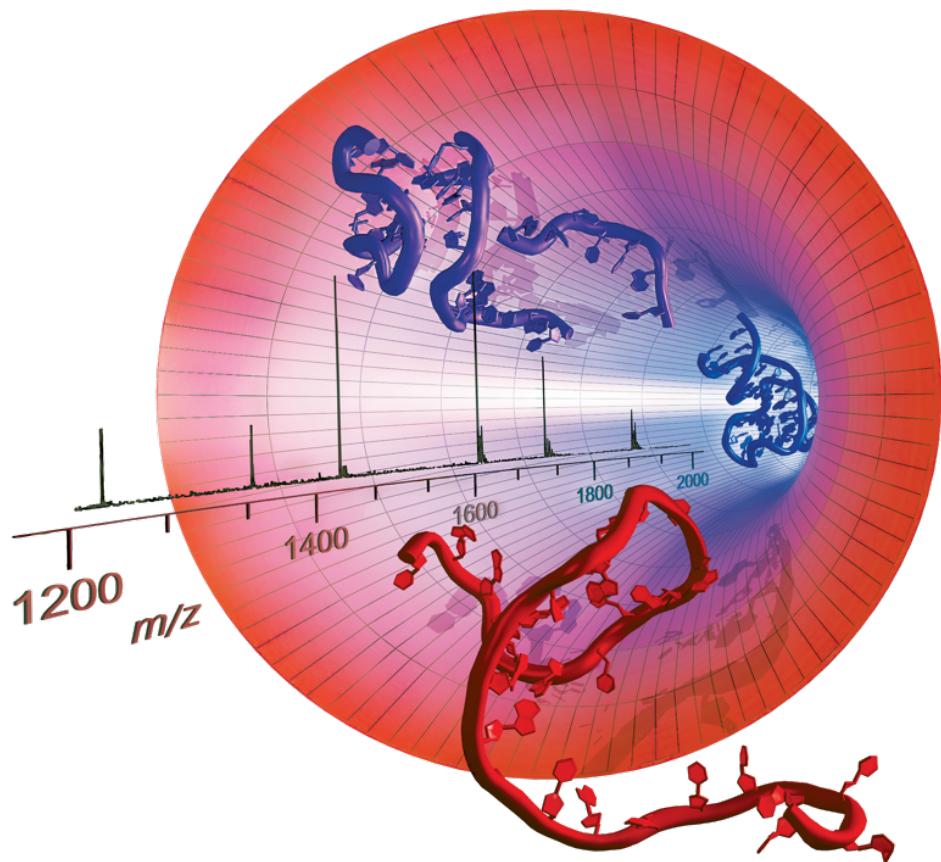


Ions and Photons in Analytical Science

Friday April 22, 2022

ETH Zurich, Hönggerberg Campus
HCI Building, Lecture Hall J7



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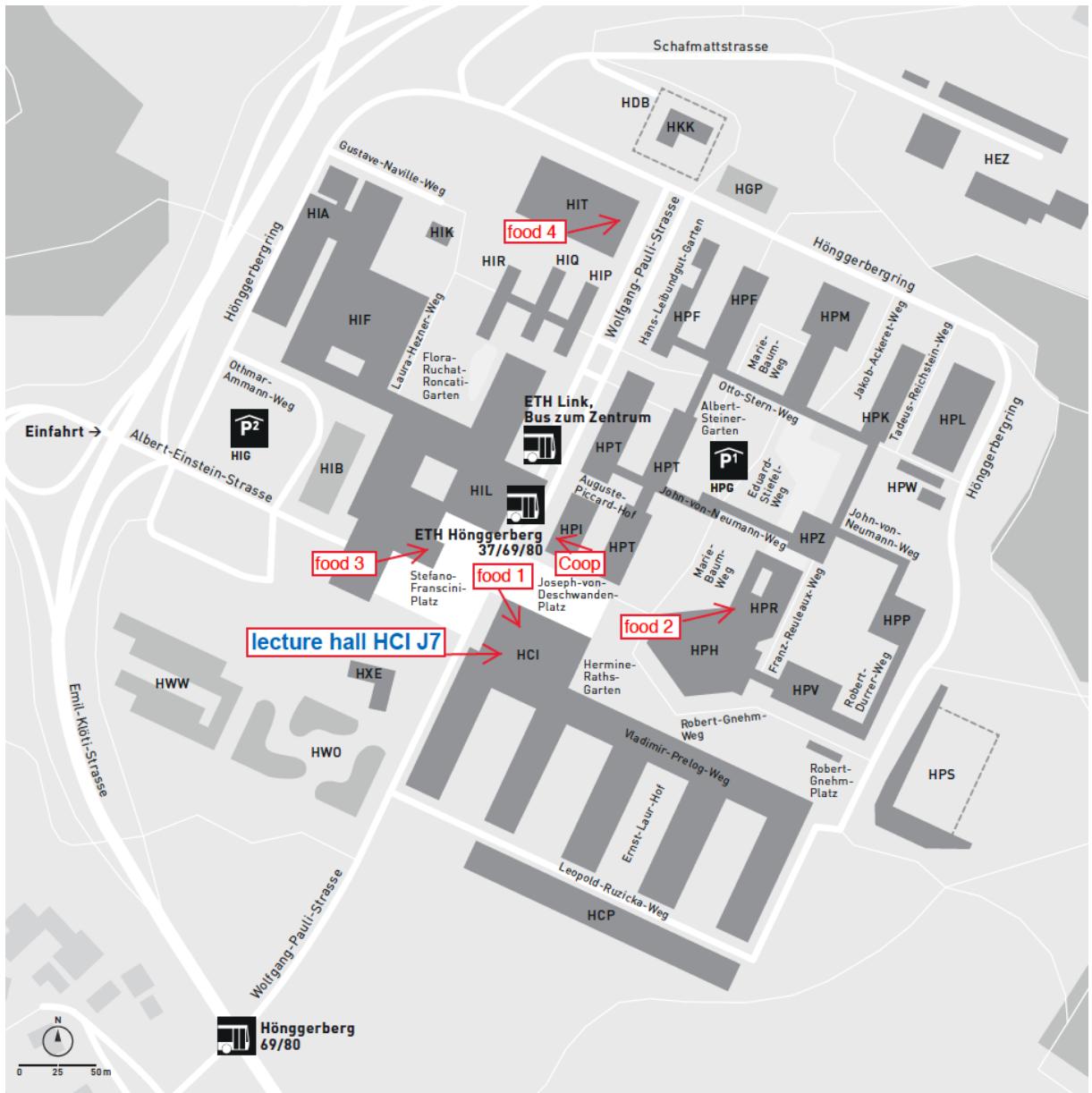
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Practical Information:



Food & Drink

Food 1	Fusion Mensa Fusion Coffee	Menu Classic/Pasta/Hot & cold buffet Bakery/Salad bar/Curries and bowls
Food 2	Counter Rest.	Pizza & Pasta/Grill BBQ, Salad buffet
Food 3	Alumni Bar	Everything in a jar
Food 4	Rice Up	Freshly prepared Asian dishes
Coop	Food store	Snacks, Sandwiches, Salads

Final Program IPAS 2021

Thursday 21.04.2022 / ETH Zurich, Hönggerberg campus / HCI Room H8		
Time	Activity / Title	Speaker
16:15– 17:15	Meet the Editor-in-Chief of <i>Analytical Chemistry</i> : Insights of a Society Journal	Jon Sweedler Univ. Illinois
Friday 22.04.2022 / ETH Zurich, Hönggerberg campus / HCI Room J7		
Time	Activity / Title	Speaker
08:15 – 08:55	Registration / Poster hanging	
08:55	Welcome	Renato Zenobi
09:00 – 09:35	Opening Talk: Fundamental advances and developments for high throughput cell analysis using ICP- <i>Time of Flight</i> Mass Spectrometry	Detlef Günther & Thomas Vonderach ETH Zurich
09:35 – 10:10	All is Analytical chemistry – what can the detection of trace molecules and ions tell us about electrocatalytic processes?	Boon-Siang Yeo Singapore National Univ.
10:10 – 10:30	Mass spectrometric toolkit for skin metabolomics	Pawel Urban Natl. Tsing Hua Univ.
10:30 – 10:50	Coffee break	
10:50 – 11:10	In-situ probing surface reaction using core-shell nanoparticle-enhanced Raman spectroscopy	Jian-Feng Li Xiamen Univ.
11:10 – 11:45	Pushing the limits of proteomics: profiling microbial communities at the protein level	Martin Pabst TU Delft
11:45 – 11:55	Sponsor talk: Vacuum Solutions in Analytical Science	Leybold GmbH
11:55 – 12:15	Poster pitches	Students
12:15 – 13:45	Lunch break / Poster Viewing	

Friday 22.04.2022 / ETH Zurich, Hönggerberg campus / HCI Room J7

Time	Activity / Title	Speaker
13:45 – 14:20	Drop by drop: Analysis of cells at high throughput	Petra Dittrich ETH Zurich
14:20 – 14:55	Ions and photons for good taste and smell	Olivier Haefliger Firmenich SA
14:55 – 15:15	Coffee break	
15:15 – 15:50	Characterisation of Short-lived Components in Atmospheric Aerosols and their Relevance for Air Pollution	Markus Kalberer Univ. Basel
15:50 – 16:25	Atmospheric Chemistry: from Combustion Aerosols to Cannabis Emissions	Vera Samburova Desert Research Institute
16:25 – 17:00	Making Single Cell Mass Spectrometry Measurements High Throughput	Jon Sweedler Univ. Illinois
17:00 – 17:15	Surprise	
17:15 – 17:30	Closing remarks	Renato Zenobi ETH Zurich
17:30 – 18:00	Apéro at Lecture hall	

Detlef Günther & Thomas Vonderach
ETH Zurich

Recent Developments in Laser ablation and Inductively Coupled Plasma Mass Spectrometry



Laser ablation inductively coupled plasma mass spectrometry has become the most widely used technique for fast imaging of a wide variety of materials, including tissues and different types of minerals. The method does not require vacuum and can deal with different sample geometries. However, the fast imaging relies on fast aerosol transport systems and fast detection systems (e.g. Time of Flight Mass Spectrometry), which have been developed and studied in the last decade. Here we report a new system which is based on the tube cell model, 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].

Argon has been the gas of choice for inductively coupled plasma mass spectrometry. However, a recently introduced nitrogen plasma reported for liquid sample introduction [2] has been coupled to a laser ablation system. Here we report first 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, some geometrical modifications on an ICP-MS have been tested to improve the throughput for single cells and nanomaterials [4]. Some details about the system and the current performance will be shown [5].

- [1] C. Neff, P. Becker, D. Günther, *JAAS* 2022, 37 (3), 677-683
- [2] M. Schild, A. W. Gundlach-Graham, A. Menon, J. Jevtic, V. Pikelja, M. Tanner, B. Hattendorf, and D. Günther. *Anal. Chem.* **2018**, 90 (22), 13443-13450
- [3] C. Neff, P. Becker, B. Hattendorf, and D. Günther, *JAAS* **2021**, 36 (8), 1750-1757
- [4] T. Vonderach, B. Hattendorf, and D. Günther *Anal. Chem.* **2021**, 93 (2), 1001-1008
- [5] T. Vonderach and D. Günther, *JAAS* 2021, 36 (12), 2617-263

Boon-Siang Yeo

National University of Singapore

All is Analytical chemistry – what can the detection of trace molecules and ions tell us about electrocatalytic processes?



Currently, more than 80% of the world's energy needs are met by burning fossil fuels. Supplies of these fuels are intrinsically limited and will eventually run out. Combustion of fossil fuels also generates CO₂, an accelerant of global warming. One solution for mitigating atmospheric concentrations of CO₂ is to electrochemically reduce them into fuels. Another is to use H₂ fuel, which can be obtained from water electrolysis. If the electricity used for driving these processes is generated from renewables, we can envisage a fuel production cycle that is closed-loop with net zero carbon emission.

An obstacle to understanding the aforementioned electrochemical reactions is the frequently low concentrations of intermediates and products generated. In this presentation, we try to identify these trace species. Using Raman spectroscopy, we have detected reaction intermediates such as OOH, which allows us to elucidate the water oxidation pathway. MoS_x has been promoted as an earth-abundant H₂-evolving catalyst. We show how the structure of amorphous MoS_x evolved during H₂ evolution. Furthermore, we have identified the S atoms therein as the catalytic-active sites responsible for H⁺ reduction. Density functional theory calculations were performed on a variety of MoS_x structures and corroborated the assignments of the observed vibrational frequencies. We further unveiled the rich chemistry of CO₂ electroreduction by detecting many hitherto-unreported higher-order hydrocarbons and oxygenates, such as those with 4 carbon atoms or more.

Pawel L. Urban

National Tsing Hua University, Taiwan

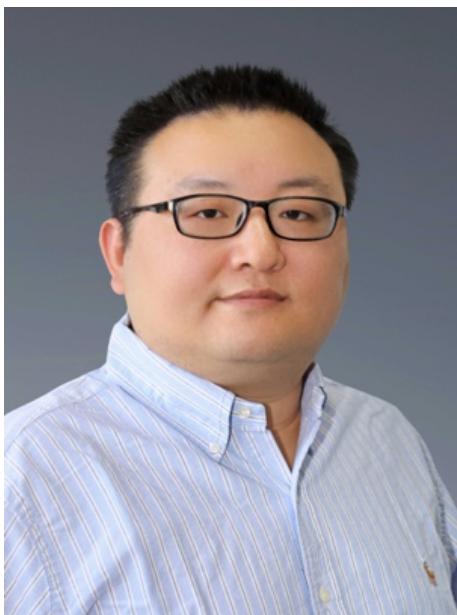
Mass Spectrometric Toolkit for Skin Metabolomics



Sampling and analysis of skin excretions provide a convenient way for non-invasive clinical diagnostics. However, collecting large amounts of sweat for analysis is cumbersome. Fortunately, the amounts of excretion specimens required for analysis by mass spectrometry (MS) are minuscule. Thus, one can avoid inconvenient sweating induction. Our team previously developed hydrogel micropatch sampling, and applied it in analysis of skin metabolites as well as topical drugs applied to skin. In one related study, patients suffering from a skin disease were screened, and several putative skin biomarkers were discovered. In that study, the hydrogel micropatches were analyzed by a customized MS interface based on desorption electrospray ionization. In another variant, we also used liquid microjunction surface sampling probe to re-extract the skin metabolites absorbed by hydrogels. Most recently, we have constructed a “vending-machine”-style robotic system, which can autonomously collect the skin excretions for MS analysis. A sampling probe with hydrogel is held by a robotic arm. The robotic arm manoeuvres the probe to press it onto the forearm of a human subject. Subsequently, it inserts the exposed probe into a custom-made open port sampling interface coupled to an electrospray ion source of a tandem mass spectrometer. Metabolites in the hydrogel are immediately extracted by a solvent liquid junction in the interface, and are analyzed by the mass spectrometer. The ion current of the target analyte is displayed on a customized graphical user interface, which can also be used to control the key components of the analytical platform. While hydrogel sampling is suitable for analysis of water-soluble analytes, we have also developed techniques for real-time detection of volatile organic compounds (VOCs) emanating from surfaces. In one variant, referred to as “PENVOC”, a robotic arm probes multiple points on the surface of a flat specimen (e.g. worn face mask or clothing) at 1-cm lateral interval, aspirating the VOCs that emanate from the specimens. The sampled VOCs are directly transferred to the atmospheric pressure chemical ionization interface of a mass spectrometer. Chemical maps of the VOC cushion above such specimens can then be plotted. The PENVOC has evolved to “mass spectroscope”, in which the operator holds a probe by hand, and approaches the probe to specified locations on human skin. The VOCs emanating from the skin at those locations are aspirated and detected. Overall, the developed techniques enable detection of different types of skin-related analytes in different analytical scenarios.

Jian-Feng Li
Xiamen University, China

In-situ probing surface reaction using core-shell nanoparticle-enhanced Raman spectroscopy



Understanding the fundamental reaction mechanism and the structure-activity relationship at a molecular level is essential for the rational design of efficient materials and devices. Such fundamental understanding is strongly dependent on the surface molecular information of the species at the electrochemical interfaces. Surface-enhanced Raman spectroscopy (SERS) can provide such information with ultrahigh surface sensitivity. However, only a few metals (like Au, Ag, and Cu) with particular nanostructures can generate strong SERS effects, greatly hindering the applications of SERS. To overcome this long-standing limitation, we developed various strategies including the “borrowing” strategy, shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), and SHINERS-satellite strategy, through the fabrication of plasmonic core-shell nanostructures, allowing in-situ SERS studies at electrochemical interfaces. Using these strategies, the dynamic process of electrocatalytic reactions, such as oxygen reduction reaction, hydrogen oxidation reaction, electrooxidation, etc., occurring on model single crystal surfaces or practical nanocatalysts have been systematically investigated. Direct spectroscopic evidence for the key intermediates, such as $^*\text{OH}$, $^*\text{OOH}$, and $^*\text{O}_2^-$, during reactions has been obtained, which is combined with theoretical simulations to uncover the reaction mechanisms or structure-activity at a molecular level. Moreover, the molecular configuration of electrochemical interfacial water on single crystal surfaces and its influence on electrocatalytic performance has been identified. Such findings not only significantly deepen the fundamental understanding of some important energy-related reactions but also open new avenues for in situ studies at surfaces/interfaces.

Martin Pabst

DU Delft, The Netherlands

Pushing the limits of proteomics: profiling microbial communities at the protein level



In nature microbes live and co-operate in complex multispecies communities, ultimately comprising the vast majority of the earth's biodiversity. Microbial ecosystems are responsible for fundamental processes within global biogeochemical cycles and moreover directly impact our well-being through close association with our bodies. A deeper understanding of their composition and metabolic activities is therefore essential in exploring how the biosphere responds to environmental changes, how to engineer microbial communities for industrial applications, and how our individual microbiomes impact health and disease.

The emergence of next-generation sequencing opened new possibilities for the characterisation of microbial communities from natural environments. However, while DNA-based approaches predict microbial diversity and genetic potential, important questions concerning biomass composition and expressed metabolic functions remain unanswered.

Therefore, the large-scale discovery and quantification of proteins from complete microbial communities through mass-spectrometry-based "metaproteomics" provides new perspectives for the field of microbial ecology. However, this emerging approach is challenged by the increased complexity of sequencing data, large reference sequence databases, and the fact that the majority of microbes remain unsequenced to date. This talk demonstrates how advanced metaproteomics approaches (aim to) overcome the above-mentioned limitations in order to obtain orthogonal proteome-level information from natural and engineered microbial ecosystems.

Petra S. Dittrich
ETH Zurich

Drop by drop: Analysis of cells at high throughput



Droplet microfluidics is a powerful method to encapsulate, manipulate and analyze individual cells at high throughput. Most assays in nL droplets, however, are based on fluorescence spectroscopy, which limits the choice of assays and multiplexing capability. Mass spectrometry, on the other hand, allows for label-free detection and identification of multiple components. Recently, we have interfaced droplet microfluidics with matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS). We use custom-made, transparent, indium-tin oxide coated targets, on which thousands of aqueous nL-droplets reside on the surface, covered by fluorinated oil. Analysis of the droplets is performed by optical and fluorescence microscopy as well as by a MALDI-MS imaging system. In this contribution, the use and versatility of the method for various applications in the field of single-cell analysis will be presented. Recently, we have created up to 300 000 hosting sites on a single target plate. Cells are seeded in parallel by exchanging an aqueous cell suspension atop the array with a fluorinated oil. Recording of mass spectra with acquisition speeds up to 15 wells per second is possible for the analysis of selected wells or the entire array. To facilitate facile alignment between microscopy and MALDI-MS data for each microwell, microwells are oriented into a binary-based optical barcode that describes their relative position. Microscopy images are decoded with image processing to determine their location in the array to target during MALDI-MS.

Olivier Haefliger
Firmenich SA, Switzerland

Ions and Photons for Good Taste and Smell



Tasty foods and beverages, and a broad range of products with a pleasant smell ranging from laundry detergent to premium perfumes, play a central role in eliciting happiness in our daily lives. Research to design, develop and continuously improve consumer-preferred flavor and fragrance ingredients and technologies is a complex multidisciplinary endeavor. Analytical scientists are actively involved in most aspects of the effort, looking for answers to a broad range of questions about the composition of matter. This presentation will give an overview of how analytical instruments relying on ions and photons are essential for the task.

Subsequently we will explore less known uses of ions and photons in the flavor and fragrance world. In particular we will show how sunlight can be leveraged to modulate the kinetics of odor release by converting odorless non-volatile precursors to volatile odorants, and its role to degrade ingredients after use and ensure their non-persistence in the environment. We will also provide an introduction to the discovery of novel taste modifiers, a type of research requiring a combination of mass spectrometers and taste buds which both rely on ions for successful detection.

Markus Kalberer
University of Basel

Characterisation of Short-lived Components in Atmospheric Aerosols and their Relevance for Air Pollution



Chemical reactions in the atmosphere are an important factor of the climate system. Greenhouse gas concentrations, for example, or the formation and concentration of aerosol particles are determined by complex chemical reactions in the atmosphere.

Reactions involving a very wide range of (organic) trace gases, emitted into the atmosphere by natural and anthropogenic sources, are often initiated by photochemical processes or are radical-initiated reactions. The identification of short-lived intermediates in such reaction schemes is an analytical-chemical challenge, but they are of key importance to determine reaction pathways in the oxidation cascade of atmospheric trace gases. Radicals and non-radical, oxidising components in aerosols are also suspected to be responsible for negative health effects of air pollution aerosol particles. Analytical method and instrument developments will be presented to characterise and quantify such short-lived reaction intermediates (e.g., Criegee Intermediates) in the gas and particle phase and how such reactive compounds are related potentially related to health relevant particle properties in the ambient atmosphere.

Vera Samburova

Desert Research Institute, Reno/NV, USA

Atmospheric Chemistry: from Combustion Aerosols to Cannabis Emissions



Environmental pollution, especially air pollution, is one of the largest environmental causes of premature death and disease. It also directly relates to local and global climate change. For example, in the past few years, due to global warming, the frequency, size, severity, and intensity of fires have drastically increased around the world. At the same time, we must more thoroughly investigate wildfire organic emissions, their chemistry, and environmental effects. Challenges have arisen in the assessment and control of other environmental organic pollutant sources, such as cannabis grow facilities, indoor household products, fuel combustion, and landfill sites. Analytical organic chemistry is an essential tool for controlling local air pollution events, as well as for researching their health effects and their effects on the global climate and the environment (water, soil, etc.). This talk will be focused on the results of comprehensive chemical characterization of different environmental organic compounds with various analytical tools: Gas Chromatography Mass Spectrometry (GC/MS), Liquid Chromatography Mass Spectrometry (UPLC-MS), and Nuclear Magnetic Resonance (NMR). The results of our research on wildfires, e-cigarette emissions, atmospheric bioaerosols, and cannabis grow facility emissions highlight the importance of speciation, characterization, and control of organic compounds in the environment.

Jonathan V. Sweedler

University of Illinois, Urbana/IL, USA

Making Single Cell Mass Spectrometry Measurements High Throughput



While the need for single cell chemical measurements of heterogeneous brain cells has been well established, the large number of cell types suggests that thousands to tens of thousands of measurements are required to characterize representative cell types in a brain region. Approaches for assaying the chemical content within populations of individual brain cells are highlighted, including mass spectrometry imaging (MSI) and single cell measurements. Using these approaches, we can measure lipids, fatty acids, neurotransmitters and neuropeptides, among others. For the high throughput measurements, the cells of interest are scattered across a microscope slide, the exact cell positions determined via optical microscopy, and mass spectra are acquired only at the cell positions. Because the spaces between the cells are not measured, the approach is efficient and rapid. Using both TOF and ICR analyzers, high acquisition rates and high information content is possible. The single cell assays allow differences in the metabolome and peptidome from supposedly homogeneous populations of cells to be explored. By obtaining information from tens of thousands of individual cells, rare cells are found and unusual neurochemicals are discovered. For select cells, follow-up capillary electrophoresis-mass spectrometry is performed. We are currently adapting the approach to work with individual cellular organelles such as dense core vesicles and mitochondria providing us with more detail on organelle heterogeneity. This has allowed us to characterize distinct populations of vesicles that contain varying peptide hormones. Our overarching goal is to uncover the complex chemical mosaic of the brain and pinpoint key cellular players involved in a range of physiological and pathological processes.