Projet MAISOE

STAE
TOULOUSE

Workshop MAISOE – RTRA – STAE

November 21-23, 2011
Relais du Bois Perché – 31160 ASPET – France

Programme

Monday, November 21, 2011

12:30 Lunch

14:00 **Welcome, RTRA STAE presentation and Introduction** (30 min)
Philippe BEHRA (INP, Laboratoire de Chimie Agro-Industrielle, UMR 1010 INRA/INPT-ENSIACET, Toulouse, France)

Convener: Mary-Lou TERCIER-WAEBER (Université de Genève, Switzerland)

Talks (40 min presentation + 20 min discussion)

14:30 Christian AMATORE (Académie des Sciences, CNRS, Université Pierre & Maire Curie, Ecole Nationale Supérieure Ulm, Paris, France): **Molecular electrochemistry and microsensors for local analysis**

15:30 George W. LUTHER, III (School of Marine Science and Policy, College of Earth, Ocean and Environment, University of Delaware, Lewes, DE, USA): **Voltammetric sensors to determine the dynamics of biogeochemical and physical processes at oxic-anoxic interfaces**

16:30 Coffee break

Talk (20 min presentation + 10 min discussion)

17:00 Claire TENDERO *et al.* (MAISOE project, Cirimat, Toulouse, France): **Material protection against corrosion and biofouling: Al_2O_3–Ag and PEEK–Ag nanostructured composite coatings for combined anticorrosion-antifouling applications**

Talks (40 min presentation + 20 min discussion)

18:00 Stephen C. Dexter and George W. LUTHER, III (School of Marine Science and Policy, College of Earth, Ocean and Environment, University of Delaware, Lewes, DE, USA): **Biofilm formation and its role in corrosion and biofouling of metals in seawater– a Mn cycling story**

19:30 Dinner

Tuesday, November 22, 2011

Convener: Bernhard WEHRLI (ETH Zürich, Switzerland)

Talks (40 min presentation + 20 min discussion)

08:30 Laura SIGG (Eawag, Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland, ETH Zürich, Switzerland): **Metal speciation analysis and its application to bioavailability to aquatic organisms**

09:30 Mary-Lou TERCIER-WAEBER (Analytical and Environmental Chemistry, Department of Inorganic and Analytical Chemistry, University of Geneva, Sciences II, Geneva, Switzerland): **Microsensors and probes for *in situ* monitoring of trace metal dynamic speciation in aquatic systems: New insights into metal biogeochemical cycles and potential impact**

10:30 Coffee break

11:00 Philippe BEHRA *et al.* (MAISOE project, LCA, GET, LAAS, LCC, LGC, LPCNO, Toulouse, France): **Trace metal dynamic speciation: application to *in situ* trace mercury microsensor**

12:30 Lunch

Convener: Ken S. JOHNSON (Monterey Bay Aquarium Research Institute, USA)

14:30 Véronique GARÇON *et al.* (MAISOE project, Legos, LAAS, LCC, LGC, OMP, Toulouse, France): **Microsensors for *in situ* measurements of dissolved macronutrients in marine systems**

15:30 Yuri P. YAKOVLEV (A.F. Ioffe Physico-Technical Institute, IBSG Co., Ltd., St Petersburg, Russia): **Optoelectronics pairs (LED's and Photodiodes) at the MID - IR spectral range (1.6-5.0 µm) for CO_2, CH_4 detection**

16:30 Coffee break

17:00 Jean-Pierre DUTASTA (École Normale Supérieure de Lyon, Laboratoire de Chimie, UMR CNRS, Lyon, France): **The chemistry of cryptophanes: applications and perspectives**

18:00 Valérie CHAVAGNAC *et al.* (MAISOE project, GET, Cirimat, LAAS, LCA, Toulouse, France): **Deep sea observatory: a need of *in situ* dissolved methane sensor**

19:30 Dinner

Wednesday, November 23, 2011

Convener: George LUTHER III (University of Delaware, USA)

08:30 Ken S. JOHNSON (Monterey Bay Aquarium Research Institute, Moss Landing, California, USA): **Sensors for long-term (years) observations of nitrate and pH and their application in ocean science**

09:30 Bernard WEHRLI (ETH Zürich, EAWAG, Swiss Federal Institute of Aquatic Science and Technology, and Institute of Biogeochemistry and Pollutant Dynamics, Switzerland): **Tracing biogeochemical processes in lakes with *in-situ* sensors**

10:30 Coffee break

11:00 **Round table** (1 h): chaired by Christian AMATORE and the different conveners

12:00 **Conclusions**: Philippe BEHRA

12:30 Lunch

14:00 Departure to Toulouse

MAISOE : Microlaboratoire d'Analyses *In Situ* pour des Observatoires Environnementaux
RTRA : Réseau Thématique de Recherche Avancée
STAE : Sciences et Technologies pour l'Aéronautique et l'Espace

Workshop MAISOE – RTRA – STAE

November 21-23, 2011
Relais du Bois Perché – 31160 ASPET – France

Abstracts

Welcome, RTRA STAE presentation and Introduction (30 min)
Philippe BEHRA (INP, Laboratoire de Chimie Agro-Industrielle, UMR 1010 INRA/INPT-ENSIACET, Toulouse, France)

Christian AMATORE (Académie des Sciences, CNRS, Université Pierre & Maire Curie, ENS Ulm, Paris, France): **Molecular electrochemistry and microsensors for local analysis**

George W. LUTHER, III (College of Earth, Ocean and Environment; School of Marine Science and Policy; University of Delaware, Lewes, USA): **Voltammetric sensors to determine the dynamics of biogeochemical and physical processes at oxic-anoxic interfaces**

Sediments and anoxic basins show a transition from oxygenated (oxic) to sulfidic (anoxic) conditions, and the pattern follows the bacterial decomposition of organic matter by oxidants [O_2, NO_3^-, MnO_2, $FeOOH$, SO_4^{2-}]. In some instances, the transition shows smooth chemical gradients, which follow an orderly diagenetic pattern and are easily modeled, but in other instances bioturbation and/or physical processes can affect the smooth chemical gradients. First, data using solid state gold amalgam voltammetric electrodes will show sediment geochemistry changes for dissolved O_2, Fe(II), Mn(II) and H_2S in marine and freshwater sediment systems. Second, data on water column chemistry changes at the interfaces found in the Black Sea, the Chesapeake Bay and other systems will show the dynamics of physical processes. The turnover of sulfidic bottom waters, which are also rich in nutrients, to the surface waters can lead to disastrous environmental consequences including fish kills harmful algal blooms.

Claire TENDERO *et al.* (MAISOE project, Cirimat, Toulouse, France): **Material protection against corrosion and biofouling: Al_2O_3–Ag and PEEK–Ag nanostructured composite coatings for combined anticorrosion-antifouling applications**

Ana-Maria Ciubotaru (Lazar)*[1,2,3], Diane Samélor[1,2], Claire Tendero[1,2], and Constantin Vahlas[1,2]

1 Université de Toulouse, CIRIMAT/INPT, 4 allée Emile Monso BP 44362, 31030 Toulouse cedex 4, France
2 Centre Interuniversitaire de Recherche et d'Ingénierie des Matériaux – UMR 5085 CNRS/UPS-INPT
3 FCS RTRA STAE, 23 avenue Edouard Belin, 31400 Toulouse, Cedex 4, France

The investigation of a complex metalorganic chemical vapour deposition (MOCVD) process is presented for the deposition of Al_2O_3-Ag and PEEK-Ag nanocomposite coatings, with the aim to combine the barrier properties of amorphous alumina and of PEEK (Poly Ether-Ether-Ketone) with the anti-fouling ones of silver nanoparticles. The process involves a hot wall reactor geometry with a deposition temperature of around 480°C and a pressure of 5 torr. Aluminium Tri-Isopropoxide (ATI) is used as precursor for the deposition of the amorphous alumina matrix on 304L stainless steel substrate, while the PEEK untreated or UV treated is used as it is as support to deposit Ag nanoparticles.

Electrochemical impedance spectroscopy and test performed at high temperature in reactive environment reveal that Al_2O_3 coatings present state of the art protection of metallic substrates (stainless steel, titanium alloys) against corrosion and high temperature oxidation [1,2].

Deposition of Ag nanoparticles is obtained by Direct Liquid Injection (DLI) MOCVD using a silver pivalate or a Ag(Fod)(PEt$_3$) solution as precursors. The study related to the dependence of Ag particles dimensions and morphology on the main process parameters was realized. Ag nanoparticles with a diameter inferior at 15 nm were obtained (Figure 1).

The obtained composite coatings are being characterized by different techniques (SEM, AFM). Also a first antifouling properties test of these materials was realized in a real environment.
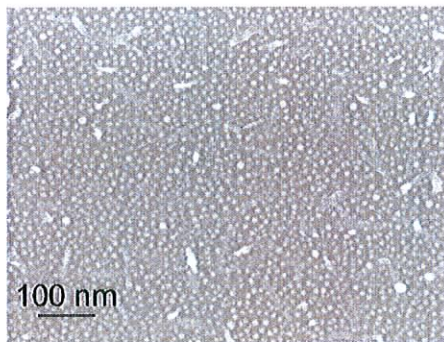

Figure 1. SEM image of Ag nanoparticles obtained using silver pivalate precursor on Al_2O_3

1. G. Boisier, M. Raciulete, D. Samelor, N. Pébère, A.N. Gleizes, C. Vahlas. Electrochemical Behavior of Chemical Vapor Deposited Protective Aluminium Oxide Coating on Ti6242 Titanium Alloy. *Electrochemical and Solid-State Letters* **11** (2008) C55-C57.
2. J.D. Béguin, D. Samélor, C. Vahlas, A.Gleizes, J.A. Petit, B. Sheldon. Evaluation of Al_2O_3 MOCVD coating for titanium alloys protection under severe conditions at high temperature. *Materials Science Forum* **595-598** (2008) 719-724.

Stephen C. Dexter and George W. LUTHER, III (School of Marine Science and Policy, College of Earth, Ocean and Environment, University of Delaware, Lewes, DE, USA): **Biofilm formation and its role in corrosion and biofouling of metals in seawater– a Mn cycling story**

Corrosion of metals is influenced by the formation of biofilms. In this work, we show data indicating that a cycle of Mn(II) oxidation and re-reduction of MnO_2 can sustain corrosion on metals. Key in this cycle is the disproportionation of Mn(III) to Mn(II) and MnO_2, and the biological (or chemical) oxidation of Mn(II) by O_2. The cycle has pH dependence and the formation of H_2O_2 can aid the cycling. In situ microelectrode profiles in the biofilms indicate that these chemical species are present. The coating of MnO_2 on metal cathodes in the absence of biofilms shows that Mn is involved with corrosion.

Laura SIGG, Philippe Bradac, Theodora Stewart, Renata Behra (Eawag, Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland, ETH Zürich, Switzerland): **Metal speciation analysis and its application to bioavailability to aquatic organisms**

Metal speciation is a key parameter for the bioavailability of trace metals to algae under freshwater conditions. Laboratory experiments and theoretical derivations have demonstrated that either the free metal ion concentrations or under certain conditions the labile metal species determine the uptake of metals by freshwater algae. Periphyton, the algal biofilm growing on solid substrates in natural waters, may be influenced by the natural polymer matrix with respect to metal uptake.

A number of analytical methods providing insights into metal speciation, as related to bioavailability under natural water conditions are available, in particular several methods for measurement of the labile metal species, which are defined by the dynamic characteristics of the method. DGT (diffusion gradients in thin films) has been used for our projects as a convenient method, by which the labile metal concentration in natural waters may be measured as a time average over hours to days. Labile metal concentrations obtained by DGT were compared to several other methods and to modelled speciation on the basis of characterization of natural organic matter by size exclusion chromatography/organic carbon detection.

Cadmium, copper and zinc accumulation in periphyton under natural freshwater conditions was related to measured speciation parameters. Labile metal concentration may be determining metal uptake by periphyton if diffusion of metals through the embedding matrix is the rate-limiting step. Characterization of this extracellular polymer matrix with respect to composition and metal binding may provide further insights.

Mary-Lou TERCIER-WAEBER (Analytical and Environmental Chemistry, Department of Inorganic and Analytical Chemistry, University of Geneva, Sciences II, Geneva, Switzerland):
Microsensors and probes for *in situ* monitoring of trace metal dynamic speciation in aquatic systems: New insights into metal biogeochemical cycles and potential impact

To enable more reliable understanding and assessment of respectively trace metal biogeochemical cycles and ecological risk in aquatic systems, the recording of high resolution data sets of specific metal fractions, coupled to master variables, is essential to both take correctly into account their spatial/temporal evolution and detect significant increase or sudden change in their concentrations. Such analyses are not feasible by using the classical approach based on total dissolved metal concentration measurements after sample collection, storage and transportation, followed by sample handling and analysis in laboratory. It requires the use of innovative analytical tools, developed taking into account specific conceptual, analytical, and technical criteria.

This will be illustrated by presenting the development of bioanalogical sensors (based on rugged, reliable modified microelectrodes), mini- and micro-integrated analytical systems and the coupling of these devices to submersible probes performed by us to allow in situ autonomous or remote high resolution voltammetric trace metal analysis and speciation coupled to master variables [1,2]. The significant advantages of such tools, vs traditional laboratory techniques, in term of spatial and temporal resolution of data, as well as the promising possibilities they lie ahead for the environmental scientists to perform cost effective, more efficient trace metal environmental monitoring [2] and pollution control [3] will be illustrated by selected examples of applications.

1. M.-L. Tercier-Waeber, M. Taillefert. Remote in situ voltammetric techniques to characterize the biogeochemical cycling of trace metals in aquatic systems. Critical review. *J. Environ. Monit.* **10** (2008) 30-54.
2. M.-L. Tercier-Waeber, T. Hezard, M. Masson, J. Schäfer. In situ monitoring of the diurnal cycling of the dynamic metal species in a stream under contrasting photobenthic biofilm activity and hydrological conditions. *Env. Sci. Technol.* **43** (2009) 7237-7244.
3. M.-L. Tercier-Waeber, M. Masson, J.-L. Loizeau, M. Sénéclauze, P. Dallemagne, A. Restrepo, L. Dussud, P. Rousseaux, S. Prigent, B. Forest. Tracking waste water effluent spreading and heavy metals they may release in coastal area using a wireless mobile sensor network, in prep. (www.mobesens.eu)

Philippe BEHRA et al. (MAISOE project, LCA, GET, LAAS, LCC, LGC, LPCNO, Toulouse, France):
Trace metal dynamic speciation: application to *in situ* trace mercury microsensor

Teddy Hezard[1,2], Maud-Alix Mader[3], Pierre-Jean Deboutière[4], David Evrard[2], Pierre Gros[2], Pierre Joseph[3], Anne-Marie Gué[3], Katia Fajerwerg[4], Bruno Chaudret[5], Brigitte Dubreuil[1], Philippe Behra[1]

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Trace metal dynamic speciation analysis is a challenge for better understanding processes and fate of trace metals in the environment. Indeed, biodisponibility, physico-chemical reactivity in aqueous phase or at solid-phase, gas-solid or gas-liquid interfaces depends strongly on the concentration of the different species. Mercury (Hg) is among the most bio-accumulated toxic trace metals in the trophic chain depending on its speciation (oxidation state and chemical species). In the different compartments of natural systems, Hg is present as inorganic complexes or as organometallic species such as methylmercury. For this reason Hg has been classified among the priority substances in the European water framework directive, the maximum permissible concentration in surface waters being at 0.07 μg L^{-1} (ca. 0.35 nmol L^{-1}). Many countries set up programs aiming at monitoring its concentration in natural systems. Two ways are possible for investigating Hg speciation: either passive in situ sensor for having a picture of averaged species concentration during a given period such as DGT (diffusion gradients in thin films) or dynamic in situ sensor in order to measure concentration of different species in a much shorter period of time. The aim of this work is to develop an analytical device which allows in situ dynamic measurement of low Hg species concentration (in the range of pmol L^{-1} to nmol^{-1}) in dissolved, colloidal and particulate phases. In order to reach this goal, a microfluidic system was developed for phase separation together with a gold nanoparticles (AuNPs) modified glassy carbon (GC) interface devoted to low Hg concentration electrochemical determination.

The microfluidic phase separation system is based on hydrodynamic filtration and brownian ratchets. It is membrane free, label free and performs separation with size of the particles as the only separation criterium. It also has the advantage of being fairly independent of the flow rate, having characteristic length of an order of magnitude higher than the particles size and using no external force field. We here present results obtained with the first generation model separator performing separation around 0.45 μm. The prototypes are Y-type microchannels made of PDMS (polydimethylsiloxane) using soft lithography technology and tested with model polystyrene fluorescent particles. We show that the threshold diameter of our systems is consistent with our theoretical predictions, achieving separation size 10 times smaller than size reported in literature.

The AuNPs-GC electrodes were prepared either by chemical synthesis or directly by means of electrochemical methods leading to nanomaterials for Hg(II) sensing.

The synthesis of AuNPs was investigated by using organometallic precursors. Two main reasons for the interest of the organometallic approach are the possibilities to get monodisperse small nanoparticles and to perform functionalization, e.g. specific ligands such as thiol compounds, at their surface. The first point is mainly responsible to a high specific area (high surface/volume ratio) and the second one is more correlated to the enhancement of the sensitivity and selectivity to Hg(II) compared to "naked" AuNPs. However, these two advantages are very often connected. Two organometallic precursors were synthesized, i.e. AuCl(THT) and AuCl(PPh$_3$) and used for the preparation of AuNPs. Different mean size (7/10/12/25/200 nm) were obtained and successfully deposited onto GC electrodes. These dense deposits still have to be tested for Hg(II) electrochemical detection by square wave anodic stripping voltammetry (SWASV).

In the case of electrodeposition, AuNPs were deposited onto GC electrodes starting from a deaerated 0.1 mol L^{-1} NaNO$_3$ solution containing 0.25 mmol L^{-1} HAuCl$_4$ (pH 3) using three different methods namely, cyclic voltammetry (CV), chronoamperometry (CA) and potentiostatic double-pulse (PDP). The AuNPs-GC electrodes exhibited significantly improved performances in the determination of 4 nmol L^{-1} Hg(II) solutions when compared to

unmodified GC and bare Au electrodes [1]. CA was found to be the best electrodeposition method for controlling the morphology, size and density of AuNPs [2]. In the optimal conditions (CA method, AuNPs size = 17 nm, NPs density = 332 μm^{-2}), the response of the AuNPs-GC electrode using SWASV was linear in the range 0.80 – 9.9 nmol L^{-1} Hg(II) with a sensitivity of 1.16 μA nmol L^{-1}. A limit of detection of 400 pmol L^{-1} was obtained for a Hg(II) preconcentration time of 5 min [2].

1. T. Hezard, K. Fajerwerg, D. Evrard, V. Collière, P. Behra, P. Gros, *J. Electroanal. Chem.* (2011) in press, doi: 10.1016/j.jelechem.2011.10.014
2. T. Hezard, K. Fajerwerg, D. Evrard, V. Collière, P. Behra, P. Gros, *Electrochim. Acta* (2011) in press, doi: 10.1016/j.electacta.2011.10.101

Véronique GARÇON *et al.* (MAISOE project, Legos, LAAS, LGC, OMP, Toulouse, France):
Microsensors for *in situ* measurements of dissolved macronutrients in marine systems

Carole Barus[1], Véronique Garçon[1], William Giraud[1,2], Justyna Jońca[1,2], Ludovic Lesven[1*], Danièle Thouron[1], Michel Armengaud[3], Nicolas Striebig[3], Maurice Comtat[2], Katia Fajerwerg[4], Pierre Lacroix[5], Jérôme Launay[5], Pierre Temple-Boyer[5], Emilie Vanhove[5]

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3 Observatoire Midi-Pyrénées – UMS
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Long term monitoring and real time transmission of collected key-parameters of marine environments such as the macronutrients silicates, phosphates, nitrates... will allow to progress in our understanding of the ocean role in climate evolution and in its interactions with the terrestrial biosphere and anthropogenic activities. In order to achieve an *in-situ* miniaturized autonomous sensor, electrochemistry has been chosen for the detection and quantification of nutrients in sea water [1].

Silicates and phosphates are non-electroactive species. Their electrochemical determination is based on the formation of a complex with molybdate. The complexes are formed by the reaction with K_2MoO_4 in an acidic solution to form the silico- and phosphor-molybdic complexes [2]. Molybdenum metal is oxidized to form molybdates and protons. To reach the needed acidic pH, a membrane is used to isolate the counter-electrode and avoid the reduction of protons formed. The complexes are then detected on gold electrode surfaces by cyclic voltammetry or chronoamperometry. The detection limit is 1 μM [3] for silicates and 0.12 μM for phosphates [4].

Experimental parameters for molybdenum oxidation have been determined and preliminary results were obtained with the 1st prototype of silicates sensor. Because the potential window for the detection of silicates and phosphates is the same, there is an obvious problem of cross interference in samples with both nutrients. Therefore, we propose three different approaches to avoid silicate interferences using differences in kinetics of complex formation, differences in electrochemistry of both complexes and influence of pH on complex formation.

Electroreduction of nitrate in seawater was investigated by cyclic voltammetry at a bare gold electrode modified by electrodeposited silver nanoparticles. A low limit of detection is achieved due to the combination of two chemical reactions coupled with electron transfer [5].

1. M. Lacombe, V. Garçon, M. Comtat, L. Oriol, J. Sudre, D. Thouron, N. Le Bris, C. Provost. Silicate determination in sea water: Toward a reagentless electrochemical method. *Marine Chemistry* **106** (2007) 489-497.
2. N. G. Carpenter, A. W. E. Hodgson, D. Pletcher. Microelectrode procedures for the determination of silicate and phosphate in waters – fundamental studies. *Electroanalysis* **17** (1997) 9, 1311-1317.
3. M. Lacombe, V. Garçon, D. Thouron, N. Le Bris, M. Comtat. Silicate electrochemical measurements in seawater: Chemical and analytical aspects towards a reagentless sensor. *Talanta* **77** (2008), 744-750.
4. J. Jońca, V. Leon Fernandez, D. Thouron, A. Paulmier, M. Graco, V. Garçon. Phosphate determination in seawater: Toward an autonomous electrochemical method. *Talanta* (2011) in press, doi.org/10.1016/j.talanta.2011.09.056
5. K. Fajerwerg, V. Ynam, B. Chaudret, V. Garçon, D. Thouron, M. Comtat. An original nitrate sensor based on silver nanoparticles electrodeposited on a gold electrode. *Electrochem. Com.* **12** (2010), 1439-1441.

Yuri P. YAKOVLEV (A.F. Ioffe Physico-Technical Institute, IBSG Co., Ltd., St Petersburg, Russia): **Optoelectronics pairs (LED's and Photodiodes) at the MID - IR spectral range (1.6-5.0 µm) for CO_2, CH_4 detection**

High power LEDs and photodiodes at the spectral range of 1.6-4.6 µm are very promising devises for the different applications such as medical diagnostics (noninvasive method for measuring glucose in blood), environment monitoring, measuring contents of oil in water and so on. A number of such relevant gases as H_2O, CO_2, CO, CH_4, N_2O, SO_2, NH_3, HF and others have strong fundamental absorption lines in the mid-infrared spectral range that are 50-500 times stronger in comparison with Near-Infrared overtone bands at shorter wavelength. Therefore such Mid-Infrared LEDs and Photodiodes (PDs) can be used for creation of optical low power consumption portable gas analyzers.

The talk will consist of four parts. The first part of the talk will be devoted to narrow band gap solid solution based on III-V compounds (GaSb - InAs, GaSb - AlSb) which were used for creation of LEDs and PDs.

The second parts of the talk will be devoted to the creation of LED's for two spectral range: (1.6-2.4) µm based on GaSb/GaInAsSb/GaAlSbAs heterostructures and (2.8-5.0) µm based on InAs/InAsSb/InAsSbP heterostructures. Design and basical optical characteristics LED's for two spectral range will be presented. Besides fundamental limitation for increasing optical power will be given.

The third part of the talk will deal with the creation and investigation of PDs for three spectral ranges: 1.2-2.5 µm based on GaSb/GaInAsSb/GaAlAsSb heterostructures, 1.5-3.6 µm based on InAs/InAsSbP heterostructures and 2.5-4.9 µm based on InAs/InAsSb/InAsSbP heterostructures.

An analysis of the photodiodes performance through the investigation of current - voltage, capacitance - voltage characteristics and spectral responsivity will be presented.

The forth part of the talk will be devoted to the application of Mid-Infrared LED's and Photodiodes in gas sensor. Principal schemes for detection of CO_2, CH_4, CO, H_2O and so on with using Mid-Infrared LED's and Photodiodes will be given. We will also present the design

of portable optical sensor for measuring water in oil based on Mid-Infrared (1.6-2.4) μm "LED matrix – Wideband Photodiodes" optopair and results of measuring water in oil.

Jean-Pierre DUTASTA (École Normale Supérieure de Lyon, Laboratoire de Chimie, UMR CNRS, Lyon, France): **The chemistry of cryptophanes: applications and perspectives**

The cryptophanes are organic molecular receptors endowed with remarkable complexation properties. They are particularly well suited for the recognition of organic cations and neutral molecules in organic solution or in aqueous media. Chiral cryptophanes are also very effective for chiral recognition (discrimination of enantiomers). One of the most important topics, recently developped, concerns the encapsulation of small gaseous molecules. For example, the complexation of xenon by cryptophanes is of great interest for the design of biosensors for medical imaging by NMR (MRI). This has been enlarged to gaseous molecules of growing interest like methane, widely available in nature and that could provide a cleaner energy resource. Thus, different approaches have been developed in recent years to functionalize the cryptophane molecules and to make them attractive for such applications. The synthesis of these molecular receptors, their properties and their potential applications, such as the recognition of biological targets (the concept of biosonde), or the recognition of gases of environmental importance, such as hydrogen or methane, will be presented.
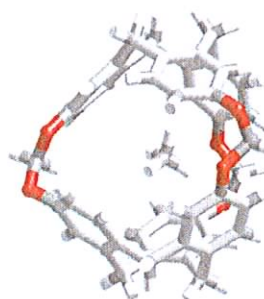
Valérie CHAVAGNAC *et al.* (MAISOE project, GET, Cirimat, LAAS, LCA, Toulouse, France): **Deep sea observatory: a need of *in situ* dissolved methane sensor**

Valérie Chavagnac[1], Cédric Boulart[1], Olivier Carraz[2,3], Han-Cheng Seat[2,3], Michel Cattoen[2,3], Thierry Bosch[2,3], Stéphane Aouba[3], Philippe Arguel[3], Françoise Lozes[3], Brigitte Dubreuil[4], Maëlenn Aufray[5], Philippe Behra[4], Alain Castillo[1], Pascal Gisquet[1]

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5 Centre Interuniversitaire de Recherche et d'Ingénierie des Matériaux – UMR 5085 CNRS/UPS-INPT

Hydrothermal systems along mid-ocean ridges are a significant source of methane for the Deep Ocean , which can be related to different geochemical processes (*e.g.* Lein *et al.*; Charlou *et al.*) [1,2]. Among them, serpentinization can produce high methane concentrations in hydrothermal fluids and strongly impact the gas flux to the water column. However dissolved gas and fluid fluxes are notoriously difficult to measure, leading to inaccuracies in the estimate of the amount of methane produced by hydrothermal systems. Moreover, significant uncertainties exist on the distribution and the patchiness of the

marine sources. These issues can be addressed by in situ chemical sensing to gain new insights on the geographical distribution of the vents and on the time variation of geochemical processes at hydrothermal sources.

Different sensing technologies and sensors currently exist but suffer from limitations (time response, hysteresis [3], which can be bypassed by optical methods associated to "intelligent" polymers. It is shown that dissolved methane can be detected and accurately measured by a surface plasmon resonance sensor associated with a methane specific binding polymer [4]. We describe two novel optical approaches based on this property. Tests of detection and calibrations are performed in the laboratory under different environmental conditions (temperature, pressure, pH). Responses of the methane specific polymer are also studied with respect of the same conditions. We present here the first results from the laboratory-based experiments.

1. A. Y. Lein, D.V. Grichuk, E.G. Gurvich, Y.A. Bogdanov. A new type of hydrogen- and methane-rich hydrothermal solutions in the Rift zone of the Mid-Atlantic Ridge. Dokl. *Earth Sci.* **375A** (2000) 1304-1391.
2. J.L. Charlou, J.P. Donval, Y. Fouquet, P. Jean-Baptiste, N. Holm. Geochemistry of high H_2 and CH_4 vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36°14'N, MAR). *Chem. Geol.* **191** (2002) 345-35.
3. C. Boulart, D.P Connelly, M.C Mowlem. Sensors and technologies for in situ dissolved methane measurements and their evaluation using Technology Readiness Levels. *TrAC Trends in Analytical Chemistry* **29** (2010) 186-195.
4. C. Boulart, M.C. Mowlem, D.P. Connelly, J.-P. Dutasta, C.R. German. A novel, low-cost, high performance dissolved methane sensor for aqueous environments. *Opt. Express* **16** (2008) 12607-12617.

Ken S. JOHNSON (Monterey Bay Aquarium Research Institute, Moss Landing, California, USA): Sensors for long-term (years) observations of nitrate and pH and their application in ocean science

Chemical sensors with lifetimes on the order of years are needed for environmental sensor networks, particularly those deployed in remote regions of the ocean. Our laboratory has developed sensors for nitrate and pH which have demonstrated reasonable stability for time periods of one year or more. The nitrate sensor is an optical instrument that measures the UV absorption spectrum of nitrate. The pH sensor is an Ion Sensitive Field Effect Transistor that is produced by Honeywell. I will briefly describe the instruments, their limitations and the work that can be done with them to monitor carbon and nitrogen cycling in the ocean.

Bernard WEHRLI (ETH Zürich, EAWAG, Swiss Federal Institute of Aquatic Science and Technology, and Institute of Biogeochemistry and Pollutant Dynamics, Switzerland): **Tracing biogeochemical processes in lakes with in-situ sensors**

From a chemist's perspective, lakes operate like large-scale reactors with gas- and heat exchange at the surface, an intense production layer in the warm and sunlit surface water coupled to enormous settling tanks for particles, where slow aerobic and anaerobic degradation processes occur. The unreacted material is either leaving the system via the outflow or accumulating with sedimentation rates of about one millimeter per year at the

bottom. In order to quantify the coupled biological and chemical processes, a system-analysis perspective is useful. Concentration profiles at high spatial resolution provide a basis to estimate turnover in reactive zones and high-frequency time series of chemical components allow the calculation of flux estimates with the eddy-covariance technique. Both applications rely on in-situ measurements with chemical sensors.

The sediment-water interface is the most reactive zone in lakes. As a consequence rather shallow stratified lakes turn anoxic within months. Further mineralization is then channeled through anaerobic processes such as denitrification, sulfate reduction and methanogenesis releasing inorganic carbon and ammonia from decaying biomass. Combining amperometric oxygen sensors with ion-selective sensors for nitrate and ammonia allowed the quantification of different mineralization processes with millimeter resolution down towater depths of 180 m. The results from a deep Swiss lake showed that oxygen consumption remained independent of depth in the oxic zone, but anaerobic processes were intensified in the deepest part.

Due to internal waves (seiches) the current regime at the lake bottom can be quite variable and the average thickness of the diffusive boundary layer is therefore subject to diurnal changes. The dynamics of oxygen exchange is best measured with the eddy covariance technique, where a fast oxygen sensor is used with an acoustic Doppler profiler. The time series of O_2 concentration readings can then be correlated to the vertical component of current velocity and the average exchange flux can be estimated for the area of the "measurement footprint" of the instrument. A study in a seiche-driven lake revealed that oxygen exchange at the sediment was limited to periods where the bottom currents exceeded 2 cm s^{-1} and the corresponding bottom shear was high enough to produce active turbulence.

Recent developments of solid-contact sensors offer the potential for improved stability in the deployment at sedimentary environments. Advances in low-level optodes and in highly amplified amperometric sensors open the analytical window to low-oxygen environments, where the most intense microbial processes occur in the water column. By combining two types of such sensors we can now quantify the dynamic regime at oxic-anoxic boundaries with sub-micromolar O_2 concentrations. Microbes living in such environments are challenged by very dynamic environmental conditions.

Round table (1 h): chaired by Christian AMATORE and the different conveners

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MAISOE : Microlaboratoire d'Analyses *In Situ* pour des Observatoires Environnementaux
RTRA : Réseau Thématique de Recherche Avancée
STAE : Sciences et Technologies pour l'Aéronautique et l'Espace