

Annual Report

CEAC

Center of Excellence
in Analytical Chemistry

2005

Impressum

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Eidgenössische Technische Hochschule Zürich
Switzerland

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Preface

Preface

by Renato Zenobi

The year 2005 marked the 10-year anniversary of the Center of Excellence in Analytical Chemistry. We decided to properly celebrate this: instead of the annual CEAC summer workshop, we held a 10-year anniversary symposium in September of 2005, at ETH Zentrum. During the preparation of this event, I and other members of the CEAC board had some doubts about the enthusiasm it would generate among scientists in the greater Zurich area. Contrary to these doubts, the day turned out to be a great success. More than twice the number of people showed up, and the program, which is reproduced in detail in this Report, was a succession of highlights of research presentations in the area of analytical chemistry and beyond. We had three keynote presentations on large-scale research installations in the area and their analytical capabilities, the Swiss Light Source at PSI (from Prof. Friso van der Veen), the new PET Center at ETH Höggerberg (from Prof. August Schubiger), and the Functional Genomics Center Zurich which is jointly operated by the ETH and the University of Zurich (from Prof. Wilhelm Gruissem). The program was completed by short research presentation by Christa McArdell (EAWAG), Irmgard Werner (ETHZ / Pharmacy), Urs Baltensperger (PSI) and Martin Kohler (EMPA) that were all of splendid quality.

A Round Table discussion concluded the day, and showed quite clearly where the strengths but also the weaknesses of our activities lie. Problem spots first: So far the CEAC has not managed to acquire a large research project. This may be related with the heterogeneity of the field, but also with the fact that many analytical chemists are "method oriented". We have also had declining attendance at our workshops and seminars. The latter trend has already been reversed, by holding the CEAC seminars at ETH Zentrum, in an old lecture hall in the beautifully renovated Old Chemistry building. It turned out that ETH Höggerberg is just too hard to reach for someone from out of town, and holding the seminars in turn at EMPA, EAWAG, PSI, and ETH, which we tried for one semester, was a bad idea. Workshops will increasingly be organized in collaboration with other organizations, for example in 2006 together with OptETH and the new Micro / Nano Science Platform at ETH; plans exist to join forces with the Division of Analytical Chemistry, Swiss Chemical Society, to put together a "Gordon Conference style" workshop / summer school in 2007. Further strengths among the CEAC activities include the successful joining of forces with bioanalytical researchers, for example in the realm of the SystemsX initiative, and the fact that ETH Zurich is one of the very few places in Switzerland where a student can get a complete and high quality education in analytical chemistry. It was pointed out by one panelist that the Swiss chemical and pharma industry has a very clear need for analytical chemists, and often has to recruit them from abroad. Our students are well prepared for the analytical challenges in this environment.

On behalf of the board of the CEAC, I would like to thank all contributors to this annual report, and the ETH Zürich, EAWAG, EMPA, and PSI for the generous financial support for continuing our activities.

Zürich, February 2006



Joint CEAC Activities

Jubiläumsveranstaltung: 10 Jahre CEAC an der Eigenössischen Technischen Hochschule (ETH) in Zürich, Schweiz

Organisation: Prof. R. Zenobi und F.T. Ford (ETHZ)

Montag, 26. September 2005

- 09.00 **U. Suter**, VP Forschung der ETH Zürich
Begrüssung
- 09.30 **R. Zenobi**, ETH Zürich
Das CEAC Vergangenheit und Zukunft
- 10.15 **M. Kohler**, Abt. Organische Chemie, EMPA Dübendorf
Langzeitgifte (POP's) – neue Herausforderungen für die Umweltanalytik
- C.S. McArdell**, Abt. Chemie, EAWAG Dübendorf
Arzneimittelrückstände in der aquatischen Umwelt: Nachweis und Bedeutung
- 11.10 **U. Baltensperger**, Lab. f. Atmosphärenchemie, PSI Villigen/AG
Analytik in der Luftreinhaltung im Spannungsfeld von PM 10 und zigtausend Einzelkomponenten
- I. Werner**, Inst. f. Pharmazeutische Analytik, ETH Zürich,
Analytik und das europäische Arzneibuch
- 11.40 **F. van der Veen**, Swiss Light Source, PSI Villigen/AG
Die Synchrotron Lichtquelle Schweiz – ein vielfarbiges Instrument für die chemische Analytik
- 13.30 **A. Schubiger**, PET Zentrum, ETH Zürich / PSI Villigen/AG
Molekulars Imaging mit Positronen Emissions Tomografie (PET)
- 14.15 **W. Gruissem**, D-BIOL & Functional Genomics Center, ETH Zürich
Vom Molekül zum Organismus – die Rolle der funktionalen Genomik in der Systembiologie

CEAC Seminars – Summer & Winter Semesters 2005

- 21.04.2005 **Prof. Andreas Hierlemann, Institut für Quantenelektronik,
ETH Zürich, Zürich, Schweiz**
CMOS-based chemical microsensor systems
- 12.05.2005 **Dr. Robert P. Eganhouse, U.S. Geological Survey,
Reston, Virginia, USA**
*Comprehensive two-dimensional gas chromatography coupled to time-
of-flight mass spectrometry (GCxGCxTOFMS): Principles and
applications in geosciences and environmental studies*
- 02.06.2005 **Dr. Ignaz J. Buerge, Eidgenössische Forschungsanstalt für
Obst-, Wein- und Gartenbau, Wädenswil, Schweiz**
*Enantioselective Degradation of Fungicides in Soils: Correlations
between Chiral Preference and Soil Parameters*
- 23.06.2005 **Prof. Stephan Borrmann, Johannes Gutenberg Universität
und MPI für Chemie, Mainz, Deutschland**
*New developments in aerosol mass spectrometry: Results from field
campaigns and from car and aircraft emissions*
- 10.11.2005 **Prof. Mattanjah S. de Vries, Physical Chemistry,
University of California, Santa Barbara, USA**
Mass spectrometry sees the light with photoionization
- 01.12.2005 **Dr. Gyula Kiss, Air Chemistry Group of the Hungarian
Academy of Sciences, University of Veszprem, Veszprem, Hungary**
*Water-soluble organic compounds in the atmospheric aerosol: from
chemical analysis to their potential role in cloud formation*
- 12.01.2006 **Prof. Walter Michaelis, Institut für Biogeochemie und
Meereschemie der Universität Hamburg, Hamburg, Deutschland**
*Compound specific carbon and hydrogen isotope analysis – new
applications in biogeochemistry and environmental chemistry studies*
- 26.01.2006 **Dr. Roman Kaiser, Givaudan Schweiz AG, Dübendorf, Schweiz**
Im Reich der Düfte – eine ölfaktorische Weltreise

WWW

The CEAC WWW address is: www.ceac.ethz.ch

Currently the following information and links can be found on the CEAC web page:

- **Who is Who:** Who belongs to the Center of Excellence in Analytical Chemistry. A list of the CEAC board of directors, with links to their WWW home pages.
- **Seminars:** a list of the special analytical seminars organized by the CEAC.
- **Workshops:** Information on the CEAC summer workshop, including registration information
- **Links:** long list of interesting analytical and chemistry links
- **CEAC Research Projects**
- **Annual Report:** The Annual Report 2005 will be made available online.

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Feature Project

Characterization of high molecular weight compounds in atmospheric particles

M. Kalberer¹, A. Reinhardt¹, M. Sax¹, R. Zenobi¹, J. Dommen², M.R. Alfarra²,
J. Duplissy², A. Gascho², A. Metzger², A.S.H. Prevot², E. Weingartner²,
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Introduction

Atmospheric aerosol particles of about 3nm–10µm in diameter play a crucial role in many aspects of the earth's climate system. In recent years it also became evident that aerosol particles pose a public health problem. There is substantial literature demonstrating that at some level of exposure morbidity and mortality rates are increased. The chemical composition of the particle is important in both, climatologic and health related issues, however, it is only poorly understood. Atmospheric aerosols contain up to 50% organic material [1], but despite a large effort in the past decades not more than about 10-20% of the organic mass could be resolved on a molecular basis [e.g. 2,3].

The organic particle fraction is either emitted directly into the atmosphere (so-called primary particles) or formed in the atmosphere as a result of chemical reactions converting volatile organic compounds into low-volatility reaction products that then partition from the gas phase into the particle phase (so-called secondary organic aerosol, SOA).

To identify and investigate their chemical composition, SOA was generated in a newly built 27-m³ smog chamber at the Paul Scherrer Institute (PSI) in Villigen, where organic particles can be studied under conditions similar to the ambient atmosphere.

Experimental

SOA was produced in photo-oxidation experiments performed in the smog chamber of the Paul Scherrer Institute. The smog chamber facility has been described in detail by [4]. Briefly, the chamber consists of a 27-m³ Tedlar bag in a wooden housing, equipped with air conditioning. Four xenon arc lamps (4 kW each) are used to simulate the solar light spectrum as closely as possible and to mimic natural photochemistry.

A SOA experiment at the smog chamber starts by flushing the primary gas components such as organics, nitrogen oxides, purified air and water vapor into the chamber where they diffuse and mix for 30-45 minutes before the experiment is started by turning on the lights. So far, three representative anthropogenic and biogenic SOA systems were investigated, i.e., 1,3,5-trimethylbenzene (TMB), α -pinene and isoprene. The experiments are usually carried out at a relative humidity of 50% in the chamber.

After starting the illumination of the reactant mixture the parent organic compound is oxidized, and typically within 0.5-2 hours particle formation is observed due to the formation of low-volatility condensable oxidation products.

During the experiments a large number of gaseous and particle components are monitored. Table 1 gives an overview of the available instrumentation and the measured parameters.

More information on the chemical and physical techniques used to analyze the oxidized particle components is given elsewhere [4-10].

Table 1: List of analytical instruments at the PSI smog chamber.

| Instrument | Monitored parameter |
|---|--|
| Rotronic Hygro Clip SC05 humidity sensor | % relative humidity (RH), temperature |
| Thermocouple type K | chamber temperatures |
| Vaisala PTA 427 pressure transmitter | ambient pressure |
| Aero Laser 5002 | carbon monoxide (CO) |
| EnviroNics S300 ozone analyzer | ozone (O ₃) |
| Monitor Labs 9841A NO _x analyzer | nitrogen oxides (NO and NO _x – NO) |
| Monitor Labs 8810 ozone analyzer | ozone (O ₃) |
| Proton transfer reaction mass spectrometer (PTR-MS) | volatile organic compounds |
| Thermo Environmental Instruments 42C trace level NO _x analyzer | nitrogen oxides (NO and NO _x -NO) |
| Gas chromatography-mass spectrometry (GC-MS) together with PUF/Filter or denuder sampling | organic compounds |
| Impactor and filter for (matrix assisted) laser desorption ionization – (MALDI) and electrospray ionization - mass spectrometry, and Fourier transform infrared spectroscopy (FTIR) | organic compounds |
| Condensation particle counter (CPC, TSI 3022) | total particle number concentration |
| Condensation particle counter (CPC, TSI 3025) | total particle number concentration |
| Scanning mobility particle sizer (SMPS, TSI 3071 and 3010 CPC) | number weighted particle size distribution |
| Wet effluent diffusion denuder/ aerosol collector (WEDD/AC) along with ion chromatography coupled to mass spectrometry | Inorganic and organic acids in gas and aerosol phase |
| Volatility tandem differential mobility analyzer (VTDMA) | particle volatility |
| Hygroscopicity tandem differential mobility analyzer (HTDMA, partly) | particle hygroscopicity |
| Aerodyne aerosol mass spectrometer (AMS) | Size resolved fingerprint of chemical composition |

Results and Discussion

Several mass spectrometric techniques were used to observe the composition and temporal changes of the SOA particles generated in the smog chamber. Kalberer et al. [5] showed for the first time that during SOA formation high molecular weight compounds (or oligomers) are formed with masses up to about 1000Da, see Figure 1. Shortly after the start of the experiment the mass spectra show only masses up to about m/z500. However, the molecular size of the oligomers grows with increasing reaction time to about m/z1000 after about 5-6hrs (Figure 1a-1d). TMB, the organic reactant in this experiment, has a mass of 120Da. Thus,

masses up to 1000Da with a very regular repetitive mass pattern are clearly the result of oligomerization reactions.

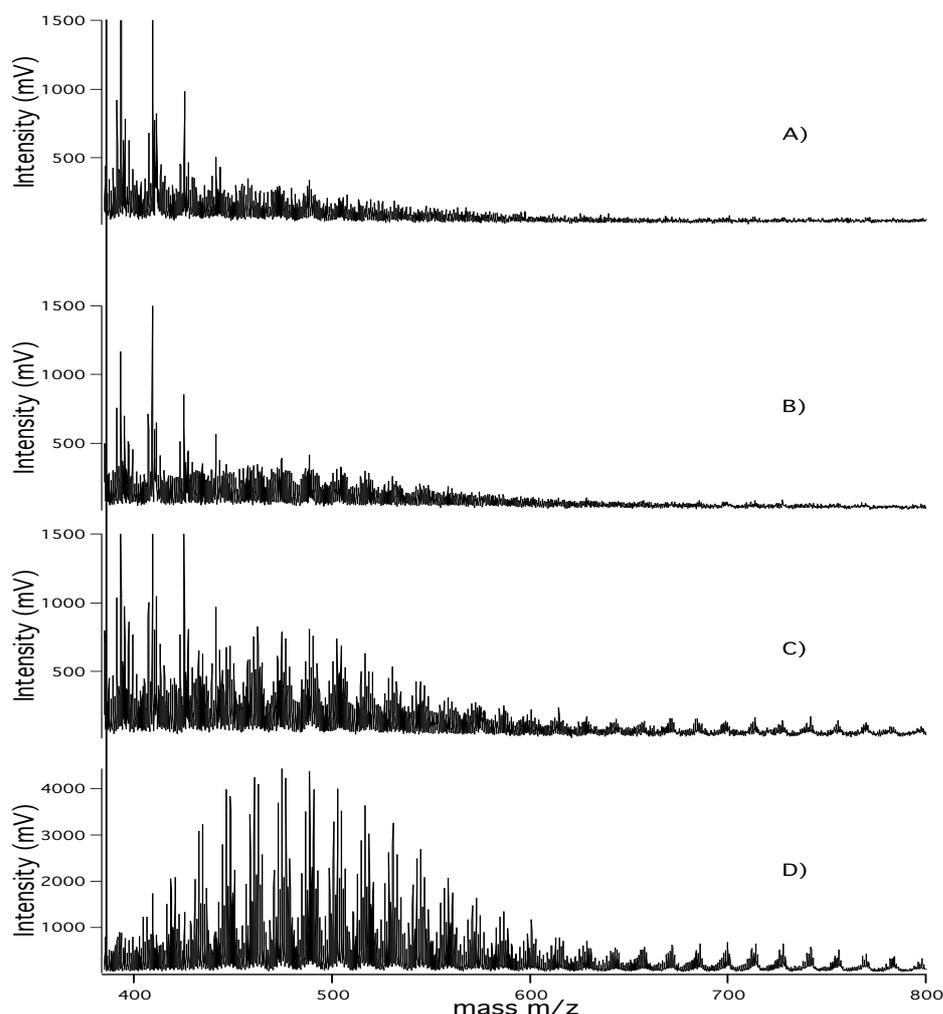


Figure 1. Temporal evolution of oligomers formed during 1,3,5,-trimethylbenzene oxidation in the smog chamber. A) Particles collected 2.5hrs after start of the experiment, B) 3.5hrs, C) 4.5hrs, and D) 6.5hrs after the start [5].

These mass spectra shown in Figure 1 were obtained with an off-line technique, i.e., particles were collected on impactor plates and then measured off-line with (matrix assisted) laser desorption/ionization mass spectrometry (LDI-MS). Recent experiments with an on-line aerosol time-of-flight mass spectrometer (ATOFMS, TSI Inc., Shoreview, USA) showed that the same oligomer patterns are also measured with single particle analysis [9] (Figure 2). The comparison of these different measurement techniques giving very similar results demonstrates that sampling or measurement artifacts can be largely excluded. This is supported by measurements with a third technique, electrospray ionization mass spectrometry, where the same oligomer patterns are measured [11].

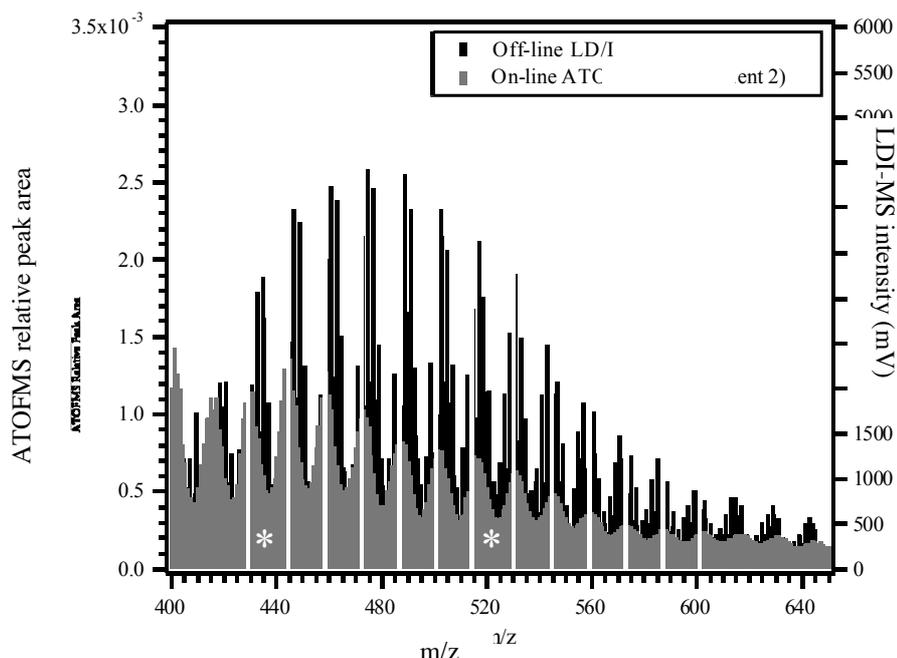


Figure 2. Overlay of on-line ATOFMS average mass spectrum and off-line LDI-MS mass spectra for 1,3,5-trimethylbenzene SOA. Because the off-line LDI-MS detects positive ions as K^+ adducts, while the ATOFMS detects deprotonated negative ions, the ATOFMS spectra have been transformed by the addition of $40m/z$ to the original mass scale for this overlay. Vertical lines have been added at increments of $m/z14$ to guide the eye (except for the instances marked with an asterisk (*), where the lines are $m/z16$ apart) [9].

Besides the oligomer formation the particle bulk is continuously oxidized over a time range of at least 20hrs as could be shown with different on-line and off-line analytical techniques. An increase in the abundance of functional groups (such as acids, or carbonyls) indicates a continuously increasing oxidation of the particle bulk and was followed with Fourier transform infrared spectroscopy (FTIR) analyses of the particles [7]. Figure 3 shows the relative increase of carboxyl and carbonyl groups with time in SOA formed during TMB oxidation.

Such an increasing oxidation was also observed with an on-line aerosol mass spectrometer, where mass fragments typical for oxidized functional groups (e.g., $m/z44$ for acids) increased with time [6] as well as with a semi-continuous ion chromatography mass spectrometric (IC-MS) analysis of organic acids in the particles [8], see Figure 3.

Concurrent with an increasing oxidation of the particles, the low-volatility particle mass fraction is increasing over more than 20hrs (see Figure 3, [5, 10]). This is partly due to the continuous formation of oligomers in the particles but also due to an increased absorption of acids and other low-volatility oxidation products formed in the smog chamber.

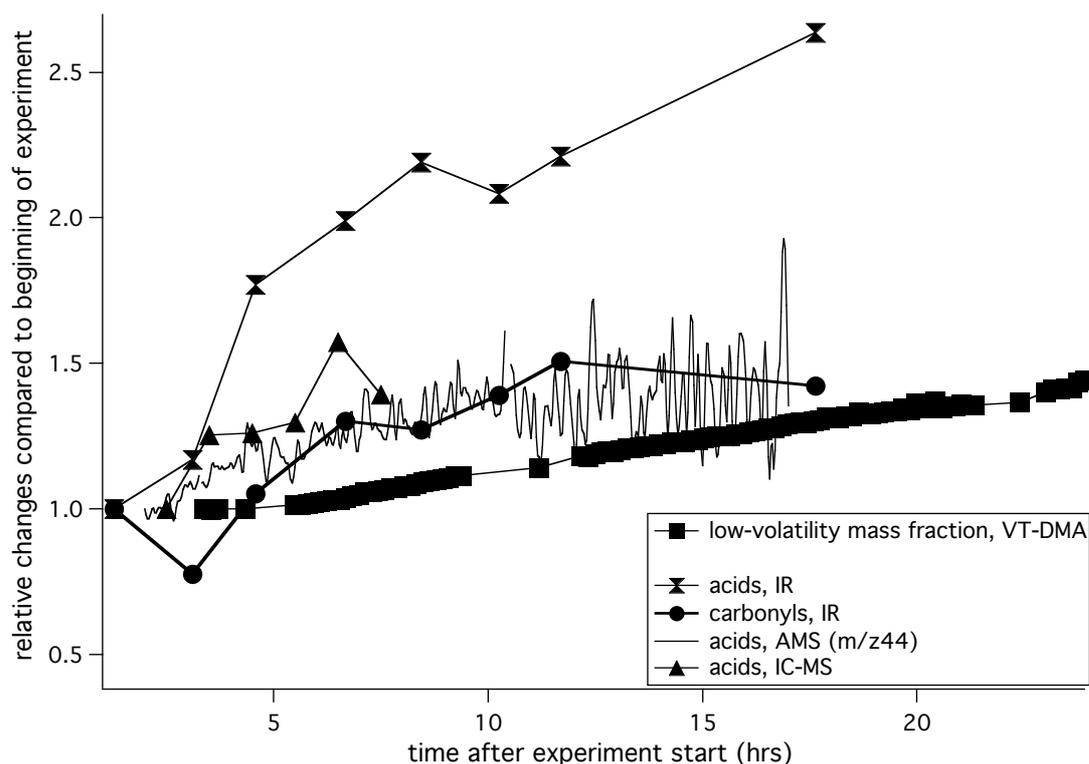


Figure 3. Increasing oxidation of TMB SOA particles was observed with various techniques, such as FTIR (for acids and carbonyls), ion chromatography and aerosol mass spectrometry (AMS). An increase of the low-volatility mass fraction is observed concurrently with this continuous oxidation.

Oligomerization seems to be a general reaction scheme in SOA formation, as it was observed in all three SOA systems investigated so far, i.e., for TMB (Kalberer et al., 2004), α -pinene (Baltensperger et al., 2005), and isoprene [12]. These findings have a number of implications for SOA modeling. Current models estimating the SOA mass formation assume a thermodynamic equilibrium of oxidation products between the gas phase and the particle phase [13]. However, the uncertainty in the specific partitioning parameters may result in huge discrepancies. A recent comparison of SOA models found predicted SOA concentrations to vary by a factor of 10 or more, where the partitioning parameters were a key difference [14].

Consequently, modeling studies addressing mechanistic aspects of SOA formation may need to readdress the current assumptions based on the oligomerization reactions proposed here. While the concept of two different vapor pressures for lumped compounds [13] might still be applicable, current interpretations of the model parameters might need to be revised.

Revised models will result in higher SOA yields, especially at higher temperature, and with different temperature dependence. Further experiments are needed to explore the absorption behavior of the high volatility fraction in the oligomerizing material. Moreover, it can be expected that these oligomerization reactions affect a number of other aerosol properties such as optical parameters, and cloud condensation nuclei potential, which are crucial for the role of aerosols in the global climate system.

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Simon Fellowship Awards

Simon Fellowship Recipients: Project Descriptions

The Wilhelm Simon Scholarship Program in Analytical and Environmental Chemistry is intended to provide research opportunities for young scientists from developing countries and from Eastern Europe / Newly Emerging States at laboratories participating in the Center of Excellence in Analytical Chemistry of ETH Zürich. It was formally started in the summer of 1995, after an agreement between the ICSC-World Laboratory in Lausanne and CEAC-ETHZ had been signed by Prof. A. Zichichi (President, World Laboratory), Prof. R. Hütter (Vice President of Research, ETH Zürich), and Prof. R. Zenobi (presenting CEAC). This support terminated in 2004. We have since continued and extended this program with own resources and in collaboration with NIDECO, the network for international development and cooperation at ETHZ. The latter funding is for post-docs (6 months) and Ph.D. students (12 months) from developing countries.

12 applications were received by the End of August 2004, and the fellowships for 2005 were awarded in November 2005. The fellows chosen for 2005 were:

- Donagh O'MAHONY (Laser and Plasma Application Group, Physics Department, Trinity College Dublin, Ireland)

- Ivan MAROZAU (Department of Chemistry, University of Aveiro, Aveiro, Portugal)

Monitoring of a laser-deposition environment by plasma analytical techniques: applications in lithium manganate thin film growth for Li-ion battery electrodes.

Donagh O'Mahony, Thomas Dumont, Stela Canulescu, Lukas Urech, Thomas Lippert, Alexander Wokaun

Materials Group, General Energy Research Department, Paul Scherrer Institut

Overview:

Lithium manganese oxide (lithium manganate) is one of the most cost-effective non-toxic and sufficiently functional cathode materials used in Li-ion batteries. At present, polycrystalline powder-based composites are used in commercial cathode production, but this leads to variations in material performance and ultimately battery failure due to inconsistencies in the particle size, morphology, crystalline orientation and electrochemically active surface area. The best approach to identifying failure mechanisms is by fabricating isolated model systems, typically as thin films with well-defined compositional and structural characteristics. However, high quality crystalline thin films of complex oxides such as lithium manganate are difficult to fabricate using conventional evaporation techniques and often require several post growth treatment steps to achieve the desired quality control. Pulsed laser deposition (PLD) is one of the most versatile techniques in use for rapid novel material synthesis and has been widely used for the growth of complex oxide thin films. It essentially involves the creation of an isolated thin film system on a substrate through the transfer of material from a target by a combination of thermal evaporation and non-thermal laser ablation processes (excimer/UV nanosecond laser). Nevertheless, selective control of the film stoichiometry is widely acknowledged as the primary growth difficulty and our films are usually $\sim 10\%$ Li-deficient compared with the target stoichiometry¹. Previously, it has been reported that for other Li-containing oxides (e.g. lithium niobate), this deficiency is related to different scattering mechanisms for the laser-ablated target species (e.g. Li, Mn, O) in the gas phase². The aim of this project was to develop one or more analytical techniques that would allow us to monitor the behavior of these species. Ultimately, we hope to improve the functionality of lithium manganate thin film structures grown via PLD by using plasma analytical techniques to advance our understanding of the dynamic interaction between the pulsed laser-produced plasma and its surrounding oxygen atmosphere.

Experimental Approach:

1. Configuration of a simple but versatile electrical (Langmuir) ion probe technique to monitor the time-of-flight dynamics of charged plasma species (i.e. electrons, ions) and the technique also served as a sensitive tool for identifying changes in the plasma deposition environment.
2. Implementation of a state-of-the-art commercial mass spectrometer system (Hiden EQP plasma diagnostics quadrupole mass spectrometer) to monitor individual species in the plasma (e.g. Li, Mn, O ions, and neutrals).
3. Correlation of plasma measurements acquired by both techniques with observations relating to film properties (e.g. growth rate, stoichiometry).

¹ Montenegro et al., *Pulsed laser deposition of thin oxide films: applications in electrochemistry*, Eds. M. Popescu, I. N. Mihailescu, Inoe Publishing House, Series: Optoelectronic Materials and Devices (ISSN 1584-5508) Volume 2, 2005, *Pulsed Laser Deposition of Optoelectronic Films* (ISBN 973-85818-2-6), pp. 207.

² *Li deficiencies in LiNbO₃ films prepared by pulsed laser deposition in a buffer gas*, J. Gonzalo, C. N. Afonso, J. M. Ballesteros, A. Grosman, and C. Ortega, *J. Appl. Phys.*, v82, pp. 3129-3133 (1997).

Results:

1. Langmuir ion probe analysis reveals that the plasma expands with a single constant velocity TOF distribution (i.e. a single peak in the TOF spectra) in high vacuum, whereas ablation in an oxygen background gas pressure of ~ 0.1 mbar leads to the separation of plasma species into two distinct groups with different TOF (i.e. a double-peak structure – see fig.1).
2. Mass spectrometry shows that the laser-ablation plasma ions are predominantly elemental Li^+ and Mn^+ , though lithium and manganese oxides have been identified (fig.3). The energy distribution spectra indicate that Mn^+ ions are the most energetic species in the plasma (fig.4).

Conclusions:

1. The double peak structure in the TOF Langmuir probe ion signals (fig.1) is characteristic of laser ablation in a background gas where the mean free path of the ablated species in the gas is of the order of the target-probe distance. The two peaks or ion groups correspond to ions that have traveled unscattered through the gas to the probe and a second group-with a later time of arrival-which has been slowed significantly due to momentum coupling with the gas. This second group may also comprise of ionized background species. We have identified that the thin film growth rate shows a strong variation with background O_2 pressure maximizes at ~ 0.2 mbar and falls off with increasing pressure (fig.2). This is close to the pressure where the second peak in the ion TOF signals begins to dominate. Thus, it seems that by slowing the plasma species, the growth rate is increased indicating that sputtering of the film by high energy (~ 100 eV) species at low background gas pressures (< 0.1 mbar) is causing significant material removal. The fall-off in the growth rate at higher pressures (> 0.2 mbar) is likely due to enhanced scattering of the ablated material away from the substrate as the gas density (and thus the mean-free path) decreases and gas-phase transport moves to a diffusive regime.
2. Although quantitative measurement of the concentration of Li and Mn species has not been carried out, the relative counts of Li^+ and Mn^+ are within 10% (fig.3). Furthermore, it seems clear that the high energy region of the energy distribution of the plasma species is dominated by Mn^+ (fig.4). At present, we are unable to clearly establish whether there is an Li-deficiency in the plasma before interacting with the background gas. However, because Li species are lighter than Mn and, from MS, appear to have lower kinetic energies, it is reasonable to expect that Li is more likely to be scattered by heavier O_2 background molecules than Mn due to its initially lower momentum.

Acknowledgements:

This work was partly funded by CEAC at ETH-Zurich under a Wilhem Simon visiting fellowship awarded to Donagh O'Mahony and co-ordinated by Dr. Thomas Lippert, head of the Materials group at PSI. We would like to thank Prof. James Lunney (Laser and Plasma Applications group at Trinity College Dublin, Ireland) and the Photonics Sources Group (Tyndall National Institute, Ireland) for facilitating the visit. We would also like to thank Dr Max Döbeli (Ion Beam Physics, ETH Zurich) for carrying out RBS measurements as part of the collaboration.

Article in preparation:

Correlation of the ion dynamics and Li deficiency in thin films of lithium manganate grown by pulsed laser deposition, Donagh O'Mahony, Thomas Dumont, Thomas Lippert, Alexander Wokaun and James Lunney.

Figures

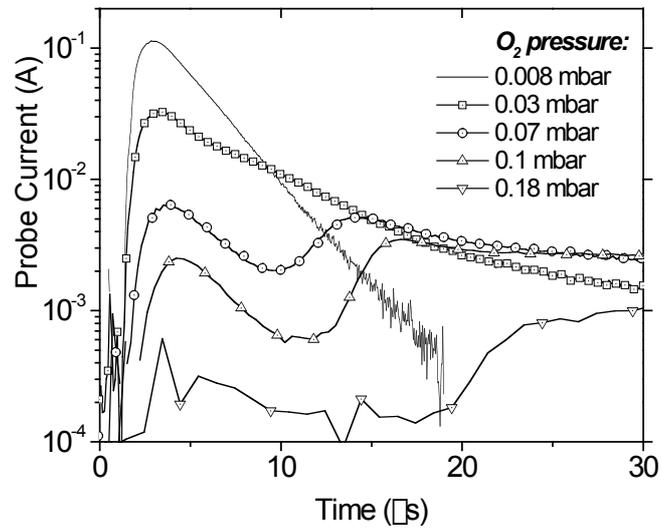


Figure 1: TOF Langmuir probe ion spectra for lithium manganate targets various O_2 gas pressures. The ion probe was positioned 4 cm from the target and ablation was carried out at 2.5 J cm^{-2} laser fluence. The technique acts as a sensitive monitoring tool for fingerprinting the optimum deposition gas pressure.

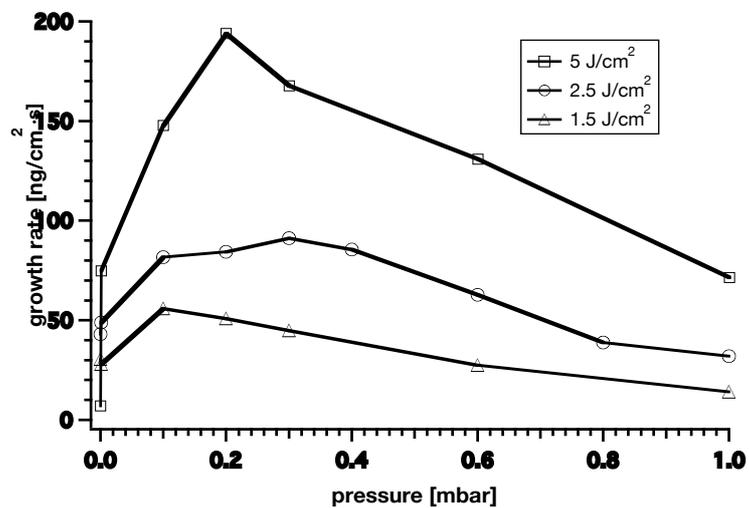


Figure 2: Lithium manganate growth rate as a function of background O_2 pressure measured by a quartz micro-balance. The various lines correspond to deposition using different fluence. Note how the growth rate maximizes around 0.1 – 0.2 mbar.

Preparation of perovskite-type oxynitride thin films by plasma assisted methods and PLD

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Materials Group, General Energy Research Department, Paul Scherrer Institut

Collaborations:

Empa: Dmitry Logvinovich, Anke Weidenkaff, Giuseppino Fortunato, ETHZ: Max Döbeli

Overview:

Perovskite-type oxynitrides exhibit interesting electrical properties and can be used as potential materials for electrical, photo- and electrochemical applications^{1,2,3}. Continuous heterovalent substitution of oxygen by nitride ions allows to tune the desired optical and/or electronic properties to the application specifications⁴. For many applications it is indispensable to use and study thin films⁵. At present the most widely used method of oxynitride films preparation is RF magnetron sputtering under reactive nitrogen plasma^{1,6}, or by thermal or plasma ammonolysis of oxide films precursors⁵. However, these techniques do not allow the preparation of films with a high control of the crystallinity. Our work is focused on the preparation of epitaxial perovskite-type oxynitride thin films by plasma assisted methods and pulsed laser deposition (PLD) and to analyze the nitrogen content quantitatively in the thin films.

Experimental:

The film deposition was carried out in a classical PLD setup and a modified version, known as Pulsed Reactive Crossed-Beam Laser Ablation (PRCLA). In this process an additional synchronized supersonic gas pulse is crossed with the ablation plume close to the target. The interaction of the plasma species with the gas pulse results in an increase of the plasma ionization degree. A KrF (248 nm) excimer laser was used for the film deposition at a repetition rate of 10 Hz and a fluence of 4.0 J/cm². All films were deposited from an SrTiO₃ target with 20000 pulses and target-substrate distance of 5.0 cm. A detailed description of the deposition techniques and experimental setups can be found elsewhere^{7,8}. The film crystallinity was studied by X-Ray Diffraction (XRD), while X-Ray Photoelectron Spectroscopy (XPS) was used for the detection and quantification of the nitrogen content in the film surface. The film stoichiometry was determined by Rutherford Backscattering Spectroscopy (RBS) using a 2 MeV ⁴He beam and a surface barrier silicon detector. The N/O ratio was calculated from Elastic Recoil Detection

¹ C. Le Paven-Thivet, L. Le Gendre, J. Le Castrec, F. Chevire, F. Tessier, J. Pinel, *Reactive sputtering deposition of oxynitride perovskite LaTiO₂N thin films*, Prog. Solid State Chem., in press.

² F. Tessier, R. Marchand, *Ternary and higher order rare-earth nitride materials: synthesis and characterization of ionic-covalent oxynitride powders*, J. Solid State Chem. **171** (2003) 143 – 151.

³ D. Yamasita, T. Takata, M. Hara, J.N. Kondo, K. Domen, *Recent progress of visible-light-driven heterogeneous photocatalysts for overall water splitting*, Solid State Ionics **172** (2004) 591 – 595.

⁴ R. Marchand, F. Tessier, A. Le Sauze, N. Diot, *Typical features of nitrogen in nitride-type compounds*, Int. J. Inorg. Mater., **3** (2001) 1143 – 1146.

⁵ R. Aguiar, A. Weidenkaff, C.W. Schneider, D. Logvinovich, A. Reller, S.G. Ebbinghaus, *Syntheses and properties of oxynitrides (La,Sr)Ti(O,N)₃ thin films*, Prog. Solid State Chem., in press.

⁶ Y. Cohen, I. Riess, *Preparation of oxynitride thin films of BaNb(O_yN)_x and LaNb(O_yN₂)_x using reactive sputtering from multiphase powder targets*, Mater. Sci. and Engineering, **B25** (1994) 197 – 202.

⁷ *Pulsed laser deposition of thin films*, ed. D.B. Chrisey, G.K. Hubler, John Wiley and Sons, 1994.

⁸ P.R. Willmott, R. Timm, J.R. Huber, *Reactive crossed beam scattering of a Ti plasma and a N₂ pulse in a novel laser ablation method*, J. Appl. Phys. **82** (1997) 2082 – 2092.

Analysis (ERDA). The sample resistance was estimated from a simple 2-point measurement with a multimeter.

Results and discussion:

Three different substrates for oxynitride films deposition were tested, i.e. STO(100), LAO(100) and MgO(100) (see Table 1). The SrTiO₃ films were typically deposited on these substrates at 700 °C with an oxygen background of 8.0×10⁻⁴ mbar and using N₂O in the gas pulse, resulting in a final deposition pressure of 1.0×10⁻³ mbar. XRD analysis of the films revealed an epitaxial film growth on STO and LAO substrates (Fig. 1A). For the MgO substrates additional reflexes were detected, which do not belong to the (X00) peak series, suggesting a nonepitaxial, i.e. polycrystalline, growth (Fig. 1B). This indicates that the lattice mismatch for MgO of -7.9% compared to the other substrates is too high for epitaxial film growth (Table 1).

The film preparation in ammonia atmosphere results in dark blue-colored films with an enhanced electrical conductivity. This suggests reduction of the growing film due to the losses of oxygen from the lattice in atmospheres with low oxygen partial pressure according to the following equation^{9,10}:



where O_o^x is a neutral oxygen position occupied by oxygen anion, $V_o^{\cdot\cdot}$ is a double positively charged oxygen ion vacancy and e^- is a free electron. The XRD analysis of films deposited in ammonia atmosphere on STO(100) substrates at different temperatures confirmed the epitaxial film growth (Fig. 2A). The detailed analysis of the diffraction patterns revealed the appearance of additional peaks, shifted to lower angles with respect to the substrate reflexes (Fig. 2B). These peaks correspond to the film and indicate an increase of the unit cell parameters of the films, compared to the STO substrates (Table 2). This behavior is most probably related to a decrease of the crystal lattice bond energy, resulting from the formation of anionic vacancies¹¹ (Eq. 1).

Two films were deposited on MgO(100) in nitrogen atmosphere at 700 °C: one using the PRCLA setup ($P_{\text{bkg}} \sim 10^{-3}$ mbar) and another one with classical PLD conditions ($P_{\text{bkg}} \sim 10^{-1}$ mbar see Table 3). Both films are colorless and exhibit a high resistance, suggesting the absence or a considerably lower concentration of electrons and anionic vacancies, compared to the samples deposited in ammonia. The XRD analysis confirmed the formation of perovskite-type films (Fig. 3A). The normalized intensity of the (110) film reflex is higher for the film, deposited in oxygen (STO-10), than for the samples deposited in nitrogen (STON-12 and STON-14 in Fig. 3B). This indicates that deposition in nitrogen atmosphere results in a higher preferential orientation of the growing film, compared to deposited in an oxygen atmosphere. The unit cell parameters of the films, deposited on MgO(100) substrates are higher compared to the single crystalline STO substrate (Tables 2, 3). This shows clearly the influence of the substrate, i.e. the lattice mismatch¹². It is noteworthy to mention that the relative intensities of the reflexes from the films deposited by PLD (STON-14) are lower than those deposited by PRCLA (STON-12 in Fig. 3A).

⁹ I.P. Marozau, V.V. Kharton, A.P. Viskup, J.R. Frade, V.V. Samakhval, *Electronic conductivity, oxygen permeability and thermal expansion of Sr_{0.7}Ce_{0.3}Mn_{1-x}Al_xO_{3- δ}* , J. Europ. Ceram. Soc., **26** (2006) 1371-1378.

¹⁰ K. S. Takahashi, D. Matthey, D. Jaccard, J.-M. Triscone, *Transport properties of reduced SrTiO₃ single crystal "thin films"*, Ann. Phys., **13** (2004) 68 – 69.

¹¹ X.Z. Liu, Y.R. Li, *Dielectric properties of multilayered SrTiO₃ thin films with graded oxygen vacancy concentration*, Appl. Phys. A **83** (2006) 67 – 72.

¹² J.H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y.L. Li, S. Choudhury, W. Tian, M. E. Hawley, B. Craigo, A.K. Tagantsev, X.Q. Pan, S.K. Streiffer, L.Q. Chen, S.W. Kirchoefer, J. Levy, D.G. Schlom, *Room temperature ferroelectricity in strained SrTiO₃*, *Nature* **430** (2004) 758 – 761.

This indicates that the higher deposition pressure in the case of classical PLD compared to PRCLA results in lower deposition rates, which has been reported previously¹³.

The results from the XPS surface analysis are presented in Fig. 4. The spectra revealed an N1s peak with a binding energy of ~399.5 eV. This binding energy value is characteristic for the nitrogen incorporated in the perovskite lattice¹⁴ and is not due to surface chemisorbed nitrogen molecules, which have a binding energy of ~402 eV¹⁵. The nitrogen concentration in the top 2 nm of the film depth, estimated from the XPS spectra analysis, is below 0.3%. However, ERDA analysis of STON-6 film yielded a nitrogen to oxygen ratio of (2.0±0.5)% in the top 100 nm of the film, which is much higher than the value obtained from XPS. This indicates a reoxidation of the film surface, which results in a lower nitrogen content in the top film layer. The quantitative composition of STON-6, determined by RBS/ERDA, is SrTi_{1.09±0.03}O_{2.70±0.09}N_{0.05±0.01}.

Conclusions:

1. Thin epitaxial SrTiO₃:N films can be prepared on STO(100) and LAO(100) substrates from a SrTiO₃ target by PLD and PRCLA in ammonia or nitrogen atmosphere.
2. Deposition in ammonia results in strongly oxygen-deficient dark films with relatively high conductivity and higher unit cell parameters compared to the STO substrate. Deposition in nitrogen yields colorless nonconductive samples with considerably lower oxygen deficiency.
3. The presence of lattice nitrogen was confirmed by XPS analysis. The bulk N/O ratio is about 2.0% while the surface nitrogen concentration is less than 0.3% most probably due to surface reoxidation.

Table 1. Unit cell parameters and lattice mismatch of the substrates used for SrTiO₃ film deposition

| substrate | a, Å | LM, % |
|-----------|-------|-------|
| STO(100) | 3.901 | 0.0 |
| LAO(100) | 3.821 | 2.1 |
| MgO(100) | 4.211 | -7.9 |

Table 2. Deposition parameters and unit cell parameters of the films deposited in ammonia atmosphere

| film | gas pulse | background | T _s , °C | a, Å |
|--------------------|---|---|---------------------|--------|
| SrTiO ₃ | - | - | - | 3.9009 |
| STON-6 | NH ₃ , 8×10 ⁻⁴ mbar | - | 650 | 3.9090 |
| STON-5 | NH ₃ , 8×10 ⁻⁴ mbar | - | 700 | 3.9081 |
| STON-7 | NH ₃ , 8×10 ⁻⁴ mbar | - | 750 | 3.9074 |
| STON-8 | NH ₃ , 8×10 ⁻⁴ mbar | NH ₃ , 5×10 ⁻⁴ mbar | 700 | 3.9095 |

Table 3. Deposition parameters and unit cell parameters of the films deposited in nitrogen atmosphere

| film | gas pulse | background | P _{deposition} , mbar | a, Å |
|---------|---|--|--------------------------------|--------|
| STO-10 | N ₂ O, 2×10 ⁻⁴ mbar | O ₂ , 8×10 ⁻⁴ mbar | 1.0×10 ⁻³ | 3.9097 |
| STON-12 | N ₂ , 8×10 ⁻⁴ mbar | N ₂ , 5×10 ⁻⁴ mbar | 1.3×10 ⁻³ | 3.9097 |

¹³ T. Scharf, H.U. Krebs, *Influence of inert gas pressure on deposition rate during pulsed laser deposition*, Appl. Phys. A **75** (2002) 551 – 554.

¹⁴ D.S. Wu, R.H. Horng, F.C. Liao, C.C. Lin, *Nitridation of (Ba,Sr)TiO₃ films in an inductively coupled plasma*, J. Non-Crystalline Solids **280** (2001) 211 – 216.

¹⁵ M.-C. Yang, T.-S. Yang, M.-S. Wong, *Nitrogen-doped titanium oxide films as visible light photocatalyst by vapor deposition*, Thin Solid Films **469** – **470** (2004) 1 – 5.

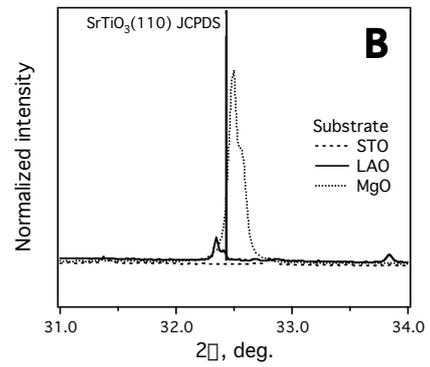
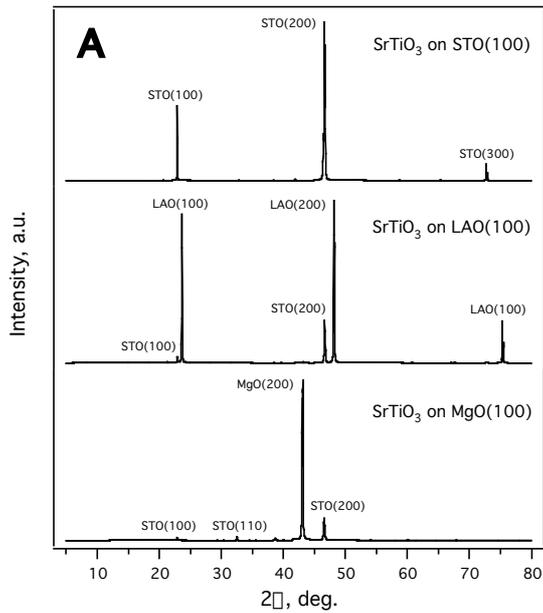


Fig. 1. (A) XRD patterns of $SrTiO_3$ films on different substrates. **(B)** Expanded plot of the STO(110) reflex.

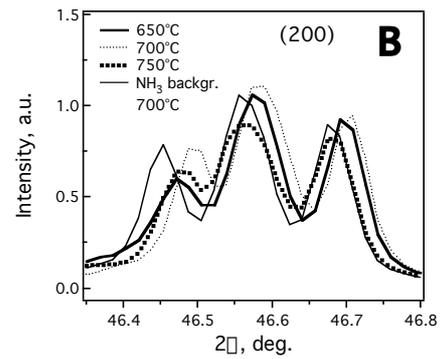
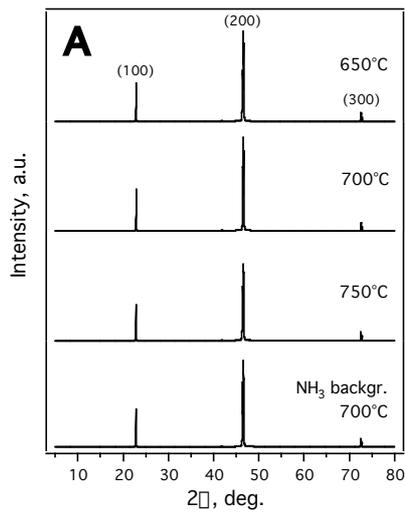
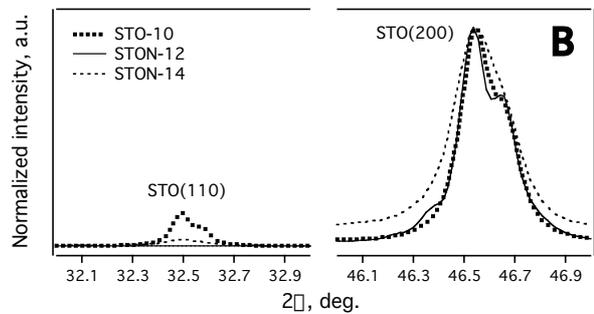


Fig. 2. (A) XRD patterns of the films deposited on STO(100) in ammonia atmosphere at substrate temperatures of 650 – 700 °C. **(B)** Expanded plot of the STO(200) reflex.



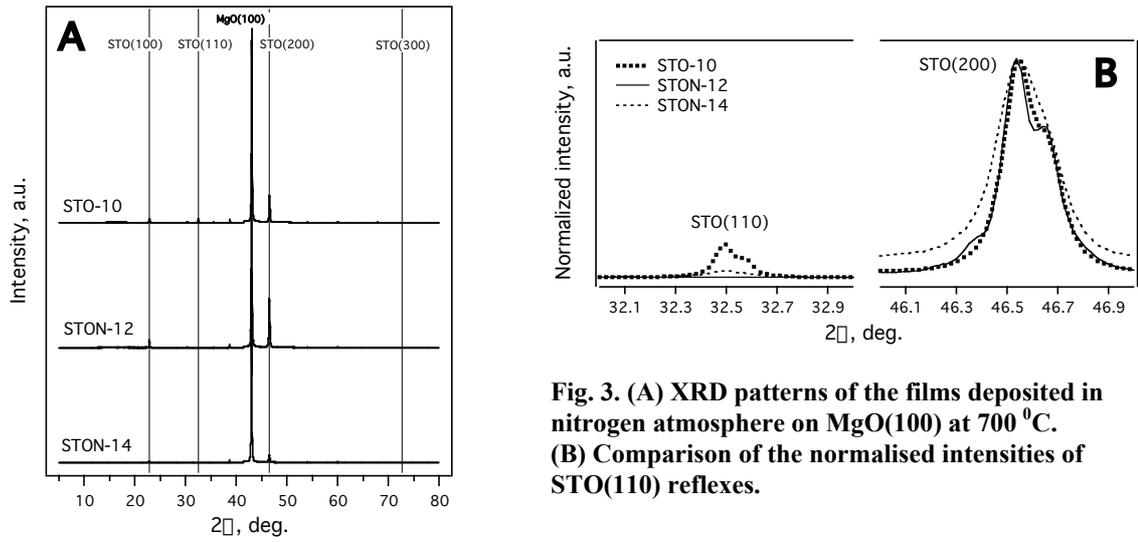


Fig. 3. (A) XRD patterns of the films deposited in nitrogen atmosphere on MgO(100) at 700 °C. (B) Comparison of the normalised intensities of STO(110) reflexes.

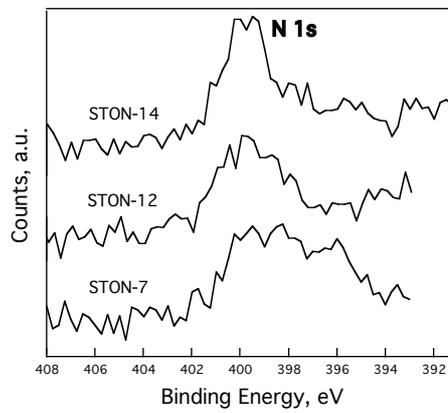


Fig. 4. XPS spectra of the SrTiO_{3-x}N_y films deposited with the PRCLA setup and an NH₃ gas pulse (STON-7); with an N₂ gas pulse and N₂ background (STON-12) and with the classical PLD setup using an N₂ background (STON-14).

Active Research at CEAC Member Laboratories

Title: Nanoscale Chemical Analysis and Spectroscopy

Researchers: Patrick Setz, Thomas Schmid, Thomas Schmitz, Christophe Vannier, Jason Yeo, Weihua Zhang, Renato Zenobi

Institute/Group: Laboratorium für Organische Chemie, ETH Hönggerberg

Project Description:

Researching the nanometer scale is currently of great relevance in many branches of modern science and engineering. As nanoscience and nanotechnology develop, powerful nanodiagnostic tools capable of recording chemical/molecular information with exquisite spatial resolution will become increasingly important. We are developing scanning near-field optical microscopy (SNOM) for nanoscale molecular analysis. SNOM is the "optical member" of the family of scanning probe microscopies and based on a subwavelength light source that is scanned above the object of interest at a distance of a few nm. In the optical near field, the illuminated area is not limited by diffraction, but merely by the size of the illumination source (50 - 100 nm). SNOM imaging can be done nondestructively and under ambient conditions.

Two main lines of research are pursued: (i) using aperture SNOM with tips designed for high optical transmission and for sustaining pulsed laser radiation, for laser ablation mass spectrometry with subwavelength spatial resolution, and (ii) apertureless SNOM, employing an external CW laser field and a metallic tip to greatly enhance the local field for "tip-enhanced" Raman spectroscopy (TERS) [1]. We have also developed a second-generation SNOM-MS instrument that combines laser ablation at ambient conditions, transport into a vacuum chamber, post-ionization / ion storage stage, and mass analysis by time-of-flight mass spectrometry [2]. Questions that are being addressed with these methodologies include the determination of the composition of thin solid films, the characterization of novel materials and elements of molecular electronics, the investigation of biological objects in their natural environment, the chemical analysis of polymer blends, and the study of chemical reactions on the surface of heterogenous catalysts.

References:

[1] C. Vannier, B. S. Yeo, J. Melanson, and R. Zenobi, *Versatile Instrument for Micro- and Nano Raman Spectroscopy*, Rev. Sci. Instrum. (in press, Jan. 2006).

[2] P. D. Setz, T. A. Schmitz, and R. Zenobi, *Design and Performance of an Atmospheric Pressure Sampling Interface for Ion Trap / Time-of-Flight Mass Spectrometry*, Rev. Sci. Instrum. (in press, Jan 2006).

Collaborations:

V. Deckert (ISAS, Dortmund/D), Veeco (Santa Barbara, CA/USA), Goodyear (Luxembourg).

Title: Environmental Trace Analysis and Aerosol Chemistry

Researchers: Christian Emmenegger, Markus Kalberer, Vera Samburova, Mirjam Sax, Renato Zenobi

Institute/Group: Laboratorium für Organische Chemie, ETH Hönggerberg

Project Description:

Organic aerosols are of importance in such different fields as global climate change, regional air quality and human health. A large fraction of the organic aerosol is emitted directly in particulate form by combustion processes. However, significant amounts are also formed in the atmosphere as a result of oxidation reactions of volatile organic compounds (VOCs), resulting in low volatility products that can thus partition into the aerosol. There is currently little knowledge about the formation and composition of these secondary organic aerosols (SOA). To study the complex compounds mixtures present in SOA, we perform controlled laboratory experiments in a flow tube reactor as well as in a smog chamber, built in collaboration with the PSI [1]. These are complemented with field experiments from urban and rural areas. The analytical tools we are using are mainly based on mass spectrometric [1, 2] and optical spectroscopy [3] methods. The scientific goals are to study the formation, composition, and chemical fate of SOA in detail, to better define the high-molecular weight fraction (so called humic acid like substances, HULIS) in ambient urban aerosols, and to push the limits for trace detection of organics in environmental samples using two-step laser mass spectrometry (L2MS) [2]. During different seasons high-volume filter samples with a 24-hour time resolution were collected and the concentration and molecular size of high molecular size compounds is determined with MALDI-MS and size exclusion chromatography-MS and size exclusion chromatography-evaporative light scattering detection. A comparison of the different methods showed that the majority of urban atmospheric HULIS have a molecular mass up to about 700 dalton. Quantitative measurements, using fulvic acid as surrogate standard, showed that the HULIS concentration is mostly between 0.5-2.0 $\mu\text{g}/\text{m}^3$ amounting to about 10-20 % of total particulate organic carbon [4, 5]. Another focus will be the investigation of particle-lung interactions and the particle properties causing negative health effects, a project started in collaboration with the university of Bern.

References:

- [1] U. Baltensperger et al., *Secondary Organic Aerosols From Anthropogenic and Biogenic Precursors*, Faraday Disc. Royal Soc. **130**, 265 - 278 (2005).
- [2] C. Emmenegger, M. Kalberer, V. Samburova, and R. Zenobi, *Diurnal Cycle Analysis of Size-Segregated Aerosol-Bound Polycyclic Aromatic Hydrocarbons with High Time Resolution*, Envir. Sci. Technol. **39**, 4213 - 4219 (2005).
- [3] M. Sax, R. Zenobi, U. Baltensperger, and M. Kalberer, *Time-resolved Infrared Spectroscopic Analysis of Aerosol formed by Photo-oxidation of 1,3,5-Trimethylbenzene and α -Pinene*, Aerosol Sci. Technol. **39**, 822 - 830 (2005).
- [4] V. Samburova, M. Kalberer, and R. Zenobi, *Characterization of High Molecular Weight Compounds in Urban Atmospheric Particles*, Atmos. Chem. Phys. **5**, 2163 - 2170 (2005).
- [5] V. Samburova, S. Szidat, C. Hueglin, R. Fisseha, U. Baltensperger, R. Zenobi, and M. Kalberer, *Seasonal Variation of High Molecular Weight Compounds in the Water-soluble Organic Fraction of Urban Aerosols*, J. Geophys. Res. **110**, D23210 (2005).

Collaborations: U. Baltensperger (PSI), H. Gaeggeler (Univ. Bern / PSI), C. Hüglin (EMPA), P. Gehr, M. Geiser (Univ. Bern).

Title: Soft Ionization Mass Spectrometry for Studying Noncovalent Interactions

Researchers: Cédric Bovet, Matthias Jecklin, Sonal Mathur, Alexis Nazabal, Tatiana Pimenova, Arno Wortmann, Renato Zenobi

Institute/Group: Laboratorium für Organische Chemie, ETH Hönggerberg

Project Description:

Soft ionization methods, in particular matrix-assisted laser desorption/ionization (MALDI), electrospray ionization (ESI), and electrosonic spray ionization (ESSI) have led to a revolution in the application of mass spectrometry (MS) to study high molecular weight biological molecules, synthetic polymers, and many other classes of compounds. What is much less known but equally interesting is that soft ionization methods allow, under carefully chosen conditions, the preservation of noncovalently bound complexes and supramolecular assemblies in the gas phase. Using MALDI, ESI, and ESSI, we investigate noncovalent complexes of biomolecular interest. Current projects include: (i) study of complex, real-world noncovalent interactions such as the inhibition or activation of the endocrine receptor by small molecules that occur in the environment, so-called endocrine disruptors. (ii) Determination of binding constants by mass spectrometry [1]. Different methods are used for this, such as ESI titration, or H/D exchange followed by MALDI readout (two novel methods called SUPREX and PLIMSTEX). We also validate these measurements by comparing against standard methods for K_d determination, such as surface plasmon resonance studies. (iii) A detailed investigation of the influence of the ESI spray on chemical equilibria in solution and how this depends on the time scale of droplet evolution relative to the time scale of the equilibrium kinetics. A thorough understanding of these effects is key for further development of ESI-MS based methods to determine accurate binding constants. (iv) The use of covalent cross-linking chemistry to stabilize large, multiprotein complexes for direct analysis by high-mass MALDI mass spectrometry using special instrumentation [2].

References:

- [1] A. Wortmann, F. Rossi, G. Lelais, and R. Zenobi, *Determination of Zinc to Beta-Peptide Binding Constants with Electrospray Ionization Mass Spectrometry*. *J. Mass Spectrom.* **40**, 777 - 784 (2005).
- [2] R. J. Wenzel, U. Matter, L. Schultheis, and R. Zenobi, *Sensitive Analysis of Megadalton Ions using Cryodetection MALDI Time-of-flight Mass Spectrometry*, *Anal. Chem.* **77**, 4213 -4219 (2005).

Collaborations: K. Wüthrich (ETHZ), S. E. Pratsinis (ETHZ), D. Moras (IGBMC / CNRS, Strasbourg, France), A. Trkola (University Hospital, Zurich), Comet AG (Flamatt), CovalX AG (Zürich), M. Suter (Eawag).

Title: MALDI Mass Spectrometry - Applications and Fundamentals

Researchers: Jürg Daniel, Alexis Nazabal, Tatiana Pimenova, Ryan Wenzel, Renato Zenobi

Institute/Group: Laboratorium für Organische Chemie, ETH Hönggerberg

Project Description:

MALDI Mass Spectrometry has emerged as an effective analytical tool for soft ionization of complex (bio-) molecules up to several 100 000 Da. In MALDI, the sample is embedded in an excess of a solid matrix, which, upon laser irradiation, assists in the volatilization and ionization of the analyte. We are contributing to a number of important areas of research with MALDI MS: (i) the analysis of polymers, the study of biomolecules, and we have had (but completed) a major activity investigating the photochemical/ thermal aging of terpenoid varnishes applied to old master paintings [1]. (ii) We are developing a continuous flow probe interface for on-line coupling of liquid separation methods with MALDI-MS [2]. (iii) As one of the very few groups in the world, we operate a novel MALDI mass spectrometer equipped with a superconducting tunnel junctions detector, made available to us through an industrial collaboration. This detector technology circumvents the familiar drop-off of the detection efficiency with increasing mass due. We are applying this instrument to detect high-mass protein complexes after stabilization by chemical cross-linking, to the mass spectrometric study of immunochemical problems and to polymer MS [3].

Our longstanding efforts in studying the fundamental principles of the MALDI ion production mechanism [4, 5] are currently focused on researching the effect of photoelectrons produced in the MALDI process, of the effect this has on ion yield, and on studying the problem of the nonuniform MALDI response for peptides generated by tryptic digestion of proteins.

References:

- [1] P. Dietemann, M. Kälin, R. White, C. Sudano, R. Knochenmuss, and R. Zenobi, *Dark Harvesting of Triterpenes Resins used for Varnishes*, Z. Kunsttechnol. Konserv. 19, 117 - 128 (2005).
- [2] J. M. Daniel, V. V. Laiko, V. M. Doroshenko, and R. Zenobi, *Interfacing Liquid Chromatography with Atmospheric Pressure MALDI-MS*, Analyt. Bioanalyt. Chem. **383**, 895 - 902 (2005).
- [3] R. J. Wenzel, U. Matter, L. Schultheis, and R. Zenobi, *Sensitive Analysis of Megadalton Ions using Cryodetection MALDI Time-of-flight Mass Spectrometry*, Anal. Chem. **77**, 4213 - 4219 (2005).
- [4] M. Dashtiev, V. Frankevich, and R. Zenobi, *Signal Enhancement in Matrix-Assisted Laser Desorption/Ionization by Doping with Cu(II) Salts*, Letter to the Editor, Rapid Commun. Mass Spectrom. **19**, 289 - 291 (2005).
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Collaborations:

Comet AG (Flamatt, Switzerland).

Title: Fourier-Transform Ion Cyclotron Resonance (FT-ICR)

Researchers: Maxim Dashtiev, Ludwig Scharfenberg, Renato Zenobi

Institute/Group: Laboratorium für Organische Chemie, ETH Höggerberg

Project Description:

Fourier-transform ion cyclotron resonance (FT-ICR) is a very powerful mass spectrometric method, celebrated for its extremely high mass accuracy and resolving power. For many applications, high-resolution measurements are very important to correctly assign peaks in the spectrum, for example to unambiguously determine a molecule's elemental composition [1]. Since the FT-ICR instrument is an ion trap, it is very well suited for studying ion-molecule reactions, for example charge transfer processes that take place after desorption in MALDI, such as gas phase protonation (cationization) reactions in the plume. We have also employed this instrumentation for the study of electron emission from MALDI targets [2].

A very important new direction of this project is the study of trapped biomolecular ions in the gas phase by laser-induced fluorescence (LIF) combined with FT-ICR [3]. These investigations are designed to answer questions about the gas-phase conformation of macromolecular ions in the gas phase, which is of high current interest. For example, there are many current debates about whether biomolecules ionized by MALDI or ESI retain their native conformation. Using single photon counting, we have demonstrated the capability to observe fluorescence resonance energy transfer in doubly labeled trapped gas-phase ions [4].

References:

- [1] V. E. Frankevich, M. Dashtiev, R. Zenobi, T. Kitagawa, Y. Lee, Y. Murata, T. Yamazaki, Y. Gao, K. Komatsu, and J. M. Oliva, *MALDI-Fourier Transform Mass Spectrometric and Theoretical Studies of Donor-Acceptor and Donor-Bridge-Acceptor Fullerenes*, Phys. Chem. Chem. Phys. **7**, 1036 - 1042 (2005).
- [2] M. Dashtiev, V. Frankevich, and R. Zenobi, *Signal Enhancement in Matrix-Assisted Laser Desorption/Ionization by Doping with Cu(II) Salts*, Letter to the Editor, Rapid Commun. Mass Spectrom. **19**, 289 – 291 (2005).
- [3] V. Frankevich, X. Guan, M. Dashtiev, and R. Zenobi, *Laser-induced Fluorescence of Trapped Gas-phase Molecular Ions Generated by Internal MALDI in an FT-ICR*, Europ. J. Mass Spectrom. **11**, 475 - 482 (2005).
- [4] M. Dashtiev, V. Azov, V. Frankevich, L. Scharfenberg, and R. Zenobi, *Observation of Fluorescence Resonance Energy Transfer in Gas-Phase Ions*, J. Am. Soc. Mass Spectrom. **16**, 1481 - 1487 (2005).

Collaborations:

F. Diederich (ETHZ), H.-J. Borschberg (ETHZ), V. Frankevich, M. Gorshkov (Moscow State Univ.)

Title: Single Cell Metabolomics

Researchers: Andrea Amantonico, Oliver Frey, Nils Goedecke, Matthias Heinemann, Andreas Hierlemann, Kai-Uwe Kirstein, Oliver Kotte, Sven Panke, Markus Pottmar, Renato Zenobi

Institute/Group: Bioprocess Laboratory, Institut für Verfahrenstechnik, ETH Zentrum
Laboratorium für Organische Chemie, ETH Hönggerberg
Physical Electronics Laboratory, ETH Hönggerberg

Project Description:

As a first step towards single-cell science, we intend to develop instrumentation for single-cell metabolomics, which is a particular challenge because it cannot be addressed via the standard '-omics'-detection methodology, i.e. fluorescence labeling. Instead, we need to develop a highly sensitive instrument that can detect on the order of 10^5 molecules of a single type in the one femtoliter of a single bacterium's cell volume. Furthermore, the technology should be amenable to high-throughput operation. We propose to achieve this through the coupling of a microfluidic cell processing and sample preparation step to a novel type of extremely sensitive mass spectrometry via an innovative fluidics/MS interface. The proposed project aims at establishing the proof of principle of the instrumental technology and at providing a first assessment of its performance and usability for biological systems science. The development is supported by investigations on intracellular stochasticity.

This project, funded through an ETHZ "INIT" proposal, has only started in mid-2005.

Title: **Optimizing Ion Sensors for Small Sample Quantities**

Researchers: Adam Malon
Tamás Vigassy
Ernő Pretsch

Institute/Group: Laboratorium für Organische Chemie, ETH Höggerberg

Project Description:

During recent years, we have developed various strategies to dramatically improve the performance of potentiometric ion sensors and have introduced ion-selective electrodes (ISEs) for a series of ions including Pb^{2+} , Cd^{2+} , and Ag^+ with detection limits in the nanomolar to picomolar range. Thanks to these improvements, potentiometry now belongs to the most sensitive techniques of ion analysis. Here, we are developing ISEs capable of measuring such low ion activities in very small sample volumes. By using the recently established labeling of biomolecules and DNA with nanoparticle-based metal (Ag) and semiconductor (CdS, PbS) tags and dissolving these metals in such small sample volumes, ISEs may, eventually, lead to potentiometric single molecule detection. One important outcome would be the DNA detection without need of amplification. By labeling enzymes with the nanoparticles, highly sensitive potentiometric immunoassays would be feasible.

References:

- [1] T. Vigassy, C.G. Huber, R. Wintringer, E. Pretsch
Monolithic capillary-based ion-selective electrodes
Anal. Chem. **2005**, 77, 3966-3970.

Collaborations:

Prof. E. Bakker, Purdue University, West Lafayette, IN, USA
Prof. J Wang, Arizona State University, Tempe, AZ, USA

Title: Potentiometric Sensors for Environmental Analyses

Researchers: Zsófia Szigeti
Tamás Vigassy
Ernő Pretsch

Institute/Group: Laboratorium für Organische Chemie, ETH Hönggerberg

Project Description:

Various Pb^{2+} -, Cd^{2+} -, Cu^{2+} -, and Zn^{2+} -selective membrane electrodes have been tested in view of their application for trace-level measurements in environmental samples. The optimal composition of the internal solution can be predicted with the help of the theoretical model developed recently. The different means of keeping this composition constant includes the use of ion buffers, ion exchangers, or a tetraalkylammonium salt added to the internal solution. The electrodes have been used for the analysis of drinking water [1] and in bio-uptake studies by yeast and plant cells [2].

References:

- [1] Zs. Szigeti, I. Bitter, K. Tóth, C. Latkoczy, D.J. Fliegel, D. Günther, E. Pretsch
A novel polymeric membrane electrode for the potentiometric analysis of Cu^{2+} in drinking water
Anal. Chim. Acta **2005**, 532, 129–136.
- [2] S. Plaza, Zs. Szigeti, M. Geisler, E. Martinoia, E. Pretsch
Potentiometric sensor for the measurement of Cd^{2+} transport in yeast and plants
Anal. Biochem. **2005**, 347, 10–16.

Collaborations:

Prof. D. Günther, Laboratorium für Anorganische Chemie, ETH Hönggerberg
Prof. E. Martinoia, Institut für Pflanzenbiologie, Universität Zürich
Prof. K. Tóth, Budapest University of Technology and Economics, Budapest, Hungary
Prof. B. Wehrli, Limnological Research Centre, Kastanienbaum

Title: Potentiometric Sensors with Internal Solid Contact

Researchers: Jolanda Sutter
Ernö Pretsch

Institute/Group: Laboratorium für Organische Chemie, ETH Hönggerberg

Project Description:

Various solid-contact ion-selective electrodes have been investigated in view of obtaining rugged responses at submicromolar sample activities. For several systems, the performance of the solid-contact ISEs is as good as, or better than, for liquid-contact electrodes with optimized inner solutions.

References:

- [1] J. Sutter, E. Pretsch
Response behavior of poly(vinyl chloride)- and polyurethane-based Ca^{2+} -selective membrane electrodes with polypyrrole- and poly(3-octylthiophene)-mediated internal solid contact
Electroanalysis, **2006**, *18*, 19–25.

Collaborations:

Prof. E. Bakker, Purdue University, West Lafayette, IN, USA

Dr. R.E. Gyurcsányi, Budapest University of Technology and Economics, Budapest, Hungary

Title: Automatic Tests of the Compatibility of One- and Two-Dimensional NMR Spectra and Chemical Structures

Researchers: Lóránt Bódis
Ernö Pretsch

Institute/Group: Laboratorium für Organische Chemie, ETH Hönggerberg

Project Description:

Today, ^1H NMR spectra can be automatically recorded with a rate of 1–2 min/spectrum so that, more and more, the interpretation has become a bottle-neck. In this project, we have further developed our previous spectra prediction program, which is now capable of estimating full ^1H NMR spectra. Various strategies of comparing the measured and predicted spectra are being developed and tested. They are optimized in view of detecting either structure incompatibilities or the presence of impurities. Additionally, a two-dimensional ^1H , ^{13}C -correlated (HSQC) spectra are being predicted and automatically compared with the measured spectra.

Collaborations:

Dr. H. Senn, F. Hoffmann-La Roche Ltd. CH-4070 Basel

Dr. P. Portmann, Upstream Solutions GmbH, CH-6052 Hergiswil

References:

- [1] L. Bodis, A. Ross, E. Pretsch
A novel spectral similarity measure
Chemom. Intell. Lab. Syst. in press.

Title: Evaluation of the figures of merit of a pulsed glow discharge time of flight mass spectrometer (GD-ToF-MS) for chemical speciation analysis and solid sampling

Researchers: Daniel Fliegel¹, Marc Gonin², Katrin Fuhrer² and Detlef Günther¹

Institute/Group: ¹Laboratory for Inorganic Chemistry
²Tofwerk, Thun

Project Description:

The figures of merit of a pulsed glow discharge time of flight mass spectrometer (GD-TOFMS) as a detector for gas chromatography (GC) analysis were evaluated [1]. The mass resolution for the GD-TOFMS was determined on FWHM in the high mass range ($^{208}\text{Pb}^+$) as high as 5500. This is significant higher than previously reported for GD-TOFMS systems [2]. Precision of 400 subsequent analyses was calculated on $^{63}\text{Cu}^+$ to be better than 1% RSD with no significant drift over the time of the analysis. Isotope precision based on the $^{63}\text{Cu}^+ / ^{65}\text{Cu}^+$ ratio over 400 analyses was 1.5% RSD.

The limits of detection (LOD) for gaseous analytes (toluene in methanol as solvent) were determined as low as several hundred ppb or several hundred pg absolute without using any pre-concentration technique. These LOD show a significant improvement of up to 3 orders of magnitude in comparison to previously reported data [3].

Furthermore, the different GD source parameters like capillary distance, cathode-anode spacing and GD source pressure with regards to the accessible elemental, structural and molecular information were evaluated. It was demonstrated that each of these parameters has severe influence on ratio of elemental, structural and parent molecular information in chemical speciation analysis and thus have to be considered carefully for chemical speciation analysis using GD-TOFMS.

This on going project will focus in the future on the further development of the glow discharge source for obtaining even better LOD and precision. Furthermore the GD-TOFMS will be coupled to new sample introduction systems to broaden the possible application area of this technique.

References:

- [1] Fliegel D, Günther D: Analytical and Bioanalytical Chemistry, 2006, *submitted*
- [2] Pisonero J, Costa JM, Pereiro R, Bordel N, Sanz-Medel A: Journal of Analytical Atomic Spectrometry 2001;16:1253-1258.
- [3] Fliegel D, Waddell R, Majidi V, Günther D, Lewis CL: Analytical Chemistry 2005;77:1847-1852.

Title: Ultra-violet femtosecond laser ablation inductively coupled plasma mass spectrometry

Researchers: Joachim Koch, Jorge Pisonero, Markus Wälle, Detlef Günther

Institute/Group: Laboratory of Inorganic Chemistry - Trace element and Micro Analysis

Project Description:

The utilization of ultra-violet femtosecond (UV-fs) laser radiation is being considered as the most promising approach to improve the general prospects of laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) concerning the isotope-selective trace element analysis of various materials. Enhanced ablation characteristics have already been reported for metals, glass, and minerals [1, 2]. Nevertheless, the application of UV nanosecond (ns) LA at 266, 213, and 200 nm still represents the most common way of solid sampling [3]. Considering UV-ns-LA-ICP-MS of metals and semi-conducting material quantification by non-matrix matched calibration appears to be problematic since strong heat diffusion into the target results in material re-distribution during LA. As a consequence, the total composition of aerosols formed can considerably deviate from the bulk value. In order to suppress heat diffusion, the laser pulse duration is supposed to fall below the so-called thermal relaxation time. According to Ref. [4], thermal relaxation in metals takes place on a time-scale of a few hundred femtoseconds, slightly depending on the conductivity of the material considered. Therefore, reducing the pulse duration down to this range has been suggested to improve the ablation characteristics and to get closer to the concept of matrix-independent, stoichiometric sampling. In the scope of this project, the general prospects of UV-fs-LA @ ~ 265 and ~ 200 nm concerning the element-selective analysis of dielectrics and metals by ICP-MS are being studied.

It has already be shown that signal ratios determined for different elemental systems such as $^{66}\text{Zn} / ^{65}\text{Cu}$, $^{208}\text{Pb} / ^{238}\text{U}$, and $^{238}\text{U} / ^{232}\text{Th}$ are hardly affected by the wavelength or laser repetition rate chosen. However, fractionation indices defined via the temporal drift of elemental ratios over two equal parts of the acquired signal were subject to systematic changes for threshold-close fluences. Corresponding ^{42}Ca -based values were found to deviate by more than 20 % from unity. In contrast, LA at higher fluences resulted in less pronounced discrepancies, falling below 5 % even for the most critical elements such as ^{66}Zn , ^{111}Cd , and ^{208}Pb .

Upcoming investigations will primarily focus on transportation, expansion, and dispersion phenomena of fs laser-produced aerosols in order to figure out potential differences to the ns case. In addition, the feasibilities of UV-fs-LA-ICP-MS for non-matrix matched calibration using, e.g., zircon and silicate glass standards will be explored.

References:

- [1] R. E. Russo, X. L. Mao, J. J. Gonzalez, S. S. Mao, *J. Anal. At. Spectrom.*, 2002, **17**, 1072
- [2] F. Poitrasson, X. L. Mao, S. S. Mao, R. Freydier, R. E. Russo, *Anal. Chem.* 2003, **75**, 6184
- [3] B. J. Fryer, S. E. Jackson, H. P. Longerich, *Can. Mineral.*, 1995, **33**, 303
- [4] B. Rethfeld, K. Sokolowski-Tinten, D. von der Linde, S. I. Anisimov, *Appl. Phys. A*, 2004, **79**, 767

Title: *In torch Laser Ablation Inductively coupled Plasma Time of Flight Mass Spectrometry, (in torch LA-ICP-ToFMS)*

Researchers: Martin Tanner, Detlef Günther

Institute/Group: Laboratory of Inorganic Chemistry / Trace Element and Micro Analysis

Project Description:

Single shot ablation maximizes the depth information of Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS) but it is very demanding in terms of data acquisition capabilities¹. Signal to noise ratios (S/N) can be improved by reduction of the aerosol dispersion which has already been shown in different studies¹⁻³. In this project laser ablation is done on a sample placed right before the ICP whereas in conventional systems the ablation takes place in a cell and the generated aerosol is transported to the ICP via tubing. The setup of the new system is inspired by a work done with LA-ICP optical emission spectroscopy (OES)⁴. It allows the ablation inside a cell (conventional) and in torch with the same laser configuration. Due to the short signal duration (few ms), in torch multi element measurement is incompatible with ICP-quadrupole MS but require an ICP-ToFMS system.

In torch laser ablation sampling was implemented to an ICP-ToFMS. The elemental and isotopic signal intensity ratios during single spot analysis were the same for in torch and in cell LA. This indicates that the same particle size distributions are formed by the laser impact and consequently sampled into the ICP. Single shot in torch LA-ICP-MS reaches the figures of merit of continuous LA in an ablation cell and provides 10 Hz LA analyses with single shot resolution⁵. The investigations focus now to improve time resolution of the analyses to further enhance S/N ratios and to get new insights in the time dependent elemental fractionation effects in LA-ICP-MS.

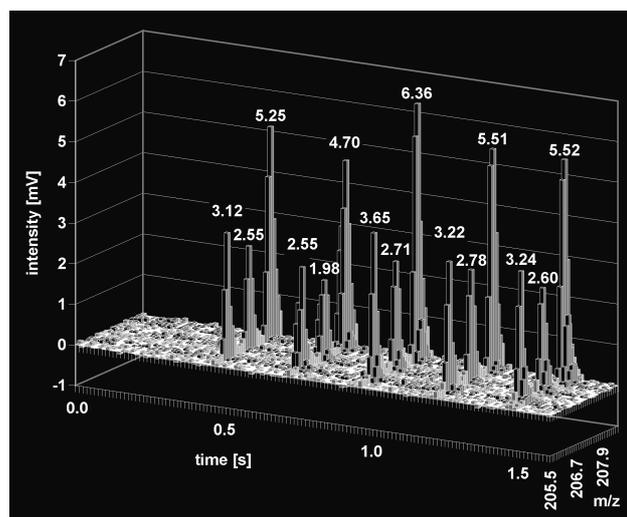


Fig. 1: ICP-TOFMS signal after 4Hz laser ablation of SRM NIST 610 inside the ICP torch. With the time resolution of 12.75ms of the instrument, each laser pulse results in 1-3 mass spectra.

References:

- 1 A. M. Leach and G. M. Hieftje, *Appl.Spectrosc.*, 2002, **56**[1], 62-69.
- 2 D. Bleiner and D. Günther, *J.Anal.At.Spectrom.*, 2001, **16**[5], 449-456.
- 3 M. Tanner and D. Günther, *J.Anal.At.Spectrom.*, 2005, **20**[9], 987-989.
- 4 X. R. Liu and G. Horlick, *Spectrochim.Acta B*, 1995, **50**[4-7], 537-548.
- 5 M. Tanner and D. Günther, *J.Anal.At.Spectrom.*, 2006, submitted

Title: Quantification of fission gases in high burnup fuel with Laser Ablation ICP-MS

Researchers: Matthias I. Horvath, Marcel Guillon*, Ines Günther-Leopold, Christian Hellwig, Andrei Izmer, Niko Kivel, Renato Restani and Detlef Günther**

Institute/Group: Laboratory for Materials Behavior, Nuclear Energy and Safety, Paul Scherrer Institut, Villigen, Switzerland
*Institute for Isotope Geology/Mineralogic Elements, ETH Zürich, Switzerland
**Laboratory for Inorganic Chemistry, Trace Elements and Microanalysis Group, ETH Zürich, Switzerland

Project Description:

Roughly 20% of all fission products are gaseous, the most important are Kr- and mainly Xe-isotopes [1]. They are solved in the fuel matrix or precipitated in nm-sized, intra-granular bubbles, in μ m-sized inter-granular pores or have been released into the plenum of the fuel rod. By reaching a burnup of 60-75 GWd/t initial heavy metal (~80% of ^{235}U has been fissioned) a so called High Burnup Structure (HBS) is formed in the rim of the fuel [2]. In this region a depletion of the noble Fission Gases (FG) in the matrix and an enrichment of FG in the pores can be observed. In model calculations it has been shown that in these pores the pressure reaches up to 30 MPa [3-5]. The knowledge of the FG distribution in the fuel is important to understand the high burnup fuel behaviour under accident conditions like reactivity initiated accident [3] and loss of coolant accident. This includes the local appearance of the FG and the microstructure.

With analytical methods routinely used for the characterization of solid samples like EPMA [5] or SIMS, the quantification of FG is difficult, since the FG in the mm-sized pores is released during sample preparation, or because of incomplete ionization of the released FG into the ultra high vacuum of the SIMS. Any analytical technique requiring sample dissolving like solution nebulization (SN) ICP-MS is not suitable, since the dissolution of the sample would result in the release of the FG.

The combination of a laser ablation system (LA) with an inductively coupled plasma mass spectrometer (ICP-MS) offers a powerful tool for this challenging task [6, 7]. This method offers the advantages of high spatial resolution with laser spot sizes down to 10 μ m and very low detection limits. The development of a suitable calibration technique for gases would allow the quantification of Xe amounts in pores in the HBS. Two different calibration strategies were evaluated and the analytical performance was compared. Via coupling with scanning electron microscope analysis (SEM) for the pore size distribution, the pressures in the pores can be estimated.

Measurements were performed on pressurized water reactor fuel with a rod average burnup of 80 GWd/t and 105 GWd/t. Fig.1 shows a transient signal of a LA-ICP-MS measurement with 8 laser ablations. These peaks were correlated with SEM pictures like in Fig. 2. The experimentally determined pressures are in the range of the modelled and calculated values of simulations [5]. Although further evaluation is still necessary, it was clearly demonstrated, that FG pressures of pores in nuclear fuel can be successfully determined with the LA-ICP-MS method.

References:

- [1] D. Olander, *Fundamental Aspects of Nuclear Reactor Fuel Elements*, ERDA Technical Information Center, Oak Ridge, Tennessee (1976), ISBN 0-87079-031-5 (v.1).
- [2] K. Lassmann, C.T. Walker, J. van de Laar, F. Lindström, *Modelling the high burnup UO₂ structure in LWR fuel*, Journal of Nuclear Materials 226 (1995) 1-8.
- [3] J. Spino, K. Vennix, M. Coquerelle, *Detailed characterization of the rim microstructure in PWR fuel in the high burn-up range 40-67 GWd/tM*, Journal of Nuclear Materials 231 (1998) 179-190.
- [4] F. Lemoine, *High burnup fuel behaviour related to fission gas effects under reactivity initiated accidents (RIA) conditions*, Journal of Nuclear Materials 248 (1997) 238-248.
- [5] W. Goll, Ch. Hellwig, P.B. Hoffmann, W. Sausser, J. Spino, C.T. Walker, *Fuel Behavior at Rod Burnups to 105 MWd/kgU: Overview on 10 Years of High Burnup Examinations at Framatome ANP*, KTG Tagung Dresden March 2006.
- [6] B. Hattendorf, Ch. Latkoczy, D. Günther, *Laser Ablation-ICPMS*, Analytical Chemistry 75, No. 15 (2003) 341A-347A.
- [7] R.E. Russo, X. Mao, H. Liu, J. Gonzalez, S.S. Mao, *Laser ablation in analytical chemistry – a review*, Talanta 57 (2002) 425-451.

Collaborations:

Swissnuclear, Institute of Polymer Physics ETHZ, Ion Beam Laboratory of Hahn Meitner Institute (ISL-HMI) Berlin.

Figures:

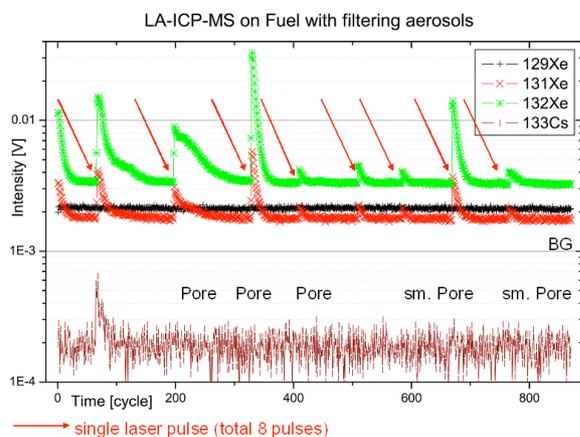


Fig.1: LA-ICP-MS on fuel in single shot mode (8 Shots). The large peaks can be correlated to opened pore(s) the small peaks to possibly opened single small pore or the retained Xe in the matrix.

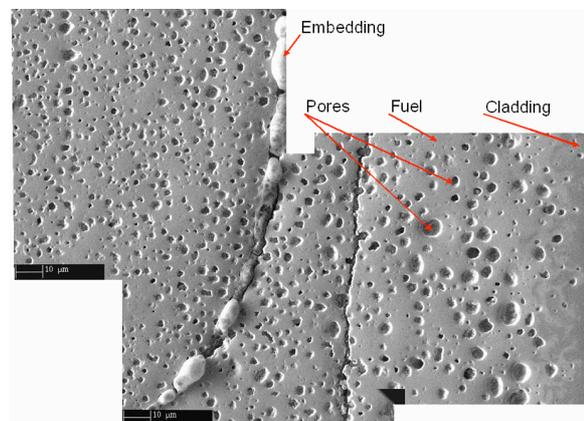


Fig.2: SEM picture of HBS of the nuclear fuel sample close to the cladding.

Title: Development of PET radiopharmaceuticals

Researchers: S.M. Ametamey, M. Honer, C. Lucatelli, P.A. Schubiger

Institute/Group: Institut für Pharmazeutische Wissenschaften, ETH Zürich

Project Description:

Positron emission tomography (PET) is an imaging modality that allows studying physiological, biochemical and pharmacological functions at a molecular level. The development and the preclinical validation of appropriate PET imaging probes for diagnostic application in neurology and oncology are of particular interest to us. With our current small animal PET scanner we achieve a volumetric resolution of 1 μ L permitting a clear delineation and visualization of small regions of interest in rodents.

Currently, our research activities are focussed on the development of new PET radiopharmaceuticals for the glutamatergic neurotransmission. This system is implicated in psychiatric and several neurodegenerative disorders including Alzheimer's and Parkinson's disease and appropriate imaging probes for this neurotransmission system are lacking. We have developed the first successful PET radiopharmaceutical that binds specifically to a subtype of the metabotropic glutamate receptor in the human brain [1]. With regard to tumor imaging, we are specifically evaluating new folic acid analogs for the imaging of folic receptor-positive tumors. A first fluorine-18 labelled folic acid derivative tested in an animal model shows promising in vivo properties [2]. Novel fluorine-18 labeled pyrimidine analogs are being developed for gene therapy monitoring using the thymidine kinase gene of the Herpes Simplex virus (HSV1-TK) as a reporter gene [3].

References:

1. S. M. Ametamey, L. J. Kessler, M. Honer, M. T. Wyss, A. Buck, S. Hintermann, Y. P. Auberson, F. Gasparini, P. A. Schubiger „ Radiosynthesis and preclinical evaluation of [11C]-ABP688 as a probe for imaging the metabotropic glutamate receptor subtype5 (mGluR5)“ J. Nucl. Med. (in press).
2. A. Bettio, M. Honer, C. Mueller, M. Bruehlmeier, U. Mueller, R. Schibli, V. Groehn, P. A. Schubiger, S. M. Ametamey ”Synthesis and preclinical evaluation of the first 18F-labelled folic acid derivative for the PET imaging of folate receptor positive tumors” J. Nucl. Med. (in press).
3. A. Johayem, S. Rai, K. Lazzatic, P. A. Schubiger, L. Scapozza and S. M. Ametamey “Synthesis and Characterization of a C-6 Nucleoside Analogue for in vivo Imaging of Herpes Simplex Virus Type 1 Thymidine Kinase Gene Expression via PET” Chemistry & Biodiversity (in press).

Title: Novel magnesium-selective electrodes for medical applications.

Researchers: Jolanta Kurz-Glebska, Rita Cannas, Stefan Spichiger, Ursula E. Spichiger-Keller.

Institute/Group: Center for Chemical Sensors and Chemical Information Technology, D-CHAB, ETHZ Technopark Zürich.

Project Description:

Magnesium-selective electrodes based on ionophores developed at ETHZ (ETH 5506, ETH 5504) and at the laboratory of K. Suzuki, Keio University, Yokohama, Japan, are the sensors which are achieving the highest selectivity to Mg^{2+} and the best discrimination of monovalent ions [1]. These ionophores are most promising to be applied to medical investigations. However, additionally to the quality of the ionophore, the design of the electrode is a crucial element. The basic theory in order to achieve the best possible performance of magnesium-selective electrodes was developed in our group [2]. The transfer of this specific know-how is the target of a project in collaboration with an industrial partner.

References:

- [1] W. Zhang, L. Jenny, and U.E. Spichiger-Keller, A comparison of neutral Mg^{2+} -selective ionophores in solvent polymeric membranes: complex stoichiometry and lipophilicity. *Anal. Sciences*, 16, 11-17, 2000.
- [2] R.Eugster, Ursula E.Spichiger, and Wilhelm Simon. Membrane Model for Neutral-Carrier-Based Membrane Electrodes Containing Ionic Sites. *Anal. Chem.* **65**, 689-695, 1993.

Collaboration

International industrial partner

Title: Project to set-up a metrological infrastructure for electrochemical analysis applied to chemistry, biotechnology and laboratory medicine at the Swiss Federal Office for Metrology and Accreditation (METAS).

Researchers: Aymeric Pellissier, Stefan Spichiger, Regula Suter, Beat Hager, Jolanta Kurz, Ursula E. Spichiger-Keller.

Institute/Group: Center for Chemical Sensors and Chemical Information Technology, D-CHAB, ETHZ Technopark Zürich.

Project Description:

It's a fundamental truth that classical analytical procedures do not respond to the same quantities as chemical sensors, biosensors and bioassays. Especially when these methods are applied and exposed to a complex specimen directly, the results deviate from wet chemical spectroscopic methods, from AAS etc. Remarkably, quantities such as *molality* and *active molality* and their units recommended by IUPAC are not used at all in practical analytical chemistry even if method comparisons reveal the differences in the results.

Start-up enterprises frequently suffer from the drawback of being unable to refer the results of sensors and bioassays developed in-house to an independent primary analytical procedure. The collaboration between the "Swiss Federal Office of Metrology and Accreditation" and CCS is focused on the development and installation of primary standard methods, primarily for electrochemical methods, on which electrodes and electrochemical instruments on the market can be traced back.

The fundamentals of electrochemical methods are well investigated and generally well accepted in the scientific community. Based on such well accepted physico-chemical fundamentals, the results yielded from electrochemical experiments under very well controlled ambient conditions are, in parallel, approximated mathematically. Results yielded by using commercialized equipment must coincide with the results yielded from the primary standard within defined limits of uncertainty.

Fundamental quantities such as *molality* and *active molality* are defined by IUPAC, and are referred to the amount of solvent in a sample. These quantities need to get generally accepted in analytical chemistry. METAS has the legal power to contribute to the efforts of European and International Bodies to achieve the international comparability of analytical results and to get through data reporting in the appropriate units.

Referenzen:

U.E.Spichiger, R.Eugster, A.Schmid, P.Gehrig, B.Rusterholz, W.Simon. Application of an Ion-Selective Magnesium Electrode on Human Blood Serum. Proceedings of an International Symposium of the Working Group on Selective Electrodes (and Sensors) IFCC/WGSE, Monterey, CA, July 19th-20th, 1990. In: R.W.Burnett, N.Gochman, G.A.Graham, A.H.Maas, R.F.Moran, A.L.VanKessel, eds. Methodology and Clinical Applications of Blood Gases, pH, Electrolytes and Sensor Technology. Utrecht: Elinkwijk, pp 279-286, 1990

Ursula E. Spichiger-Keller, Ed. (1998), Chemical Sensors/Biosensors for Medical and Biological Applications. Weinheim: Wiley-VCH.

International Federation of Clinical Chemistry and Laboratory Medicine, Scientific Division, Working Group on Selective Electrodes. R.W. Burnett, P.D'Orazio, N. Fogh-Andersen, K. Kuwa, W.R. Külpmann, L. Larsson, A. Lewenstam, A.H.J. Maas, G. Mager, U. Spichiger-Keller. IFCC recommendation on reporting results for blood glucose. Clinica Chimica Acta 307, 205-209, 2001.

International Federation of Clinical Chemistry and Laboratory Medicine, Scientific Division, Working Group on Selective Electrodes (2002). Burnett RW, Hartford (US), Covington AK, Newcastle upon Tyne (UK), D'Orazio P, Lexington (US), Fogh-Andersen N, Copenhagen (DK), Kuwa K, Tsukuba (JP), Külpmann W, Hannover (DE), Larsson L, Linkoping (SE), Lewenstam A, Åbo-Turku (FI), Maas AHJ, Utrecht (NL), Mager G, Bad Homburg (DE), Spichiger-Keller U, Zürich (CH). GUIDELINES FOR SAMPLING, MEASURING AND REPORTING IONIZED MAGNESIUM IN UNDILUTED SERUM, PLASMA OR WHOLE BLOOD.

International Federation of Clinical Chemistry and Laboratory Medicine, Scientific Division, Working Group on Selective Electrodes (2002). Burnett RW, Hartford (US), Covington AK, Newcastle upon Tyne (UK), D'Orazio P, Lexington (US), Fogh-Andersen N, Copenhagen (DK), Kuwa K, Tsukuba (JP), Külpmann W, Hannover (DE), Larsson L, Linkoping (SE), Lewenstam A, Åbo-Turku (FI), Maas AHJ, Utrecht (NL), Mager G, Bad Homburg (DE), Spichiger-Keller U, Zürich (CH), Zijlstra WG, Groningen (NL), RECOMMENDATION FOR MEASURING AND REPORTING IONIZED CHLORIDE IN UNDILUTED BLOOD PLASMA AND SERUM.

Collaborations:

S. Wunderli, U. Feller, Swiss Federal Office of Metrology and Accreditation, Wabern, Switzerland.

Swiss Enterprises

Specific Research Institutes and Universities involved in electrochemistry

Title: A nanoparticulate matrix for the development of gas-selective sensors

Researchers: Jorge Fernandez-Sanchez, Rita Cannas, Stefan Spichiger, T. Nezel, T. Roth, R. Steiger, Ursula E. Spichiger-Keller.

Institute/Group: Center for Chemical Sensors and Chemical Information Technology, D-CHAB, ETHZ Technopark Zürich.

Project Description:

Nanoparticulate inorganic materials constitute a promising substrate to develop gas-selective chemical sensors with high resistance to heat and gamma irradiation. CCS recently got access to nanostructured ink-jet papers produced at Ilford, Marly, Switzerland. Various paper qualities made from different metal oxides and additives are accessible where the porosity, the pore volume and the pore size are well defined [US 6,156,419 patent]. Referred to the chemistry of the metal oxide, the surface charge of the pores can be negative or positive. The influence of electrostatic interactions on the specific chemical reaction of an organometallic compound adsorbed within the pores and the target gas was studied. The ink-jet papers were shown to be indeed resistant to gamma-irradiation and to autoclavation (humidity and heat) opposite to plasticized polymer membranes.

Organometallic complexes (OMCs) such as phthalocyaninato Fe(II), Ru(II)- and Ir(III) complexes as well as pH- and pCO₂-sensitive indicators with appropriate pK, in addition to additives were dissolved in a volatile solvent and applied to the nanostructured film by spin-coating. The analytical performance of these films to the varying partial pressure of specific gases was investigated. Organometallic compounds were synthesized and synthetically modified in collaboration with the group of Prof. M. Graetzel, EPFL, in order to study the interactions between the surface of the mesopores and the specific OMC. In conclusion, the stability of the chemical compounds insulated within the mesopores and the homogeneity of the films is improved compared to solvent polymeric membranes. In addition, the chemically modified nanostructured film responds within seconds to the target gas.

The chemical reactions going on within the nanoporous structure were investigated using the internal special optical equipment for the investigation of gas-selective sensors and sensor arrays. The chemical mechanisms were investigated by solution NMR and the SBSR-technique which is used with FTIR-ATR-spectroscopy at CCS. The characteristics of the films were correlated to the specific parameters of nanoporosity (see results).

References:

- [1] J. Fernandez-Sanchez, T. Roth, R. Cannas, Md. K. Nazeeruddin, M. Graetzel, U.E. Spichiger-Keller, Novel oxygen sensitive complexes for optical oxygen sensing (submitted)
- [2] J. Fernandez-Sanchez, T. Nezel, R. Steiger, U.E. Spichiger-Keller, A novel optical NO₂- selective sensor based on phthalocyaninatoiron(II) incorporated into a nanostructured matrix, *Sensors & Actuators B* 113 (2006) 630-638.

[3] Jorge F. Fernández-Sánchez^{1,2*}, Stefan Spichiger², Rita Cannas², Rolf Steiger², Ursula E. Spichiger-Keller², Novel nanostructured materials to develop oxygen-sensitive films for optical sensors, *Anal. Chim. Acta* (in print).

[4] Jorge F. Fernández-Sánchez,^{†‡*} Ignacio Fernández-Nieves,[§] Paul S. Pregosin,[§] and Ursula E. Spichiger-Keller[†], CO and NO₂ Sensing by Phthalocyaninatoiron(II) Incorporated into Nanostructured Layers: X-Ray, H-1 and C-13 NMR and Photophysical Investigations, *Helv. Chim. Acta* (submitted).

Collaborations:

Md. K. Nazeeruddin, M. Graetzel, EPF, Lausanne
R. Steiger, R. Beer, ILFORD Imaging, Marly, Switzerland
Ignacio Fernández-Nieves, P.S. Pregosin, ETH Zürich

Summary of a selection of relevant results:

Oxygen-selective films based on luminescence quenching:

The incorporation of the OMCs into the nanopores increases their **luminescence quantum yield** up to 85% (excitation at 400 nm, emission λ_{\max} at 530 nm) for the Ir(III) complexes (bis(2-phenylpyridinyl)-N⁴,N⁴,N⁴,N⁴-tetramethyl-(4,4'-diamine-2,2'-bipyridine) iridium(III) chlorate) and the **sensitivity to molecular oxygen** by a factor of >40 (Stern-Volmer constant) for the Ru(II)-complex ETH^T 3003 (tris(4,7-bis(4-octylphenyl)-1,10-phenanthroline) ruthenium(II)) (excitation at 460 nm, emission λ_{\max} at 620 nm).

Surprisingly, the total pore volume and the pore size played a crucial role for the sensitivity of the luminescence quenching reaction whereas the reaction was insensitive to the chemistry of the nanostructured metal oxides. The co-incorporation of Ir(III) complexes and ETH 3003 allowed to achieve an efficient fluorescence energy transfer (FRET) between both due to the dense package of the OMCs within the nanoparticulate material. The nearly ideal overlap of the electromagnetic spectra of N-926 and ETH 3003 results in a nearly complete transfer of energy between both compounds.

Nanoparticulate optical films selective to nitrogen dioxide:

A phthalocyaninatoiron(II) complex solubilized in a number of amine solvents such as p-decylaniline, benzylamine and dioctylamine [6] showed promising performance in view of the selective detection of the NO₂-partial pressure in air of 50% humidity [5]. Incorporated into a nanoparticulate film, a detection limit of 20 ppm NO₂ was achieved (approx. 40 $\mu\text{g m}^{-3}$). The role of the amine which has to solubilize the OMC is involved in a ligand exchange reaction with NO₂ and CO (absorption λ_{\max} at 659 nm). This reaction and the influence of a temperature of 60°C was investigated by solution NMR in collaboration with P. Pregosin (ETHZ). The structure of the solubilized complex was investigated by X-ray.

In contrast to the Ru(II)- and Ir(III)-complexes, the coordination of NO₂ to and the ligand exchange with the solubilized phthalocyaninatoiron(II) complex only occurred if the surface of the mesopores was positively charged.

[5] a) T. Nezel, Investigation and development of selective polymeric liquid membranes for the optical detection of NO₂ with chemical sensors, PhD Thesis, Diss ETH No 14602, Swiss Federal Institute of Technology, Zurich, 2002.

Title: Dynamic Operation Mode for Physisorption-based Chemical sensors

Researchers: Adrian Kummer, Thomas Burg, Andreas Hierlemann

Institute/Group: Laboratorium für Physikalische Elektronik, Dept. Physik, ETH Hönggerberg

Project Description:

The target was to explore the possibility to discriminate analytes based on their non-equilibrium signals in polymer-coated capacitive chemical microsensors (1-3). The analyte uptake in the chemically sensitive polymer layers of 3 to 7 mm thickness has been analyzed using a diffusion model and the dynamic sensor response data (1-3). The shapes of the response profiles have been calculated analytically. Despite the simplifications in the model, the observed transient signal profiles could be described accurately. The comparison of the measured diffusion coefficients (on the order of 10^{-12} m²/s) with literature values measured at similar concentration levels showed good agreement. The diffusion times of water and the first aliphatic monohydric alcohols in the polymers are strongly correlated to their molecular size. The discrimination of these substances based on dynamic sensor data of a single sensor could be demonstrated. In particular, the analysis of mixtures of analytes with similar chemical behavior (water/ethanol or methanol/ethanol) by means of analyzing the response profile of single exposure steps or by applying a series of decreasingly long alternating target gas exposure and carrier gas exposure steps has been performed.

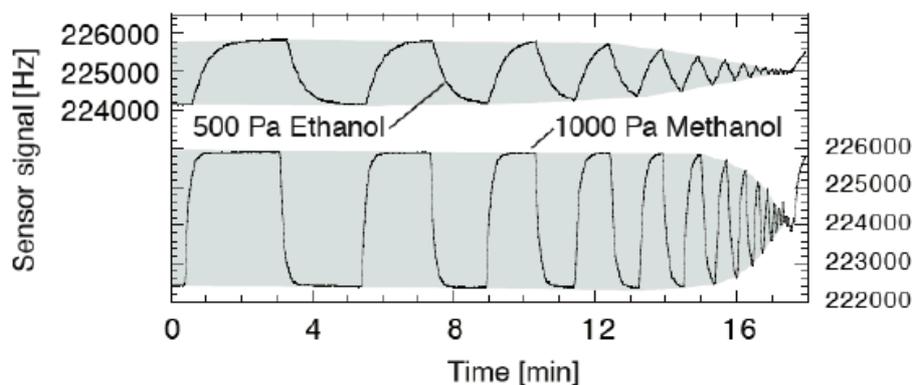


Fig1. Sensor signals for a series of concentration steps of decreasing lengths from 160 down to 1 second. The envelope of the response profile is highlighted in gray. It is analyte-specific and depends on the analyte absorption and desorption times in the respective polymer.

References:

- (1) Adrian M. Kummer, Thomas P. Burg, and Andreas Hierlemann, Transient Signal Analysis Using Complementary Metal Oxide Semiconductor Capacitive Chemical Microsensors, **Anal. Chem.** 2006, 78, 279-290.
- (2) A. Kummer, A. Hierlemann, H. Baltes, Tuning sensitivity and selectivity of CMOS-based capacitive chemical sensors, **Anal. Chem.** 76 (2004) 2470-2477.
- (3) A. Kummer, A. Hierlemann, Configurable electrodes for capacitive-type sensors and chemical sensors, **IEEE Sensors** 2006, 6, 3-10.

Title: The FGCZ Mass Spectrometry Platform – Collaborative Approaches at the Interface of Analytical Chemistry and Biology

Researchers: Dorothea Rutishauser, Peter Gehrig, Bernd Roschitzki, Bertran Gerrits, Frank Potthast, Christian Ahrens, Mike Scott, Wilhelm Gruissem, and Ralph Schlapbach

Institute/Group: Functional Genomics Center Zurich, Uni/ETH Zurich

Project Description:

The use of mass spectrometry (MS) in the life sciences is a hallmark development in the recent shift of the biological sciences towards more technology-based and (semi-) quantitative approaches in elucidating complex biological systems. While classical and mostly one-dimensional MS as a tool for protein identification remains important, several new applications of analytical chemistry technologies have found their way into the characterization of highly diverse sets of molecules, including proteins and peptides, carbohydrates, lipids, and small organic compounds resulting from metabolic processes.

The MS platform at the Functional Genomics Center Zurich (FGCZ) provides a sophisticated analytical infrastructure and application expertise that can be accessed by biologists and chemists working at the ETH or the University of Zurich (for details please visit www.fgcz.ch). The FGCZ supports a number of pre-fractionation technologies, including 1D and 2D combinations of nano-LC and cap-LC systems, as well as 2D-gel electrophoresis. These pre-fractionation technologies interface flexibly with a broad range of mass spectrometers including tandem MS systems of classical 3D and linear ion trap, quadrupole TOF, MALDI-TOF/TOF, and combined ion trap–FT-ICR instruments.

Research is carried out in close collaboration between user groups and experienced FGCZ staff to address a wide range of analytical questions from the identification of exotic peptides in insects or quantitative cancer biology studies in humans to membrane protein analysis of plant cells. Using the most advanced technologies and bioinformatics support, researchers can investigate not only the breadth and depths of proteomes in great detail, but also discover and map small chemical protein modifications that are emerging as important biological regulators.

Together, the combined expertise in the Center of Excellence in Analytical Chemistry and in the FGCZ provides scientists in Zurich an unsurpassed infrastructure and environment for analytical research.

Selected References:

Potthast F., Ocenasek J., Rutishauser D., Pelikan M., and Schlapbach R.
Database independent detection of isotopically labeled MS/MS spectrum peptide pairs.
J Chromatogr B. 2005; 817(2):225-30.

Baginsky S, Kleffmann T, von Zychlinski A, Gruissem W. Analysis of shotgun proteomics and RNA profiling data from Arabidopsis thaliana chloroplasts. J Proteome Res. 2005 ;4(2):637-40.

Scheurer S.B., Rybak J-N., Roesli C., Brunisholz R.A., Potthast F., Schlapbach R., Neri D. and Elia G. Identification and relative quantification of membrane proteins by surface biotinylation and two-dimensional peptide mapping. *Proteomics* 2005; 5(11):2718-2728.

Selected Collaborations:

S. Baginsky, W. Gruissem (D-BIOL, ETH Zurich)

G. Elia, D. Neri (D-CHAB, ETH Zurich)

R. Aebersold (D-BIOL, ETH Zurich)

R. Zenobi (D-CHAB, ETH Zurich)

J. Jiricny (IMCR, University of Zurich)

E. Hafen (Inst. of Zoology, University of Zurich)

Title: Probing the interaction of cadmium with the rainbow trout estrogen receptor using ICP/MS and MALDI-TOF

Researchers: Victor J Nesatyy, Adrian A. Ammann, Marc J.-F. Suter

Institute/Group: Department of Environmental Toxicology, Eawag

Project Description:

The widely reported negative effects on the reproductive system observed in aquatic organisms and their possible link to endocrine active chemicals (EACs) present in the environment gave raise to public concern worldwide. Recent studies indicated that certain heavy metals, including cadmium (Cd), can mimic the effects of the endogenous estrogen receptor (ER) agonist 17 β -estradiol, and lead to estrogen receptor activation.

In order to identify Cd-binding sites in the ER ligand-binding domains we utilized modern ICP/MS and MALDI-TOF techniques as well as radio-ligand assays. Identification of the *rt*ER-LBD residues involved in Cd interactions was done using peptide-mass fingerprinting after chemical derivatization of the fusion protein shielded by Cd against various types of chemical modification. The degree of modification of exposed residues allowed to identify amino acids involved in Cd-binding [1].

The mechanism of ER activation by Cd may include a number of conformational changes. This was investigated using a combination of H/D exchange and MALDI-MS. The extent of Cd induced conformational changes was determined by comparing peptide map patterns for the deuterated samples with and without ligand pre-equilibration. Our data obtained using dried-droplet spotting showed significant MW shifts for the deuterated samples in comparison to the control. However, no difference between deuterated samples with and without Cd/E2 pre-equilibration was observed. The use of the thin-layer spotting method resulted in a significant decrease in the signal intensity and peptide coverage in comparison to the peptide maps obtained using the dried-droplet method. But again it did not indicate distinguishable conformational changes for Cd or E2 pre-equilibration versus the control. The lack of conclusive data on the ligand induced ER conformational changes may suggest minimal differences in the H/D exchange rates between reportedly different conformations of the liganded and unliganded ER.

References:

V.J. Nesatyy, B.V. Rutishauser, R.I.L. Eggen, M.J.-F. Suter, *Identification of the estrogen receptor Cd-binding sites by chemical modification*, *Analyst* **130**, 1087-1097 (2005).

Collaborations:

Swiss National Research Programme 50
R Zenobi (ETHZ)
EU-Project EDEN, member of the CREDO cluster

Title: Endocrine Disrupting Compounds in the Aquatic Environment

Researchers: Marc J.-F. Suter, Adrian A. Ammann, Rik I.L. Eggen, Anja Liedtke
Victor Nesatyy, René Schönenberger, Étienne L.M. Vermeirssen,
A. Christiane Vögeli

Institute/Group: Department of Environmental Toxicology, Eawag

Project Description:

Investigations on exposure to endocrine disrupting compounds in the environment have entered the 2nd research decade. While today the environmental exposure situation is reasonably well understood, linking it to observed effects is much more difficult, as is the corresponding risk assessment. Various reasons can be listed for this: i) the variability of environmental concentrations is rarely taken into account, ii) the classic effect pathway for endocrine disruptors is via nuclear receptors, however, there are also other modes of action which are currently less well understood, iii) it is not entirely clear how to deal with mixtures, particularly if the mode of action is dissimilar,

For these reasons our research has focused on internal concentrations in aquatic organisms, because they better reflect the history and levels of exposure than plain environmental exposure measurements. We have analyzed bile (short time storage) and adipose tissue of bream and whitefish, using bioassay-directed fractionation. A good approximation of internal concentrations that circumvents the need to expose and then sacrifice fish is the use of passive sampling devices. We could show that the estrogenicity measured in bile of exposed brown trout very well matched the estrogenicity sequestered by the passive sampling device [1]. However, this technique only reflects physicochemical properties and no physiological response of an exposed organism.

Feminisation of male gonads and the production of “female” proteins are the classic biomarkers in endocrine disruptor research. Current advances allow for a more detailed and subtle analysis, particularly with respect to rapid changes at the level of the genome and proteome. Using two-dimensional LC coupled to mass spectrometry we could show that zebrafish eggs exposed to cadmium or estradiol had different proteome maps compared to controls, clearly indicating different modes-of-action.

References:

E.L.M. Vermeirssen, O. Korner, R. Schönenberger, M.J.-F. Suter, P. Burkhardt-Holm, *Characterization of environmental estrogens in river water using a three pronged approach: active and passive water sampling and the analysis of accumulated estrogens in the bile of caged fish*, Environ. Sci. Technol. **39**, 8191-8198 (2005).

Collaborations:

Swiss National Research Programme 50
R Zenobi (ETHZ), P Hunziker (Uni ZH)
EU-Project EDEN, member of the CREDO cluster

Title: Chlorin Index: a new parameter for organic matter freshness in sediments

Researchers: Carsten J. Schubert

Institute/Group: Department of Surface Waters, Eawag

Project Description:

Total chlorins, comprising degradation products of chlorophyll, have been used recently to reconstruct paleoproductivity from marine sediment cores. Here, we report on a new index, the Chlorin-Index (CI) that proves to be a helpful tool for rapidly estimating organic matter freshness in marine sediments. The CI is a ratio between the fluorescence intensity of a sediment extracted with acetone and treated with hydrochloric acid and the original sediment extract. It represents the ratio of chlorophyll and its degradation products deposited in the sediments that could still be chemically transformed and those that are inert to chemical attack. The ratio is lower in sediments that include freshly deposited phytoplankton material and higher in older, more degraded sediments. We measured this new parameter on surface sediments, and sediments from several short and a long sediment core from different oceanic settings. CI values range from 0.2 for chlorophyll a to 0.36-0.56 for fresh material deposited on the shelf off Namibia to values around 0.67 in sediments off Chile and Peru to values up to 0.97 for sediments in a deep core from the northeastern slope of the Arabian Sea. We have compared the CI to rates of bacterial sulfate reduction, as a direct measure of organic matter reactivity and to other degradation indices based on amino acid composition. We conclude that the CI is a reliable and simple tool for the characterization of organic material freshness in sediments in respect to its degradation state.

References:

C.J. Schubert et al., *Chlorin Index: a new parameter for organic matter freshness in sediments*, *Geochem. Geophys. Geosyst.* **6**, (2005).

Collaborations:

Jutta Niggemann, Gabriele Klockgether, Tim G. Ferdelmann (Biogeochemie, Max Planck Institute, Bremen)

Title: Assessing river-groundwater exchange in the regulated Rhone River (Switzerland) using stable isotopes and geochemical tracers

Researchers: Markus Fette, Rolf Kipfer, Carsten J. Schubert, Eduard Hoehn, Bernhard Wehrli

Institute/Group: Department of Surface Waters, Eawag
Department of Water Resources and Drinking Water, Eawag

Project Description:

Modern flood protection projects are often combined with measures for river restoration, which enlarge the river bed to improve the flow capacity during peak discharge. For the planning of such projects it is essential to quantify the river-groundwater exchange. To address this question in the highly regulated upper Rhone River basin, a combination of stable isotope techniques with geochemical and transient tracers has been used. The $\delta^{18}\text{O}$ signal in precipitation decreases towards more negative values with a slope of 0.34 ‰ per 100 m altitude, precipitation during winter was about 5.5 ‰ more negative than in summer. Since in winter about 55% of the water in the River Rhone comes from high alpine hydropower reservoirs with a known $\delta^{18}\text{O}$ value, this isotopic signature provides direct information of the source region and the seasonality in samples from groundwater wells. On a spatial scale SO_4^{2-} measurements help to constrain groundwater components, because the tributaries and groundwater sources south of the Rhone are rich in SO_4^{2-} with concentrations of more than 12 mM in spring water. In winter the Rhone water reaches concentrations of up to 1.5 mM, and during snowmelt in summer, this value drops below 0.5 mM. Finally the transient tracer $^3\text{H}/^3\text{He}$ is used to estimate groundwater inflow in deep gravel pits and to calculate an average travel velocity in the alluvial aquifer of about 1.7 km a^{-1} .

References:

M. Fette, R. Kipfer, C.J. Schubert, E. Hoehn, B. Wehrli, *Assessing river-groundwater exchange in the regulated Rhone River (Switzerland) using stable isotopes and geochemical tracers*, Appl. Geochem. **20**, 701-712 (2005).

Title: Two-Dimensional Isotope Analysis to Decipher Biodegradation Processes

Researchers: Luc Zwank, Michael Berg, René P. Schwarzenbach

Institute/Group: Department of Water Resources and Drinking Water, Eawag
ETHZ (Environmental Organic Chemistry)

Project Description:

Compound-specific analysis of stable carbon and hydrogen isotopes was used to assess the fate of the gasoline additive methyl tert-butyl ether (MTBE) and its major degradation product tert-butanol (TBA) in a groundwater plume at an industrial disposal site. We developed a novel approach to evaluate two dimensional compound specific isotope data with the potential to identify reaction mechanisms and to quantify the extent of biodegradation at complex field sites. Due to the widespread contaminant plume, multiple MTBE sources, the presence of numerous other organic pollutants, and the complex biogeochemical and hydrological regime at the site, a traditional mass balance approach was not applicable.

The isotopic composition of MTBE steadily changed from the source regions along the major contaminant plume (-26.4‰ to +40.0‰ (carbon); -73.1‰ to +60.3‰ (hydrogen)) indicating substantial biodegradation. Constant carbon isotopic signatures of TBA suggest the absence of TBA degradation at the site. Published carbon and hydrogen isotope fractionation data for biodegradation of MTBE under oxic and anoxic conditions, respectively, were examined and used to determine both the nature and the extent of in situ biodegradation along the plume(s). The coupled evaluation of two dimensional compound specific isotope data explained both carbon and hydrogen fractionation data in a consistent way and indicate anaerobic biodegradation of MTBE along the entire plume. A novel scheme to re-evaluate empiric isotopic enrichment factors, ϵ , in terms of theoretically based intrinsic carbon (12k/13k) and hydrogen (1k/2k) kinetic isotope effects (KIE) is presented. Carbon and hydrogen KIE values, calculated for different potential reaction mechanisms imply that anaerobic biodegradation of MTBE follows a SN₂-type reaction mechanism.

Furthermore, our data suggest that additional removal process(es) such as evaporation contributed to the overall MTBE removal along the plume, a phenomenon that might be significant also for other field sites at tropic or subtropic climates with elevated groundwater temperatures (25°C).

References:

L. Zwank, M. Berg, M. Elsner., T.C. Schmidt, R.P. Schwarzenbach, S.B. Haderlein, *New Evaluation Scheme for Two-Dimensional Isotope Analysis to Decipher Biodegradation Processes: Application to Groundwater Contamination by MTBE*. Environ. Sci. Technol., **39**, 1018–1029 (2005).

Collaborations:

Torsten C. Schmidt, , Stefan B. Haderlein (Eberhard-Karls University Tuebingen)
Martin Elsner (University of Toronto)

Title: **Bacterial Biosensor for Rapid and Accurate Analysis of Arsenic in Highly Variable Groundwater Samples**

Researchers: Pham Thi Kim Trang, Michael Berg

Institute/Group: Department of Water Resources and Drinking Water, Eawag

Project Description:

Every day quality measurements of drinking water usually rely on chemistry. However, for arsenic, which is contaminating potable water in millions of groundwater wells in Asia, this is no trivial business. Arsenic quantification requires the use of expensive machines, whereas chemical field test kits are notoriously unreliable at lower arsenic concentrations. We have successfully validated a completely different analytical method, in which engineered bacteria emit light when encountering arsenite. Such so-called bacterial biosensors have been developed before, but have not much been applied to real-world samples. Current estimates are that, e.g., 150 million people in the West-Bengal and Bangladesh area, over 10 million in Vietnam and over 2 million in China are exposed to unacceptable arsenic intake through potable water consumption

A bioluminescence-producing arsenic-inducible biosensor based on *Escherichia coli* was used as the reporter organism. Specific protocols were developed with the goal to avoid the negative influence of iron in groundwater on arsenic availability to the biosensor cells. 194 groundwater samples were collected in the Red River and Mekong River Delta regions of Vietnam, and analyzed both by atomic absorption spectroscopy (AAS) and by the arsenic biosensor protocol. The biosensor performed well at and above arsenic concentrations in groundwater of 7 µg/L, with an almost linearly proportionally increase of the bioluminescence signal between 10 and 100 µg As/L (r^2 of 0.997). Comparisons between AAS and arsenic biosensor determinations gave an overall average of 8.0% false negative and 2.4% false positive identifications for the biosensor prediction at the WHO recommended acceptable arsenic concentration of 10 µg/L, which is far better than current chemical field test kits can provide. The simple protocol by which the bacterial biosensors performed accurately in chemically very different groundwaters, thus holding promise for wider screening campaigns in Asia and other areas suffering from arsenic pollution in drinking water resources.

References:

Pham Thi Kim Trang, Michael Berg, Pham Hung Viet, Nguyen Van Mui, Jan Roelof van der Meer. *Bacterial Bioassay for Rapid and Accurate Analysis of Arsenic in Highly Variable Groundwater Samples*. Environ. Sci. Technol. **39**, 7625–7630 (2005).

Collaborations:

Jan Roelof van der Meer (University of Lausanne, Department of Fundamental Microbiology)
Pham Hung Viet, Nguyen Van Mui (Hanoi University of Science)

Title: **The Use of High Resolution ICP MS in Aquatic Research**

Researchers: Adrian A. Ammann

Institute/Group: Department of Environmental Toxicology, Eawag

Project Description:

The best sensitivity available in multi-element determination covering about 80% of the elements in the periodic table makes ICP MS the method of choice for determination of total elemental composition especially for low concentrated trace elements and also makes it the preferred element specific detector in element speciation analysis.

Insufficient performance (DL, reliability) of our old quadrupole ICP MS forced us to replace it. At the end of a scrutinized evaluation it was clear that only a high resolution double focusing magnetic sector field ICP MS (HR ICP MS) instrument could fulfill our needs. The most useful benefit of the HR ICP MS is its superior sensitivity which is about 100 times better than that of a simple quadrupole instrument. In most cases this allows sample to be diluted, thereby reducing or eliminating matrix interferences without diluting relevant pollutants below the instrument detection limit. With this instrumentation low concentrations of highly toxic elements (Cd, Hg, Pb etc) can now be directly determined and thus their chronic effects assessed. Many of the remaining interferences can be separated from the target elements by higher resolution settings. In highest resolution, however, DL are raised to that of a simple quadrupole instrument.

When working with biologically active molecules the HR instrument's ability to detect small fragment ions in addition to elements, becomes important. For instance a protein is sensitively tracked by HR ICP MS based on bound metals, while characteristic fragments detected at the same time provide additional information. Thus the approximate number of peptide bonds can be determined and related to other elements (e.g. S, P) or to the bound metals.

The HR instrument is also heavily used in element speciation analysis by chromatography. In order to detect as many elements as possible in transient signals of only about 10s duration, shortest acquisition times are required. The higher the sensitivity the shorter the acquisition times that can be chosen. Additionally, fast (1 ms) electric switching between masses within $\pm 30\%$ of the actual magnet mass can be performed circumventing the inertia of a magnet (40-60 ms). This makes the HR ICP MS a fast and hence useful multi element detector for chromatography.

Title: Quantification of glyphosate and aminomethylphosphonic acid in water using automated online solid phase extraction-liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS)

Researchers: Irene Hanke, Heinz Singer, Juliane Hollender

Institute/Group: Department of Environmental Chemistry, Eawag

Glyphosate is one of the most important herbicides worldwide. The trace level determination in water is difficult and in many cases the robustness is limited due to the polar character of the zwitterionic molecule. This is one of the main reasons why only few environmental data are available despite the high use of glyphosate. To overcome this problem an automated analytical method for the quantification of glyphosate and its major metabolite aminomethylphosphonic acid (AMPA) at the ng/L level in surface and groundwater has been developed. The method is chiefly automated and thus allows the rational measurement of a large number of samples (approach see [1]).

The method is based on the derivatization of the analytes with 9-Fluorenylmethyloxy-carbonylchloride (FMOC-Cl) followed by an enrichment step with solid phase extraction (SPE), which is coupled online to a high performance liquid chromatography-tandem mass spectrometer. The transformation of the very polar analytes into the corresponding FMOC-derivatives [2] helps to improve the performance of enrichment, separation and detection. Our results demonstrate that the content of the organic solvent is the most important influencing factor for a fast and complete derivatization. At an acetonitrile content of 10% the reaction with FMOC-Cl is completed after two hours at room temperature. Tests with surface and waste water have shown that the high reaction yield is not affected by the sample matrix. Experiments to optimize enrichment and purification of samples using different phases show an almost complete enrichment on modern copolymeric (Oasis-HLB, Strata-X) or mixed-mode copolymeric phases, even with waste water samples with an acetonitrile content of 5 to 10%. A fast elution has been achieved best with the copolymeric phase Strata-X. Refocusing and a good chromatographic separation of the FMOC-derivatives on a C18 column were accomplished by adding water to the online transferred SPE-eluate. A selective detection of the FMOC-derivatives was obtained by electrospray ionization (negative mode) on a triplequad mass spectrometer running in the SRM-mode. Measurements of ambient water samples show the applicability of the method for the determination of glyphosate and AMPA.

Literature:

[1] Stoob, K., et al., *Fully automated online solid phase extraction coupled directly to liquid chromatography-tandem mass spectrometry: Quantification of sulfonamide antibiotics, neutral and acidic pesticides at low concentrations in surface waters*. J. Chrom. A, **1097**(1-2), 138-147 (2005).

[2] Nedelkoska, T.V. and G.K.-C. Low, *High-performance liquid chromatographic determination of glyphosate in water and plant material after pre-column derivatisation with 9-fluorenylmethyl chloroformate*. Anal. Chim. Acta **511**, 145-153 (2004).

Collaborations:

This project was partly funded by the Swiss Federal Office for the Environment FOEN

Title: **β -blockers in Municipal Wastewater Treatment**

Researchers: Alfredo C Alder, Philipp Richle, Christa S McArdell

Institute/Group: Swiss Federal Institute for Environmental Science and Technology (EAWAG)

Project Description

The β -adrenergic blockers (betablockers) comprise a group of pharmaceuticals that are mostly used in the treatment of cardiovascular disorders such as hypertension, cardiac arrhythmia or ischemic heart disease. After intake these drugs are excreted with urine either as the active substance or as metabolites. Human-use pharmaceuticals enter sewage effluents unchanged or metabolized via urine and feces and by improper disposal and eventually reach municipal wastewater treatment plants. To study the removal of selected β -blockers, field studies were performed in a full-scale activated sludge treatment plant.

Wastewater samples were enriched by solid-phase extraction, and analysed by reversed-phase liquid chromatography coupled to tandem mass spectrometry using positive electrospray ionization. Atenolol-d7, sotalol-d6 and propranolol-d7 were used as surrogate standards. Recoveries from treated wastewater were above 80% for atenolol, sotalol and propranolol. Recoveries of metoprolol, which was quantified with the non-ideal standard propranolol-d7, were around 50%. The overall precision (n=6) ranged between 3 and 6%. The limit of quantification varied between 10 and 20 ng/L.

First results in two full-scale activated sludge treatment plants indicated that elimination in wastewater treatment plants is incomplete, and therefore residual amounts are discharged to ambient waters. The removal from the wastewater stream during wastewater treatment was 74-82% for atenolol, 32-36 % for sotalol, 31-43% for metoprolol and 26-33% for propranolol. Concentrations measured in treated waste wastewater ranged between 400-680 ng/L for atenolol, 240-250 ng/L for sotalol, 100-160 ng/L for metoprolol and 30-120 ng/L for propranolol. The results indicate that elimination in wastewater treatment plants is incomplete, and therefore residual amounts are discharged to ambient waters.

Collaborations:

EU-Project ERAPharm

Title: Detection of Emissions of Non-Regulated Oxidized Volatile Organic Compounds by Advanced GC-MS Technology (ENOVO)

Researchers: Geir Legreid, Stefan Reimann and Johannes Staehelin

Institute/Group: Laboratory for Air Pollution/Environmental Technology, Empa
Institute for Atmospheric and Climate Science, ETHZ

Project Description:

Oxidized Volatile Organic Compounds (OVOCs) are toxic to human health and precursors for tropospheric ozone and secondary organic aerosols. Climatological data in the atmosphere is limited as the chemical analysis of this group of compounds is far from straightforward. Consequently, assessments of sources based on real-world observations are practically not available. The successful development of an automatic system for measuring OVOCs in air samples was performed as a part of the PhD project ENOVO at Swiss Federal Laboratories for Materials Testing and Research (Empa) and the Institute for Atmospheric and Climate Science (IACETH) of the Swiss Federal Institute of Technology (ETHZ). The compounds of main interest were C₁-C₅ alcohols, C₂-C₆ carbonyls and selected VOCs. The compounds were measured during the following campaigns:

- Four seasonal campaigns at the high Alpine background site of Jungfraujoch (3580 m asl)
- Four seasonal measurement campaigns at an urban site (Zürich, Kaserne)
- One measurement campaign in the Gubrist highway tunnel [1]
- One measurement campaign in a small Swiss village (Roveredo) in winter for measuring biomass burning (during the AEROWOOD campaign)

The high Alpine station at Jungfraujoch in the Swiss Alps and was a unique location for studying the chemistry of the lower free troposphere and transport phenomena. The seasonal differences were of interest as well as the different sources for the OVOCs. Primary source regions for these compounds were identified from back-trajectory analysis, and their source strengths will be calculated from average ratios of the OVOCs versus carbon monoxide (CO) concentrations during pollution events. The OVOCs are not only emitted from anthropogenic and biogenic sources, but also produced by oxidation processes in the atmosphere which complicates the interpretation. Source profiles from the urban measurements in Zurich, the highway tunnel and Roveredo will be used to distinguish the influence of primary and secondary OVOCs at the high Alpine background site.

References:

[1] G. Legreid, S. Reimann, M. Steinbacher, J. Staehelin, D. Young, and K. Stemmler, *Measurements of OVOCs and NMHCs in a Swiss highway tunnel for estimation of road transport emissions*, Environ. Sci. Technol., (2006), submitted.

Collaborations:

A. Prevot, J. Dommen (PSI)

P. Simmonds, D. Young (University of Bristol, UK)

Title: Determination of ammonia in ambient air using photoacoustic spectroscopy

Researchers: Christoph Hueglin, Andrea Fischer, Peter Graf, Beat Schwarzenbach, Brigitte Buchmann

Institute/Group: Air Pollution / Environmental Technology Laboratory, Empa, 8600 Dübendorf

Project Description:

Ammonia is a relevant atmospheric pollutant. Deposition of gaseous ammonia and ammonium aerosol through dry and wet deposition contributes to both acidification and eutrophication of ecosystems. Ammonia has a relative short atmospheric lifetime and is deposited fairly close to its sources. Ammonia is able to neutralize acids and forming particulate ammonium, which can be transported over long distances. In order to assess the effects of reduction measures, as well as to study the role of ammonia on secondary aerosol formation processes, accurate and reliable measurement systems for ambient ammonia are needed.

A photoacoustic system designed for long-term measurement of ammonia in ambient air was developed in close cooperation with Omnisens SA (Lausanne, Switzerland). The system uses a CO₂ laser and a properly designed resonant photoacoustic cell to achieve ammonia detection at sub-ppb level [1]. To account for the signal of interfering species (i.e. H₂O, C₂H₄, CO₂, and NH₃ resulting from thermal dissociation of particulate ammonium nitrate) a set-up that consists of two sampling lines (sample and reference line) is used. The two sampling lines are identical, except that the reference line includes a citric acid coated diffusion denuder for selective removal of NH₃. A multi-channel sampling system is used to switch between the two sampling lines. The ambient NH₃ concentration is derived from the difference of consecutive measurements of NH₃ in the reference and sample line. Two of these instruments are currently successfully applied within the Swiss National Air Pollution Monitoring Network (NABEL).

References:

[1] S. Schilt, L. Thévenaz., M. Niklès, L. Emmenegger, Ch. Hueglin. (2004). *Ammonia monitoring at trace level using photoacoustic spectroscopy in industrial and environmental applications*. Spectrochimica Acta Part A, 3259-3268.

Collaborations:

Omnisens SA (Lausanne)

Title: Endocrine Disrupting Chemicals in the Air (ENDAIR) – Bioassay-Based Investigation of Endocrine Disrupters in Diesel Exhaust

Researchers: Daniela Wenger, Andreas Gerecke and Norbert Heeb

Institute/Group: Laboratory of Organic Chemistry
Empa, Swiss Federal Institute for Materials Science and Technology

Project Description:

Endocrine disrupting chemicals (EDCs), released from the technosphere into the atmosphere, are suspected to cause negative health effects in humans and wildlife as they interfere with the hormone system. Inhalation of EDCs might represent an important exposure pathway that should be considered in human risk assessment. However, the extent of exposure to endocrine disruptors in the air is not well studied.

The project ENDAIR aims to provide insights into the exposure of humans and animals to airborne EDCs. To this end, we develop analytical tools to detect and characterize endocrine disruptors in airborne samples, e.g., in diesel exhaust, atmospheric particulate material, indoor dust, and cigarette smoke/particles. We combine biological methods with chemical analysis via bioassay-directed fractionation of extracted samples. Chemically activated luciferase expression (CALUX) bioassays are implemented to quantify endocrine activity mediated either by the human estrogen receptor (estrogenic compounds) or the aryl hydrocarbon receptor (AhR-ligands, e.g. TCDD-like compounds). Active substances in fractionated samples are characterized by GC/HRMS and LC/MS/MS.

So far, we investigated the endocrine activity of diesel exhaust. Diesel engines are a source of potential airborne EDCs and inhalable particulate matter, which may be associated with endocrine disruptors. We analyzed complete exhaust samples from a diesel engine. The samples were collected with and without exhaust gas after-treatment by two particle filter systems.

The latest results of our study show that diesel exhaust collected without particulate trap contains estrogen receptor ligands (335 pg 17 β -estradiol equivalents/m³ diesel exhaust) as well as aryl hydrocarbon receptor ligands (16 to 55 ng 2,3,7,8-TCDD equivalents/m³ diesel exhaust). The amount of estrogen receptor ligands in 1 m³ diesel exhaust is comparable to 0.001% of a common birth control pill. The highest amount of aryl hydrocarbon receptor ligands measured in 1 m³ diesel exhaust corresponds to the estimated yearly uptake of dioxins via food of an average adult in Europe [1]. Further, we could show that particle filter systems reduce aryl hydrocarbon receptor ligands in diesel exhaust by more than 80%. Estrogen receptor ligands in diesel exhaust collected with particulate trap could not be detected so far.

References:

[1] German Federal Environmental Agency, *Comments on the Opinion of the Scientific Committee on Food on the Risk Assessment of Dioxins and Dioxin-like PCBs in Food*, 2002.

Collaborations:

Renato Zenobi (ETHZ), Hanspeter Nägeli (University of Zurich).

Title: Brominated flame retardants and other endocrine disrupting chemicals in the ecosystem of Lake Thun - environmental fate and correlation to biological effects (FLEET)

Researchers: Christian Bogdal, Martin Kohler and Peter Schmid

Institute/Group: Laboratory of Organic Chemistry, Empa Dübendorf

Project Description:

Brominated flame retardants (BFRs), currently produced at an annual rate of several 100,000 tonnes, are added to polymeric materials, textiles or electronics to reduce their flammability. As there is evidence that many BFRs are persistent, bioaccumulative and toxic, the presence of these halogenated organic compounds has become of growing concern to scientists over the past decade.

The first and main part of the present project, applied to the ecosystem of Lake Thun, consists in assessing the environmental fate of BFRs. To this end, concentrations of several BFRs are measured in different compartments such as water, fish, sediment, plankton, and air. Results of chemical analysis of these field samples are interpreted in terms of sources, sinks and temporal trends of BFRs. Additionally, a model, evaluating mass balance and environmental partitioning of BFRs in Lake Thun will be established in collaboration with ETHZ.

The second part aims to determine whether the occurrence of gonad malformations of whitefish in Lake Thun, emerging since 2000, can be related to increased concentrations of xenobiotic compounds in fish. For this objective, a larger range of persistent organic pollutants is analysed in fish, and a possible link to fish malformations is investigated. Besides BFRs and polychlorinated biphenyls (PCBs), concentrations of polychlorinated naphthalenes (PCNs) in sediment and fish are examined. PCNs have been used world-wide as technical mixtures until the years 1980, and in Switzerland, PCNs, known as persistent, toxic and endocrine active chemicals, have been employed in fog ammunition in World War II.

Sampling of surface sediment, sediment cores, plankton and fish was organised and achieved. Contaminant time trends will be investigated by isotopic dating and chemical analyses of sediment cores. Surface sediments have already been analysed for PCNs, and concentrations of about 0.6 ng/g dry sediment were found. This represents normal background contamination levels, being in the same range as for comparable sites reported in the literature (0.2 - 6 ng/g dry weight). The congener patterns showed a predominance of lower chlorinated and more volatile congeners.

Collaborations:

Martin Scheringer, Konrad Hungerbühler (Safety and Environmental Technology Group, ETHZ); Michael Sturm, Erwin Grieder (Surface Waters, Eawag); Anja Liedtke, Christiane Vögeli, Marc Suter, Rik Eggen (Environmental Toxicology, Eawag); Pascal Vonlanthen, Alan Hudson (Fish Ecology and Evolution, Eawag); David Bittner, Carlo Largiadèr (Zoological Institute, University Bern); Markus Zeh, Daniel Scheidegger, Ueli Ochsenbein (Water Protection Laboratory, Canton Bern).

Title: The historical record of brominated flame retardants and other persistent organic pollutants in a Swiss lake sediment core

Researchers: Martin Kohler¹⁾, Markus Zennegg¹⁾, Paul C. Hartmann²⁾, Michael Sturm²⁾, Erika Gujer¹⁾, Peter Schmid¹⁾, Andreas C. Gerecke¹⁾, Norbert V. Heeb¹⁾, Hans-Peter Kohler²⁾, and Walter Giger²⁾

Institute/Group: ¹⁾Swiss Federal Institute for Materials Science and Technology (Empa), Überlandstrasse 129, 8600 Dübendorf, Switzerland.
²⁾Swiss Federal Institute of Aquatic Science and Technology (Eawag), Überlandstrasse 133, 8600 Dübendorf, Switzerland.

Project Description:

Brominated flame retardants are used to reduce the flammability of combustible materials, such as plastics and textiles. The global market demand for brominated flame retardants is increasing and exceeds 200,000 t/y. The environmental safety of these chemicals is currently discussed controversially. While the acute toxicity of brominated flame retardants is low, evidence for neurotoxic and endocrine disrupting effects is growing. Concerns have been raised by the detection of these chemicals at steadily increasing concentrations in environmental and biological samples world-wide.

Concentrations of brominated flame retardants were measured in a dated sediment core taken from Greifensee, a small 32 m deep lake on the Swiss plateau east of Zürich [1]. The sampled core spans the time period between 1848 and 2001. Brominated flame retardants appeared in the early 1980s, while the concentrations of other persistent organic pollutants, such as DDT, PCB and PCDD/F, peaked in the 1960s. After a short rise in the early 1980s, the lower brominated diphenylethers, corresponding to the technical Penta- and OctaBDE products, were levelling off at concentrations below 2 ng/g dry weight (dw). In contrast, the sediment concentration of decabromodiphenyl ether (DecaBDE), a widely used flame retarding additive today [2], is rising quickly. The current doubling time for DecaBDE is 8.9 years, putting today's DecaBDE sediment concentration (7.3 ng/g dw) in the same range as the sediment concentration observed for PCB, today.

References:

- [1] M. Kohler, M. Zennegg, P. C. Hartmann, M. Sturm, E. Gujer, P. Schmid, A. C. Gerecke, N. V. Heeb, H.-P. Kohler, and W. Giger, *The historical record of brominated flame retardants and other persistent organic pollutants in a Swiss lake sediment core*, Abstract Book of the 15th Annual Meeting of SETAC Europe, Lille, France, May 22-26, 2005, p. 213.
- [2] A. C. Gerecke, P. C. Hartmann, N. V. Heeb, H.-P. Kohler, W. Giger, P. Schmid, M. Zennegg, M. Kohler, *Anaerobic Degradation of Decabromodiphenyl Ether*, Environmental Science & Technology, **39**, 1078 – 1083 (2005).

Collaborations:

Martin Scheringer and Konrad Hungerbühler, Safety and Environmental Technology Group, Institute for Chemical and Bioengineering, ETH Zürich.

Title: Method development for high salt content analysis to investigate solubility limitations of aqueous Ni and isotopic exchange of ^{63}Ni in cementitious systems

Researchers: A. Ulrich¹, E. Wieland²

Institute/Group: ¹EMPA, Swiss Federal Laboratories for Materials Testing and Research
Überlandstrasse 129, 8600 Dübendorf, Switzerland
Lab 131 Laboratory for Solid State Chemistry and Analysis
²PSI, Paul Scherrer Institut, Nuclear Energy and Safety Department,
Laboratory for Waste Management, 5232 Villigen PSI, Switzerland

Project Description:

The behaviour of stable nickel and ^{63}Ni in cement systems has been investigated in batch-type experiments under conditions corresponding to the initial stage of cement degradation. Therefore, stability tests using ^{63}Ni -labelled solutions mixed with an artificial cement pore-water (ACW) have been carried out. Thus, analysis methods for the determination of the trace and ultratrace elements in high salt content solutions had been developed using inductively plasma optical emission spectrometry (ICP-OES), inductively coupled plasma quadrupole-mass spectrometry (Quad-ICP-MS) as well as high-resolution magnetic sector field plasma mass spectrometry (HR-ICP-MS). The results revealed that a Ni-containing precipitate was formed at high Ni concentrations, which limits the concentration of dissolved Ni. The concentration of dissolved Ni in cement suspensions seem to be controlled by the partitioning of stable Ni between the cement matrix and the cement pore water. The dissolved Ni concentration was found to be independent of the solid-to-liquid ratio, suggesting that a solubility-limiting process was involved in controlling the partitioning of stable Ni between HCP and ACW. The concentration of dissolved Ni, calculated based on the assumption that the partitioning of stable Ni is caused by a reversible linear sorption process, predicts a strong increase in the concentration of dissolved Ni with increasing S/L ratio. This was clearly contradicted by the experimental results. This finding provides supporting evidence that a solubility-limiting process controls the concentration of dissolved Ni in cement systems. An additional argument against linear sorption was provided from measurements of the sorption isotherm using stable Ni, which showed only a small increase in the concentration of dissolved Ni, while the concentration of added Ni varied over several orders of magnitudes. The results support the idea that a solid-solution aqueous-solution system involving Ni may account for the behaviour of stable Ni in cement systems. The distribution ratio for the partitioning of ^{63}Ni between pristine HCP and ACW is consistent with literature data obtained under similar experimental conditions. The R_d value determined on Ni loaded HCP samples increase with increasing concentration of stable Ni in HCP. The uptake of ^{63}Ni by pristine and Ni loaded HCP can be interpreted in terms of an isotopic exchange process with the stable Ni inventory. The distribution coefficient, α , of the exchange process, indicates that only a small portion of the inventory of stable nickel is accessible to isotopic exchange.

References:

[¹] E. Wieland, J. Tits, A. Ulrich, M.H. Bradbury: Experimental evidence for solubility limitation of the aqueous Ni(II) concentration and isotopic exchange of ^{63}Ni in cementitious systems, *Radiochim. Acta* 94, 2006, 29-36.

Collaborations:

I. Hagenlocher (NAGRA - National Cooperative for the Disposal of Radioactive Waste Switzerland).

Title: Risk assessment for secondary emissions of diesel particulate trap systems

Researchers: A. Ulrich¹, A. Wichser¹, N. V. Heeb², L. Emmenegger³

Institute/Group: EMPA, Swiss Federal Laboratories for Materials Testing and Research
Überlandstrasse 129, 8600 Dübendorf, Switzerland
¹Lab 131 Laboratory for Solid State Chemistry and Analysis
²Lab 132 Laboratory for Organic Chemistry
³Lab 134 Laboratory for Air Pollution /Environmental Technology

Project Description:

Most particulate traps efficiently retain soot of diesel engine exhaust but the potential hazard to form secondary emissions has to be controlled. The DPF regeneration is mainly supported by metal additives or metallic coatings. Certain noble or transition metals can support the formation of toxic secondary emissions such as dioxins, PAH, Nitro-PAH or other volatile components. Furthermore, particulate trap associated additive metals can penetrate through the filter system or coating metals can be released from coated systems. The VERT test procedure was especially developed to assess the potential risks of a formation of secondary pollutants in the trap. The present study gives an overview to the VERT test procedure. Aspects of suitability of different fuel additives and coating metals will be discussed and examples of trap- and additive induced formation of toxic secondary emissions will be presented.

References:

- [1] N Heeb, A Ulrich, L Emmenegger, J Czerwinski, A Mayer, M Wyser: Secondary emissions risk assessment of diesel particulate traps for heavy duty applications, SAE Paper 2005-26-014, 329-338.
- [2] A Mayer, J Czerwinski, M Wyser, M Kasper, N Heeb, A Ulrich, L Emmenegger, H Egli, W Scheidegger: Filtration Efficiency, Secondary Emissions and Reliability of Particle Filter Systems in Underground Workplaces, Proceedings of the 8th International Mine Ventilation Congress, Brisbane, 6-8 July 2005.

Collaborations:

J. Czerwinski (University of Applied Sciences, Biel-Bienne, Switzerland)
M. Wyser (Swiss Agency for the Environment, Forests and Landscape, Bern, CH)
H.Egli, W. Scheidegger (SUVA)
A. Mayer, TTM Mayer AG, Niederrohrdorf, CH
M. Kasper, T. Mosimann (Matter Engineering)

Title: **The Influence of different Lubrication Oils on Particle Emissions of TDI-Engine**

Researchers: A. Ulrich, A. Wichser, G. Müller

Institute/Group: ¹EMPA, Swiss Federal Laboratories for Materials Testing and Research
Lab 131 Laboratory for Solid State Chemistry and Analysis,
Überlandstrasse 129, 8600 Dübendorf, Switzerland

Project Description:

Due to increasing concern about health effects of fine and ultra-fine particles from combustion engines, the diesel particle filter technology (DPF) is a key technology for heavy duty and passenger cars to appropriately reduce the particle emissions. In this respect, a very important parameter is the irreversible plugging of particle filters with non-combustible ashes. The quality of lubrication oil, especially the ash content has a certain influence on regeneration intervals of diesel particle filters. Therefore, in the present study, the effects of different lubrication oils on particle mass and size distribution as well as the composition of the particle emissions were investigated. The test engine was a modern heavy duty diesel engine without particle filter system.

A main goal of the project was the investigation, how different lubrication oils influence the particulate emissions under different conditions and to assess the contribution of oil to the total emissions. It should be studied if and how the composition (e.g. additive packages) of the oils influences the total emissions. The comparison of non-doped lubrication oils with especially doped oils should enlighten the contribution of the oil to the particle formation.

References:

- [¹] J. Czerwinski, J.-L. Pétermann, A. Ulrich, G. Mueller, A. Wichser: Particle Emissions of a TDI-Engine with Different Lubrication Oils, SAE Paper 2005-01-1100.
- [²] J. Czerwinski, J.-L. Pétermann, A. Ulrich, G. Mueller, A. Wichser: Emisja czastek stalych z silnika TDI z roznymi olejami smarujacymi - Particle Emissions of a TDI-Engine with Different Lubrication Oils, PTNSS Silniki Spalinowe Czasopismo naukowe - Combustion Engine Scientific Magazine, PL ISSN 0138-0346, Rok. XLIV, Vol. 2, 2005, 46-55.
- [³] A. Ulrich, A. Wichser, J. Czerwinski: The Influence of different Lubrication Oil Types on the Particle Emissions of a Diesel-Heavy Duty Engine, in preparation.

Collaborations:

J. Czerwinski (University of Applied Sciences, Biel-Bienne, Switzerland)

Title: Method development for spatially resolved chemical investigations of corrosion processes at aluminium alloys - a feasibility study

Researchers: A. Ulrich, M. Gysler

Institute/Group: EMPA, Swiss Federal Laboratories for Materials Testing and Research
Überlandstrasse 129, 8600 Dübendorf, Switzerland
Lab 131 Laboratory for Solid State Chemistry and Analysis

Project Description:

Corrosion is an important issue in materials science and engineering. A detailed understanding of corrosion mechanisms is fundamental for an effective prediction and minimization of corrosion damage and evident for sustainable material science and development. The initial corrosion usually attacks at the weakest location, normally surface defects such as grain boundaries, inclusions, segregations or precipitates. Thus, the investigation of local chemical changes is of increasing interest in the corrosion research. Therefore, a research project has been launched with the goal to develop a localized analytical procedure for spatially resolved and element specific chemical in-situ characterisations of corrosion processes. Within a diploma thesis a first feasibility study had been carried out to study if a downsizing and miniaturisation of such in-situ tests is possible and which and how different parameters influence the dissolution rate of specific elements in various aluminium alloys. After an appropriate method development, optimization and validation, several tests were carried out, first, on the basis of droplet experiments such as the effect of the type of the attacking media, concentration, pH and the impact time as well as different surface treatment and surface finishing of the studied aluminium alloys. All samples were analysed by inductively coupled plasma mass spectrometry (ICP-MS). Regarding miniaturisation, first tests with respect to media purity and optimized detection limits were carried out. Secondly, first investigations on miniaturisation by variations of the wetted area size were performed. This work will be continued in form of a PhD thesis starting in January 2006.

References:

^[1] M. Gysler: *Charakterisierung der Korrosionsbeständigkeit von Aluminiumlegierungen*, Diplomarbeit EMPA/ZHW (2005)..

Collaborations:

Prof. Krähenbühl, Prof. Siegenthaler (University of Bern)
P. Schmutz, EMPA

Title: Seasonal profiles of sulphur, phosphorus and potassium in Norway spruce

Researchers: T. Barrelet^{1,2}, A. Ulrich¹, U. Krähenbühl²

Institute/Group: ¹EMPA, Swiss Federal Laboratories for Materials Testing and Research
Lab 131 Laboratory for Solid State Chemistry and Analysis,
Überlandstrasse 129, 8600 Dübendorf, Switzerland
²University of Bern, Department for Chemistry and Biochemistry,
Freiestrasse 3, 3012 Bern, Switzerland

Project Description:

Seasonal profiles of sulphur, phosphorus and potassium content in the wood of Norway spruce trees have been established for the first time. This became possible by a novel use of LASER ablation coupled to HR-ICP-MS for measuring these elements in drill cores. This technique combines excellent spatial resolution with superior detection power, and makes it possible to measure low element concentrations even in relatively narrow year rings. Despite its low quantity in wood, sulphur is an important macronutrient for plants and seems to display seasonal variations of its concentration, which corresponds to actual presumptions of sulphur metabolism in plants. A similar seasonal pattern was also found for phosphorus, another crucial element in tree nutrition. This was unexpected, because it was previously assumed that the distribution of phosphorus remains constant throughout the year. Potassium, the third element measured, seems to be accumulated especially in the latewood. The found profiles suggest a seasonal variation, thus uncovering new aspects of Norway spruce (*Picea abies*) metabolism.

References:

- [¹] T. Barrelet, A. Ulrich, H. Rennenberg, U. Krähenbühl: Seasonal profiles of sulphur, phosphorus and potassium in Norway spruce wood, *Plant Biology* 2006, accepted.
- [²] T. Barrelet: Norway Spruce as an Environmental Archive for Sulphur Dioxide, Inauguraldissertation der Philosophisch-naturwissenschaftlichen Fakultät der Universität Bern, 2005.

Collaborations:

F.H. Schweingruber, D. Nievergelt and J. Esper (WSL, CH),
J. Kaplan (Botanical Institute, University of Bern, CH)
H. Rennenberg, (University of Freiburg im Breisgau, Germany)

Title: Railway Traffic - A Source of Fine Particles?

Researchers: P. Lienemann¹, C.N. Zwicky¹, N. Bukowiecki^{1,3},
A. Wichser¹, A. Ulrich¹, M. Hill², R. Gehrig²

Institute/Group: EMPA, Swiss Federal Laboratories for Materials Testing and Research
Überlandstrasse 129, 8600 Dübendorf, Switzerland
¹Lab 131 Laboratory for Solid State Chemistry and Analysis
²Lab 134 Laboratory for Air Pollution /Environmental Technology
³PSI, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

Project Description:

Public transportation systems are promoted especially in urban areas to reduce the use of individual vehicles. Compared to light duty vehicles, trains operated by electric engines have obviously negligible aerosol emissions per passenger and distance. However, particulate emissions caused by railway traffic are detectable. Material abrasion from tracks, wheels, brakes and the overhead traction line enhance the concentration of typical railway specific elements in ambient air. To get representative information about the contribution of railway traffic to the local immission of particulate matter with particle sizes below 10 micrometers (PM₁₀), a field study was performed covering a time period of one year. The chemical composition of the aerosol samples was determined with x-ray fluorescence spectrometry (WD-XRF). The calibration for XRF was performed using various aerosol filters quantified by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) after microwave digestion. The measurement campaign involved daily sampling at three measuring sites influenced by railway traffic together with an urban background site without local railway exposition (Zeughaus). The sampling sites were situated at the entry to the main railway station of Zurich (Röntgenstrasse, Gamperstrasse) as well as at a very busy railway line with more than 700 trains per day (Juchhof). The aerosol particles were sampled on quartz filters in a distance of ~10 m from the railway tracks. To study the distance dependence of the railway induced concentrations of railway relevant elements such as iron, manganese and copper, additional samples were taken at Juchhof in a distance of 36 m and 120 m from the railway track. The substantial daily variations of the elemental concentration are due to meteorological influences based on atmospheric dilution and transportation processes. In a distance of 10 m from the railway tracks the PM₁₀ concentration was 1.5 – 2.0 µg/m³ higher than at the urban background site, which contained an average of 21.5 µg/m³ PM₁₀ particles. The additional fine particles caused by railway traffic consist mainly of iron. Compared to the average background concentration of ~0.6 µg/m³ iron at the Zeughaus sampling site, the iron content of the aerosol in 10 m from the railway tracks was with ~2 µg/m³ about three times higher. The iron concentration decreased drastically with increasing distance from the railway track. Similar behaviour showed the also railway relevant elements copper and manganese.

References:

^[1] N. Bukowiecki, M. Hill, R. Gehrig, C. Zwicky, P. Lienemann, F. Hegedus, G. Falkenberg, E. Weingartner, U. Baltensberger, *Trace Metals in Ambient Air: Hourly Size-Segregated Mass Concentrations Determined by Synchrotron-XRF*, Environ. Sci. Technol., **39**, 5754-5762, (2005).

Collaborations:

BAFU (former BUWAL), SBB, PSI (Villigen), INFRAS (Zurich)

Title: Origin investigation of bloomery iron from northern Switzerland

Researchers: M. Senn-Bischofberger A. Wichser, A. Ulrich

Institute/Group: EMPA, Swiss Federal Laboratories for Materials Testing and Research
Überlandstrasse 129, 8600 Dübendorf, Switzerland
Lab 131 Laboratory for Solid State Chemistry and Analysis

Project Description:

The knowing of the origin of metallic waste products on archaeological sites is of particular interest for the investigation of historical manufacturing techniques and trade ways.

Therefore, the knowledge about the chemical composition is essential. In spite of the heterogeneity of the waste samples, it is possible to group the waste products according to their origin on the basis of the determined chemical composition.

The Jura region was also in former times an important region for iron smelting sites also due to proximity to ore deposits. The history in iron smelting reached even back to the Iron Age and the Swiss steel industry is still located in this region. Historical iron production techniques are based on a reduction of the iron to the solid state. Compared to modern steel the gained bloomery iron is usually very heterogeneous. Therefore, the use of LASER Ablation inductively plasma mass spectrometry (LA-ICP-MS) is especially attractive due to the excellent multi-element detection sensitivity and the high spatial resolution. Defined zones of the iron objects have been analyzed using LA-ICP-MS. Commercially available metallic standard reference materials were used for the calibration.

A goal of this study was the identification of typical elemental patterns, which allow definite classifications and an assignment to individual origin sites. Of special interest were the elements phosphorus, arsenic, nickel, cobalt and copper, which exist in various concentrations and ratios in the different iron samples. The patterns are representative fingerprints for the used iron ores. Based on these fingerprints, which were preserved during the manufacturing process, a correlation between the investigated metallic object and the origin of the iron is possible. The metallographic and chemical analyses of about 120 iron objects were carried out, mainly consisting of metallic forging waste.

References:

- ^[1] M. Senn Bischofberger, Das Schmiedehandwerk im nordalpinen Raum. Internationale Archäologie, Naturwissenschaft und Technik, Vol. 5 (Rahden/Westf.) 2005.

Collaborations:

Swiss National Museum (ZH); Office de la Culture, Sections archaeology and palaeontology (JU); Section archaeology (ZH); Department of Prehistory, University of Zurich

Title: Ultratrace Anion Analysis in High-Purity Applications

Researchers: R. Figi, C. Schreiner, O. Nagel

Institute/Group: ¹EMPA, Swiss Federal Laboratories for Materials Testing and Research
Lab 131 Laboratory for Solid State Chemistry and Analysis,
Überlandstrasse 129, 8600 Dübendorf, Switzerland

Project Description:

The achievable detection limits in ultratrace anion analysis in high-purity industrial applications are strongly limited by the available materials and equipment. Therefore, method development for ultratrace anion analysis requires systematic Investigations of all applied equipment. For example commercially available plastic vials for storing the eluted liquid samples are manufactured with materials containing several additives which might potentially release anionic contaminants, thus degrading the blank quality and determination limits (DL).

References:

^[1] . R. Figi et al., *Microchimica Acta* *Microchim Acta* 150, (2005), 199–209.

Collaborations:

Methrom AG, Switzerland

Title: Trace gas and $\delta^{13}\text{C}$ - CO_2 analysis by FTIR spectroscopy

Researchers: J. Mohn and L. Emmenegger

Institute/Group: Empa, Materials Science and Technology, Laboratory for Air Pollution / Environmental Technology, Duebendorf

Project Description:

Fourier Transform Infrared (FTIR) spectroscopy is a versatile tool for gas analysis. Applications are widespread from real-time measurement of industrial processes to environmental monitoring of trace gases [1, 2]. The quality of the analytical result, however, is strongly dependent on task-specific optimization of the system which includes hardware configuration, quantification algorithm and calibration strategies.

We developed a method based on a portable, commercially available, 0.5 cm^{-1} resolution FTIR spectrometer which allows simultaneous on-line analysis of multiple trace gases (CO_2 , CH_4 , N_2O , CO) as well as the $^{13}\text{C}/^{12}\text{C}$ isotopic ratio of atmospheric CO_2 ($\delta^{13}\text{C}$ - CO_2). The analytical setup was improved to reach high temperature and pressure stability and an exceedingly good spectral signal to noise ratio. Our method requires no sample preparation other than optional drying and can be applied directly to ambient air. For $\delta^{13}\text{C}$ - CO_2 we designed a calibration procedure that is distinctly different from the concepts published so far [3, 4], using a set of multicomponent standards that were prepared from CO_2 emission sources with characteristic isotopic composition and quantified by Isotope Ratio Mass Spectrometry (IRMS). For quantification, a robust partial least square (PLS) algorithm was used. Validation for the trace gases was performed at a measuring site of the Swiss National Air Pollution Measuring Network (NABEL), achieving a precision of 0.1 - 0.3 % for CO_2 , CH_4 and N_2O , and 0.9 % for CO . Laboratory results for $\delta^{13}\text{C}$ - CO_2 are very promising with a precision (Allan variance) of 0.3 ‰, showing its potential to study environmental processes with distinctive isotopic signatures.

References:

- [1] J. Mohn, U. Beck, K. Zeyer and L. Emmenegger, *Calibration of reactive process gases for the characterization of semiconductor processes by FTIR*, J. Mol. Struct. **744**, 247-253 (2005).
- [2] J. Mohn, A.M. Forss, S. Bruhlmann, K. Zeyer, R. Luscher, L. Emmenegger, P. Novak and N. Heeb, *Time-resolved ammonia measurement in vehicle exhaust*, Int. J. Environ. Pollut. **22**, 342-356 (2004).
- [3] M.B. Esler, D.W.T. Griffith, S.R. Wilson and L.P. Steele, *Precision trace gas analysis by FT-IR spectroscopy. 2. The $^{13}\text{C}/^{12}\text{C}$ isotope ratio of CO_2* , Anal. Chem. **72**, 216-221 (2000).
- [4] S. Söderholm, N. Meinander and J. Kauppinen, *The $^{13}\text{C}/^{12}\text{C}$ isotopic ratio determined by FTIR spectroscopy*, Proc. 11th International Conference on Fourier Transform Spectroscopy (ICOFTS-11), Athens, American Institute of Physics, 1997.

Collaborations:

Prof. N. Buchmann, ETHZ, Inst. of Plant Sciences

Title: X-ray absorption spectroscopy (XAS) investigations on Ni uptake mechanisms in cement

Researchers: M. Vespa, R. Dähn, D. Grolimund, E. Wieland, A. M. Scheidegger

Institute/Group: Waste Management Laboratory, Paul Scherrer Institute (PSI), Villigen

Project Description:

Cement-based materials play an important role in multi-barrier concepts developed worldwide for the safe disposal of hazardous and radioactive wastes. Cement is used to condition and stabilize the waste materials and to construct the engineered barrier systems (container, backfill and liner materials) of repositories for radioactive waste. In this study, Ni uptake by hardened cement paste has been investigated with the aim of improving our understanding of the immobilization process of heavy metals in cement on the molecular level. X-ray-absorption spectroscopy (XAS) coupled with diffuse reflectance spectroscopy (DRS) techniques were used to determine the local environment of Ni in cement systems. The Ni-doped samples were prepared at two different water/cement ratios (0.4, 1.3) and hydration times (1 hour - 1 year) using a sulphate-resisting Portland cement. The metal loadings and the metal salts added to the system were varied (50 up to 5000 mg/kg; NO_3^- , SO_4^{2-} , Cl^-). The XAS study showed that for all investigated systems Ni(II) is predominantly immobilized in a layered double hydroxide (LDH) phase, which was corroborated by DRS measurements [1]. Only a minor extent of Ni(II) precipitates as Ni-hydroxides ($\text{Ni}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$). This finding suggests that Ni-Al LDH, rather than Ni-hydroxides, is the solubility-limiting phase in the Ni-doped cement system.

References:

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Title: Climate relevant research at the Jungfraujoch within the Global Atmosphere Watch Project

Researchers: Ernest Weingartner, Bart Verheggen, Julie Cozic, Martin Gysel, Günther Wehrle, Urs Baltensperger

Institute/Group: Paul Scherrer Institut, Laboratory of Atmospheric Chemistry

Project Description:

The Global Atmosphere Watch (GAW) program is an activity overseen by the World Meteorological Organization (WMO). It is the goal of GAW to ensure long-term measurements in order to detect trends and to develop an understanding of these trends. With respect to aerosols, the objective of GAW is to determine the spatio-temporal distribution of aerosol properties related to climate forcing and air quality up to multi-decadal time scales. The GAW monitoring network consists of 23 Global (including now the Jungfraujoch, which was upgraded from a Regional to a Global station) and some 300 Regional stations. While Global stations are expected to measure as many of the key variables as possible, the Regional stations generally carry out a smaller set of observations.

The following aerosol parameters are continuously measured on the Jungfraujoch: aerosol optical depth, major ionic components in two size fractions, scattering and hemispheric backscattering coefficient at various wavelengths, absorption coefficient at various wavelengths, and the aerosol number concentration. For most parameters a continuous 11-year record is now available (see <http://aerosolforschung.web.psi.ch/onlinedata>). In addition, dedicated field campaigns were performed in order to determine the response of the aerosol particles to increased relative humidity [1,2,3] and to study the interaction of aerosol particles with clouds [4]. More than 900 hours of in-cloud measurements of the aerosol and hydrometeor properties were made during intensive field campaigns in order to parameterize the aerosol partitioning in natural, mid-latitude, mixed-phase clouds. The activated fraction was observed to decrease with increasing ice mass fraction (IMF) from approximately 0.6 in summer liquid phase clouds (IMF = 0) to less than 0.2 in mixed-phase clouds (IMF > 0.05). The latter is attributed to the Wegener-Bergeron-Findeisen mechanism whereby ice crystals grow at the expense of liquid water drops, releasing formerly activated aerosols back into the interstitial phase. The observed partitioning into the ice phase was used to predict the ice crystal number concentration in a general circulation model, resulting in a significantly smaller shortwave aerosol indirect effect on climate than is generally found.

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Collaborations: Meteoswiss, Payerne; University of Applied Sciences, Windisch; EMPA, Dübendorf; Institute for Atmospheric and Climate Science, ETH Zürich; Institut für Troposphärenforschung, Leipzig, Germany; Institute of Atmospheric Physics, DLR Oberpfaffenhofen, Germany; University of Manchester, England; University of Mainz, Germany; Universität Darmstadt, Germany; University of Helsinki, Finland.

Title: Evaluation of Aerosol Road Traffic Emissions in Switzerland by Chasing Experiments and Dynamometric Tests

Researchers: Silke Weimer^{1,2}, René Richter², Daniel Schreiber¹, Anna Maria Forss¹, Stefan Krähenmann², Claudia Mohr², Jan Stilli¹, Claudio Rüdý¹, Martin Mohr¹, André Prévôt², Christian Bach¹, Urs Baltensperger²

Institute/Group: ¹ Internal Combustion Engines Laboratory, EMPA
² Laboratory for Atmospheric Chemistry, Paul Scherrer Institut

Project Description:

For the assessment and understanding of the atmospheric processes that involve aerosols, it is necessary to study more aerosol properties than just the particulate mass. The combination of chasing experiments and dynamometric tests allows to determine real-world and quantitative emission measurements of vehicles at various driving conditions (e.g. different speeds, different road gradients). The goal is to assess the emitted aerosol size distributions, the solid (i.e. the non-volatile) aerosol size distributions, the aerosol surface, and the aerosol number. The PSI mobile lab, described in [1], was redesigned to allow for controlled chasing experiments, implementing a bag sampler. Individual vehicles were tested both by the chasing and the dynamometric test method and emissions plumes of a larger number of randomly chosen vehicles in regular traffic were and will be used to get more statistics.



Figure 1. The PSI mobile lab chasing a test vehicle (picture: Silke Weimer).

The instruments inside the mobile laboratory include a Condensation Particle Counter (CPC), a Micro Soot Sensor (MSS), a Scanning Mobility Particle Sizer (SMPS), a Diffusion Charger (DC), a Fast Mobility Particle Sizer (FMPS), as well as CO₂ and NO_x gas analyzers. The chasing experiments are performed at the Military Airport in Dübendorf and compared to test bench measurements conducted at the EMPA. In a distance of around 10 m the tested vehicles are chased at different velocities.

One goal is the investigation of the relevance of the nucleation mode under ambient conditions. Hence, the experiments take place in warm and cold seasons.

The size distribution measurements of diesel engines showed for warm seasons that the soot mode at a particle diameter of 60 nm was repeatable and seen in the test bench and chasing experiments (Fig. 2). We did not find a nucleation mode for velocities up to 80 km/h. In contrast, we experienced a distinct nucleation mode in regular highway traffic at temperatures around -7 °C. One aim will be to investigate the physical and chemical properties of the aerosol particles with a diameter smaller than 50 nm for one specific vehicle by chasing and test bench measurements for cold seasons.

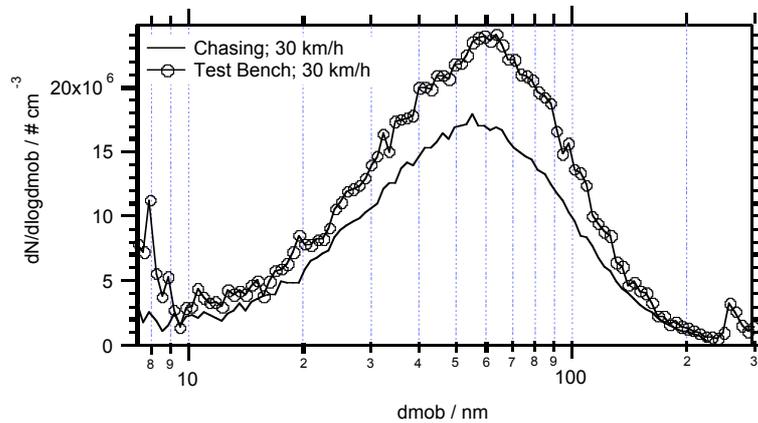


Figure 2. Size distributions of a test vehicle in a chasing and a test bench experiment.

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Collaborations:

U. Lohmann (ETHZ)

Title: Lipidomics in Clinical Diagnostics

Researchers: Ines Burkard, Arnold von Eckardstein, Katharina Rentsch

Institute/Group: Institut für Klinische Chemie, Universitätsspital Zürich

Project Description:

Our research goal is the identification and evaluation of biomarkers for the preclinical diagnosis of atherosclerosis. Such disease markers would imply a major advancement towards the current medical practice, where cardiovascular high-risk patients are identified by the presence of multiple or extreme risk factors. Compared to this conventional strategy, disease markers are expected to increase the sensitivity and specificity in the identification of patients who will develop major coronary events in the near future and will hence indirectly improve the prevention of cardiovascular disease. Disease biomarkers of atherosclerosis are also expected to be very helpful in the monitoring of anti-atherosclerotic interventions.

Enzymatic oxidation of cholesterol into oxysterols and bile acids plays a key role in the regulation of cholesterol homeostasis. Via oxysterols and bile acids, cholesterol can be eliminated from specific organs and cells (e.g. liver, brain, macrophage). Among the oxysterols, 24S- and 27-hydroxycholesterol are of potential diagnostic interest since their plasma concentrations may reflect the cholesterol metabolism of the brain and macrophages, respectively. 5,6-secosterol and its aldolization product are the products of ozone-driven oxidation of cholesterol and have been suggested to serve as new biomarkers for the early and non-invasive detection of ongoing atherosclerotic inflammation processes.

Liquid chromatography mass spectrometry (LC-MS/(MS)) methods have been developed for the determination of 24S- and 27-hydroxycholesterol [1] as well as for 15 conjugated and non-conjugated bile acids [2] and 5,6-secosterol and its aldolization product [3]. A collective of healthy individuals has been analyzed in order to establish reference values of the different markers and to unravel associations and correlations with demographic and anthropometric measures as well as clinical biochemical markers. The influence of daytime, food intake and menstrual cycle on the concentrations of 24S- and 27-hydroxycholesterol as well as the different bile acids have been studied [4].

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Collaborations:

G. Waeber (Universität Lausanne)

Title: **The use of LC-MS(/MS) as an analytical tool in the drug monitoring laboratory**

Researchers: Ursula Gutteck, Arnold von Eckardstein, Katharina Rentsch

Institute/Group: Institut für Klinische Chemie, Universitätsspital Zürich

Project Description:

Liquid chromatography with mass spectrometric detection (LC-MS) is nowadays an indispensable analytical tool for the quantification of drugs and drug metabolites in serum and plasma in the course of therapeutic drug monitoring. Electrospray ionization (ESI) allows an easy and sensitive detection of many drugs but is incriminated with ion-suppression due to co-eluting endogenous substances from the patient samples. In addition, the ionization process can be saturated, which leads to restricted linearity. In order to optimize the analytical quality of our assays for more than 100 different drugs, we are testing each analyte for its ionization behaviour using atmospheric pressure chemical ionization (APCI). This ionization mode is more destructive but offers a wide linear range and is less sensitive to ion suppression. If the ionization process results in a sufficient sensitivity the assay has to be fully validated for its use in a clinical laboratory. The goal of this project is to use APCI wherever possible. In addition different new methods have been introduced in our laboratory. For the optimal treatment of a single patient with a brain tumor a sensitive LC-MS method has been developed and validated for the quantification of celecoxib [1]. The already existing LC-MS method for the quantification of 9 different antiretroviral drugs was completely modified and the first non-peptidic proteinase inhibitor was included into the procedure [2]. Aripiprazol is a new atypical antipsychotic drug which needs drug monitoring due to its interaction potential with other drugs. Therefore, an LC-MS method has been developed and validated.

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Collaborations:

Numerous different clinicians from the university hospital Zurich or other hospitals in Switzerland

6

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Group Prof. R. Zenobi, Laboratorium für Organische Chemie, ETH Höggerberg

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Group of E. Pretsch, Laboratorium für Organische Chemie, ETH Höggerberg

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Group Prof. P. A. Schubiger, Institut für Pharmazeutische Wissenschaften, ETH Zürich

M. Bruehlmeier, B. Kaser-Hotz, R. Ackermann, C.R. Bley, M. Wergin, P. A. Schubiger, S. M. Ametamey "Measurement of tumor hypoxia in spontaneous canine sarcomas" *Veterinary Radiology and Ultrasound* **46(4)**, 348-354 (2005).

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Collaborations

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A project between ETHZ and Eawag investigates conformational changes in the estrogen receptor induced by the heavy metal cadmium.

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