypochlorite species obtained via electro-oxidation of chlorides at the anode and (·OH) radicals generated during water discharge. The apparent pseudo-first order rate constant for the removal of colour was equal to 2.54 x 10⁻⁴ s⁻¹ under conditions of free pH evolution. The control of pH at the acidic level at the value of 4.5 resulted in an over 30-fold increase of the reaction rate. Less encouraging results obtained during the comparative chemical oxidation of pollutants by hypochlorite ions indicate that electrochemical oxidation is preferred to the commonly applied chemical treatment. Interesting results were also obtained for direct anodic oxidation of cyanides, a reaction which proceeded simultaneously with the formation of the catalytic film of Cu oxides on the electrode. This was possible for low agitation rates, as otherwise film was sheared from the electrode surface. A shearing rate γ and shearing stress τ acting on the anode surface were quantified by a polarographic method consisting in measuring the limiting diffusional current I_L of the reduction of ferricyanide ions on the cathode. This method gives generally results which agree accurately with the laser Doppler measures. The experiments performed using a solution containing a mixture of 2 x 10⁻³ M potassium ferricyanide, 5x 10⁻² M potassium ferrocyanide and 0.5 M sodium hydroxide as supporting electrolyte served to define the average limiting current I_L , that can be related to the average surface shear rate by appropriate equations, which are reported in the Poster. An alternative biological treatment for azo dyes was also tested. When the azo dyes are subjected to anaerobic treatment they can undergo, by contrary to what is observed under aerobic conditions, a reductive cleavage with a rupture of the -N=N- bond and formation of aromatic amines. A study undertaken to elucidate the influence of the ratio between the concentration of the dye and that of additional carbon, on the performance of anaerobic reactor treating synthetic textile wastewater containing the Procion Brilliant Red H-EGXL dye, was performed using a fed-batch reactor, operated under isothermal conditions at 30 °C, with different feed. Removal of colour from the synthetic textile wastewater has been shown to be feasible in the reactor operating under anaerobic/anoxic conditions, provided the dye concentration in the feed being lower than 2.2 g/L. However, the obtained effluent contained still the organic load and nitrogen and it was necessary to apply a post treatment using electrochemical oxidation.

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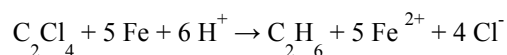
Application of ultrasonically produced nano zero-valent iron for the degradation of chloroethenes

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Halogenated pollutants, such as chlorinated ethenes, are the most often found contaminants in subsurface environments. In recent years, it has been demonstrated that zerovalent iron (ZVI) can be used to dehalogenate chloroethenes and chloroethanes due to hydrodechlorination. For example, perchloroethene (PCE) is essentially reduced completely to ethane with ZVI:



In-situ zerovalent iron permeable barriers have been implemented for the treatment of chlorinated solvents contaminated groundwater. However, the construction of permeable barriers is very expensive due to high investment costs. The direct application of nanosized materials in the subsurface represents a more cost-efficient alternative. Nanoscale iron particles would provide enormous flexibility for *in situ* applications. However, pure iron nanoparticles have no protective shell on the surface and hence they are not stable in contact with air. On the contrary, they are pyrophoric and burn spontaneously upon exposure to air.

Therefore, a new sonochemical method was developed to prepare air stable iron nanoparticles in the presence of commercial edible oils. The sonochemistry leads to the formation of iron nanoparticles surrounded by a polymer. Air stability was demonstrated for several months. Our study focussed on the dechlorination activity of the novel nanoparticles.

The air-stable nanoparticles were added to polluted groundwater samples containing approx. 1 mg/l PCE. As a result, the new material proved to be efficient for PCE dechlorination. More than 50 % of the initial PCE was completely dechlorinated to ethene and ethane. As compared to conventional ZVI, that is used for Permeable Reactive Barriers, the reactivity of the nanomaterial is approx. 10 times higher. The experiments demonstrate the high potential of the material for environmental remediation.

Keywords: chloroethenes, nanoparticles, dehalogenation, groundwater, remediation

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Dechlorination activity and microbial population dynamics after exposure to an electric field

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Chloroethenes are hazardous environmental pollutants frequently detected in groundwater and soil. Natural occurring microbial degradation processes of chloroethenes are known to be limited by the availability of electron donors (e.g. H_2) and acceptors (e.g. O_2). In recent years, electrode applications were increasingly considered to stimulate microbial remediation processes. The aim of the project at the TZW is to use electrodes to enhance microbial degradation of chloroethenes via water electrolysis. The electrochemical formation of hydrogen and oxygen will be used to generate zones favourable for microbial dechlorination.

In general, understanding the effects of electric currents and electrochemical reactions on microorganisms is a pre-requisite for successful electro-bio-processes development. Therefore, the dynamic changes in a VC dechlorinating enrichment culture were investigated during exposure to an electric field and subsequent incubation, applying DNA analysis by denaturing gradient gel electrophoresis (DGGE).

A vinylchloride (VC) dechlorinating enrichment culture was exposed to an electric field and samples were taken for activity and DGGE analysis. After DGGE analysis, a major distinctive DNA band could be seen in all samples which presumably represents the VC dechlorinating organism. Dechlorination activity could be correlated to band thickness. In samples showing microbial dechlorinating activity the bands were more dominant indicating that more DNA was present in these samples due to microbial growth.

In summary no shift in bands could be detected in the enrichment culture throughout the incubation period and along the electrolysis. The dechlorinating activity correlated with DNA band thickness and decreased with increasing exposure to the electric field. Inhibiting effects were only observed at very high current intensities ($I = 350\text{mA}$, Electrode area = 20 cm^2 , Volume: 900 mL) and additional chemical analysis revealed that these effects were due to the electrochemical formation of toxic by-products rather than directly related to the electric field. Furthermore, at electric field intensities required for field conditions no effects on microorganism activity could be

observed.

The same experimental procedure can be applied to study the sensitivity of different bacteria to electric fields and electrochemical reactions. The bands of interest have been cut out from the DGGE gels and the DNA was amplified using PCR in preparation for sequencing. This will allow the identification of relevant bacterial species present in the enrichment cultures.

Acknowledgment: The authors gratefully acknowledge financial support by the COST office, AIF Otto von Guericke, EPSRC, BUCKINGHAM Group Contracting and FIRST FARADAY.

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Assessment of the potential for electrochemical stimulation of TCE biodegradation in a contaminated soil

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Due to their extensive use as industrial solvents, dry cleaning agents and degreasers, chlorinated solvents are extremely common contaminants in soil and groundwater. Chlorinated solvents released into the sub-surface may result in the presence of free-phase (dense non-aqueous phase liquid; DNAPL) chlorinated solvent contamination, which will persist for decades and act as long-term sources of groundwater contamination. All chloroethenes are either known or suspected carcinogens and therefore their presence in the environment is of major concern. Microbial degradation mechanisms for chlorinated ethenes are often limited in the field by a lack of electron donors and electron acceptors.

The purpose of this STSM is to assess the potential for electrochemical stimulation of TCE biodegradation in a contaminated soil. Specifically it will look at the enhancement affects of hydrogen and Fe(III), compounds which may be generated by electrochemical processes. Two soil cores (from a depth of 1.5m to 6m) were taken anaerobically from a TCE contaminated site in the UK using a sonic drilling technique. Each core consisted of three 1.5 m length filled plastic liners, with a 15cm diameter. From the same site, 60 litres of groundwater were taken anaerobically from 6 bore holes. The initial stage of this work was to establish the extent of contamination throughout the soil core profiles. The cores were therefore analysed for TCE and metabolite concentrations using Gas

Chromatography. Samples were also analysed for chloride and sulphate concentrations using Ion Chromatography. The ground water was tested for O₂, pH, chlorinated solvents, sulphate and chloride.

The in-depth chemical analysis of the soil cores showed that complete dechlorination from TCE to ethene had occurred in parts of the profile. This indicates that dechlorinating organisms are present in the soil. However, dechlorination of the contaminants is likely to be limited by the availability of electron donors. In order to assess the enhancement effects of hydrogen and Fe(III), soil samples from the most contaminated parts of the cores were homogenised and used for the set up of flow column experiments and microcosms. Groundwater sampled from a borehole in between the two soil cores was also used for these experiments. Three microcosms containing sediment and groundwater were amended with acetate, iron and iron plus acetate. Three microcosms containing only groundwater were amended with acetate, iron and hydrogen. It is hypothesized that in the microcosms and flow columns with hydrogen and acetate added, dechlorination will be greatly enhanced. Weekly sampling of the microcosms and flow columns will take place to assess biodegradation rates. In addition, soil samples will be investigated for the presence of specific dechlorinating microorganisms and for overall shifts in the microbial community using molecular techniques.

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Ultrasound-assisted extraction of pine needles for elemental analysis

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The microwave accelerated dissolution has become the main sample pre-treatment method for elemental analysis in different kind of environmental samples¹. The microwave based methods are powerful but those methods are usually time consuming and tedious. An alternative and faster sample pre-treatment method is an ultrasound-assisted extraction which has been validated also for several sample matrices.²

In this study the ultrasound-assisted extraction followed with ICP-OES is validated for the determination of element concentrations in pine needles. The microwave digestion procedure (BCR 100, Beach leaves) was used as a reference method for ultrasound-assisted extraction procedure. The need for

analysis of pine needles is based on their ability to be good indicators of both environmental contamination and available nutrient content of soil. The increased interest on the analysis of pine needles in Finland is due to the use of energy wood ash as a fertilizer in forests.

Efficient and cost effective method of extraction for the determination of element concentrations in pine needles was developed. A standard reference material (SRM) or real sample of about 250 mg was accurately weighed into a 100 ml plastic screw-top bottle into which 5 mL of water and 5 mL of *aqua regia* was added. The bottle was closed and placed into a 650 W, 35 kHz, Model Transsonic 820/H ultrasonic water bath (ELMA, Singen, Germany). The optimized sonication procedure lasted 9 minutes and was carried out at a temperature of about 50 °C.

The determined element (Al, Ca, Cd Cu, Fe, K, Mg, Mn, Na, P, and Zn) concentrations were highly comparable with the certified concentrations of the SRM 1575 (Pine needles). The element concentrations determined with both ultrasound-assisted extraction and microwave digestion followed with the ICP-OES were also statistically tested and significant differences were found for Fe, Mg and P only.

The main advantages of the ultrasound-assisted extraction, when compared to conventional methods, are the speed of extraction (9 min), high sample treatment capacity (50 samples at the same time) and low reagent usage resulting in low nitrate and chloride concentrations when *aqua regia* is used. The ultrasound-assisted extraction procedure is carried out at low temperatures and pressures, which resulting in capability to extract sample without loss of easily volatile elements such as arsenic and mercury.² When centrifuge tubes are used, the sample solutions can be centrifuged instead of filtering, which is necessary for the sequential extraction procedures.³

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Analysis of Chlorobenzenes in Environmental Water Samples using Microwave-Assisted with Ionic-Liquids Liquid-Phase Microextraction

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Liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are the most commonly used sample pre-treatment methods for the isolation and/or enrichment of chlorobenzenes. Solid-phase microextraction (SPME) is an alternative preconcentration method for aqueous samples in which analytes partition between the stationary phase on a SPME fibre and the sample is achieved after equilibrium. An interesting and recently introduced alternative to traditional extraction techniques is liquid-phase microextraction (LPME), which is based on the miniaturisation of the traditional liquid-liquid extraction method by greatly reducing the solvent to aqueous ratio. This is performed by using a single-drop of organic solvent or a small length of porous hollow fiber-protected solvent.

Headspace single-drop microextraction (SDME) has proved to be rapid, inexpensive, simple, precise, virtually solventless and sensitive technique for the analysis of chlorobenzenes in water samples, representing an excellent alternative to traditional and other recently introduced methods¹.

The present work investigates, for the first time, the possibility of using microwave to assist the microextraction of eight chlorobenzenes in water samples. In addition, ionic liquids will be evaluated to generate the single-drop, to produce the microextraction on headspace modality.

Experimental variables will be evaluated and optimized by means of experimental design and the optimized method will be validated with real samples.

Keywords: Chlorinated benzenes; headspace SDME; ionic liquid; microwaves; water analysis.

Acknowledgements: The authors would like to thank the financial support of the Spanish Government (projects n. DPI2002-04305-C02-01, PTR1995-0581-OP-02-01, PROFIT2004-23-122 and CAL03-078-C3-2). L.V also thanks Vicerrectorado de Investigación, Desarrollo e Innovación of University of Alicante for her scholarship and COST (European Science Foundation, EU) for her grant.

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Selective modification at tyrosine residues by the electrochemical, sonoelectrochemical and sonochemical nitration of lysozyme

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Selective modification at tyrosine residues by the electrochemical, sonoelectrochemical and sonochemical nitration of lysozyme Walton, David J. 1; Heptinstall, John1, Mercer, Sadie1, Peterson, Ian R.1; Matters, Dominic1; Escalapez-Vicente, M^o Deseada2; Iniesta, Jesús2 Cooper, Helen J3 1School of Science and the Environment, Center for Molecular and Biomedical Science, Coventry University, Coventry CV1 5FB, United Kingdom 2Physical Chemistry Department, Alicante University, Alicante 03080, Spain 3 School of Biosciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom. Examination of the electrochemical, sonoelectrochemical and sonochemical modification of proteins and other bioactive molecules may result in the production of novel proteins, enzymes and other bioactive species, in comparison with traditional methodologies such as protein engineering and the use of chemical reagents. The aim of this is to produce electrosynthetically nitrated proteins and to manipulate the nature of that modification either by the use of ultrasound irradiation during electrolysis or by simple exposure of an aqueous protein solution to an ultrasonic field. We show that the above techniques have various consequences for the labelling of proteins, for their specific immobilisation, use in biosensors, the production of novel modified proteins for pathophysiology of oxidative dysfunction, and the microencapsulation of proteins in polymeric microspheres. Hen egg white lysozyme (HEWL) was treated in pH9 aqueous buffer by electrochemical, sonoelectrochemical and sonochemical reaction in the presence of sodium nitrite. Site specific nitration and the stability of lysozyme during these treatments was evaluated by UV-vis spectroscopy, HPLC, direct mass spectrometry, enzyme linked immunosorbent assay (ELISA) and by determining the enzyme activity before and after nitration. In earlier work we showed the electrochemical nitration of HEWL to be selective for tyrosine 23 initially, followed by bisnitration at tyrosine 20 with no trisnitration at tyrosine 53 [1]. Now in this presentation we assess the simultaneous ultrasonic irradiation of the electrosynthesis of HEWL using a 40 kHz 180 w ultrasonic cleaning

bath, resulting in different mono to bis nitration ratios at the same residues compared to those in a silent system. Sonication of aqueous lysozyme solutions with and without sodium nitrite was also performed and to the best of our knowledge we show for the first time the sonochemical nitration of HEWL in the presence of a nitrogen source such nitrite [2].

Keywords: Lysozyme, protein stability, ultrasound, free radicals, nitration.

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