*CH*analysis 2022

6th Meeting of the Swiss Analytical Scientists
Dorinth Resort Blüemlisalp, Beatenberg
May 19-20, 2022

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Program *CH*analysis 2022

Thursday, 19th May 2022

13.00 Conference Opening
Marc Suter, Vice-President SCS Division of Analytical Sciences (DAS)

Session 1 – Chairs: Marc Suter, Davide Bleiner

13.05 Invited Lecture
Lenny Winkel, Eawag
«Analytical advancements improve insights into the biogeochemical cycle of selenium»

Contributed Lectures

13.35 **Emanuel Billeter**, Empa
«Operando analysis of hydrogen in solids and on surfaces»

13.50 **Filippo Longo**, Empa
«Hard X-ray photoelectron spectroscopy and electrochemical impedance spectroscopy as new approach for surface properties analysis»

14.05 **Carlos Triana**, UniZH
«Advancements in laboratory XAFS instrumentation for the investigation of electrocatalysts for water splitting»

14.20 **Pitchnaree Kraikaew**, UniGE
«Capacitive readout of ion-selective electrode by electronic control for high precision measurements»

14.35 Coffee Break

Session 2 – Chairs: Franka Kalman, Christoph Meyer

15.20 Invited Lecture
Behnam Ahmadian Baghbaderani, Lonza
«Robust and reliable analytical methods: critical requirement for industrialization of cell and gene therapies»

Contributed Lectures

15.50 **Anika Hoffmann**, HES-SO
«Novel RP-HPLC based assay for selective and sensitive endotoxin quantification»

16.05 **María Fernanda Cifuentes Girard**, UniGE
«Analysis of diastereomeric pyrrolizidine alkaloids in tea samples by liquid chromatography and supercritical fluid chromatography vacuum differential
mobility spectrometry-mass spectrometry»

16.20 **Silvia Mallia**, METAS
«Improved analytical methods for PAHs and Hg in selected food matrices»

16.35 Poster session and Aperitif

18.30 Dinner

21.00 Get-together Party

Friday, 20th May 2022

Session 3 – Chairs: Eric Bakker, Hanspeter Andres

09.00 Simon-Widmer Award Lecture
Andrew DeMello, ETH Zürich
«The past, present and future of microfludics: a personal perspective»

Contributed Lectures

09.30 *Christian Berchtold*, FHNW
«LC-MS and GC-MS methods for sweat analysis as alternative biofluid in metabolomics»

09.45 *Yoshiki Soda*, UniGE
«Hyper-polarizing organic phase and its use for polyion sensing in blood plasma»

10.00 *Gunnar Schwarz*, ETH Zürich
«Complementing lectures with videos depicting case studies in instrumental element analysis»

10.15 Coffee Break

Session 4 – Chairs: Bodo Hattendorf, Stefan Schürch

10.45 Invited Lecuture
Detlef Günther, ETH Zürich
«Between fundamentals and applications – the important role of analytical chemistry»

Contributed Lectures

11.15 *Tara Forrest*, UniGE
«Submersible probe with in-line calibration and symmetrical reference element for long-term continuous measurements»

11.30 *Marco C. Knobloch*, Empa
«R-based Automatic high-resolution mass Spectra Evaluation Routine (RASER) for the rapid analysis of chlorinated paraffins and olefins»

11.45 *Nikolai Huwa*, Eawag
«Investigation of phosphorylation dynamics within the mTOR signalling pathway in zebrafish PAC2 cells by means of mass spectrometry-based targeted proteomics»

12.00 Invited Lecture
Marco Baity Jesi, Eawag
«Machine learning as a tool to predict toxicity of chemicals»

12.30 General Assembly of the Division Analytical Sciences (DAS) of the Swiss Chemical Society

13.00 End of the *CH*analysis 2022

Analytical advancements improve insights into the biogeochemical cycle of selenium

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Trace elements (metals, metalloids, non-metals) play a major role in human and animal health. Certain trace elements are toxic, even at very low concentrations. Other trace elements, referred to as micronutrients, are essential to humans and other organisms, however only in specific concentration ranges. To prevent over- or underexposure of trace elements, it is essential to better understand their cycling and distributions in the various environmental compartments, such as in soils, plants, ground- and surface water and the atmosphere. As the chemical speciation of trace elements largely determines their environmental mobility and bioavailability for uptake by plants and other organisms, it is of key importance to be able to identify and quantify trace element species in various environmental compartments. Furthermore, past research in environmental geochemistry has mainly focused on inorganic speciation of trace elements; however, in the environment, many trace elements occur in organic forms which remain largely unexplored due to the challenges posed by their analysis.

In this talk, I will present how advancements in analytical chemistry help elucidate the inorganic and organic speciation of the trace element selenium (Se) and therefore its environmental pathways and processes. Selenium, which is naturally present in rocks, soils, water and air, but also introduced into the environment via anthropogenic processes, is an essential micronutrient at low concentrations but toxic at to organisms at higher concentrations. Examples will be given of how liquid and gas-phase chromatography coupled to inductively coupled plasma mass spectrometry gives new insights into the speciation of Se in marine algae, the atmosphere and in soils. Finally, it will be shown how this information can be used to better understand processes connecting the different compartments and thus the overall biogeochemical cycle of selenium.

Operando analysis of hydrogen in solids and on surfaces

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Metal hydrides are an interesting class of materials not only for hydrogen storage but also for catalyzing hydrogenation reactions. Exemplary for these processes is the activity of early transition metal hydrides towards the ammonia synthesis reaction.[1] At first glance, the presence of large amounts of hydrogen in/on the catalysts should be beneficial to the catalytic process. Upon closer inspection, it was found that the catalytic activity of metal hydrides compared to metals is decisively influenced by electronic changes induced by hydrogen uptake.[2] The conceptual difficulty arises from the interrelation of bulk and surface hydrogen concentration. To determine the bulk hydrogen concentration of a large number of materials we have developed a combinatorial high throughput method for neutron imaging.

The analysis of hydrogen on surfaces is based on in situ membrane hydrogenation of thin films in combination with reflecting electron energy loss spectroscopy (REELS).[3] This method enables time resolved surface hydrogen concentration measurements as a function of the applied hydrogen pressure. The combination of a high throughput method for bulk hydrogen concentration determination with careful analysis of pristine surfaces will enable fast screening of hydride forming compounds for hydrogenation catalysis.
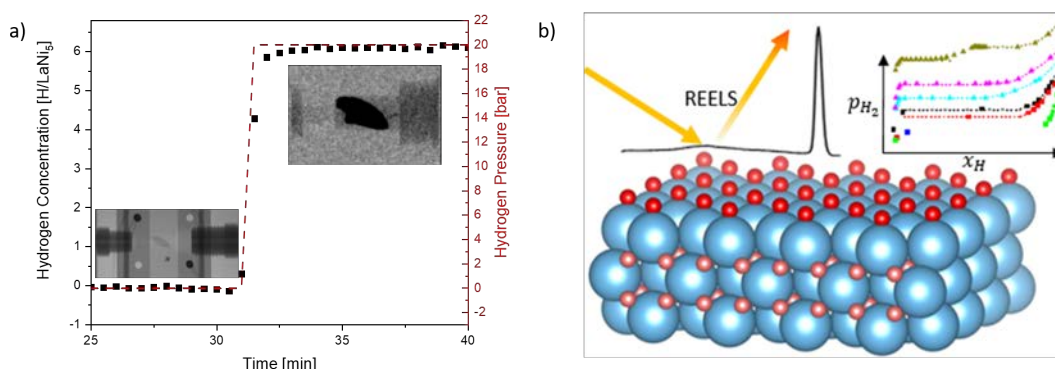

Figure 1. a) Bulk hydrogen concentration measurement by neutron imaging. b) Schematic representation of REELS measurements on TiH_2 surfaces.

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[1]   Y. Kobayashi et al., *J. Am. Chem. Soc.* **139** (2017), 18240.
[2]   E. Billeter et al., *Chem. Phys. Chem.* **20** (2019), 1398.
[3]   E. Billeter et al., *J. Phys. Chem. C,* **125** (2021), 25339.

Acknowledgement

Hard X-ray photoelectron spectroscopy and electrochemical impedance spectroscopy as new approach for surface properties analysis

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Energy storage is pivotal for a swift implementation of a renewable energy economy, but still awaits a technically and economically feasible large-scale solution. Alkaline water electrolysis represents a promising method used for hydrogen production particularly due to robustness, efficiency, durability and cost.[1] These advantageous have their in origin in the use of a simple setup and the use of abundant and cheap materials, e.g., Ni (alloys) as electrode material. The peculiarity of Ni can be related to its ability to form various compounds with hydrogen and oxygen (e.g., NiH_x, NiO, $Ni(OH)_2$, $NiOOH$).

X-ray photoelectron spectroscopy is the ideal tool to probe the chemical and electronic structure of surfaces, including electrodes. However, standard methods are restricted to ultra-high vacuum conditions; and even near ambient pressure photoelectron spectroscopy [2] may deliver falsified results of the surface during operando conditions, because the great number of (secondary) photoelectrons excited during photoexcitation. We therefore propose a different strategy to probe the extended surface post-mortem by photoemission, and link the thus obtained materials characterization to the true operando technique electro-chemical impedance spectroscopy (EIS) performed in parallel. A sophisticated sample station attached to an X-ray photoelectron spectrometer with standard (XPS: Al-Kα radiation) and hard X-ray excitation (HAXPES: Cr-Kα radiation) allows the preparation and monitoring of oxide/hydroxide layer thickening as a function of potential and time, from which an improved understanding of the properties of electrode surfaces can be drawn. The above- introduced Ni and nickel oxide/hydroxides surface serve as a relevant example of this approach.
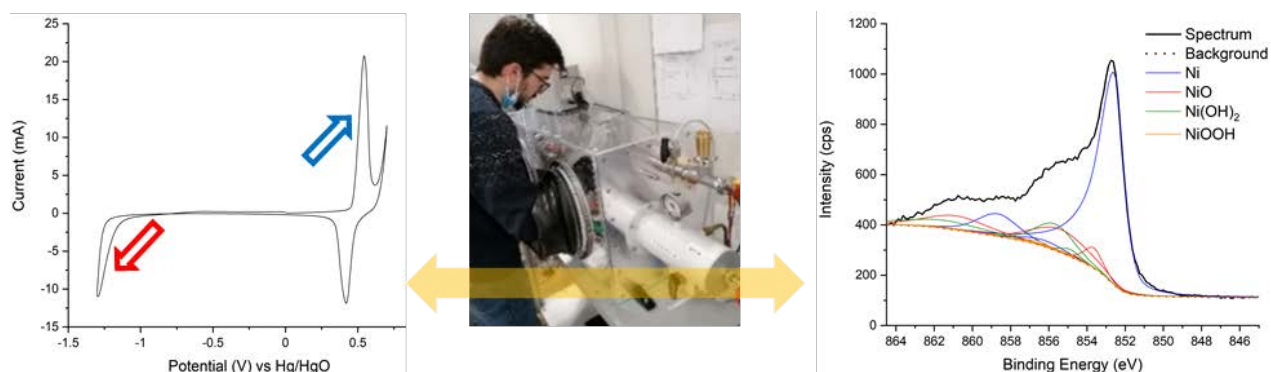

Figure 1: Cyclic voltammogramm (left) of Ni in 1M KOH prepared in an Ar-glove box attached to an XPS/HAXPES instrument (right panel: HAXPES of cycled Ni-electrode).

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Advancements in laboratory XAFS instrumentation for the investigation of electrocatalysts for water splitting

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Rational design of efficient electrocatalysts for industrial water splitting is essential to produce sustainable hydrogen fuel. However, understanding catalytic mechanisms under reaction conditions remains a major challenge. This is because the characterization of active species requires the use of front-line experimental techniques at high-energy synchrotron radiation sources to achieve the highest atomic-scale resolution. Fortunately, recent advancements in high-performance laboratory X-ray spectrometers offer synchrotron-quality resolution to access hard X-ray techniques at the lab without compromising on energy resolution. We present recent advances in laboratory X-ray absorption spectroscopy (XAS) instrumentation (Figure **1a**), and their applications to the investigation of electrocatalysts for water splitting. The tabletop XAS in-lab instrument permits the acquisition of X-ray absorption near edge spectra (XANES), giving insight on the valence state and electronic configurations of active catalytic centers, and the extended X-ray absorption fine structure (EXAFS), offering information of interatomic distances, coordination numbers, and disorder in the coordination shells (Figure **1b**).[1] The element-selectivity of the in-lab XAS instrument offers an exceptional technique to prove the atomic-level coordination environment, electronic and chemical states of active catalytic sites under reaction condition, no matter they are crystalline or amorphous catalysts.[2] The enhancement of the spectrometer capabilities to achieve adequate XAS signal-to-noise ratio will be discussed. The use of additives, attaining high performance at low/high energy ranges, sample preparation and design of electrochemical cells for *in situ*/*operando* experiments will be further examined (Figure **1c**).
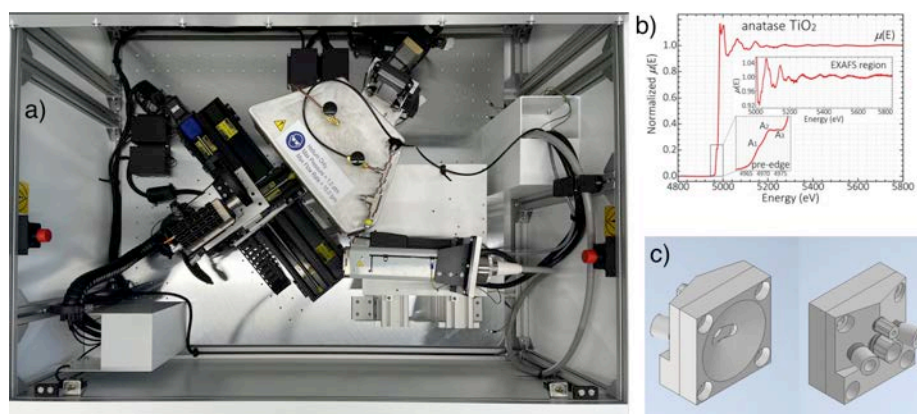
Figure 1. **a**) Laboratory X-ray absorption spectroscopy (XAS) instrument easyXAFS300. **b**) Representative XAS spectrum of anatase TiO_2. **c**) Home-designed electrochemical cells for *in situ*/*operando* XAS experiments.

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Capacitive readout of ion-selective electrode by electronic control for high precision measurements

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Constant potential coulometric readout of ion-selective electrode is known to improve sensitivity by producing a current signal that is easier to identify than that of direct potentiometric measurement. The current spike is measured and integrated, giving charge information that is proportional to logarithmic ion activity. The general coulometric readout utilizes an ion-to-electron transducing material as a capacitive layer for solid-contact ion selective electrode (SC-ISE).[1] In this case, the charge transfer process may be limited by the capacitive behavior of the transducer, resulting in a long response time and a current drift from the zero baseline. We presented recently for the first-time the use of an electronic capacitor instead of a solid-contact material to overcome the main drawbacks of constant potential capacitive readout.[2] The capacitor can be simply adapted to amplify the current signal so that it is optimally suitable for each application. Importantly, the current baseline drift is minimized owing to the ideally capacitive behavior of electronic capacitor. In that work, the electronic capacitor is discharged after each sample measurement by sequentially introducing a reference solution, which is required for a certain time to acquire again a zero potential difference.

To improve this method for practical use, we report the use of an electronic circuit to automate the control of the capacitive readout principle.[3] The open-circuit potential (OCP) of the reference solution is measured and stored by the potentiostat. In this method, the OCP value can be applied directly to the sample solution resulting in a sharp current spike. Discharging the capacitor is executed by short circuiting after each chronoamperometric measurement. Hence, the reference solution is no longer needed, resulting in shorter response time. Furthermore, the development of a portable device for constant-potential coulometry is presented. A small potentiostat along with dedicated electronic circuits are integrated and fitted in a small box (18.5 cm width × 10.7 cm length × 3.6 cm height with a weight of 370 g). A range of capacitors (22 – 220 µF) are integrated in the device, which can be automatically chosen by the control software. The device, the so-called PotentioCap, was evaluated in standard pH solutions and stabilized seawater samples using a hydrogen-selective electrode placed in series with a capacitor. The results of transient current and integrated charge over time correlates well with that from capacitive readout using a benchtop potentiostat with an external electronic circuit.

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Robust and reliable analytical methods: critical requirements for industrialization of cell and gene therapies

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Over the last few decades, a wide range of cell and gene therapies have emerged including the viral vector-based gene therapies, autologous and allogenic cell therapies. These therapies offer potential solutions to treat devastating diseases such as cancer, diabetes, or neurodegenerative disorders. In order for these therapies to have widespread therapeutic significance and become readily available, it is necessary to address multiple challenges associated with the Chemistry, Manufacturing and Controls (CMC) strategy including establishment of a phase appropriate manufacturing process, sampling plan, process analytics, and product release testing and logistics. Development of phase-appropriate, robust and reliable analytical methods is the primary requirement for development of robust and commercially viable manufacturing processes. A well-designed testing strategy is required to ensure adequate characterization of the final product (and intermediate materials generated throughout the process) can be achieved through implementation of reliable analytical methods as in-process monitoring, in process decision making assay or release testing during the manufacturing campaign. Here, we are going to review some of the current challenges associated with the development of appropriate analytical methods for cell and gene therapies and particularly highlight our approach, at Lonza, towards the development of robust and reliable analytical methods to properly test and characterize cell and gene therapy products. Using a cell therapy application as a case study, we will specifically highlight the testing strategy and our rationale towards choice of analytical methods implemented in the manufacturing process while ensuring reliability and robustness of the assay.

Novel RP-HPLC based assay for selective and sensitive endotoxin quantification

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Endotoxin testing in pharmaceuticals and injectables is a crucial requirement for patient safety. This paper presents a novel instrumental analytical endotoxin quantification assay.[1] It uses common analytical laboratory equipment (HPLC-FLD) and allows quantifying endotoxins in different matrices from about 10^9 EU / mL down to about 40 EU / mL (RSE based). Test results are obtained in concentration units (*e.g.* ng endotoxin / mL), which can then be converted to commonly used endotoxin units (EU / mL) in case of known pyrogenic activity. During endotoxin hydrolysis, the endotoxin specific rare sugar acid KDO is obtained quantitatively. After that, KDO is stoichiometrically reacted with DMB, which results in a highly fluorescent derivative. The mixture is separated using RP-HPLC followed by KDO-DMB quantification with a fluorescence detector. Based on the KDO content the endotoxin content in the sample is calculated. The novel chemical endotoxin assay is economic and has a small error. Its applicability was demonstrated in applied research. Endotoxins were quantified in purified bacterial biopolymers, which were produced by Gram-negative bacteria. Results were compared to LAL results obtained for the same samples. A high correlation was found between the results of both methods. Further, the new assay was successfully utilized for the development of novel endotoxin specific depth filters, which allow efficient, economic and sustainable endotoxin removal e.g. during DSP. Further, endotoxin content development was monitored in the supernatant of *E. coli K12* and *P. putida* bioreactors from inoculation until harvest. With that an easy to install tool is available to optimize reactor conditions with respect to the development of the endotoxin content during cultivation, a task difficult to achieve using the LAL assay. Those examples demonstrate that the new chemical endotoxin assay has the potential to complement the animal-based biological LAL pyrogenic quantification tests, which are accepted today by the major health authorities worldwide for the release of commercial pharmaceutical products and bring the endotoxin assay to the 21st century.

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Analysis of diastereomeric pyrrolizidine alkaloids in tea samples by liquid chromatography and supercritical fluid chromatography vacuum differential mobility spectrometry-mass spectrometry

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Recently, the monitoring of pyrrolizidine alkaloids (PAs), classified as phytotoxic compounds, in food matrices has gained of interest. PAs are a complex mixture of diastereomers and more than 600 PAs and their N-oxides forms were identified in over 6000 plants. Many LC-MS and GC-MS assays have been developed, but requires extensive sample preparation and long analyses times, and methods with higher throughput are needed. In the present work, the potential of vacuum DMS (vDMS) for reducing LC analysis time while maintaining good selectivity is investigated for the analysis of diastereomeric PAs in tea samples. In addition, the performance of supercritical fluid chromatography-mass spectrometry (SFC-MS) is an attractive alternative to LC for reducing analysis time and is capable of resolving the diastereomeric PAs.

Diastereomeric PAs were analysed in tea samples. Epi-jacobine and atropine were used as internal standards. Samples were extracted using H_2SO_4, centrifuged and filtered. Extracts were analysed on various systems: 1) short LC-vDMS-MS, 50 x 1.0 mm C_{18} column (5 min) in trap/eluted setup using $MeOH/H_2O$ (15/85; v/v), 0.1%FA 2) LC-MS/MS method using C_{18} column, 150 × 2.1 mm (12 min). 3) SFC-MS/MS method (7 min) using CHIRALPAK® IG-3, 3.0 x 100 mm, 3 μm SFC column. Analyte detection was performed either on LCMS-8050 QqQ or on 8060 QqQ mass spectrometer (Shimadzu) and prototype vDMS cell (33 mbar pressure).

Four sets of PA diastereomers were investigated. Intermedine, echinatine, lycopsamine, indicine (*m/z* 300) and their N-oxide forms; intermedine-N-oxide, echinatine-N-oxide, indicine-N-oxide, lycopsamine-N-oxide (*m/z* 316) have no selective fragments under CID and coeluted in LC. Senecivernine and senecionine (*m/z* 336) cannot be distinguished by MS/MS and they partially coeluted in LC. Jacobine is the only diastereomer (*m/z* 352) that has a selective fragment (*m/z* 352>155) and can be distinguished from retrorsine, while senecivernine-N-oxide and senecionine-N-oxide (*m/z* 352); have different retention times.
For SFC-MRM/MS all diastereomers are resolved using the CHIRALPAK® IG-3 SFC column under ternary gradient. vDMS has shown to be powerful approach for the separation of isomeric analytes and to improve detection selectivity. Solvent, correction and dispersion voltage, temperature and pressure were optimized in vDMS to achieve separation of diastereomers. The combination of short LC column with trap/elute setup and vDMS and detection in SIM mode enabled simplified sample preparation, reduced the analysis time and improved selectivity compared to classical LC-MS method. In addition, LC-vDMS-MS enables accurate quantitation of 10/14 diastereomeric PAs with higher throughput (<1h), compare to reported LC-MRM/MS method in which 9/14 diastereomers could be separated and SFC-MRM/MS in which all diastereomers are fully resolved but requires time consuming sample preparation (>3h). Finally, PA diastereomers were successfully analysed in 20 tea samples using the short LC-vDMS-MS method and compared to LC-MRM/MS and SFC-MRM/MS methods.

Improved analytical methods for PAHs and Hg in selected food matrices

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Contaminants in food may pose a serious health risk. For this reason, very sensitive methods are needed to detect the presence of these analytes in trace and ultra-trace amounts in complex food matrices. The national reference laboratories for processing contaminants (NRL-PC) and for metals and nitrogenous compounds (NRL-MN) in food at the Federal Institute of Metrology METAS work on the development of reference methods and reference materials for reliable food analysis. One of the major tasks of our NRLs is to compare different extraction and analytical methods for food contaminants. As a first example, we present a fast extraction/clean-up method for GC-MS/MS analysis of polycyclic aromatic hydrocarbons (PAHs) in food supplements containing botanicals. As a second example, we compare two analytical methods (ICP-MS and direct mercury analyzer) for the determination of mercury in skimmed milk and offal. Advantages and limitations of these methods are discussed. One of the future objectives of our NRLs is to develop faster extraction and clean-up processes with low solvent consumption for a large number of food contaminants.

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The past, present and future of microfludics: a personal perspective

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Since the concept of the miniaturized total analysis system was introduced by Michael Widmer and Andrea Manz in 1990, there has been a continual and rapid evolution of microfluidic systems for use in the chemical and biological sciences. Interest in microfluidic technology has been driven by concomitant advances in the areas of genomics, proteomics, drug discovery, single cell analysis, high-throughput screening and diagnostics, with a simple need to perform high quality and rapid experiments on small sample volumes. Interest in microfluidics has been stimulated by the fact that physical processes can be more easily controlled when instrumental dimensions are reduced to the micron scale, with a range of seductive features accompanying system miniaturization. These include the ability to process small volumes of fluid, enhanced analytical performance, reduced instrumental footprints, low unit costs, facile integration of functional components and the ability to exploit atypical fluid behaviour.

My lecture will discuss why we have been motivated to use microfluidic systems for chemical and biological experimentation over the past twenty-five years and will focus particularly on studies that exploit the spontaneous formation of droplets to perform a variety of experiments and the development of novel platform for clinical diagnostics.

LC-MS and GC-MS methods for sweat analysis as alternative biofluid in metabolomics

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Background: Sweat is a promising but still insufficiently studied matrix in the field of metabolomics research. Compared to blood, saliva, hair, or urine sweat appears less complex, since the concentration of proteins (saliva), lipids, phospholipids (blood), or urea (urine) are significantly lower. Therefore, the sample preparation process for mass spectrometry might be simplified. From a diagnostic point of view, the analysis of this alternative biofluid is an opportunity to find yet undiscovered biomarkers. Sweat represents short term ongoing metabolic processes comparable with blood or saliva.[1–3] The sampling allows theoretically the access to samples from people outside of a hospital, without an additional infection risk. This is important to support diagnostics in low-income countries, especially for vulnerable patients such as children. However, one of the challenges of sweat analysis is the low concentration of biomarkers and the low sample volume (25 – 200 µL). Methods for the analysis of sweat using LC-MS and GC-MS have been developed to investigate potential markers for tuberculosis. However, this contribution focusses on the development and execution of the methodical part only.

Method: Sweat samples were collected using an iontophoresis technique combined with pilocarpine. To achieve sufficient statistical data (including technical replicates), the methods were optimized to operate with a sample volume of less than 30 µL. Measurement were performed on a LTQ Orbitrap XL LC-MS and a Leco GC-TOF-MS. For the GC-TOF-MS analysis, a method based on Fiehn (2016)[4] was developed.

Results: By LC-MS, about 6400 features were found. Typical amino acids and even antibiotic drugs have been detected. By GC-TOF-MS 128 metabolites out of about 2800 detected features have been identified by retention time index and electron impact spectra matched with the Fiehn Library.

Conclusion: LC-MS and GC-MS are feasible approaches for sweat analysis if sufficient sample volume is available. The basis for future studies, including specific sampling recommendations, was developed.

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Hyper-polarizing organic phase and its use for polyion sensing in blood plasma

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Ion-selective optodes (ISOs) have emerged as an optical variant of ion-selective electrodes (ISEs) allowing the optical detection of ionic species based on ion exchange between analytes and optical reporters. Being freed from external equipment, ISOs have been miniaturized down to the nanoscale (<100 nm) using various optical signal transducers such as chromoionophores, solvatochromic dyes and quantum dots. While the nanoISOs have shown promising performance for the detection of small ions such as alkali ions (K^+, Na^+, Li^+) and biologically relevant ions (Ca^{2+}, Mg^{2+}, Cl^-), those for polyion quantification have suffered from severe interference in the complex samples whole blood, blood plasma and serum. Indeed, the signal of ISOs in plasma was found to already saturate in the absence of the target polyion in our experiment and as reported earlier.[1]

In this contribution we will describe a newly developed sensor working through a novel sensing mechanism based on "hyper-polarizing organic phase" where the solvatochromic dye is strongly polarized by the negatively charged organic molecule DNNS (dinonylnaphthalenesulfonate ion) which is known to be a good ligand of protamine, an arginine-rich polycationic protein.[2] The solvatochromic dye accordingly shows a high polarity signal in the organic phase, which is, surprisingly, higher than that in an aqueous environment. In the presence of protamine, DNNS incorporated in the nanoparticle-based sensor interacts with protamine rather than the solvatochromic dye, turning the optical signal back to non-polarity. In this manner hyper-polarization is used as an optical signal transduction mechanism.

The newly developed sensor has shown greatly improved selectivity where even arginine, the main repeating moiety of protamine, does not induce signal transduction at all while the conventional ion-exchange type exhibited interference from arginine. Several thermodynamic parameters involving DNNS/protamine and DNNS/arginine interaction will be shown to explain the cause of this improved selectivity. Owing to the high selectivity, this sensor has enabled polyion detection in plasma for the first time as an optical nanoparticle-based sensor. The sensor was finally applied to quantify heparin, a polyanionic saccharide used as an anticoagulant during surgery, in various patient plasma samples.

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Complementing lectures with videos
depicting case studies in instrumental element analysis

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During the pandemic, much lecturing was done via videoconferences or recorded lessons and experiments. The latter have now become so widespread that they will likely be used more continuously for the planning of and as a support of courses dealing with instrumental techniques in particular. Even if videos do not provide hands-on experience, they can make places and processes tangible in a lecture hall. Particularly in analytical chemistry classes, it is often impractical to bring either the instruments to the students or all students to the instruments to explain them. Similarly, some procedures may take too long or take place in different locations: field sampling, sample preparation, instrumental analysis, etc.[1] Still, the selection of videos available for teaching analytical chemistry is limited, especially for advanced topics. Here we present our experience with videos complementing analytical chemistry lessons with examples to familiarize undergraduate students with instrumental techniques. Furthermore, we provide a more detailed account on how we planned, produced, and utilized a video to review course content at the end of the semester. The analytical case study presented focused on the determination of magnesium in two well water samples with emphasis on flame atomic absorption spectroscopy, while also comparing results with inductively coupled plasma optical emission spectroscopy and titration measurements. During the lecture, we engaged students by asking them for suggestion on how to carry out the measurements before showing the respective video sections. A survey among the students revealed a remarkably positive response to this approach. We conclude with practical advice for planning and producing similar video to visualize case studies.

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Between fundamentals and applications – the important role of analytical chemistry

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The major challenges of our times request sustainability in everything we are planning in the future. Environmental protection, discovery of new resources, characterization of new and lightweight materials, material replacement and reduction in the construction industry, food production and safety and life science and medicine are important topics, among others, where analytical chemistry plays a major role. The availability of the entire portfolio of analytical techniques is of utmost importance while constant refinement and development is required in order to provide high compatibility and flexibility for applications in the aforementioned research fields.

The group for Trace Element and Micro Analysis at ETH Zurich studied a variety of instruments, processes and methods related to element analysis and isotope ratio determinations. Instruments were developed which become more and more applied. For example, a significantly improved prototype inductively coupled plasma time of flight mass spectrometer (ICP-TOFMS) led to the renaissance of TOF-MS instruments and they are now commercially available (TOFWERK AG, Thun Switzerland). These instruments contribute to knowledge generation in many fields of research, e.g. in life science, medicine, geology and chemistry. Here we report a new sample introduction system for laser ablation generated aerosols introduced into an ICP-TOFMS, which has recently been developed and tested in our group. The aerosol washout and the improvements in terms of image acquisition time will be discussed.[1]

For many decades Argon has been the plasma gas of choice for ICP-MS, even though alternative gases have been proposed and tested. To exploit the possibility of Argon substitution, a recently introduced Nitrogen plasma source (Radom, Milwaukee, USA)[2] has been studied in combination with laser ablation. We also report results on direct solid analysis by LA-ICP-MS using nitrogen as plasma gas.[3]

Finally, the analyses of single cells gained significant attention using a cy-TOF-MS. Therefore, the geometry of the ICP-MS has been modified to improve the throughput of single cells and nanomaterials.[4] The system and the current performance will be presented.[5]

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Submersible probe with in-line calibration and symmetrical reference element for long-term continuous measurements

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Nitrogen plays an essential role in plant and crop growth, promoting photosynthesis, which is essential for a healthy ecosystem. Although nitrogen is naturally present in the atmosphere, plants mostly absorb it through the soil. To enhance plant growth and therefore productivity, nitrate fertilisers have been used routinely in agriculture all over the world. At the same time, due to leaching in the groundwater or surface runoff, nitrate pollution has become an increasing concern for water pollution. In 1991, the European Commission (EC) established a decree aiming to reduce nitrate pollution and prohibit further pollution.[1] Since this directive, the use of nitrate-based fertilisers has been more adequately regulated and systematic water quality monitoring has been implemented. Although recent trends show a decrease of nitrate levels and an increase of the general water quality, the monitoring process is not uniform and still rather tedious. The current strategy relies on fixed sampling stations and punctual sampling at strategic sites, which both require manpower and expensive measurement techniques making it impossible to ensure a constant monitoring of nitrate levels.

Submersible potentiometric probes have been used previously in environmental studies,[2] but they require a pump to drive the sample towards the measuring site. To enable constant monitoring, the pump would have to run continually, which would lead to unreasonable power consumption.

We present here a new nitrate-selective submersible probe that can perform independent and continuous measurements over an extended period of time. In this case the sensing head is located directly in contact with the sample allowing for constant monitoring without any additional power. An in-built miniature low consumption peristaltic pump can be pre-programmed to perform a one-step calibration at a predetermined time interval to correct for underlying drifts that would bias the results. To reduce the temperature dependency on the sensor signal, a new reference element based on the principle of electrochemical symmetry has been tested and implemented into the probe. This probe has been successfully deployed in Lake Geneva and the Arve river during field campaigns and the nitrate levels that were measured on-site were comparable with those of traditional measurements methods. Due to its low power consumption and drift correction, it is estimated that this system can run maintenance-free for several months.

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R-based Automatic high-resolution mass Spectra Evaluation Routine (RASER) for the rapid analysis of chlorinated paraffins and olefins

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Technical chlorinated paraffins (tCPs) are produced in large scales of 1 million t/y and are used in various applications as plasticizers and flame-retardants in plastic and as metalwork fluids.[1] They are complex mixtures with millions of constitutional and stereo-isomers of poly-chlorinated *n*-alkanes with carbon-chain lengths of C_{10}-C_{30} (C-homologues) and variable chlorination degrees of Cl_3-Cl_{20} (Cl-homologues). Technical CP mixtures can contain up to 10^8 isomers.[1] Because of their toxicity and environmental risks, the use of short-chain CPs (C_{10}-C_{13}) has been restricted and SCCPs are regulated as persistent organic pollutants (POPs) under the Stockholm Convention.[2] This forced a shift to a production and use of medium-(C_{14}-C_{17}), long- (C_{18}-C_{21}), and very long- chain ($C_{>21}$) CPs. The analysis of CPs is challenging because of mass spectrometric interferences of the numerous isomers, the absence of suitable reference materials and the presence of side-products or transformation products such as chlorinated olefins (COs).

We applied liquid-chromatography coupled to an atmospheric pressure chemical ionisation method with a high resolution mass selective detector (LC-APCI-Orbitrap-MS) to study complex mixtures of up to 1320 homologues of CPs and olefinic transformation products. Such spectra are indeed complex, containing up to 30'000 relevant signals. An R-based Automatic Spectra Evaluation Routine (RASER) was self-developed and used to read-out defined CP and CO signals of specific homologues. With it, C- and Cl-homologue distributions of CPs and COs are obtained. The procedure reduced the workload required for the spectra evaluation from weeks to hours. Visual validation of measured and expected isotope clusters and the reconstruction of full scan mass spectra showed the presence of hundreds of CP- and CO-homologues. Mass spectrometric abundances were highest for medium-chain CPs and COs. CO-homologues were detected in abundances up to 10 % with respect to CP-homologues

The soft ionization technique applied favours the formation of quasi-molecular chloride-adduct without formation of fragment ions. The high mass resolution allowed to distinguish CPs and olefinic materials. RASER provide the possibility evaluate complex spectra of technical CP-mixtures containing up to 30'000 ions. This procedure can be applied to CP containing materials of different origin such as environmental samples or plastic from consumer products. The potential of the method was evaluated on sewage sludge (this contribution) and plastic materials we are exposed to in daily live.

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Investigation of phosphorylation dynamics within the mTOR signalling pathway in zebrafish PAC2 cells by means of mass spectrometry-based targeted proteomics

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Currently, thousands of fish are being used annually to perform toxicity tests needed to inform environmental risk assessment of chemicals and products. To reduce the use of animals, alternative (non-animal) toxicity testing methods need to be developed. Recently, the first fish cell line-based assay for the determination of acute toxicity to fish was adopted as an OECD test guideline.[1] This assay provides a measure of chemical effects on cell viability, which can be linked to fish mortality *in vivo*. However, being relatively short-term, this assay does not measure effects on cell population growth and hence cannot be directly used to predict *in vivo* effects on fish growth, another important ecotoxicological endpoint. To obtain growth-relevant measures, one could extend the assay by several days and use the change in cell numbers as a proxy for fish growth.[2] Another approach could be to monitor chemically induced molecular changes known to affect cell growth and proliferation. One of the major cellular signalling pathways known to be involved in the regulation of cell growth and proliferation in eukaryotes is the mechanistic target of rapamycin (mTOR) pathway. There are also indications that the mTOR pathway could be involved in the mediation of chemical effects on growth, but these interactions have not yet been systematically explored, especially in aquatic organisms such as fish. In this project, we are using *in vitro* cultured zebrafish (*Danio rerio*) PAC2 cells as a model to investigate the architecture and functionality of the mTOR pathway, as well as its susceptibility to chemicals and the concomitant effects on growth and proliferation of fish cells. The initial steps included: i) selection of the zebrafish counterparts for the main proteins comprising the mTOR signalling pathway in mammals; ii) identification of putative phosphorylation sites on our targets through comparative analyses with help of PhosphoSitePlus;[3] (iii) development of mass spectrometry based assays to monitor the abundance and phosphorylation changes of selected proteins as described in.[4,5] Our approach will enable the monitoring of protein phosphorylation dynamics by using mass spectrometry instead of relying on antibody-based methods. This would provide a significant methodological advancement since the respective antibodies for non-mammalian proteins are not always available. The subsequent experiments will expand our knowledge about the mTOR-mediated signalling and its role in growth regulation in fish cells, as well as its potential disruption by chemicals. This knowledge in turn could provide an avenue to develop a new non-animal toxicity test for predicting chemical effects on fish growth without using the actual fish.

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Machine learning as a tool to predict toxicity of chemicals

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One of the pillars of modern civilization is the ability to synthesize and/or use an enormous range of chemicals, which allow for new and improved products and serve as pharmaceuticals, pesticides, food additives and the like. However, in order to maintain a healthy biodiversity, it is crucial to know the impact of these chemicals on the organisms of the ecosystems where they are diffused. Usually this is done through in-vivo testing. Yet, beyond its obvious ethical implications, in-vivo testing is not scalable to large amounts of taxa and chemicals, because of its strong requirements in terms of time, money, and highly-trained personnel. Machine learning comes in as a viable alternative with the potential of allowing us to explore the impact of large numbers of chemicals on many taxa: harmlessly, quickly and cheaply. We develop machine learning models that can quickly infer the mortality of a chemical on a certain fish species and highlight the importance of including information on both chemical and taxonomy as input features. We then analyze ways of comparing the reproducibility of in-vivo experiments with machine learning models trained on similar data, finding that there is no perfect method. Although comparisons between in-vivo and in-silico methods need to be taken with a grain of salt, machine learning presents as a potentially valid alternative to animal testing.

Poster Presentations

Marcel Aebli, ETH Zurich (#01)
«Disorder in cesium lead halide nanocrystals»

Pascal Becker, ETH Zurich (#02)
«Impact of ablation cell design in LA-ICP-MS quantification»

Polyxeni Damala, University of Geneva (#22)
«Characterization of PEDOT used as ion-to-electron transducer with eQCM»

Veysel Demir, Eawag, Dübendorf (#18)
«Glutathione S-transferase (GST) expression repertoire in a zebrafish embryonic cell line and its regulation by GST model substrate 2,4-dinitrochlorobenzene (CDNB)»

Chiara Fabbretti, ETH Zurich (#06)
«Europium and samarium anomalies in wastewater treatment plants of Windisch and Aarau»

Fabienne Gräppi, FHNW (#17)
«LC-MS and GC-MS methods for sweat analysis as alternative biofluid in metabolomics»

Yousuf Hemani, Empa, Dübendorf (#09)
«Compressive signal collection for dynamic tabletop X-ray absorption spectroscopy (XAS) »

Selim Kazaz, Empa, Dübendorf (#13)
«Operando REELS of hydrogen selective membrane systems»

Kilian Koch, Empa, Dübendorf (#26)
«Digital lab-workflows with OpenBIS»

Kevin Kraft, Empa, Dübendorf (#07)
«Hollow-cored toroidal-coil (HTC) detector for fast transient signals in ICP-MS»

Monique Kuonen, ETH Zurich (#03)
«Nitrogen plasma as ion source for inorganic mass spectrometry»

Canwei Mao, University of Geneva (#23)
«Miniaturized solid-state ionophore-based microelectrode for ion transfer Voltammetry: stability problems»

Claudia Masucci, Empa, Dübendorf (#15)
«Known and unknown of direct air capture amine materials»

Gabriel J. Mattos, University of Geneva (#19)
«Instrumental control of an enzyme immunoassay using ion-selective membrane electrodes and pulsed chronopotentiometry»

Oscar Mendo Diaz, Empa, Dübendorf (#16)
«Fast evaluation of complex high-resolution mass spectra of chlorinated paraffins (CPs) and chlorinated olefins (COs) in plastic consumer products»

Thomas Muggli, University of Bern (#08)
«Swab spray mass spectrometry: An ambient ionization method for the analysis of surfaces»

Christoph Neff, ETH Zurich (#04)
«Advanced technology for high throughput LA-ICP-TOFMS element imaging»

Marin Nikolic, Empa, Dübendorf (#14)
«Can H/D exchange by neutron imaging anticipate the conversion of hydrogenation catalysts? »

Robin Nussbaum, University of Geneva (#21)
«Hyperpolarized solvatochromic nanosensors embedded in agarose gel towards heparin sensing in blood»

Di Qu, Empa, Dübendorf (#10)
«Polymer ablation using extreme ultraviolet pulses»

Oksana Shliakhtun, Empa, Dübendorf (#11)
«VLS flat field spectrometer for extreme ultraviolet radiation. Design and analysis for LIXS»

Ayian Speck, University of Geneva (#24)
«Self-referencing pulstrode: Further optimization and new electrode designs»

Miruse Suloska, Empa, Dübendorf (#12)
«Investigation of nanoparticle enhanced emission in laser induced X-ray spectroscopy (NE-LIXS) »

Nikolai Y. Tiuftiakov, University of Geneva (#20)
«Carbonate optical nanosensors: New mechanisms and their advantages»

Yaotian Wu, University of Geneva (#25)
«Self-powered potentiometric sensor based on optical signal transduction with liquid crystal display»

Zuqiang Xu, ETH Zurich (#05)
«Laser ablation with funnel-focused mass spectrometry for improved resolution and analysis speed»

Disorder in cesium lead halide nanocrystals

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Cesium lead halide $CsPbX_3$ (X = Cl, Br, I) perovskite semiconductor nanocrystals (NCs) increasingly mesmerize researchers because they exhibit outstanding optoelectronic properties. One of the remaining hurdles is an atomistic structure determination due to their soft structure and their small size. We addressed this challenge by using nuclear magnetic resonance (NMR) spectroscopy.[1] This accessible technique can not only give insights into the elemental composition, but also into structural properties without having to manipulate or even damaging the labile samples during the measurements. The NC cores of colloidal solutions of perovskite semiconductor NCs could be studied in depth with solution NMR for the first time. The determination of surface and core sites could be done by probing various size selected NCs with an edge length between 3 and 12 nm. In doing so, a correlation between the chemical shift and the band gap of the NCs was observed, which was already predicted by theory. Furthermore, the distortions of the core structure induced by the dissimilar monodentate and zwitterionic capping ligands was studied, quantified, and could be correlated with their optical properties. *Ab initio* molecular dynamics simulations performed on various sizes of $CsPbBr_3$ NCs confirmed our observations. In mixed halide $CsPb(Br/Cl)_3$ NCs, an anion gradient was observed for the first time. These findings showcase the great potential of solution NMR in shedding light on the structure of colloidal semiconductor NCs.

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Impact of ablation cell design in LA-ICP-MS quantification

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been used routinely in the past few decades for the analysis of samples in geology, biology, material sciences, forensics and more. Large volume ablation cells are predominantly used, which mix the laser generated aerosols in a large volume and allow for the acquisition of stable signals for applications such as isotope or bulk analysis. For purposes that require spatial information, such as imaging and depth profiling, low dispersion laser ablation cells have been developed to resolve individual laser pulses. These cells commonly use a two volume approach, where samples are placed on a 3D-stage within a large volume, below a much smaller volume with a narrow opening in-between.[1,2]

In this work, the differences of the aerosol transport between these two types of ablation cells were investigated in terms of quantification accuracy. Transport phenomena of the laser generated aerosols were studied based on their particle size distributions and elemental ratios. The differences between low and high dispersion were investigated, as well as the effect of further aerosol stretching after the low dispersion ablation cell and the three setups were compared in regards to reproducibility and accuracy.
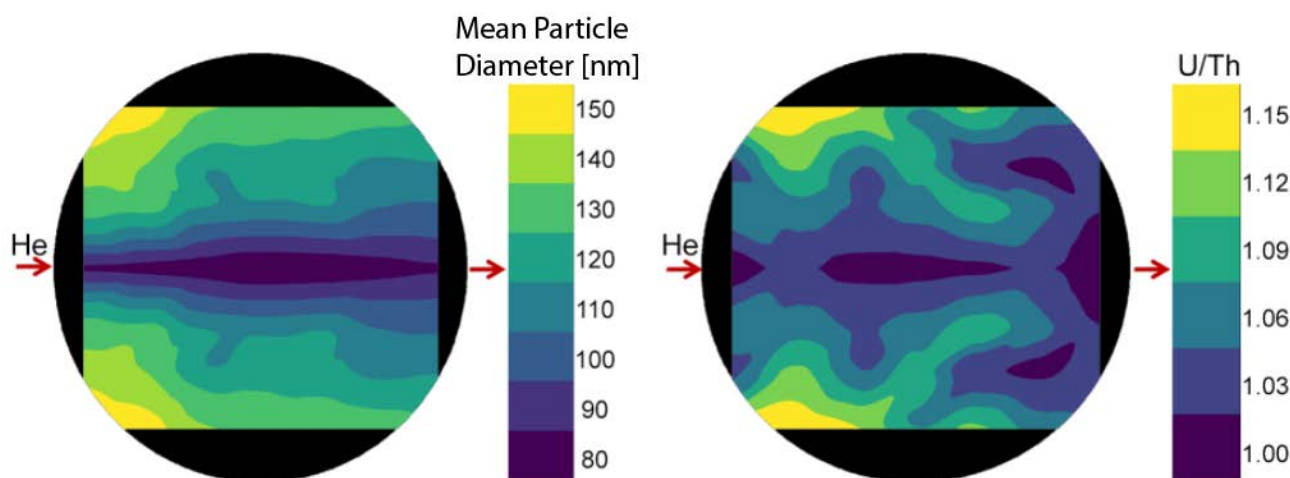
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Characterization of PEDOT used as ion-to-electron transducer with eQCM

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Conducting polymers have been studied with great interest over the last decades as they may offer unique ion-to-electron transduction properties and help to improve electrochemical performance of electrochemical sensors. Some of the most common materials used in the field of electrochemistry include poly(3-octylthiophene) (POT), polypyrrole (PPy), poly(aniline) (PANI) and poly(3,4-ethylene-dioxythiophene) (PEDOT). Although the choice of the polymer is a compromise of many aspects, the use of certain PEDOT derivatives can be advantageous in view of the reported drawbacks manifested by other polymers such as POT, which is known to be light sensitive.[1] PEDOT is prepared via electrochemical polymerization from a solution of the monomer and a supporting electrolyte. The resulting polymer is positively charged and incorporates doping ions from the electrolyte, which act as charge compensators.[2] As of today, several studies have examined the influence of the supporting electrolyte on the electrochemical and mechanical properties of the resulting film.[3,4] As evidenced,[5] the structure of the film and the level of water uptake can significantly influence the potential stability of sensors based on the non-hydrophobic form of PEDOT. Its hydrophobic derivatives, including PEDOT-C_{14}, have not been studied to such an extent. The enhanced hydrophobicity of PEDOT-C_{14} makes it particularly suitable for use as an ion-to-electrode transducer in potentiometry.[6]

In the present study, we examine how different supporting electrolytes with doping ions of varying size and properties (e.g. lipophilicity), change the physicochemical properties of the film during the electropolymerization of certain EDOT derivatives. Using eQCM we monitor changes of the polymer structure (mass growth, viscoelasticity) and electrochemical behavior (capacitance, ion-exchange properties). By comparing different PEDOT materials used as ion-to-electrode transducers, we show how the shift to a hydrophobic derivative could help us adjust and predict their electrochemical behavior with greater accuracy. This knowledge is valuable for building stable potentiometric sensors as well as novel voltammetric sensors with desired charge- and ion-transfer properties.

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Glutathione S-transferase (GST) expression repertoire in a zebrafish embryonic cell line and its regulation by GST model substrate 2,4-dinitrochlorobenzene (CDNB)

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The number of chemical compounds used in various products and applications is increasing steadily, raising the demand for more testing data to inform risk assessment. At the same time, there is an urge to replace, reduce and refine (3R) the use of animals in toxicity testing, a challenge posed from scientific and ethical perspectives. Alternative testing methods offer promising innovations catering to both demands, as they can enable high-throughput screening without animal use. In aquatic risk assessment, assays with zebrafish (Danio rerio) embryos (i.e., non-protected life stages[1]) and rainbow trout (Oncorhynchus mykiss) cell lines (i.e., RTgill-W1[2] and RTgutGC[3]) have been successfully positioned as an alternative to using adult fish. Since the zebrafish embryo test still requires maintenance of adult fish for breeding purposes, possibilities to use zebrafish cell lines instead are also being explored.[4] One limitation to the broader application of these alternative models for toxicity assessment has been the insufficient knowledge about their capacity to biotransform chemicals, i.e., their spectrum of expressed biotransformation pathways. One such pathway is the mercapturic acid pathway, which protects organisms from harmful electrophilic compounds. Recently, the functionality of the mercapturic acid pathway and hence the capacity to detoxify electrophiles has been demonstrated in both zebrafish embryo and the zebrafish embryonic cell line, PAC2, using a nontoxic concentration of a reference substrate, 1-chloro-2,4-dinitrobenzene (CDNB).[5,6] The first step in this pathway, glutathione conjugation of an electrophile, is catalyzed by the glutathione S-transferase (GST) enzymes. Using mass spectrometry-based targeted proteomics, we demonstrated that both zebrafish embryo and the PAC2 cell line express a broad repertoire of GST isoforms that might have partially overlapping functions.[5,7] Although some GST substrates have been reported to regulate the expression of GST enzymes previously, exposure to a non-toxic concentration of CDNB did not cause significant changes in GST expression. Here, we exposed the PAC2 cells to 10%, 20% and 50% effect concentrations (EC10, EC20 and EC50, respectively) of CDNB to understand GST expression responses to higher substrate concentrations.

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Europium and samarium anomalies in wastewater treatment plants of Windisch and Aarau

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The increasing use of Rare Earth Elements (REEs) for technological applications will likely lead in increased amounts REEs discharged to the environment, with only poorly understood consequences for the receiving compartments. Results from initial screening studies demonstrated the presence of most of the REEs in wastewater [1] and sewage sludge samples [2] collected for more than 60 wastewater treatment plants in Switzerland. Of special interest is the fraction of REEs which is related to anthropogenic activities and in selected sewage sludge samples high fractions of Ce, Sm, Eu and Gd were associated with anthropogenic activities. Additional sampling campaigns confirmed exceptionally high concentrations of Sm and Eu in sewage sludge collected from the wastewater treatment plants of Windisch and Aarau.
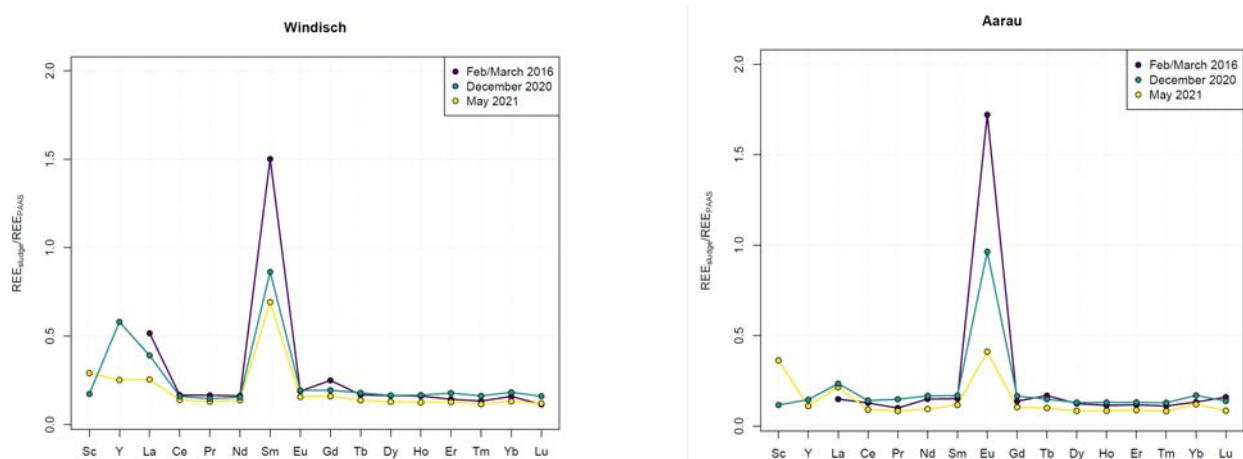
In this work, the Sm and Eu anomalies from the Windisch and Aarau WWTPs were, therefore, studied in further detail. Sewage sludge samples were analyzed by triple-quadrupole inductively coupled mass spectrometer (ICP-MS) and normalized to the Post Archean Australian Shale (PAAS). This revealed that PAAS normalized Eu and Sm concentrations were higher compared to their neighboring (PAAS normalized) REEs, suggesting a substantial (anthropogenic) contribution of Sm and Eu to the respective wastewaters. A single-particle time-of-flight ICP-MS (sp-ICP-TOFMS) system was used to analyze the particulate and dissolved fractions of REEs in influent and effluent wastewater, and to estimate the removal efficiency of REEs during wastewater treatment. Low dissolved concentrations of Eu and Sm were found both in the influent and effluent, and no Eu NPs were observed, but Sm NPs were detected. However, the presence of high levels of Eu and Sm in the sludge indicate that further investigation is necessary.

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LC-MS and GC-MS methods for sweat analysis as alternative biofluid in metabolomics

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Background: Sweat is a promising but still insufficiently studied matrix in the field of metabolomics research. Compared to blood, saliva, hair, or urine sweat appears less complex, since the concentration of proteins (saliva), lipids, phospholipids (blood), or urea (urine) are significantly lower. Therefore, the sample preparation process for mass spectrometry might be simplified. From a diagnostic point of view, the analysis of this alternative biofluid is an opportunity to find yet undiscovered biomarkers. Sweat represents short term ongoing metabolic processes comparable with blood or saliva.[1–3] The sampling allows theoretically the access to samples from people outside of a hospital, without an additional infection risk. This is important to support diagnostics in low-income countries, especially for vulnerable patients such as children. However, one of the challenges of sweat analysis is the low concentration of biomarkers and the low sample volume (25 – 200 µL). Methods for the analysis of sweat using LC-MS and GC-MS have been developed to investigate potential markers for tuberculosis. However, this contribution focusses on the development and execution of the methodical part only.

Method: Sweat samples were collected using an iontophoresis technique combined with pilocarpine. To achieve sufficient statistical data (including technical replicates), the methods were optimized to operate with a sample volume of less than 30 µL. Measurement were performed on a LTQ Orbitrap XL LC-MS and a Leco GC-TOF-MS. For the GC-TOF-MS analysis, a method based on Fiehn (2016)[4] was developed.

Results: By LC-MS, about 6400 features were found. Typical amino acids and even antibiotic drugs have been detected. By GC-TOF-MS 128 metabolites out of about 2800 detected features have been identified by retention time index and electron impact spectra matched with the Fiehn Library.

Conclusion: LC-MS and GC-MS are feasible approaches for sweat analysis if sufficient sample volume is available. The basis for future studies, including specific sampling recommendations, was developed.

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Compressive signal collection for dynamic tabletop X-ray absorption spectroscopy (XAS)

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X-ray Absorption Fine-Structure Spectroscopy (XAFS) is a powerful analytical technique, which works with almost any sample environment, as compared to X-ray crystallography, for obtaining elemental and chemical information in many fields such as biosciences, material sciences, catalysis and physical chemistry.[1,2] XAFS utilizes a large bandwidth radiation that is tuned sequentially to capture the entire spectrum where the resolution is dependent on the monochromator. The entire scanning of certain samples can take relatively long times. High brightness, essential for enough sensitivity, can be destructive for certain samples. Time resolved XAFS needs complex optical setups and fast signal processing techniques to resulting in a data deluge. Source features are obtained at synchrotron beamlines. Few of these exist worldwide, with limited access due to large amount of proposals.

Ideally, one would like to have a single shot acquisition of the entire spectrum, where the entire scanning should be faster than the chemical reaction being studied. Furthermore, the source should at low sample damage intensity, without sacrificing information and the required resolution should be close to few meV. Advantageously, this method should be available in each laboratory.

Aim of this study was to develop a data processing method, which can match and compliment as much as possible such requirements. Compressed Sensing (CS) is a well-known procedure in signal processing used to acquire and reconstruct undersampled data sets without losing any important information about the signal. Taking advantage of the sparsity of the spectral signal in a fixed basis and when sampled randomly, the data acquisition can be dynamic, where in one case the sampling rate is varied or in the second case the acquisition time. Aided by convex optimization solvers, faster and reliable data acquisition is possible with competent data reconstruction.
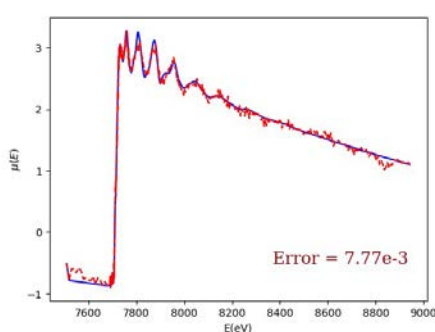
Figure 1: Reconstructed signal (red) vs reference signal (blue). Comparison for a Co foil, which is sampled randomly at 30%.

This research shows as a proof of concept, the advantages and limitations of the compressed sensing technique for XAFS data acquisition using a laboratory X-ray source. The results from many different samples tested with the code show that even with as less as 30 % of data sampling, the error for reconstruction of the XAFS spectrum is less than or equal to 1%. Example of Co foil is shown in Figure 1. The reconstructed raw data also translates reliably for K-space and R-space analysis. A big advantage is pre-emptive studies of unknown samples. The limitation is more peaks in the spectral signal means more sampling is required for complex signals. Therefore, compressed sensing for XAFS is useful for fast and reliable data acquisition with low noise, within a few minutes on tabletop.

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Operando REELS of hydrogen selective membrane systems

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In a future scenario with hydrogen as an energy carrier, the separation and purification of the energetically costly hydrogen will become even more important than today.[1] Here, we make use of an experimental model system (consisting of a V thin film coated Pd membrane) to study material combinations for hydrogen selective membranes, in which the surface properties of the system can be modified intentionally.[2] The *in situ* preparation allows for observation of ultra-clean hydrogenation and the quantification of the permeation kinetics and the surface elemental characterization by XPS/AES. We determine the (sub-) surface hydrogen concentration by *operando* reflecting electron energy loss spectroscopy (REELS) as a function of pressure and temperature, from which the surface hydrogen pressure-composition isotherms are derived (Figure 1). The energy dependence of REELS reveals that VH_x exhibits a hydrogen concentration gradient. We demonstrate the existence of a rate-limiting step by direct observation of the dependence of the permeation on the hydrogen content in the Pd/V composite membrane. Modelling of the permeation behaviour yields activation energies in good agreement with other hydrogen absorbing thin film systems [3] for the overall process, the dissociation at the Pd surface, the diffusion in the membrane, and the dissociation at the V surface.
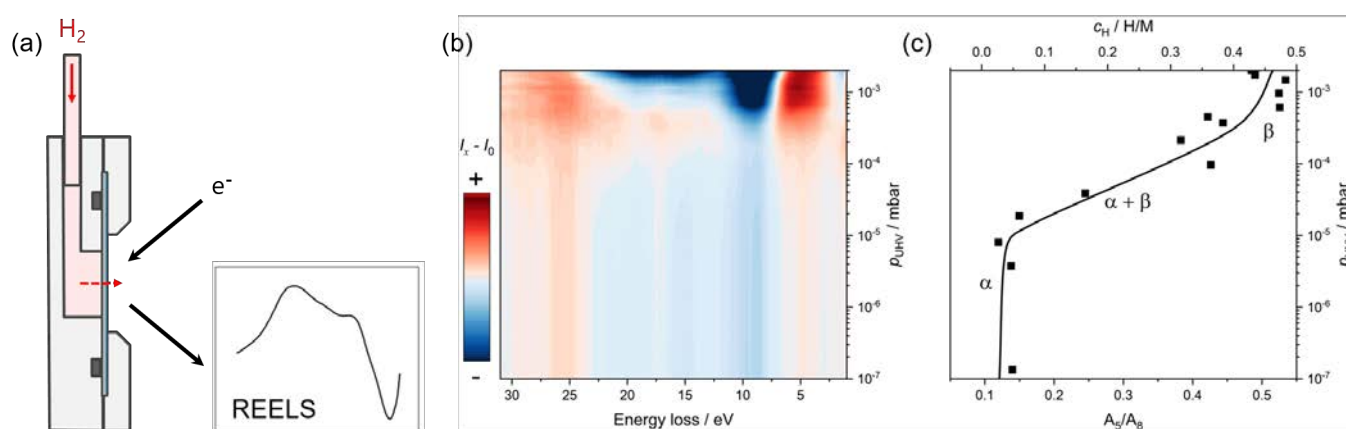

Figure 1:   (a) Schematic representation of the membrane setup for electron spectroscopy. (b) REELS difference spectra of VH_x (x = 0 – 0.3) recorded at 100 °C under increasing hydrogen pressure from which a surface hydrogen pressure-composition isotherm (c) can be derived.

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Digital lab-workflows with OpenBIS

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In recent years, digitalization of scientific recording has grown in importance. Especially to comply with the FAIR principles (findable, accessible, identifiable, and reusable) for open data, electronic laboratory notebooks and other tools are necessary considering the increasing amount of data collected.

In this work, we use the tool openBIS developed by the ETH Zurich to implement digital lab-workflows. These workflows include data wrangling, data pre-processing and data analysis. Implementation was done using additional open-source python-based tools such as pandas, FastAPI, pybis, and matplotlib. An execution plan for workflow digitalization is proposed which includes the following main steps: (i) identification of needs, (ii) fit-gap analysis, (iii) testing-phase, (iv) implementation and (v) management. The developed plan will be used to digitize various lab-workflows with openBIS and adapted if necessary. In a later stage, implementation of a version-control system Renku to manage methods and data processing as well as automation of the scientific recording will be in focus.

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Hollow-cored toroidal-coil (HTC) detector for fast transient signals in ICP-MS

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Mass spectrometry methods are used from elemental analysis to the identification of large organic compounds. For all the mass filters a longer signal acquisition time leads to improved spectra and a wider m/q range that can be scanned. Mass analyzers instead such as Time-Of-Flight enhance their performance with short transients.

However, limitations from space charge and/or the requirement to compress the time-domain m/q phase-spread do limit the use for ultrafast transient from small sample amounts. In Fourier transform (FT) mass spectrometry one looks at the frequency domain, which help to overcome time-domain constratints. However, in methods like orbitrap-MS and ICR-MS the m/q range can only be investigated at a narrow dynamic range due to the space charge effect, making longer measurement times and higher sample uptake necessary for obtaining the complete mass spectra.[1] Furthermore, the longer transient will lead to spectra with a better resolution, sensitivity and signal to noise ratio.[1]

In depth profiling analysis of coatings using Laser ablation ICP-MS, where depth resolved elemental composition is of interest, the measurment time cannot be simply extended. To circumvent this problem, we realized an induction detector that can measure different ions simultaneously. The hollow-core toroidal (HCT) detector is a differerentiator.[2] It measures changes in the ion current wavefunction. As the induction goes, the sensitivity is all the best for faster current changes. This dramatically enhances the sensitivity for ultrafast transients and makes it blind to DC background. Figure 1 shows the basic proposed setup for the HTC detector in an ICP-MS.

In this work we show preliminary experimental results from measurments with the coil and investigate which data treatment methods that are readily used in orbitrap-FT-MS and ICR-FT-MS could also be applied to this new detector.[3]
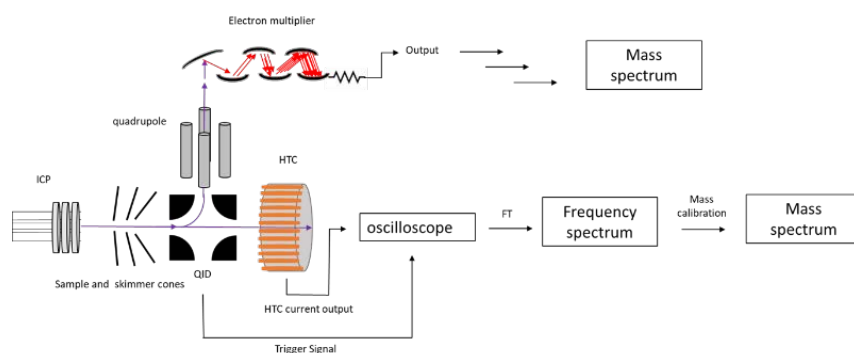

Figure 1: Scheme of the HTC detector placed inside an ICP-MS and
           the working steps for obtaining a mass spectra.

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Nitrogen plasma as ion source for inorganic mass spectrometry

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Nitrogen based plasmas have gained increasing attention as an alternative ion source for inductively coupled plasma mass spectrometry (ICPMS) as nitrogen is environmentally friendlier and more cost-effective than argon. While early plasma generation approaches using nitrogen were limited by their lower operating power,[1,2] a high-power nitrogen sustained microwave inductively coupled atmospheric pressure plasma (MICAP)[3] has been introduced recently. This novel source was coupled to a quadrupole mass spectrometer in our lab and is currently investigated for its figures of merit in element and isotope analyses of aqueous solutions.
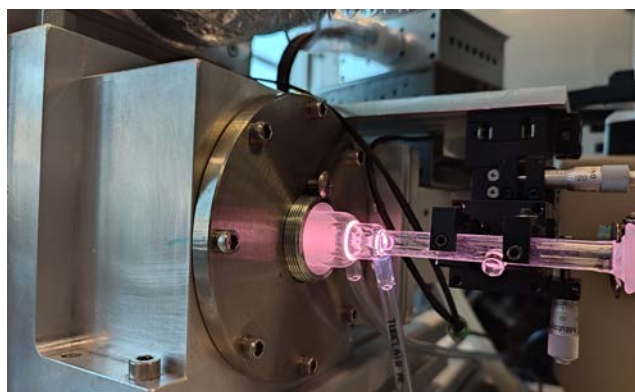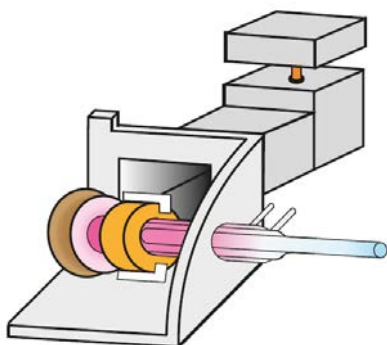
The influence of forward power and nebulizer gas flow rate on sensitivity, plasma background, and polyatomic ion formation was analysed. The plasma background ions decreased with increasing nebulizer gas flow rate and decreasing power, while atomic ions could be assigned to one of three groups based on their dependence on the operating conditions. The distinction between the groups can generally be explained by physical-chemical properties of the elements such as mass, ionization energy and oxygen bond strength. However, while indicators of gas temperature (e.g. CeO^+/Ce^+ formation ratios) imply that similar temperatures can be reached in Ar and N_2 plasmas, the highly abundant NO in the latter limits the attainable sensitivity for elements with high ionization energy to a greater degree. To investigate to which extent the use of N_2 as plasma gas affects the gas dynamics during the extraction of the plasma into the MS, different geometries of the vacuum interface were studied by varying the sampler to skimmer distance, changing the sampler orifice size and employing an additional interface pump. Despite N_2 plasmas having different characteristics during the supersonic expansion compared with that of Ar, the attainable sensitivity could barely be improved by the tested modifications.

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Miniaturized solid-state ionophore-based microelectrode for ion transfer Voltammetry: stability problems

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Liquid based capillary microelectrodes have been well explored for ion transfer at the interface between two immiscible electrolyte solutions and many attempts to design ion-selective microelectrodes emerged based on it.[1] However, there has been a gap in producing durable and stable solid-state ion-selective microelectrodes for voltammetric ion sensing applications.[2] Some designs could be applied to a potentiometric readout, but a voltammetric control would be more attractive for numerous applications.[3] Here we show promising results with thin film K-selective microelectrode of 10 μm diameter interrogated by cyclic square wave voltammetry (CSWV). Using PEDOT-C14 as transducing layer and polyurethane as membrane matrix prevents the loss of ion sensing components. And the microelectrode can show a good Nernstian response. The logarithmic selectivity coefficients over sodium and calcium are found as -4.2 and -12.7 respectively, which meets the requirement for physiological measurements. Importantly, the difficulty of developing voltammetric thin film solid-state microelectrodes was found coincidently, as the water layer deteriorated the stability and reproducibility more seriously when the electrode dimensions were reduced to the micrometer scale. As a rougher transducer layer was electrodeposited on the gold surface, the performance of the microelectrode would deteriorate, as confirmed with AFM morphology studies. The results may be able to help researchers develop versatile applications in the future.

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Known and unknown of direct air capture amine materials

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One of the proposed technologies to reduce greenhouse gas concentration in the atmosphere relies on direct air capture (DAC) using sorbent materials. These can be discharged for storage or feedstock commercialization in a cycling approach between capture and release. For CO_2, amine-functionalized polymers have been proposed.[1] The latter are able to reversibly bind CO_2 from air by forming carbamates and then release it upon moderate heating at low pressure and followed by a new DAC cycle.

The increasingly rapid development of amine-based adsorbents for the removal of CO_2 is already at commercial-scale implementation. In the last decade, significant progresses have been made in understanding the CO_2-amine interaction. Said et al.[2] proposed a unified six membered mechanism to propose all possible interactions of CO2 with amines and water. Unfortunately, the CO_2 capturing capacity rapidly degrades with cycle. This has been attributed to parasitic chemical pathways such as oxidative degradation and other deactivation processes. The level of information on the chemical pathways is clearly determined by the depth of analytical coverage.

Spectroscopic techniques along with Mass Spectrometry techniques allow the investigation of such mechanisms as well as the formation of not yet identified compounds.

The adsorbent was characterized by FTIR, ATR, XPS, SEM, ICP-MS, ToF-SIMS and GC-MS before and after the exposure to air under different conditions.

As a result of the data achieved, a special cell for operando chemistry is being realized for the real time detection of organic groups as well as elemental traces. Data integration is promising to generate important insight, but presents a number of discussed challenges.

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Instrumental control of an enzyme immunoassay using ion-selective membrane electrodes and pulsed chronopotentiometry

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A new potentiometric enzyme immunosensor principle is evaluated for the detection of antigenantibody interactions at the cation responsive membrane surface without the need to add the enzyme substrate, which acts as the ion marker in the backside inner solution. This is accomplished by a triple pulse protocol to control the delivery of the enzyme substrate from the inner solution to the sample side using pulsed chronopotentiometry (Fig. 1).[1] First, a zero current measurement (I) gives a stable open circuit potential (OCP) of the system. The second step of the protocol consists of a controlled anodic current pulse (II) of defined magnitude and duration (i = 1µA and t = 1.5 s, in this case), which leads to a flux (J) of enzyme substrate (choline, Ch^+) through the ion-selective membrane (m). The anodic pulse is followed by a zero current measurement pulse (III). During this time, the previously extracted ions are consumed by the enzyme (choline oxidase, ChOx) after a sandwich enzyme immunoassay, resulting in different OCP measurements since the ion-selective membrane is responding to the Ch^+ concentration. At steady-state, the flux across the membrane is equal to the contribution from the flux across the aqueous diffusion layer in the sample side in addition to the enzyme reaction, which is described by the Michaelis-Menten kinetic model.

In the sandwich immunoassay, the target analyte to be measured is bound between two primary antibodies, each binding to a different epitope of the antigen. The monoclonal antibody on the surface of the electrode (capture antibody) captures the antigen from the sample; the polyclonal ChOx-labeled antibody (detection antibody) binds directly to a different site of the antigen. At equilibrium, the amount of bound ChOx labeled antigen-antibody complex is directly proportional to the concentration of antigen from the sample, resulting in different OCP (III) measurements.[2] The ion-selective membranes are surface-modified with an antibody using click chemistry between alkyne-PEG-NHS molecules and azide groups from the modified poly(vinyl chloride) of the membrane. The antibodies are covalently immobilized based on the interaction between NHS ester-activated and primary amines from the antibody structure. The surface modification is characterized by electrochemical impedance spectroscopy, fluorescence microscopy, and contact angle measurements.
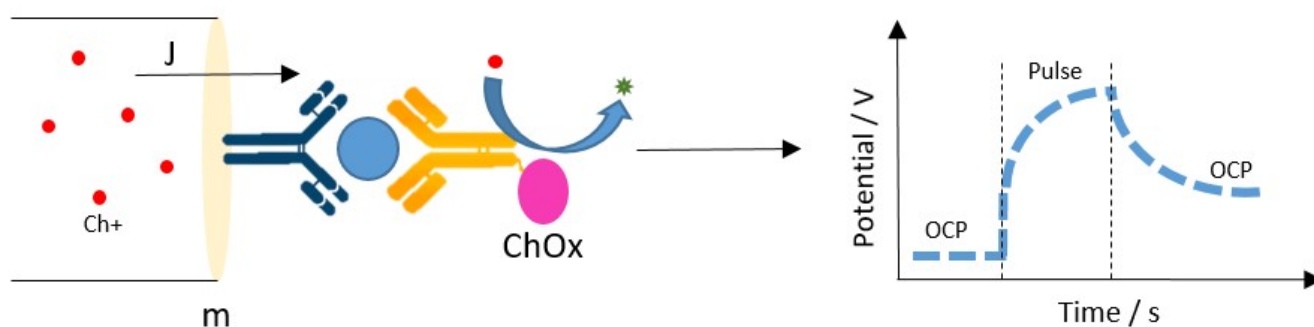

Figure 1. Schematic representation of the sensing principle.

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Fast evaluation of complex high-resolution mass spectra of chlorinated paraffins (CPs) and chlorinated olefins (COs) in plastic consumer products

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Chlorinated paraffins (CPs) are high production volume chemicals with production rates of about 1 million t/y. CPs are widely used in plastic materials both as plasticizers and flame-retardants.[1] Technical CPs are produced in non-selective processes through radical chlorination of n-alkanes. This results in complex mixtures of millions of constitutional isomers and stereoisomers. CPs are produced with carbon-chain lengths of C_9-C_{30} (C-homologues) and with chlorination degrees of Cl_3-Cl_{20} (Cl-homologues). In other words, such a technical CP-mixture applied in plastic material can contain up to 400 C-Cl-homologue classes. Mass spectra of such CP-mixtures can contain up to 20'000 ions of ^{12}C-/^{13}C- and ^{35}Cl-/^{37}Cl isotopologues.

Furthermore, such spectra are interfered with ions of chlorinated olefins (COs), which are an important family of CP transformation products. The formation of COs and chlorinated di-olefins (CdiOs) was observed during thermal exposure of CPs[2] and during exposure of CPs on reactive metal surfaces formed during metalwork.[3]

We have developed an LC-APCI-Orbitrap-MS method that is able to resolve such complex mass spectra. As will be demonstrated here, the newly developed R-based automatic spectra evaluation routine (RASER) has been used to identify and extract specific ions of the various isotope clusters of different CP- and CO-homologues. The applied soft-ionization technique, which supports the formation of chloride-adduct [M+Cl]$^-$ ions, together with the high resolution of the Orbitrap-MS of 140'000 are crucial to solve the conundrum.

We will demonstrate the potential of our new approach on four CP-containing plastic materials from widely used consumer products. The combination of a soft-ionization technique, a mass spectrometer with high resolution and the automatic data evaluation with RASER allowed us to distinguish about 660 different CP- and CO-homologues, which corresponds to mass spectra with about 11'000 ions. The new RASER method will be presented in a separate contribution. Its potential will be demonstrated on plastic materials commonly found in Swiss households (this work) as well as on Swiss sewage sludge samples.

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Swab spray mass spectrometry: An ambient ionization method for the analysis of surfaces

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In the past two decades, a myriad of ambient ionization mass spectrometry techniques have been presented. Among them "swab spray", which is based on direct ion generation from swabs, has demonstrated a great potential for clinical and forensic applications.[1] Basically, the swab head enables easy and effective sample collection on various surfaces and acts as a depleting sample reservoir during analysis. Ionization is induced by solvent flow and the high voltage directly applied to the swab head by the help of a custom-made ion source. The formation of a visible Taylor cone, jet region, and spray plume, where the analyte ions undergo electrospray-based ionization, is observed.

In the current work, the effects of ion source parameters, swab head properties, and solvent composition are investigated.
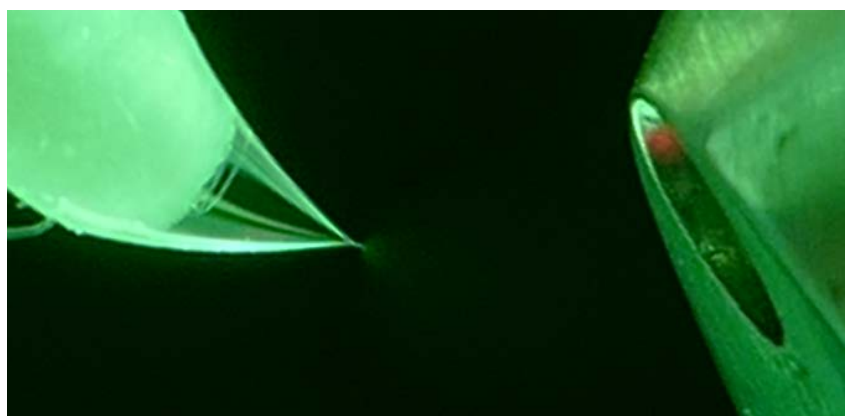

Figure 1: Generation of a Taylor cone, droplet jet, and spray plume at the tip of a swab.

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# Advanced technology for high throughput LA-ICP-TOFMS element imaging

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Laser ablation inductively coupled plasma time-of-flight mass spectrometry (LA-ICP-TOFMS) element imaging provides valuable information of the distribution of major to trace elements within solid materials. For example, the element distribution can give insights into geological processes and genesis of minerals and rock formations.[1]
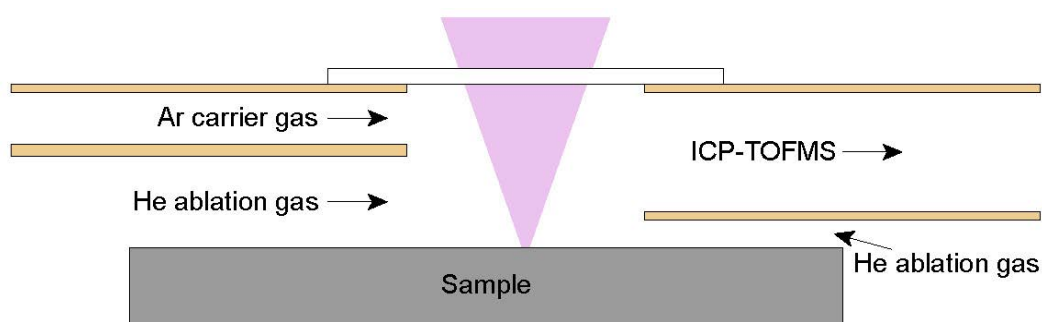
Here, we present the parallel flow ablation cell (PFAC) in combination with the imaging control system (ICS) to increase the throughput and applicability for element imaging. The PFAC is a modification of the tube cell design[2] and allows fast and reliable aerosol transport. The signal duration of 0.25 ms (full width at 10% of the maximum) is the shortest achieved so far for laser ablation sample introduction and ICP-MS detection. The ICS synchronizes the control of the translation stage, the laser and the TOFMS data acquisition and therefore allows an almost automated analysis. In addition, the combined control of the three devices allows the imaging of custom ablation area masks fitting the sample structure. Multiple laser pulse patterns can be chosen according to the application. For example, a single pulse mode can be used for fast scanning of the area of interest or a hole drilling mode to achieve lower limits of detection. The triggered data acquisition for every ablation position led to binned pixel data in relation to the sample position. This simplifies the data evaluation and allows a more automated image generation, and reduces the time for data evaluation. The capabilities are exemplified by the measurement of common reference materials for LA-ICP-MS and by quantitative element imaging of geological samples.

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Can H/D exchange by neutron imaging anticipate the conversion of hydrogenation catalysts?

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Hydrogenation reactions are crucial in a renewable energy scenario, notably to facilitate the production of hydrocarbons from hydrogen. The reactions are catalyzed by specific catalysts consisting of metal nano-particles on an oxide support. The chemical function of the support is unclear [1]. Hydrogen after dissociative chemisorption may migrate over the oxide surface and thereby promote the transport to and from the reactive sites [2]. Verification of this so-called hydrogen spillover and particular its effect on the reaction kinetic is an analytical challenge, because the quantitative detection of dynamic hydrogen at relatively low concentrations (c << 1 at.%) is difficult.

We developed a combinatorial setup for neutron imaging, capable of measuring up to 69 samples simultaneously under identical conditions (temperature/pressure) to quantify the amount of hydrogen in different hydrogenation catalysts.

For this, hydrogen/deuterium exchange measurements at temperatures between 20 to 350°C and at a pressure of 1bar were performed on Ni deposited on reducible and non-reducible supports. The measurements are the starting point of a universal database of hydrogenation catalysts. To correlate the catalytic activity with H/D exchange observed by neutron imaging, the CO_2 conversion of each catalyst CO_2 as a function of pressure, temperature, and space velocity was measured. The multitude of samples measured simultaneously allowed to analyze the dependence of the activity on specific properties such as metal particle density. This yields additional insights of the generally good correlation between hydrogen-deuterium exchange and catalytic activity.
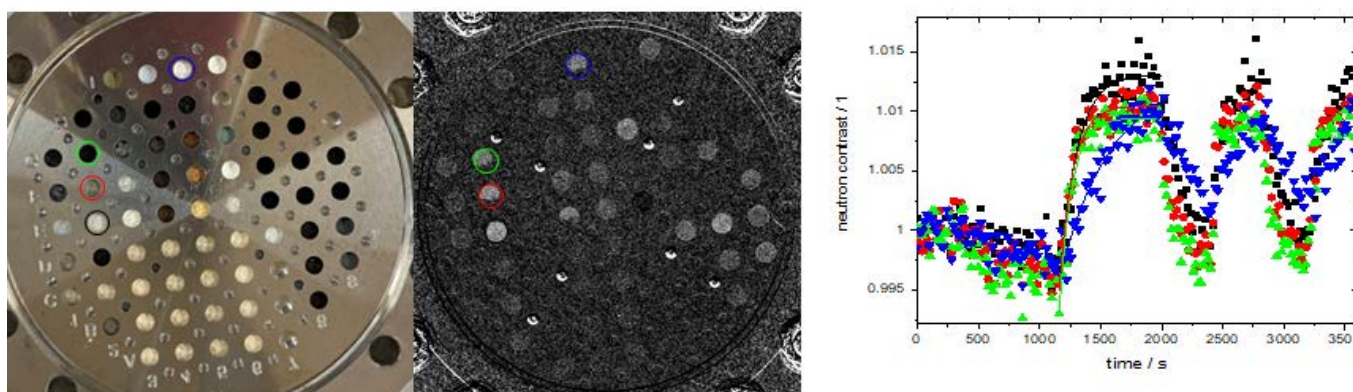

Figure 1: Left: optical micrograph of the combinatorial sample stage. Middle: Neutron image during H-D exchange. Right: Kinetics of H-D exchange as measured by neutron contrast.
Samples: Al O (blue); Ni 0.5%-at on Al O (black); Ni 5%-at on Al2O3 (red); Ni 40%-at on Al O (green)

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Hyperpolarized solvatochromic nanosensors embedded in agarose gel towards heparin sensing in blood

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Heparin is a polyanionic anticoagulant extracted from natural sources and used in numerous surgical procedures. Its typical concentration in the blood steam ranges from 0.1 to 5 IU/mL and varies with time due to its clearance from the body. Too low of a heparin concentration increases clotting risk, whereas excessive levels can induced uncontrolled bleeding. Thus, it is crucial to be capable of quickly measuring heparin levels. The effects of heparin may be reversed via polyionic binding with protamine, an arginine-rich protein that can be used as an antidote in the case of heparin overdose.

The current gold standard of heparin determination is the anti-Xa assay. Since it is a fluorescence-based method, it requires significant sample processing times as it cannot be performed in whole blood. The demand for a more suitable analysis tool encouraged the development of more convenient heparin quantification methods.

Meyerhoff and coworkers achieved pioneering work on protamine and heparin detection since 1994 with ion selective electrodes[1] and optical sensors.[2] Our group recently developed emulsion-based particles sensitive towards protamine containing a solvatochromic dye as signal transducer.[3] The nano-optodes showed a significant absorbance shift in the presence of protamine, no pH cross response and were successfully used to quantify heparin levels in hospital patients' plasma. However, this approach still required sample treatment since it was unsuitable for whole blood detection owing to its high background absorbance.

Agarose gels have been previously used to embed optodes for ion detection.[4] Our protamine sensors were embedded in agarose gel, poured in commercially available polystyrene cuvettes and pictures were taken after protamine addition on top of the gel. The nanosensors showed the desired absorbance shift in presence of protamine when embedded in the gel. Here, however, the mixing between protamine and the nanoparticles was limited by protamine diffusion into the gel. Previous works using embedded nanosensors to detect cations utilized a distance-based readout. Such approach could not be applied to protamine or heparin sensing because physiological concentrations were much smaller. Thus, an intensity-based quantification method was developed here with spectral unmixing,[5] allowing us to monitor the signal change induced by protamine diffusion over time. This method gave promising results for both protamine and heparin quantification in whole blood samples.

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Polymer ablation using extreme ultraviolet pulses

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Laser ablation microanalysis is well established to perform a rapid and spatially resolved microanalysis. The sample utilization efficiency (fraction of measured mass versus amount of sampled mass) is extremely inefficient, as low as a few ppm. This causes a large sample damage and limits the sensitivity. The use of short wavelength radiation has been proposed to enhance the absorption and thus eliminate the heat-affected zone.[1] Sub-destructive sampling with extreme ultraviolet radiation (EUV, λ= 5-50 nm) has potential applications in microanalysis due to its strong absorption cross-section with any matrix. This radiation can excite the electrons and ionize the surface molecules or atoms efficiently. Obviously, it is important that the sampling is stoichiometric and possibly free of matrix effects.In order to achieve a better understanding of EUV photon and material interaction as well as the chemical processing on various material surfaces, the PMMA and PTFE samples were primarily irradiated by a pseudospark XUV source without focusing in our laboratory. Time-of-flight secondary ion mass spectroscopy (Tof-SIMS) was applied to observe the chemical processing on the surface. According to the fragments from the Tof-SIMS spectra, it is obvious that EUV photon is able to break both the main chain and the side chain in the polymers. Interestingly, the fluorine in PTFE depletes after the EUV irradiation, since it can generate volatile clusters with O and H in vacuum and desorb from the surface. X-ray photoelectron spectroscopy (XPS) results presents also the surface oxidation and fluorine depletion of PTFE. Additionally, the wettability of both polymer increased after EUV treatment, because there are more O generated and remained on the surface. This study presents a wide range of possibilities for the further development of the surface modification/microanalysis by XUV irradiation/ablation.
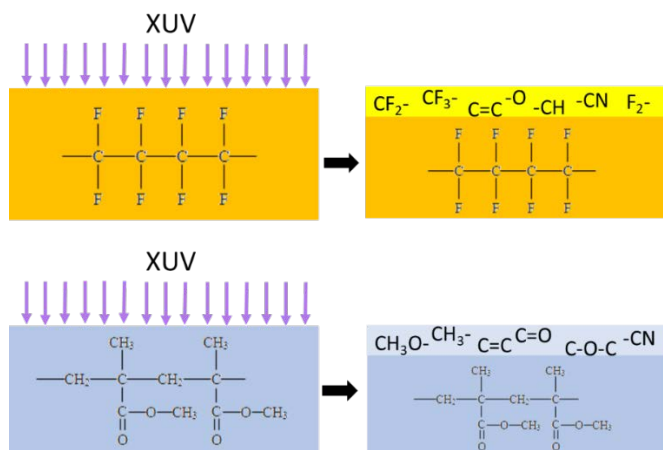

Figure 1: Schematic of the interaction between XUV and polymer matrices

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# VLS flat field spectrometer for extreme ultraviolet radiation. Design and analysis for LIXS

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Extreme ultraviolet (XUV) spectrometer is a crucial intrument for characterization of plasma and XUV spectrocopy. The flat-field XUV spectrometer with a variable-line-spacing (VLS) grating is able to focus the light onto a flat image plan, which is beneficial for the CCD camera.[1] An XUV spectrometer for the 11 to 62 nm is essential to detect a wide range of XUV emission. According to the specification of the grating, the distance between grating center and focal plane is 469 mm and the flat image plane is 110 mm. Due to the limitation of the CCD chip size (27.5 μm) and bellow statics, two construction methods are proposed: scanning the spectrum with a CCD moving along the focal plane and shifting the focal planealong the CCD chip surface. Thus, there is great interest in the total system error of these two methods. It can be estimated by using mathematical modeling, based on the initial distribution of the source radiation and the geometry of the optical system.
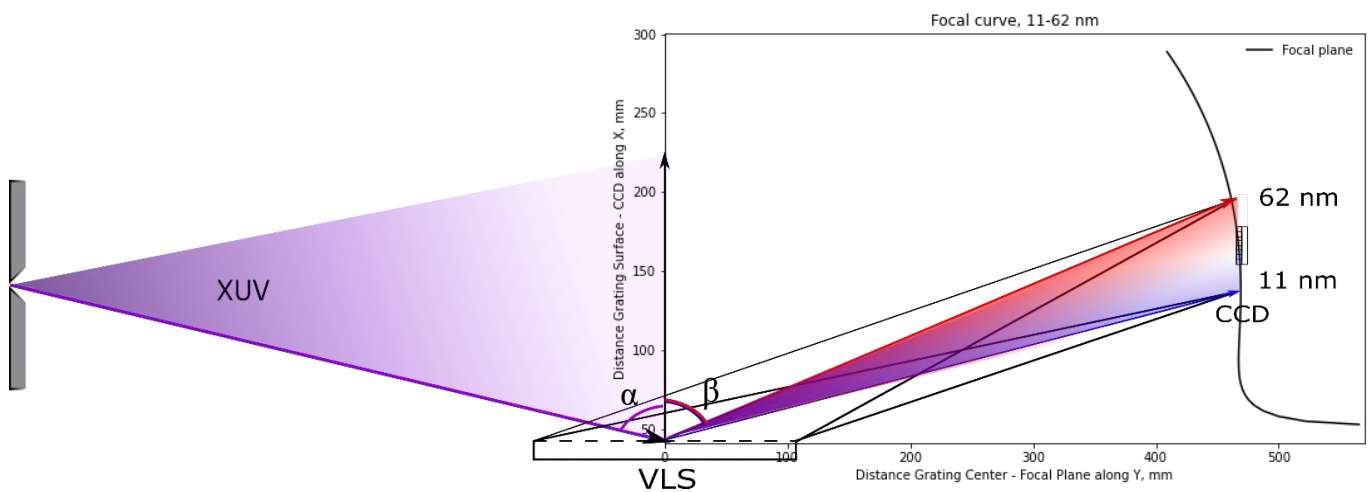
[1]   Qu D., Bleiner D., *J. Anal. Atom. Spectrom.* 2020, 35(9), 2011-2022.

Self-referencing pulstrode: Further optimization and new electrode designs

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With an ever-increasing world population and life expectancy, public health often ranks as the second sector in terms of budgetary spending worldwide. Finding ways to reduce the costs, whether it is in the preventive care or therapeutic domain, is a crucial component of developing a sustainable health system. As a result, Point-of-Care Testings (POCTs) and wearable sensors have attracted a tremendous interest in the past decades. As opposed to traditional analysis, which are costly and time-consuming, POCTs and wearable sensors present, among others, the following advantages: they are cost-effective and allow rapid or continuous measurements, which lead to better reaction time and thus fewer costly complications.[1] Electrochemical sensors in that regards represent a good example of POCTs.

The reference electrode is an essential component of an electrochemical system, resulting in a high research activity in that domain.[2] The gold standard remains the Ag/AgCl double junction reference electrode. However, owing to its electrolyte-filled inner compartment its design is cumbersome and impractical for wearable sensors applications, which require miniaturization. From that point of view, all-solid state reference electrodes provide a promising alternative.

Gao *et al.* proposed a solid-state reference electrode which relies on an Ag/AgI element and acts as a pulstrode to self-generate a reference potential.[3] The pulstrode protocol consists of four distinct steps: 1) potentiometric measurement of the initial state of the system (OCP), 2) a cathodic current pulse, leading to the reduction of Ag^+ into Ag and the local release of a controlled amount of iodide, 3) measurement of the EMF (reference pulse) 4) application of the original OCP to regenerate the system into its initial state. The protocol has proven its reliability in terms of precision and stability over cycles on a macro-electrode. This work investigates the application of the pulstrode protocol to different electrode designs such as a fine silver wire acting as a micro-electrode or screen-printed electrodes provided by the Swiss Center for Electronics and Microtechnology. Additionally, an attempt to improve the robustness of the described system against sample convection and sample density fluctuations was made by covering the electrode surface with an agarose gel layer.

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Investigation of nanoparticle enhanced emission in laser induced X-ray spectroscopy (NE-LIXS)

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In analytical Chemistry, fast measurements and easy sample preparation are two important factors for a method for the investigation of solid surfaces. One technique that fulfils these requirements is Laser Induced Breakdown Spectroscopy (LIBS). In recent years it was found out that the emission signal can be increased by coating the sample with a thin layer of gold or silver nanoparticles.[1] This technique is called NELIBS (nanoparticle enhanced LIBS). The emission signal enhancement through nanoparticles depends on the distance between the nanoparti-cles on the surface and can be controlled by the concentration of the used nanoparticle solution to coat the sam-ple.[2] This pre-treatment of the sample further enhanced the capabilities of LIBS by allowing the elemental quan-tification at ppb levels with a single laser shot.[3]

In our study, we investigate the same phenomenon in the wavelength region of 5 to 20nm using Laser Induced X-ray Spectroscopy (LIXS) to determine if this technique of emission signal enhancement can also be used for LIXS. Our experimental setup can be seen in Figure 1. We will prepare samples with different gold nanoparticle concen-tration and use 10nm, 50nm, 100nm and 200nm sized nanoparticles and determine the optimal concentration for each size for the emission signal enhancement. Additionally we will compare and investigate the signal enhance-ment achieved with NELIBS.
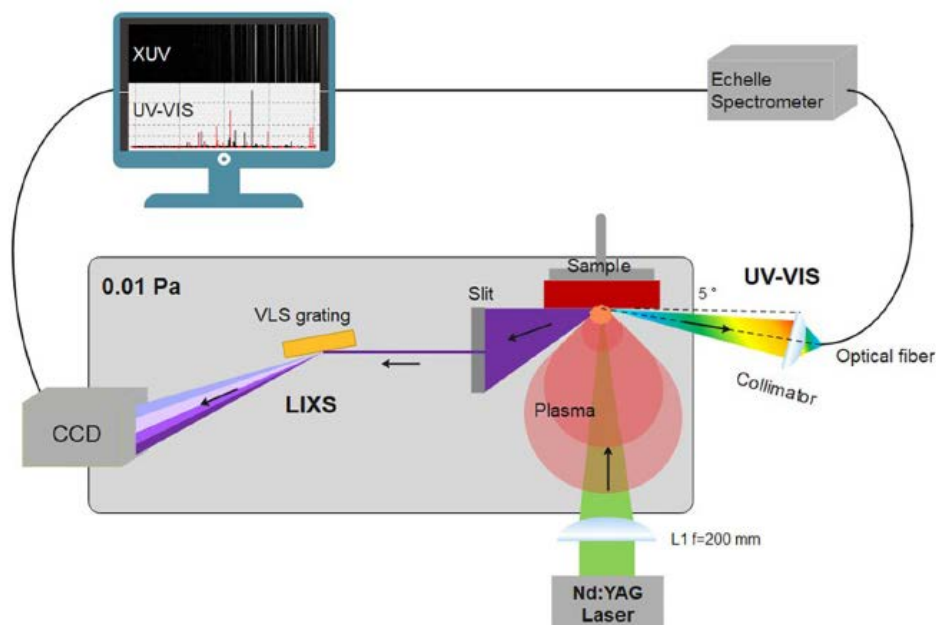

Figure 1: Experimental setup of the LIXS setup. Wavelength is 532nm of a Nd:YAG Laser focused with a lens onto the target. The target and spectrometer is placed in a vacuum chamber and the XUV (and also UV-Vis) signal are collected radially using a fiber optic and CCD camera.[4]

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Carbonate optical nanosensors: New mechanisms and their advantages

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In Situ concentration profile mapping of carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and dissolved carbon dioxide (CO_2) in natural waters (rivers, lakes etc.) as a function of depth is highly relevant for environmental analysis and might serve as a source of insight into the evolution mechanisms of such complex ecosystems. Numerous solutions for both potentiometric and optical sensing of carbonate and carbon dioxide in aqueous and gaseous samples have been proposed over the years,[1] yet such practical tools for spatially resolved analysis as emulsion-based nanooptodes have generally been overlooked.

We are here describing carbonate-selective nanosensors based on either a chromoionophore or a solvatochromic dye as an optical reporter. The sensing appears to predominantly take place on the surface of the nanoparticle and is subject to an influence from lipophilic cations present in the sample transferring into the sensor phase. This is successfully used to enhance sensor performance by adding a second dye into the sample with the subsequent use of a ratiometric readout (Fig. 1). We note that sample alteration is unfavorable for routine *in situ* applications of carbonate-selective nanoparticles. A thorough mechanistic study is carried out, the dual solvatochromic dye approach is expanded and the nature of the interactions between the dyes is investigated.
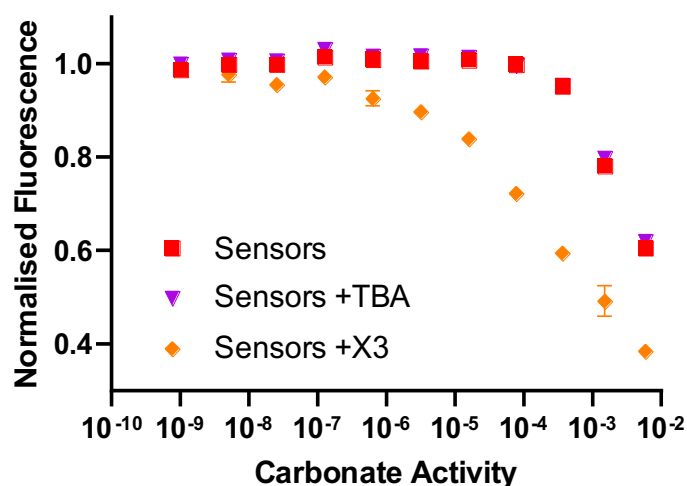

Figure 1. Solvatochromic carbonate sensor response modulated by the addition of a second dye, X3, to the sample solution.

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Self-powered potentiometric sensor based on optical signal transduction with liquid crystal display

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Self-powered sensors are attractive because they are environmentally friendly and allow for sensor miniaturization. However, developing self-powered potentiometric sensors is still quite challenging because only limited energy can be harvest by this measurement principle.

A new type of self-powered ion-selective potentiometric sensor is illustrated here that requires very little power. For the first time, the potential of a glass pH electrode of very high impedance (130 M Ω) is directly read out optically. This is accomplished by a liquid crystal display (LCD) as the electrochromic transduction principle. The LCD gives a significant change of transmission upon applying an external voltage within a certain range. The transmission process requires a very small charge on the order of 100 pC to be transferred across the membrane owing to its low capacitance of ca. 50 pF.

For the LCD to be turned on, the cell voltage needs to be boosted by the addition of additional Zn/Zn2+ elements placed in series. Also, the LCD is found to give a time-dependent absorbance decrease, which may be due to reversible radical reactions at the underlying ITO electrode as a constant voltage is applied.[1] This is mitigated by adding a high resistance element in series to attenuate the associated decay, capturing the optical signal for 4 s and then short-circuiting the LCD for at least 5 s. This results in repeatable recovery of the LCD absorbance for an optical readout of adequate precision. The absorbance is found to decrease with increasing pH, which can be used to measure any sample of interest.
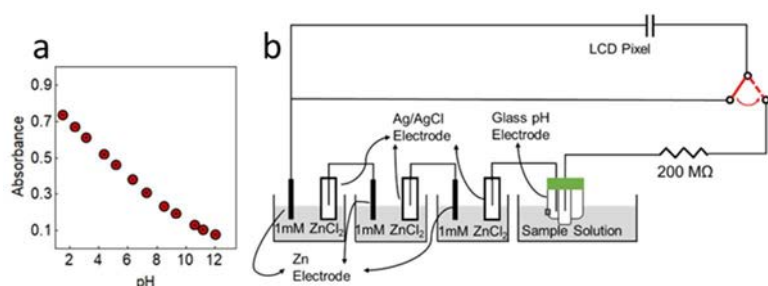

Figure 1. A) Direct LCD absorbance response to pH from a glass electrode. B) Scheme of the sensor circuit.

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Laser ablation with funnel-focused mass spectrometry for improved resolution and analysis speed

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Spatially resolved element analysis has been used and applied widely in forensic science, geochemical analysis, biological imaging, etc. LA-ICPMS is of great interest in performing such analyses due to its high sensitivity, availability and robustness.[1] However, the substantial operating cost and extensive amount of argon gas as well as spectral inferences pose a limitation to this technique.[2, 3] Thus, a femtosecond laser ablation funnel-focused mass spectrometer (LAFUMA) system for high-speed, high sensitivity element imaging is currently developed.

LAFUMA comprises a positioning system, a femtosecond-laser source for desorption and ionization, custom-made convergent-divergent nozzle (CD nozzle) and ion funnel, ion optics connected to a time of flight mass spectrometer. The femtosecond laser allows for directly sampling and ionization while causing a minimal heat affected zone,[4, 5] thus preserving the structure of the adjacent sample regions. Compared to conventional laser ablation mass spectrometry methods, where ions are typically generated in high vacuum, the design of LAFUMA shall provide a higher sensitivity through ablation/ionization within a bath gas before a CD nozzle and an rf-only ion funnel transfer the ions into the MS. The previously described prototype instrument (Querci et al) has been further modified to now include a sample positioning system and an improved ion optics downstream the ion funnel. Initial experiments with the new setup were carried out to determine suitable operating conditions with respect to gas flow rates, pressure in the sample chamber.

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Wabern, 3. May 2022

Invitation for the General Assembly of the Division Analytical Sciences of the Swiss Chemical Society

Date: **Friday, 20th May 2022**

Time: **12:30 to 13:00**

Place **Dorinth Resort Blüemlisalp, Beatenberg**

Agenda

1. Opening of the General Assembly by the president
2. Nomination of scrutineers
3. President's report
4. Treasurer's report
5. Election of board members – approval of the board
6. Outlook
7. Individual proposals
8. Miscellaneous

With my best wishes

Hanspeter Andres

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