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MIR Spectroscopy beyond trace levels - environmental and industrial applications

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Advances in mid-IR quantum cascade laser (QCL) technology have triggered an impressive progress in instrumental developments. This progress is in line with a continuous quest for high-precision and selective measurements of a large variety of molecular species, as well as for compact, robust and field deployable gas analyzers. Correspondingly, the applications cover very diverse areas, including environmental sciences and industrial process control. Recent trends include the miniaturization of QCL spectrometers and multi-component instruments that are based on multi-wavelength QCLs [1].

Nitrogen dioxide (NO_2) is one of the most prominent examples. QC laser based trace gas analysis is well suited for remote locations with very low NO2 mixing ratios. Using an astigmatic Herriott sample cell with 200 m optical path length, a precision of 3 ppt and 10 ppt for $NO_2$and NO, respectively was obtained for continuous, on-site measurements under predominantly free tropospheric air conditions at the high-alpine station Jungfraujoch [2].

The fact that isotope ratios of atmospheric trace gases contain highly valuable information about their sources and sinks triggered numerous instrumental developments based on QCL spectroscopy, because laser based methods can deliver real-time data with high temporal resolution and precision. This is illustrated by 6 years *in-situ* isotope ratio measurements of CO_2at Jungfraujoch [3]. Furthermore, laser spectroscopy is inherently specific to structural isomers having the same mass, and thus capable to perform site-specific isotopomer N_2O measurements [4,5].

Fast detection is illustrated by the development of a patented analyzer for leak detection of aerosol can propellants. The instrument allows detecting small leaks with high speed (‹ 10 ms) and sensitivity (1 ppm), allowing the industrial testing of up to 750 cans per minute [6].

The concept of “multi-color” spectroscopy has been explored based on a dual-wavelength QCL [7]. The active region of this laser consists of two different active layers stacked on top of each other, optimized for a broadband emission at 1600 $cm^{-1}$and 1900 cm^{-1}, while single-mode emission at the desired wavelengths is ensured by a succession of two distributed-feedback (DFB) gratings with different periodicities. A prototype spectrometer allows fast (10 Hz) operation during automotive exhaust emission measurement and ambient air monitoring in a suburban environment [8].

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[2] B. Tuzson et al., Selective measurements of NO, NO_2 and NO_y in the free troposphere using quantum cascade laser spectroscopy, Atmos. Meas. Tech., **6**, 927–936 (2013).

[3] P. Sturm et al., Tracking isotopic signatures of CO_2 at Jungfraujoch with laser spectroscopy: analytical improvements and representative results, Atmos. Meas. Tech. **6**, 423–459 (2013).

[4] J. Mohn et al., Site selective real-time measurements of atmospheric N_2O isotopomers by laser spectroscopy, Atmos. Meas. Tech. **5**, 1601–1609 (2012).

[5] P. Wunderlin et al., Isotope signatures ofN_2O in a mixed microbial population system: Constraints onN_2O producing pathways in wastewater treatment, EST, 47 (3), pp. 1339-1348 (2013).

[6] J. Jágerská et al., Highly sensitive and fast detection of propane and butane using a 3 µm quantum cascade laser, Appl. Opt., **52**, 4613–4619 (2013).

[7] J. Jágerská et al., Dualwavelength quantum cascade laser for trace gas spectroscopy,” Applied Physics Letters 105, 161109–161109–4 (2014).

[8] Jágerská et al., Simultaneous measurement of NO and NO_2 by dual-wavelength quantum cascade laser spectroscopy. Optics Express 23(2): 1512-1522 (2015).

Detection and identification of non-covalent interactions with SPRi-MALDI MS

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In pharma and life science research, there is a lot of interest for fast and accurate screening methods. The coupling of SPRi and MALDI MS technologies meet the strong demand for high-throughput analysis and identification of biomolecular interactions. In addition it provides information on binding kinetics and binding affinity in real time.

SPR measurements were performed on the SPR Plex II (Horiba, Palaiseau, France) working with polyoxyethylene functionalized gold slides including NHS-esters for immobilizing ligands. Mass spectrometric detection was done with a commercial MALDI TOF mass spectrometer (Ultraflex II TOF, Bruker Daltonics, Bremen, Germany) and the gold slide was mounted to an adapter target. The measurements were performed in the linear positive ion mode with standard settings and a “smartbeam” laser with proper energy. Each mass spectrum was the average of 2000 laser shots acquired at random sample position.

We will show an investigation of off-target binding of various DARPins. DARPins (designed ankyrin repeat proteins) rival antibodies for target binding, but are genetically engineered and more robust. It is known that the DARPin off7 interacts specifically with maltose binding protein (MBP) [1]. MBP is part of the maltose/maltodextrin system, which is a sophisticated regulatory and transport system involving many proteins. The binding specificity of DARPins with a mixture of important proteins will be determined while DARPins are immobilized. In an inverse experiment, MBP (0.4 mg/ml) was immobilized and a mixture of DARPins (off7 and a non-interacting DARPin, E3_5) was injected.

The K_D was determined based on the measured SPR data and resulted in 4.39 nM (± 0.03), which fits very well with the theoretical value of 4.40 nM [1]. A MALDI MS measurement on the SPRi-chip directly after the SPRi experiment verifies the specific interaction between off7 and MBP due to the mass spectrometric identification of off7 and no other protein.

The coupling of surface plasmon resonance and mass spectrometry enables the multiplexed investigation of specific interactions out of a crude mixture with no need of purification, separation steps or labeling in real time, as shown for the interacting partners off7 and MBP.

[1] H. K. Binz et al., *Nature Biotechnol*, **2004**, 22, 575-582

Quick and easy NMR titration using slice-selective experiments to study concentration gradients in agarose gels

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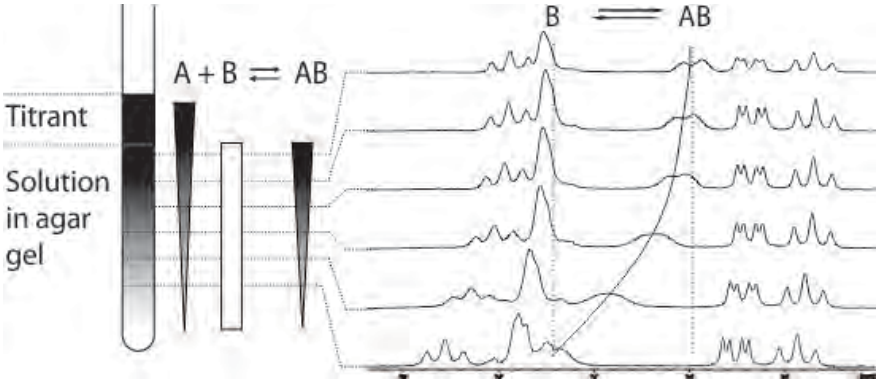
NMR titration is a long recognised method for determination of equilibrium constants or thermodynamic parameters of reactions, but suffers from the drawback of being time consuming. Recently, spatial-selective NMR spectroscopy for reaction monitoring was proposed[1]. The method relies on slow diffusion of one of the reaction components into a polystyrene gel, containing the other, thus resulting in a spatially dependent sample composition along the NMR tube. Following a similar approach we present the use of agarose gels as the medium for single-experiment NMR titrations in water. It was used to study the inclusion of paracetamol in cyclodextrine macrocycle as a model reaction. The agarose gels benefits from a very simple and reliable sample preparation. Moreover, we observed no interaction between the matrix and the compounds under study and obtained high-resolution spectra, identical to those obtained from solution samples.



One of the main advantages of the proposed method is its speed achieved by performing the slice selective experiments in an interleaved manner, thus affording the acquisition of quantitative spectra in 1-10 minutes. In addition to the room temperatures measurements, the variable temperature NMR titration has been also investigated, as the agarose gels possess the attractive property to lower the freezing point of water making it possible to study water solutions up to -8 C.

[1] T. Niklas, D. Stalke, M. John, *Chem. Commun.*, **2015**, 51, 1275-1277.

High-speed, high-resolution, multi-elemental imaging of geological samples

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Elemental imaging has recently gained a lot of attention in the field of geology, biology and medicine, where the characterization of micro-structures and the evaluation of elemental distributions across heterogeneous samples are of major relevance.
Until now, most instrumental approaches applied in either two or three dimensional imaging studies were comprised of a laser ablation system coupled to a scanning (quadrupole or sector-field) mass analyzer. The fundamental operating principle of those systems did not allow simultaneous multi-element detection. In order to enable shot by shot detection, the system had to be operated at low laser repetition rates which made it suffer from spectral intensity skew errors and accounted for an extended data acquisition time. Laser spot sizes of a few 10s of microns were commonly applied impairing high lateral resolution.
Here we report the coupling of an ArF excimer laser ablation system (λ=193 nm) to a prototype ICP-TOF mass analyzer enabling high-speed, high-resolution, multi-elemental imaging of geological specimens.
Operating a low-dispersion laser ablation tube cell, minimum signal widths of 9 ms were obtained when ablating NIST 610 (full width at 1% peak maximum). The system's capability to run at 100 Hz laser repetition rate while maintaining baseline separation of individual transient signals was demonstrated. Limits of detection in the low µg/g range were observed for most trace elements. Full mass spectra can be acquired at a speed of up to 33 kHz.
Following the thorough characterization of the new setup performing different imaging experiments on standard reference materials, this LA-ICP-TOFMS setup was applied in quantitative two and three dimensional imaging studies dealing with various geological specimens including a cesium infiltrated Opalinus clay thin section with pyrite inclusions and a meteorite sample. Laser spot sizes varying from 1.5 to 5 µm and a laser repetition rate of 20 Hz were applied. The results of these studies will be compared to the findings made by synchrotron based X-ray tomography. Advantages and shortcomings of both techniques will be discussed.

Electromembrane extraction: a new technical development.

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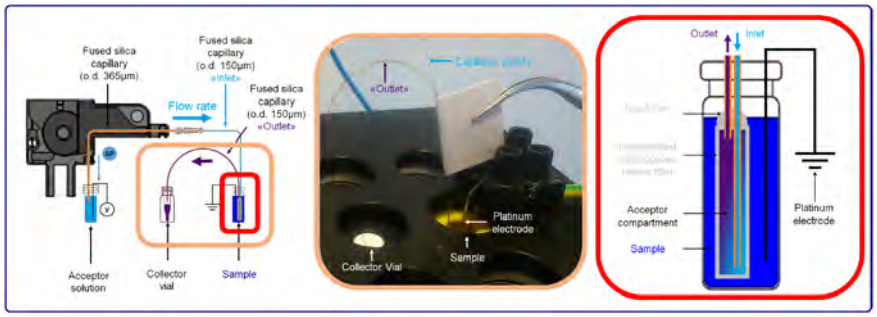
Introduction

Electromembrane extraction (EME) is a relatively recent electro-assisted extraction method [1]. EME consists in the migration of charged compounds under an electrical field, through a supported liquid membrane (SLM) impregnated on a microporous hollow-fiber. This method has already shown high potential for the extraction of low molecular weight basic compounds of medium polarity. In this study, a new set-up of EME device was developed. The main attribute of this original device, directly inspired from microdialysis, relies in the continuous refreshment of the acceptor compartment, enabling higher preconcentration factors compared to the conventional static set-up, and good recoveries.



Methods

Standards solutions (50 ng/mL) of 15 neuropeptides were extracted with the new EME set-up. For the first time to our knowledge, a polypropylene hollow-fiber with a 50 µm wall thickness was used. Pressure and voltage were applied thanks to an Agilent Electrophoresis 7100 CE system. Several parameters such as the SLM composition (nature of the organic solvent and carrier), the voltage, the extraction time, and the flow rate of the acceptor phase were evaluated towards preconcentration factor and recovery. Extracts were analyzed by RP-UHPLC-MS/MS with SRM using an Agilent QqQ 6490 MS system. Preconcentration factors and recoveries were estimated by comparison with a standard solution injected in the same conditions.

Results

Although alcohols have been described the most suitable solvents for peptide extraction, the addition of decanone to a nonanol SLM (1:1, v/v) stabilized the extraction process and offered better results for a few peptides. The addition of DEHP as a carrier to the SLM was found to enhance the selectivity for polar peptides. The high electrical field (ca. 200/cm) significantly influenced the extraction process. High extraction times (up to 45 min.) had no significant influence on the preconcentration factor, but greatly improved recovery (up to 70%). Decreasing the flow rate of the acceptor phase enabled a high preconcentration factor (up to 50-fold).

[1] Stig Pedersen-Bjergaard, Knut Einar Rasmussen, *Journal of Chromatography A*, **2006,** 1109(2), 183-90.

Drug quantification in blood within microstructures for Point-of-Care Therapeutic Drug Monitoring

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[1]University of Applied Sciences Western Switzerland

Many modern therapeutics involved for instance in the treatment of infections, cancer or in post-transplant therapies require Therapeutic Drug Monitoring (TDM) owing to their narrow therapeutic range. Currently this process is demanding for the patients, as several milliliters of blood are required, slow and costly, as the sample need to be transferred to a central laboratory, and suffer of limited efficacy, as the results are difficult to interpret for a non-specialist. To overcome these problems, we aim at providing a simple, rapid and sensitive solution by develop a compact and cost-effective Point-Of-Care drug quantification device based on miniaturized competition assay. Preliminary results have demonstrated the feasibility of downsizing FPIA and shown that two prototypical drugs: Tobramycin and Tacrolimus, an antibiotic and an immunosuppressant can be quantified using minute amounts (only 20 µl) of human blood. For Tobramycin, the assay could be further miniaturized down to just one µl of human serum while preserving its performance. Moreover, the assays could be transposed into different microstructures using a custom-made Fluorescence Polarization instrument, as a first step towards a Point-Of-Care Therapeutic Drug Monitoring device.

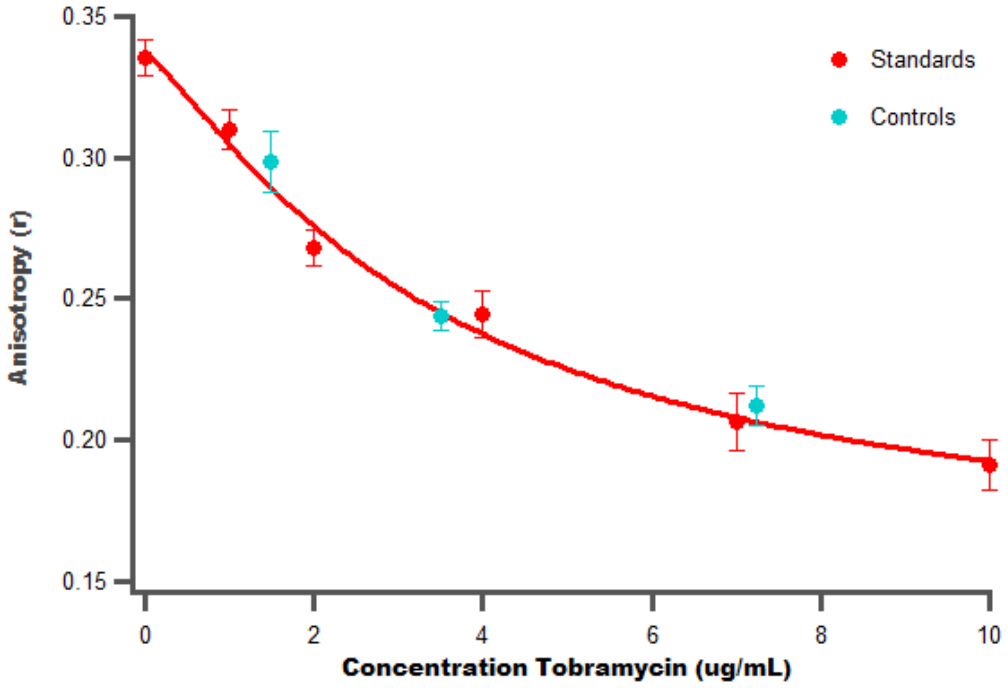

Fig.: Fluorescence Polarization Immunoassay (FPIA) calibration curve with a novel Tobramycin derivative for Tobramycin quantification using minutes amount of blood

Sanavio B and Krol S (2015) On the slow diffusion of point-of-care systems in therapeutic drug monitoring. *Front. Bioeng. Biotechnol.* **3**:20.

Thin Layer Ionophore-Based Membranes for Multianalyte Detection

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[1]University of Geneva

A novel concept is introduced here that allows one to detect multiple ions simultaneously using a single ion-selective membrane. This is demonstrated with thin plasticized polymeric membranes (less than 300 nm in thickness) containing up to two ionophores in addition to a lipophilic cation-exchanger that is back side contacted with a film of electropolymerized poly(3-octylthiophene) (POT) as an ion-to-electron transducer.

The operating principle is shown in Figure 1a, illustrating a membrane that contains lithium and calcium ionophores simultaneously. An anodic scan partially oxidizes the POT underlayer, which results in the expulsion of cations from the membrane at an appropriate potential. Distinct ion transfer waves appear in the obtained voltammogram owing to the different standard ion transfer potential of the cations involved in the process (Figure 1b). Moreover, each peak shifts to more positive potentials with increasing activity of the corresponding cation according to the Nernst equation. In other words, calibration curves analogous to potentiometric sensors are found for lithium and calcium, independent of the concentration of the other cation.

The basis of the developed concept is established for lithium and calcium accompanied by a response model that agrees well with the experimental results.[1] This is the first time that a selective potentiometric multianalyte analysis is achieved with an ion-transfer electrochemical technique. Current efforts in our laboratory aim to explore different membranes containing multiple ionophores to analyze several cations in the same sample using a single electrode.

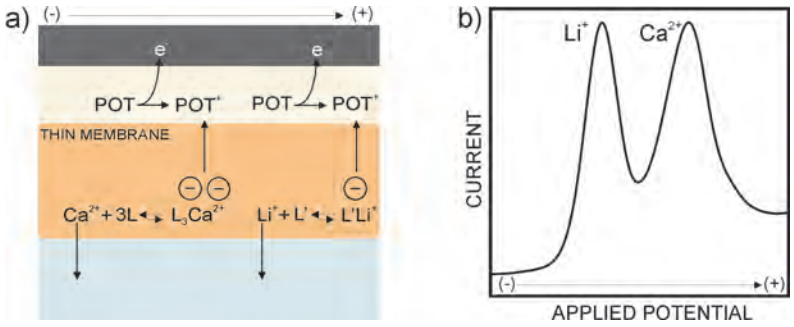

Fig. 1a) Scheme of the electrochemical process (L=calcium ionophore and L'=lithium ionophore). **b)** Voltammograms obtained for equimolar concentrations of lithium and calcium.

[1] G.A. Crespo, M. Cuartero, E. Bakker, submitted to Analytical Chemistry (2015).

Multistage Transversal Modulation Ion Mobility Spectrometry: Reducing the Voltage Required for High Resolution IMS for pre-existing mass spectrometers.

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[1]SEADM S.L., [2]ETH Zurich

Commonly used IMS techniques provide a pulsed output of ions, which requires interfacing of these instruments to very fast Mass Spectrometers (such as ToF). Our goal is to develop an Ion Mobility Spectrometer (IMS) that can be coupled with any pre-existing MS, and which does not require a fast IMS-to-MS synchronization.
Transversal Modulation IMS (TMIMS) combines an axial electric field and a transversal-oscillating electric field that provides a continuous output of mobility selected ions. It can also be operated in full transmission mode, and at atmospheric pressure. These features make it a very versatile IMS solution for pre-existing mass spectrometers. We have developed two prototypes that demonstrate the possibilities of the instrument. However, these systems still require further improvements to meet final user requirements: (i) the transmission must be increased, (ii) the voltage of the instrument inlet must be reduced to manageable levels, (iii) the oscillating voltages must be reduced.

Here we present a new instrument that uses a ladder of six small TMIMS stages, each powered with a square wave with a voltage of 1KV. This voltage is about six times smaller than the one used in previous prototypes, and it can be easily handled with low-cost electronic components. According to simulations (COMSOL), selected ions are sequentially focused to the center of each slit of the ladder, while non-selected ions accumulate lateral displacements as they traverse the TMIMS ladder. As a result, despite the low deflection voltages used, ions are deflected away from the TMIMS outlet as if a much higher deflection voltage was used, providing high resolving powers with low voltages.

The inlet of the new instrument was grounded, thus facilitating coupling with standard ions sources. The outlet was coupled through a resistive capillary with a LTQ mass spectrometer (Thermo). The resistive capillary transfers the ions from the outlet electrode of the TMIMS (which was powered at 8kV) to the inlet of the MS. We used two different sources to test the performances of TMIMS ladder. Our experiments with the new prototype show that, as expected, although the resolving power of each isolated TMIMS stage is poor, the resolving power of the ladder is comparably much better. Additionally, by comparing the shape of the spectra when only some stages of the ladder are powered, we could show that the ladder also improves the robustness against over-current limitations: when too large currents are inputted through the TMIMS inlet, space charge spreads the ions beam, thus broadening the peaks in the spectra. In the ladder, space charge effects are restricted to the first stage, allowing the rest of stages to function normally.

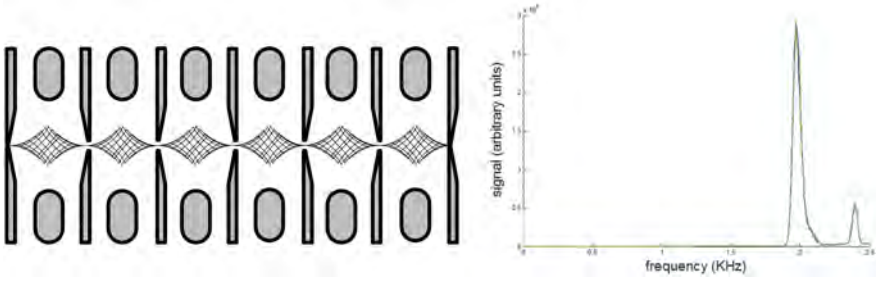

Figure: (left) Scheme of the TMIMS ladder, and simulated trajectories of the selected ions through the TMIMS ladder; (right): Tetraheptylammonium signal measured at the MS as a function of the frequency of the oscillating field.

Fourier optical beam shaping of femtosecond laser pulses for high resolution depth profile analyses by LA-ICPMS

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Element-selective depth profile analyses of high-tech materials, including thin films and multilayer systems, have gained importance over the past years in order to keep up with the ever growing standards concerning control and optimization of manufacturing processes. Here, technologies utilizing ion beam probes such as secondary ion mass spectrometry (SIMS) and Rutherford backscattering (RBS) [1] are most frequently chosen due to their high depth resolution, sensitivity, and selectivity. By comparison, laser ablation (LA)-based photonic probes in combination with, *e.g.*, inductively-coupled plasma (ICP)MS have rarely been applied in this context, even though they offer the feasibility of atmospheric sampling and, therefore, a high throughput of specimen. Furthermore, up-take rates of ‹ 10 nm per shot have been reported [2] when femtosecond (fs) laser sources are employed, which potentially allows to perform depth profile analyses with resolutions in a range of 100 nm and below. For this, a homogenization of the laser radiation delivered to the sample surface is required to ensure the formation of craters with steep walls and flat bottoms and, in this way, to suppress mixing of material originating from different layers in the course of analyses. However, ahigh-grade beam homogenization has remained challenging since most of the design concepts applicable are accompanied by either beam distortion and/or stretching of the laser pulse duration.

In this study, a Fourier transformation (FT)-based two-step optical processing scheme for the generation of homogenized laser intensity profiles in an objective`s focal plane was conceived, which rests on the delivery of diffracted beams. Initially, the laser radiation is truncated by a circular aperture to let pass only the inner region of the beam where intensity gradients are smallest and uniformity is highest. Downstream the aperture, the beam diffracts along its path to form an Airy disk in the far field (1^{st} FT). Finally, the diffracted radiation is focused by an aberration-corrected objective lens to re-transform the Airy disk into a homogenous spot at the sample surface (2^{nd}/reverse FT). The performance of this scheme concerning shape, morphology, and general appearance of craters formed in borosilicate glass by fs-LA @ 400 nm wavelength and 150 fs pulse duration was tested under both, helium atmosphere and ambient air. Crater shapes, morphologies, and up-take rates per shot were examined using optical and confocal microscopy as well as scanning electron microscopy.

[1] D. Abou-Ras et al., Microsc. Microanal., 2011, 17, 728-751.
[2] J. Pisonero et al., Anal. Chem.,2007, 79, 2325-2333.

High resolution laser ablation depth-profiling mass spectrometry

A. Riedo[1], V. Grimaudo[1], P. Moreno-García[1], M. B. Neuland[1], M. Tulej[1], P. Broekmann[1], P. Wurz[1]*

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Accurate investigations of chemical heterogeneity of solid materials is a highly demanding task in various fields of applications, ranging from purity control of high performance material in industrial application, tissue analysis in medical diagnostic or investigation of surface weathering in space research. Laser depth-profiling combined with mass spectrometric analysis is one of the most powerful methods which offers high vertical resolution together with highly sensitive chemical analysis.

In our recent studies we analysed the chemical composition of various solid materials by means of depth profiling method. The chemical analysis were conducted by combining a fs-laser ablation/ionisation ion source (~190fs, λ = 775nm, laser spot diameter Ø ~15µm) with a miniature reflectron time-of-flight mass spectrometer (LMS).[1,2] Electrochemically deposited copper samples bearing spatially-confined impurity layers were used as platform for the development of a novel quantitative depth-profiling technique. These samples were fabricated under galvanostatic conditions by means of an additive-assisted plating procedure, which is used in the semiconductor industry for the fabrication of small sized copper interconnect architecture of Si-based logic and memory devices.[3,4] This plating procedure, however, suffers from incorporation of additives, which causes the formation of defects within the embedding copper material decreasing the performance and life time of the integrated circuits. The understanding of the embedding conditions and the quantitative chemical analysis of these impurity layers becomes mandatory to improve the filling procedure within this industrial sector.

The quantification of the mean ablation rate by means of optimising the laser irradiance and single shot experiments allowed for optimal depth profiling conditions with unprecedented vertical resolution in the sub-nm range. The actual instrument performance, which includes the high vertical and lateral resolution, the high detection sensitivity reaching ~10ppb concentration (atomic fraction) of elements within a sample material, and the high dynamic range of more than eight orders of magnitude enables high precision and quantitative chemical analysis of the grain boundary sites where the impurities within the copper deposit are incorporated. Our present capabilities in laser ablation mass spectrometry complement and improve significantly upon previous SIMS measurements providing a better understanding of the incorporation of distinct additives.

[1] A. Riedo et al., *J. Anal. At. Spectrom.,* **2013**, 28, 1256-1269.
[2] M. Tulej et al., *Geostand. Geoanal. Res.,* **2014**, 38, 441-446.
[3] V. Grimaudo et al., *Anal. Chem.,* **2015**, 87, 2037-2041.
[4] P. Moreno-García et al. to be submitted to *Electrochemistry Communication*.

Single-walled Carbon Nanotubes (SWCNTs) for Bioanalyte Sensing

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Nanomaterials offer distinct chemical and optical properties that are advantageous in a breadth of bioanalytical applications, including the development of highly selective and sensitive sensors [1]. Polymer-wrapped single-walled carbon nanotubes (SWCNTs), in particular, have been used to develop optical sensors selective towards a variety of biomolecules, including nitric oxide (NO) [2], riboflavin (vitamin B2), and the hormone, estradiol. These sensors use SWCNT fluorescence to quantitatively monitor analyte concentration. The selectivity of these sensors is tuned by engineering the polymer wrapping, which imparts the nanotube with molecular recognition capabilities. Because SWCNT fluorescence is strongly affected by the nanotube environment, perturbations in the environment caused by analyte adsorption and desorption result in fluorescence changes. Previous studies have shown that analyte concentration modulates SWCNT fluorescence with sensitivities that can even extend down to the single-molecule limit.

SWCNT-based optical sensors have been used in the quantitative, spatiotemporal measurement of biomolecules in several biological systems, including mammalian cells, *in vivo* models [3], photosynthetic organelles [4] and, most recently, whole plant leaves [5]. This presentation summarizes the recent developments and applications of the field, as well as our ongoing endeavors in engineering a new generation of optical nanosensors.

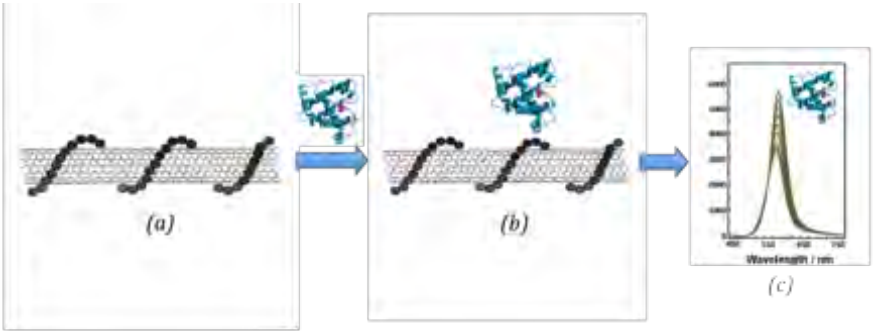

Figure 1. Schematic representation of SWCNT-based optical sensors for bioanalyte detection:
(a) SWCNT wrapped with surfactant, polymeric, or biological coatings.
(b) Binding of the bioanalyte to the SWCNT (blue molecule).
(c) Change in SWCNT optical signal (fluorescence emission).

[1] A. A. Boghossian et al., *Chem. Sus. Chem*. **4**, 848 (2011).
[2] Z. W. Ulissi et al., *Nano Letters* **14**, (2014).
[3] J.H. Kim et al., *Nature Chemistry* **1**, 473 (2009).
[4] A. A. Boghossian et al., *Advanced Energy Materials* **3**, 881 (2013).
[5] J. P. Giraldo et al., *Nature Materials* **13**, 400 (2014).

Variable Q1 windows for MS acquisition and predicted LC retention time ranges for LC-SWATH-MS analysis

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[1]Life Sciences Mass Spectrometry, University of Geneva and Lausanne

The analysis of metabolomics samples by LC-MS commonly allows the detection of hundreds of compounds. Precursor ion intensities can span over several orders of magnitudes. Data dependent acquisition (DDA) methods often miss the acquisition of MS/MS spectra for low intensity compounds which cannot be used for quantification. Data independent acquisition (DIA) methods like SWATH are emerging to obtain all MS/MS spectra for qualitative and quantitative analysis.

SWATH uses Q1 windows with a certain width to obtain all MS/MS spectra within a *m/z* range. It is important to note that ramped collision energies (CE) are commonly applied. As such reference MS libraries with composite MS/MS spectra which cover the whole expected CE range from 10 – 100 eV are needed for improved MS/MS matching. We developed such a MS metabolomics library which includes 528 compounds from all the major human metabolite classes.

Depending on sample complexity SWATH data acquisition can lead to multiplexed MS/MS spectra when several co-eluting precursor ions are acquired in the same Q1 window. To address this issue, we propose to use variable Q1 windows. We developed the in-house software SwathTuner to calculate optimal window widths based on the *m/z* and TIC distribution of the LC-MS features detected in the sample.

For many compounds and especially isomers a good MS/MS matching is not always sufficient for unambiguous identification. In these cases, we propose to use predicted LC retention time ranges based on a linear regression between the retention times for a set of isotopic labeled metabolites and their log D values.