

# Imaging the Chemistry of Materials Kinetics

Andreas Borgschulte, Emanuel Billeter, Alessia Cesarini, Yousuf Hemani, Marco Knobloch, Kevin Kraft, Filippo Longo, Claudia Masucci, Marin Nikolic, Di Qu, and Davide Bleiner\*

**Abstract:** The kinetics of most chemical energy storage and conversion processes is rate-limited by the mass transport through matter. There is an uncertainty on the corresponding kinetic models, especially if based solely on kinetic theory. Henceforth analytical strategies coupled to setups, in order to capture data for overcoming this limitation, are essential. *Operando* chemical imaging of the kinetics process supports the identification of rate-limiting barriers and definition of actionable kinetic insights. After an overview of the chemical and physical processes in various energy storage/conversion systems, and examples of chemical imaging applied on them, analytical challenges are discussed with particular focus on novel methods and fundamental limitations. Despite convincing success technologies, various scientific challenges of *operando* chemical kinetics await solution. Apart from technical improvements of the analysis instrumentation, promising developments are seen in advanced digital science.

**Keywords:** Analytical chemistry · Chemical imaging · Kinetics · Instrumentation



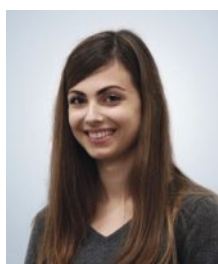
**PD Dr. Andreas Borgschulte** is a physicist with focus on applied spectroscopy. He received his doctorate in physics from TU Braunschweig (D) in 2002. After postdoctoral position at VU Amsterdam (NL) and the Helmholtzzentrum Geesthacht (D), he started exploring the hydrogen world as group leader of the group Hydrogen Spectroscopy at Empa. He shares his ideas and experience as lecturer at University

Zurich and ETH Zurich.



**Emanuel Billeter** obtained his Bachelor's and Master's degrees in chemistry from ETH Zurich. For his Master thesis, he studied highly doped graphitic materials, a material class under investigation for applications in batteries and hydrogen storage, at Montana State University. Since 2018 he is a PhD student in the Laboratory for Advanced Analytical Technologies at Empa, where he studies metal hydride surfaces and catalysis using a custom built surface science system for

*in situ* hydrogenation of metals.



**Alessia Cesarini** studied at ETH Zurich, where she obtained her BSc and MSc degrees in chemistry. During her master studies she approached the field of catalysis with a thesis work on CO<sub>2</sub> conversion to CH<sub>3</sub>OH. Afterwards, she began her doctoral studies in heterogeneous catalysis at Empa in collaboration with the Department of Chemical and Bioengineering, ETH Zurich (Prof. Dr. J. A. van Bokhoven). Her

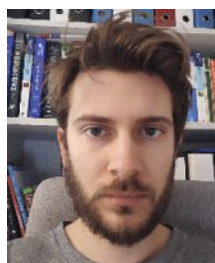
research focuses on developing a new process for the conversion of light olefins in jet fuel range products.



**Yousuf Hemani** has a Master of Science in Photonics from University of Eastern Finland. He did his Master thesis at DESY, Hamburg, and is currently carrying out his PhD thesis at Empa on Tabletop X-ray Absorption Spectroscopy.



**Marco Knobloch** did both his BSc and MSc at the University of Applied Science (ZHAW) in Wädenswil. Since 2019, he is a PhD in chemistry in the laboratory of Advanced Analytical Technologies, Empa, whose research focuses on chlorinated paraffins in the environment, the study of their transformation processes and the development of analytical strategies.



**Kevin Kraft** obtained his BSc in Biochemistry at the University of Zurich. He worked in the group of Prof. Raimund Dutzler on the Inhibition of the prokaryotic divalent metal transporter ScaDMT by nanobodies for his bachelor thesis. He has a MSc in Biochemistry from University of Zurich and did his thesis in the group of Prof. Roland Sigel investigating the folding pathway of a groupIIB intron with smFRET

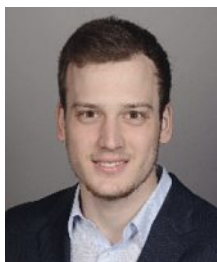
TIRFM. Since 2020 he is a PhD student at Empa.



**Filippo Longo** obtained his Bachelor's degree in Chemistry at the University of Messina with an experimental thesis on H<sub>2</sub>S in petroleum product at the laboratories of Milazzo's Refinery. He obtained his Master's degree in Chemistry at the University of Ferrara. He graduated *summa cum Laude* with an experimental thesis on the synthesis of ruthenium complexes on ruthenium nanoparticles for the photoassisted hydrogen evolution *via* water splitting at the Autonomous University of Barcelona. Since 2021, he is a PhD in chemistry in the Laboratory for Advanced Analytical Technologies, Empa.



**Claudia Masucci** obtained her Bachelor's degree in Chemistry at the University of Rome Tor Vergata and graduated with an experimental thesis on VOC in environmental matrices by headspace gas chromatography at the Italian Air Force. She has a Master's degree in analytical chemistry from the Sapienza University of Rome. She graduated *Summa cum Laude* with an experimental thesis on the evaluation of a portable Raman spectrometer as an analytical tool in the pharmaceutical industry at Universitat Autònoma de Barcelona. Since 2021, she is a PhD student at Empa.



**Marin Nikolic** received his Master's degree in chemistry from the University of Zurich in 2018. His Master thesis focused on the photo-electrochemical water splitting, which he did in the group of Prof. David Tilley. After his Master's, almost two years of industrial work experience followed in Dow AG and in Dottikon ES AG. He started his PhD in late 2020 at Empa.



**Di Qu** received BSc in both civil engineering and geo-environmental engineering at Sichuan University and at TU-Clausthal, respectively. In 2018, she did Master thesis work on nickel-based catalysts for OER in Jülich Forschungszentrum and obtained her MSc in sustainable energy technology at RWTH Aachen. Since 2019, she is a PhD candidate at Empa.



**PD Dr. Davide Bleiner** got his PhD in 2002 at the ETH Zurich in the group of Detlef Günther. He had postdoctoral positions at Empa and University of Antwerpen, and then in 2007 joined the ETH Zurich as Senior Assistant in the Laboratory for Energy Conversion. In 2010 he received an SNF Professorship Grant at the University of Bern. Since 2014 he is the head of Advanced Analytical Technologies at the

Empa. In 2016 he got his habilitation *Venia Legendi* with PhD from the University of Zurich under the lead of Greta Patzke and Roger Alberto. He is member of the graduate school for chemical and molecular science of the University of Zurich. He also teaches classes in analytical science at the ETH and University of Zurich as a Privatdozent. Since 2021 he joined the board of the Division Analytical Science of the Swiss Chemical Society.

## 1. Advanced Materials Processes

### 1.1 Kinetics is Key

The success of modern materials science is a direct consequence of the development of analytical methods. The sought properties of steel, *e.g.* its elasticity and hardness, have their origin in the elemental and crystal structure of the complex material. This example is representative for the structure–performance relationship as the principal scientific question in materials science, sometimes depicted as Ashby plots.<sup>[1]</sup> Historically, the dynamic nature played only a niche role. As an example, in the pioneering work by the father of ultrafast spectroscopy, Ahmed Zewail allocated a time scale of around 100 ns for the martensitic transformation in steel.<sup>[2]</sup> The work received only little attention, because the results do not lead directly to an improvement of the sought properties of the material of interest. This changes drastically when dealing with energy conversion and storage devices as needed for a future renewable energy scenario. Here kinetics plays a crucial role.<sup>[3]</sup>

As a popular example, the kinetic performance of a battery is directly linked to the dynamics of materials transformations. Any insight into the atomistic phenomena is helpful in improving the performance of such electrochemical devices. Modern approaches to high-performance ion-conducting materials now include measurements of hopping rates by solid-state nuclear magnetic resonance (NMR) to be compared to transport measurements.<sup>[4]</sup> Another prominent field of application is (electro)catalysis: *operando* IR spectroscopy has become a standard tool to unravel the reaction mechanisms on liquid–solid and gas–solid interfaces;<sup>[5]</sup> to mention just a few examples.

In addition to empirical improvements of technical parameters such as charging time in batteries or turnover frequencies in catalysis, the aim of *operando* research is to attribute the empirical relationships to elementary reactions. Although most reactions are long known, the identification of the rate-limiting step is painstaking and requires sophisticated analytical tools. An enlightening example is the rate-limiting step in hydrogen selective metal membranes. Depending on the external and internal conditions applied, the rate-limiting step may be diffusion inside the membrane or surface limited at the outer surfaces of the membrane.<sup>[6]</sup>

### 1.2 Kinetics Needs a Picture

An interesting aspect of kinetics is that it is only defined with the existence of an interface. Here, the perturbation of fields and/or matter starts, and thereby defines the time axis. This means that time and space are interrelated. Any method probing the dynamics of a system must thus be dimensionally resolved, either directly by the spatial resolution of the analytical method, or indirectly by the spatial boundaries of the experiment. In reality, there exist quite a range of interfaces such as

- Gas/Solid interfaces
  - Bubbles, Porosity
- Liquid/Solid
  - Fluid or Melt inclusions
- Liquid/Liquid and Solid/Solid
  - Defects, Polycrystals

One-dimensional interfaces (surfaces and interfacial layers) are conceptually most simple, and thus often studied without the exact knowledge of the interface. Many surface science methods are based on the assumption of a flat surface, *e.g.* depth profiling by cycling sputtering/XPS analyses, which is often used even without the ideal geometry as rough approximation.<sup>[7]</sup> For complex interfaces, imaging techniques are indispensable, however.

The type of interface determines the kinetics of mass and energy migration in addition to the physical phenomena such as diffusion, phase transformation, convection, irradiation, growth and self-assembly. In the following, we describe a few archetypical

examples in energy storage and conversion devices depicting the general methodology as well as the challenges accompanying it.

### 1.2.1 Kinetics of Hydrogen Storage

Hydrogen is the ideal energy carrier, if safe and efficient storage is available.<sup>[8]</sup> Hydrogen storage in metal hydrides is a promising solution to this problem, but the performance parameters do not satisfy the need of technical applications yet.<sup>[9]</sup> It is worth noting that the hydrogen storage challenge would be solved if the kinetics of hydrogen sorption in light metal hydrides were sufficient around room temperature. The hydrogen capacity, *i.e.* the hydrogen storage density of a couple of light weight metal hydrides is high enough.<sup>[10]</sup> During hydrogen absorption in classical metal hydrides such as  $\text{LaNi}_5\text{H}_x$  there are various steps involved:<sup>[11]</sup> the dissociation of the hydrogen molecule and the transport of the chemisorbed hydrogen towards the subsurface and adjacent diffusion in the bulk, and finally the phase transformation from the hydrogen solid solution into the hydride phase (and *vice versa*). Hydrogen sorption kinetics is governed by the kind and dimensionality of the interface. At first approximation, one simplifies the geometry to a static, one-dimensional interface (usually the surface). However, some metal hydrides such as  $\text{MgH}_2$  form a transient interface complicating reaction kinetics.<sup>[12]</sup> Most lightweight metal hydrides are so-called complex metal hydride systems, which are composites at least in one hydrogenation state.<sup>[9,13]</sup> The description of sorption kinetics depends on the knowledge of the underlying morphology changes.

Electron microscopy is the standard technique to study the complex structure of archetypal hydrogen storage materials. Most hydrogen storage materials such as Ti-doped  $\text{NaAlH}_4$  consist of agglomerates of particles. It was found that the distribution of elements on the microscale changes markedly after cycling.<sup>[12]</sup>

In the case of the reactive hydride composite  $\text{LiBH}_4\text{-MgH}_2$ , the segregation of compounds takes place on a macroscopic scale, because  $\text{LiBH}_4$  becomes liquid at operation temperatures.

The complexity of hydrogen storage materials perpetuate in the sorption kinetics. Therefore, empirical kinetic analysis methods such as the so-called *Johnson-Mehl-Avrami* model are used.<sup>[17]</sup> Here, the fraction of transformed material  $f$  evolves with time  $t$  as in Eqn. (1):

$$f(t) = 1 - \exp(-K \cdot t^n) \quad (1)$$

In addition to the kinetic constant of the process  $K$ , the model gives a fit parameter  $n$ , which is related to the physical phenomenon (diffusion or phase transformation) and the dimensionality of the interface. This procedure is highly debated because of too many degrees of freedom.<sup>[18]</sup> The scientific discussion would greatly benefit from novel temporal and spatially resolved *operando* methods corroborating the specific outcome of kinetics analyses.

However, currently, time-resolved chemical imaging is studied only on model systems such as metal hydride *thin films* by a variety of imaging methods such as optical microscopy (Fig. 1a), Raman imaging, surface near field optical microscopy (SNOM, Fig. 1b). The aerial resolution of optical imaging is limited by the Abbe limit. This limit can be circumvented by making use of the local near fields, pushing the limit down to 20 nm. The latter was used to follow the hydrogenation of Mg thin films (Fig. 1b). Indeed, in contrast to expectations from kinetic analyses, the hydrogen sorption kinetics does not follow a continuous diffusion but is a stepwise sequential hydrogen absorption in small grains. If sub-micrometer resolution is sufficient, less demanding far field optical methods are powerful tools to follow a variety of time- and space dependent chemical transformations. Although Fig. 1a is only a snapshot of the growing hydride interface in epitaxial yttrium thin films, the image gives a good impression how the hydrogen diffuses along grain boundaries in the material. Such relatively simple optical methods can be extended to yield quantitative information, *e.g.* optical microscopy images reveal hydrogen diffusion coefficients in metal hydrides,<sup>[19]</sup> magneto-optical Kerr microscopy probes hydrogen diffusion in magnetic alloys,<sup>[20]</sup> hydrogen exchange in borohydride by Raman spectroscopy,<sup>[21]</sup> to mention just a few applications.

### 1.2.2 Catalysis for Hydrogen Production and Conversion

Catalysis is a key topic in renewable energy conversion, as the overall efficiency of the round trip cycle of an energy carrier relies on the efficiency of the individual conversion steps, *e.g.* from electricity to hydrogen, further refinement of hydrogen into other renewable fuels, chemical storage, and back conversion into electricity, mechanical work, or heat. The corresponding reactions are catalyzed by well-developed catalysts. Such catalysts are complex materials. Obviously, imaging methods are crucial to characterize the structure of the catalyst from the micro- to the macroscale.<sup>[22]</sup> In addition, chemical imaging helps to identify the active sites, particle size and distribution, and changes during catalysis such as segregation and coking (Fig. 2). Classical catalysis research focusses on the identification of intermediates at a catalyst's surface, usually by non-imaging *operando* spectroscopy such as diffuse reflectance infrared FT Spectroscopy (DRIFTS) and inelastic neutron scattering (INS).<sup>[23]</sup> However, the distribution of adsorbates during catalysis follows temporal and spatial patterns, first recognized by pioneering work of the Ertl group<sup>[24]</sup> on a mesoscopic scale, phenomena, which require temporally resolved chemical imaging.

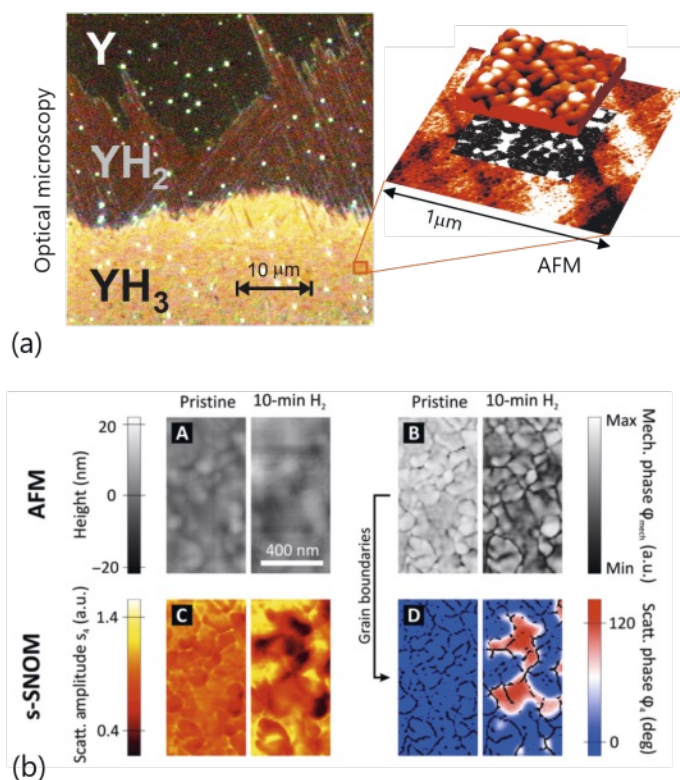


Fig. 1. *Operando* chemical imaging of hydrogenation in metal hydride thin films: (a) optical micrograph of a hydrogen diffusion front in yttrium thin films loaded from the bottom.<sup>[14]</sup> The hydrogen uptake in yttrium thin films needs a catalytic coating made of Pd-nano particles.<sup>[15]</sup> (b) AFM and SNOM picture of free standing thin Mg films showing the switching of grains as small as 20 nm.<sup>[16]</sup>

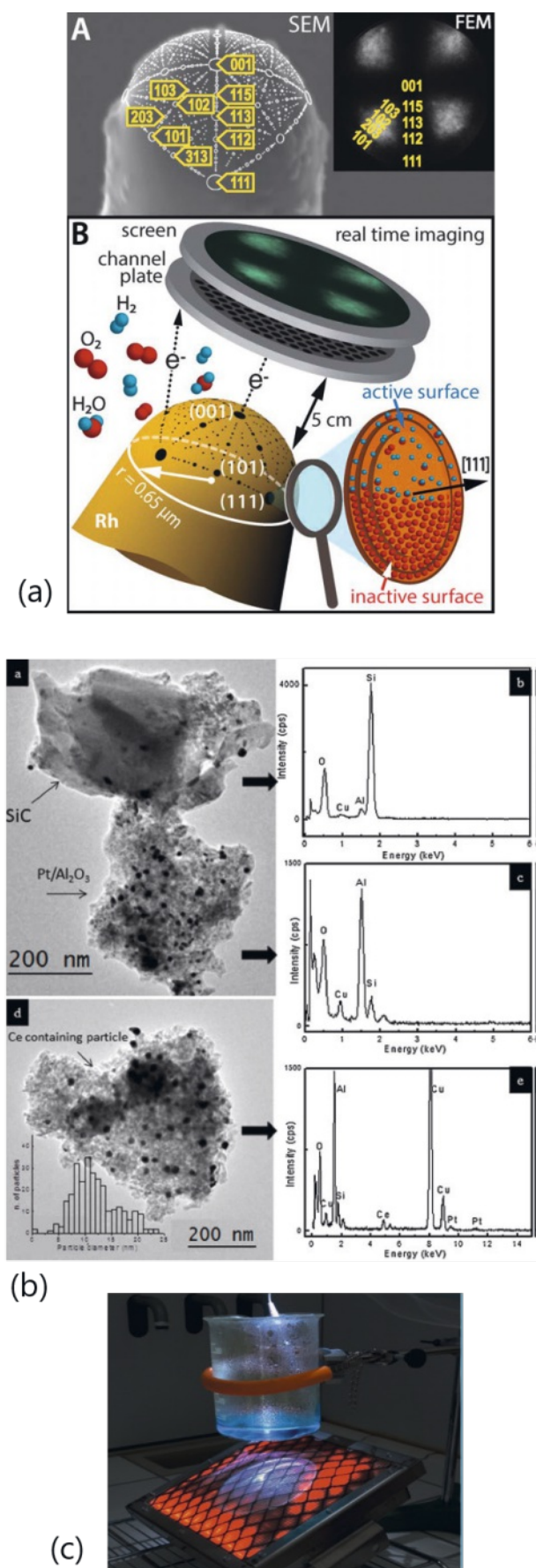


Fig. 2. (a) *Operando* chemical imaging of kinetic oscillations during hydrogen combustion on a single particle.<sup>[25]</sup> (b) SEM picture of hydrogen oxidation catalyst and EDX-spectra indicating the distribution of noble metal catalyst and oxide support.<sup>[26]</sup> (c) Catalytic hydrogen burner. In addition to the designed catalyst shown in (b), a special reactor design is needed for full conversion.<sup>[27]</sup>

Recently, such patterns have been observed also on the atomistic scale for the hydrogen oxidation reaction (Fig. 2a) on a single noble metal particle. The spatial structures translate into temporal oscillations of the reaction indicating a subtle interplay of the occupation of sub- and surface sites. The effect limits the full conversion of this simple exothermic reaction, despite using one of the best catalyst material available. For applications such as catalytic hydrogen burners, catalytic particles are usually deposited on oxide supports, which in addition to being a simple mechanical support seem to promote the reaction kinetics. *Operando* chemical imaging has helped in clarifying the role of the oxide, in particular to follow hydrogen spillover promoted by some, but not all oxides.<sup>[28]</sup> Full conversion for efficient heat generation needs sophisticated catalytic burner setup (Fig. 2c) using the optimized catalyst shown in Fig. 2b.

Heat generation is a relatively simple conversion method, more demanding is the conversion of chemical energy into electricity and/or mechanical work. Here, fuel cells are very promising, relying on efficient electro-catalysts embedded into gas diffusion electrodes and ion conducting membranes. Imaging techniques have long supported the development of conventional fuel cell components<sup>[29]</sup> as well as novel developments such as cataluminescent energy conversion.<sup>[30]</sup> The study of electro-chemical interfaces is the challenge par excellence. Although not different from a fundamental point of view, the chemical imaging of the liquid-solid interface is most challenging.<sup>[12,32]</sup>

### 1.2.3 Chemical Engineering

Eventually, the power performance of an energy conversion device, be it a catalytic reactor or a fuel cell, is determined by the kinetics over all length scales from the atomistic catalyst to the macroscopic mass and heat transport on the meter range. The direct visualization of mass flow, concentration of reactants, intermediates and products, and the density of active catalyst supports the design and optimization of large-scale reactors, which corresponds to chemical imaging on a large scale. Currently, imaging by probing the proton by nuclear magnetic resonance (MRI) and by neutron scattering has generated striking results.

Bouchard *et al.*<sup>[31]</sup> studied the hydrogenation reaction of propylene to propane by hyper-polarized MRI imaging (Fig. 3a). The imaging analysis provides the spatial distribution of the conversion and the flow field (not shown) and thereby the distribution of the active sites in the catalyst. Similar analysis was applied on industrial catalyst monoliths and related technical structures.<sup>[33]</sup> The power of the MRI method is clearly the differentiation of different chemical states of hydrogen (*e.g.* propane from propylene). A drawback is the long measurement time required. Here, time-resolved neutron imaging is advantageous with demonstrated time resolution in the ms range both for periodic as well as non-periodic phenomena. Imaging by neutron scattering has difficulties in distinguishing chemical states, although also this is possible. Its great advantage is the compatibility to the harsh conditions present in catalysis,<sup>[34]</sup> heat storage<sup>[35]</sup> and fuel cells.<sup>[29a]</sup> As an example, Fig. 3b shows the time and space resolved evolution of the water produced during sorption enhanced methanation in a 40 cm long prototype reactor.<sup>[32]</sup>

## 2. Imaging Data for ‘Actionable Insights’

Seeing is believing. Tracking kinetics actions across a material involves multiple critical dimensions, such as: *what* chemistry does one observe, *how much* of it, *where* it is located and/or transported, and *when* and *how long* that chemistry happens. Being able to pattern the spatial and temporal dimensions with the required accuracy and precision permits to relate the observed structures to a function, and from there to the dynamics of a material process.

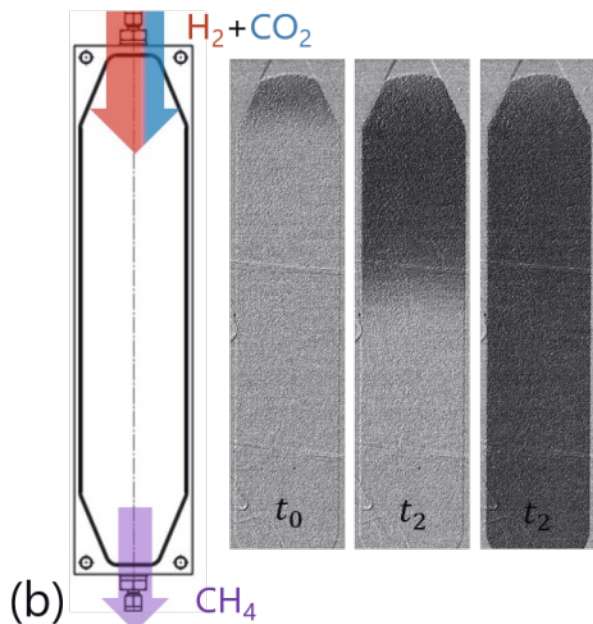
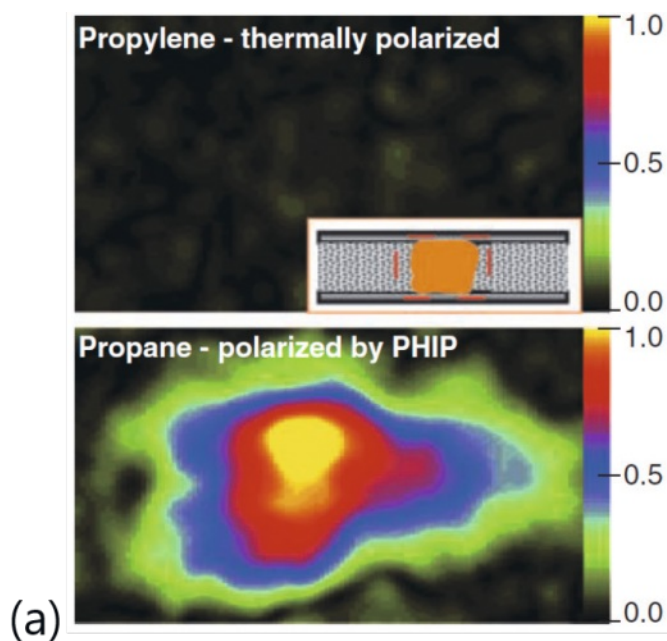


Fig. 3. (a) MRI image of thermally polarized propylene (top panel). The approximate position of the imaging field of view is indicated by the dashed red lines in the inset showing the reactor setup. The bottom image shows p-H<sub>2</sub>-polarized propane. From ref. [31]. (b) Time resolved neutron images of the water accumulation in a sorption enhanced methanation reactor.<sup>[32]</sup>

A number of techniques are available for capturing data on some of these particular phenomena (Fig. 4). The utilization of existing measurement methods is *analytical technology*. However, the creation of a methodology for the reliable experimental use of it or for a task beyond state-of-the-art, is the research subject of *analytical science*. This is an important aspect to highlight, because while many popular techniques are commercially available, those discussed here are at research level. While the layman perception of ‘analytics’ overemphasizes the technological aspects of data capturing, the science of measurement is make or break.

Analytical science is in transformation. Traditionally it was all about determining robust linear (Pearson’s) coefficients to calibrate and quantify. Modern analytical science focuses on the design and evaluation of methods for extracting non-obvious chemical patterns. The emergence of underlying structures is another

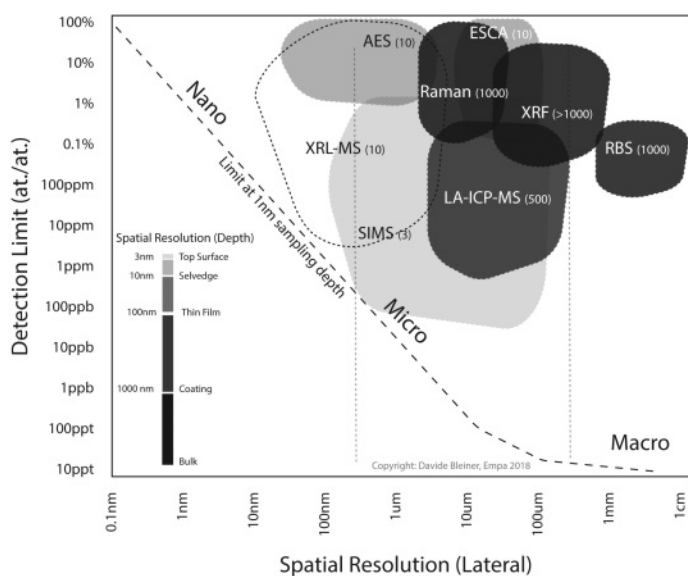


Fig. 4. Selection of popular microanalytical techniques with respect to their lateral resolution and detection limit (in parenthesis the approx. depth resolution is given in nm). One notes that there is a Poisson limit in the bottom left corner. Legend: AES: Auger Electron Spectroscopy, ESCA: Electron Spectroscopy for Chemical Analysis (aka XPS), LA-ICP-MS: laser ablation inductively coupled plasma mass spectrometry, RBS: Rutherford Backscattering Spectrometry, SIMS: Secondary Ion Mass Spectrometry, XRF: X-ray Fluorescence Spectrometry, XRL-MS: X-ray Laser Mass Spectrometry.

essential aspect to frame the kinetics and purity of a material. The retrieval of ‘actionable insights’ is not a consequence of a technology. Analytical science is the active part of a measurement method, to stand out between a data-modelling and a process-modelling approach.<sup>[36]</sup>

On the road towards analytical science innovating analytical technology, one begins with ‘real-world’ domain-specific questions. Domain expertise always guides the analytical scientist. The design of an analytical solution, centered on data generation and processing, must abide by a few fundamental limits. Obviously, materials scientists wish for unlimited power in figures of merit, such as sensitivity, resolution, dynamic range, spectral range, and also tool access. An educated scheme provides a way to address problems in imaging the kinetics of materials that have a potential impact.

Furthermore, characteristic scales of analyte heterogeneities, *i.e.* whether major, minor, trace or ultratrace, over order of magnitudes in space (nano, micro, macro) or time (femto, nano, milli, *etc.*) represent a deeper insight than a bulk analysis with extremely high accuracy and precision. Non-dimensional analysis on migration processes utilizes data matrices to operate with state-of-the-art digital techniques.

Henceforth, the times of classical materials analysis as started by lab bench luminaries such as C.R. Fresenius<sup>[37]</sup> are over and restricted to routine analysis. A combination of semi-quantitative and smart techniques can lead to unprecedented insights in materials science, out of reach for the classical ‘zero dimensional’ wet analysis of the bulk.

A final point to be mentioned in analytical research, is the environmental impact of an analytical laboratory. Anastas<sup>[38]</sup> published more than twenty years ago the twelve principles of green analytical chemistry and further updates. It is imperative, also for the analytical lab, to take concrete action to minimize the use of chemicals and carbon footprint, especially if this converges with a scientific advancement of the field.

Making ‘impossible’ measurements possible is the result of worldwide research to overcome the limits. International research

institutions, *e.g.* NIST, NIMS, BAM, ISAS, ETH, EPFL, *etc.* as well as research groups at Universities (*e.g.* see the power list of the magazine *Analytical Scientist*, that featured our group in the 2019 survey) are investing significant funding. It is important that Switzerland keeps its leading position, which is the effort of the Division of Analytical Sciences (DAS) of the Swiss Chemical Society.

## 2.1 Chemical Visualization at its Limits

While analytical technology (*i.e.* the instruments you bought for your laboratory) has reached a high level of capability, some chemical insights are still beyond the state-of-the-art. In the following, a few exemplary cases are shown that indicate current limits in the possibilities for chemical analysis. As much as *domain* materials science makes progress by trial-and-error on a given structure or compound, so the analytical scientist has to create and validate new inspection methods combining theory and experimentation.

### 2.1.1 Limited Detection Power at Nano-Scale

The shrinking of sampling to nano-scales has a major impact on the capability to detect chemical components. The reduction of sampling cardinality obviously drops the mean signal. As quantification depends on counting statistics, there is often insufficient counting to keep up the sensitivity at the nano-scale. For secondary methods, diluted components may be handled by a more prolonged signal accumulation. In direct microanalysis this is not possible because the measurement process is destructive. The bracketing sensitivity ( $s$ ), which is the slope of the calibration curve (*i.e.* signal per analyte amount) predicts the detection limit (DL) as follows (Eqn. (2)):

$$DL = \frac{3\sqrt{\sigma_o^2}}{s} \quad (2)$$

where  $\sigma_o^2$  is the variance of background noise. The variance is related here to instrumental uncertainty, and must be distinguished from  $\sigma_1^2$ <sup>[39]</sup> that is the variance associated to the objective material heterogeneity. Ideally, one needs  $\sigma_o^2 \ll \sigma_1^2$  to be able to map the chemical inhomogeneity, especially for defect inspection and/or local kinetic processes. As shown elsewhere in detail,<sup>[40]</sup> the sensitivity scales inversely with the sampled volume, especially at nano-scale, such that at high spatial resolution the DL is always degraded. Henceforth, for a given depth and width of mass sampling, one can predict what is the ultimate limit of detection with the available Poisson counting. Such DL may be further degraded if the instrument has a noisy readout and/or the material is porous, which further lowers the counting.

Therefore, besides the enhancement of the sensitivity, it is essential to develop strategies for the sinking of the instrumental noise  $\sigma_o$  and approach the theoretical Poisson detection limit ( $DL^\circ$ ). In fact, the ultimate limit is estimated by Eqn. (3):

$$DL^\circ \sim \frac{A}{m} \sigma_o 10^{-24} \quad (3)$$

where  $A$  is the molar mass and  $m$  is the sampled mass. Experimental DL's are typically orders of magnitude higher than  $DL^\circ$ .

Led by this consideration, our group managed to improve the detection limit of laser-induced breakdown spectroscopy (LIBS), a rapid and spatially resolved technique. Our approach was not based on trying to enhance the sensitivity, as traditionally done.

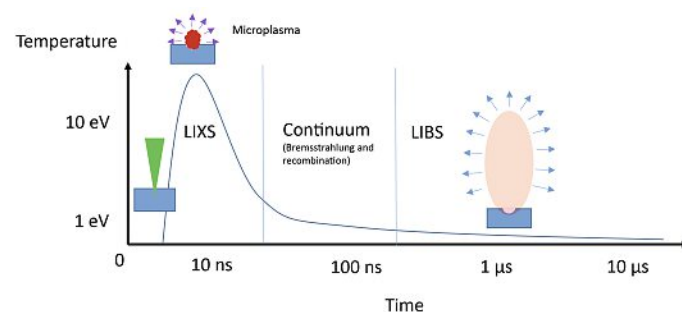
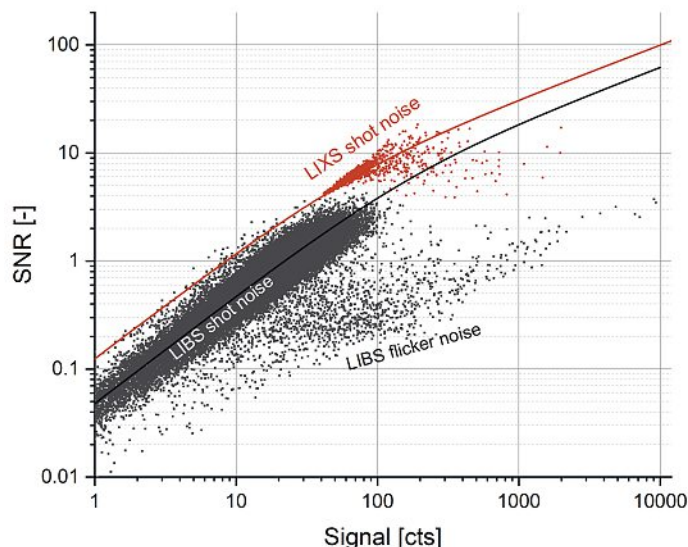


Fig. 5. Top: Noise structure in LIBS vs LIXS. The noise structure is composed by a Poisson component of shot noise and a flicker component given by the laser-induced plasma fluctuation. Bottom: Qualitative profile of the temperature evolution in laser induced plasma. The temperature increases rapidly in few ps, and as the plasma expands the temperature drops. In the early stage, the plasma emits X-rays, and over ns and longer the emission red-shifts into the optical domain.

Rather, the method looked to drastically sink the instrumental noise. It must be said that noise in LIBS comes both from the count rate and breakdown plasma expansion (Fig. 5, top).

A substantial background reduction is possible by means of shifting the observation to the short wavelength emission, *i.e.* soft X-rays. This emerges in the early stages of the laser-induced plasma breakdown. Fig. 5 summarizes this new approach and results published by Qu *et al.*<sup>[41]</sup> show the benefits for the characterization of Li and F in precursor materials for batteries. This technique using soft X-rays detection has been called LIXS as an evolution of the acronym LIBS.

### 2.1.2 Matrix-Effect Limited Dynamic Range

Besides pushing the detection power for high purity and contamination inspection, analytical science has another challenging application: predicting the upscaling behavior of materials inspected at the lab scale. Research done on small 'test model' samplings should serve as a template for large-scale implementation. The classical reductionist's approach to extrapolate linear effects has been shown to be very limited. The transfer to industrial plants is one such example, *e.g.* the up-scaling of the sorption enhanced methanation discussed in section 1.2.3, and direct air capture functionalized polymers installed into 24/7 demonstrators. The complexity of data structure makes important properties evident at macro-scales (so-called *emergence*). In fact, data are generated through a process of abstraction. 'Captured data' are *per se* not more objective

than ‘exhaust data’, but the analytical scientist equipped with all necessary domain-understanding can ‘sense check’ and test null hypotheses (see the ‘DIKW’ pyramid from T.S. Eliot 1934<sup>[42]</sup>).

The possibility of multiscale observation requires a dynamic range. The alternative of sample dilution and/or pre-concentration, as known in wet analytical chemistry, is less attractive for materials science, if at all possible. It would require practices of sample extraction and/or digestion that would homogenize the bulk. The minor deviations that cannot be observed or statistically consolidated in the test model may turn out to cause degradation and plants may stop working. The rapid investigation approach that is typical of academic as well as industrial research is often at odds with the need for consolidated data over the full life cycle of a material. For that, one needs dynamic range to be able to track phenomena over a wide magnitude range. It is also noteworthy to mention that an extension of the dynamic range implies a reduction in sensitivity.

A further challenge is that of linearly consistent and concomitant analysis of major, minor and trace/ultratrace components. The combination of trace and major components may induce substantial *matrix effects*, with the occurrence of non-linearities. The latter makes the quantification less robust.

For students, it is often difficult to visualize the nature of matrix effects, and how these affect a measurement. One can argue that in simple terms it is about the collective chemical interaction between atoms and molecules in materials. Each material has its chemistry, which turns out into different matrix effects. In fact, using a classic example from optical spectroscopy, a physical treatment can help visualize this aspect.

Following the discussion by Mayerhöfer *et al.*<sup>[43]</sup> one can trace a quantitative relation between the concentration and the absorbance with full physical insights on the molar oscillator strength, damping constant, and frequency. While Beer’s law predicts a linear relation between the dielectric function and the concentration, this linearity is not generally transferred to the index of refraction. The complex index of refraction is not a property of matter (as the dielectric function is) but a property of light waves in the respective materials.

Indeed, the molar attenuation coefficient is itself a function of concentration, oscillator strength and oscillator displacement. Therefore, Beer’s law is a special limit of the physical framework, which does not hold in the detailed case of kinetic interactions as investigated within a chemical framework. Analytical research must thus address matrix effects as the rule, rather than as an empirical exception.

### 2.1.3 Limited Imaging Resolution at Ultrafast Time-Scales

The capability to visualize the distribution of chemicals provides unique insights on diffusion, heterogeneity and zoning, and also the onset of degradation. Chemical visualization can be carried out with two complementary approaches: (i) mapping or (ii) imaging. While the layman language tends to confuse them, they are substantially different based on instrumental grounds (Fig. 6).

Mapping is the process of spot by spot sequential capturing of spatially zero-dimensional signals, which are then post-processed to reconstruct the 2D/3D spatial distribution. On the other hand, imaging is the process of full field simultaneous projection of 1D/2D signals by a transfer function to a block storage.

While the spatial resolution in mapping depends on the *sampling* spot size, in imaging it is dictated by the *detector* pixel size. While the field of view in mapping is dictated by the scanning range, in imaging it is dictated by the collection aperture. Finally, while the spectral skew in mapping is given by the scanning step, in imaging is the exposure lapse. *Spectral skew* is the offset between data points nominally attributed to the same instant, but experimentally collected in different ones.

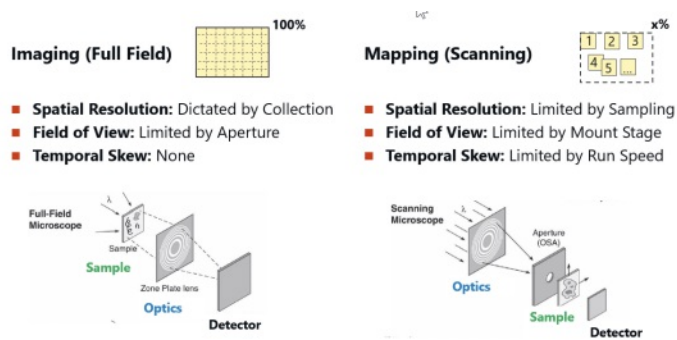


Fig. 6. Chemical visualization methods, by means of imaging (full field capturing) or mapping (scanning capturing). Note the differences in what determines the resolution, the field of view and the temporal skew.

In general, mapping is more flexible when the characteristic time scale of the chemical process is long. Imaging on the other hand, is more suitable for a snapshot analytics, *e.g.* in *operando* spectroscopy. In summary, imaging techniques do not produce significant temporal dispersion but a non-negligible spatial dispersion due to the collection bandwidth and geometry. Therefore, a special class of imaging techniques, so called ‘*lensless methods*’<sup>[44]</sup> tend to overcome this bottleneck by means of a computational retrieval of the object from a coherent diffraction pattern.

A further point is about the temporal resolution and the ability to collect chemical movies. Chemical movies are extremely insightful in kinetic studies. The so-called time-bandwidth product, *i.e.* the fact that all the shortest is the exposure time, the wider is the collection bandwidth is a fundamental limit, which could be traced back to the uncertainty relation.

Fig. 7 shows how the spectral resolution of a selection of advanced sources for optical spectroscopy distributes as a function of the pulse duration. One sees that there is a fundamental trade-off given by the Fourier complementarity between the exposure time and spectral bandwidth. Therefore, corresponding figures of merit can be indicated, and depending on the specific analytical requirements, one approach or the other will turn out more suitable.

One important point is the distinction between differential and integrative methods. The former are often non-destructive, while the latter mostly offer better resolution while the sample consumption is to be taken into account.

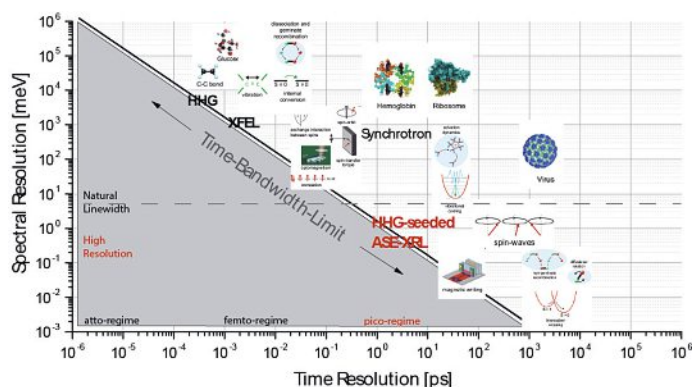


Fig. 7. Time-bandwidth limit that shows a tradeoff between spectral resolution and temporal resolution. Below a fundamental limit there is no possibility to measure. Depending on the source type, specific chemical applications can be accessed. Legend: ASE-XRL: Amplified Spontaneous Emission X-ray Laser, HHG: high harmonic generation, XFEL: X-ray Free Electron Laser.<sup>[45]</sup>

The down-scaling of the object size is not only a limitation for the analysis, rather it is an objective limit also the operation of devices at ultrasmall scale. For instance, the so-called ‘*Boltzmann tyranny*’<sup>[46]</sup> defines the fundamental thermionic limit of the sub-threshold swing of a MOSFET at 60 mV/decade at room temperature, and therefore precludes lowering of the supply voltage and the overall power consumption.

As the magnitude approaches the quantum scale, the resolution is not a simple continuum function of the means, but is sensibly driven by the variances and covariances. As analytical instrumentation is a system of electrical and mechanical components, these challenges are also important for the realization of high-performance and miniaturized devices. The use of short wavelengths has pushed the scaling down of the spatial resolution in both microscopy and lithography.

As discussed elsewhere (see ref. [47]), we have developed a unique setup for the generation of X-ray laser lines on a tabletop. State-of-the-art X-ray lasers are attached to particle accelerators, of hundreds of meters in size. The system developed in house has a footprint of approx. 20 m<sup>2</sup>. The main characteristic is that of the ultranarrow linewidths of  $\Delta\lambda/\lambda < 10^{-5}$  that corresponds to less than a meV. Such narrow lines are important for high-resolution spectroscopy and/or Raman spectroscopy in the X-ray. As the pulse duration is ps to ns, the exception linewidth combines with a high temporal resolution for a large number of chemical processes in materials science.

#### 2.1.4 Limited Duty Cycle for Non-Target Analysis

Performing an analytical measurement is not an open survey process to explore the sample. It is instead a statistical experiment, testing a null hypothesis. Therefore, order of magnitude knowledge on the compounds is essential to orient the search. So-called *target* analysis is thus effective and efficient to produce *quantitative* information. On the other hand, the time-consuming and poorly sensitive survey screening of an unknown material, as it is done in *non-target* analysis, is mainly leading to *qualitative* information.

The extraction of information is split over the channels of the measurement: if the analyte menu is large, the duty cycle will suffer. The duty cycle may be limited by instrumental factors, *e.g.* filtering, scanning, latency, data transfer, *etc.* but also by materials factors. For instance, the collection of fluorescence (whose pulse duration is shorter than a few nanoseconds), using a detector integrating over several microseconds, suppresses the average count rate.

Maximization of the duty cycle is a recurring challenge in analytical science. Adaptive collection, for instance, makes sure that one captures the data *full bin*. This overcomes the tradeoff between filtering for high resolution and scan density. The optimization of duty cycle is of course limited because the setup has physical dimensions, *e.g.* detector size, frame rate.

As discussed in section 2.3.2, a novel concept of charged particle detection, *i.e.* electrons and/or ions, has been patented in our group.<sup>[48]</sup> The particles are detected by means of an inductive image current picked up by a Rogowski-like coil. This technology, called hollow-core toroidal (HCT) coil, permits the simultaneous determination of the full range of analytes at 100% duty cycle. The transient signals are Fourier Transformed (FT) and calibrated, in order to obtain a kinetic energy spectrum (electrons)<sup>[49]</sup> or a mass-to-charge spectrum (ions). The enhancement of the duty cycle is thereafter not in tradeoff with the resolution, which depends on the duration of the transients.

#### 2.1.5 Limited Dimensionality for Target Analysis

Research to minimize the measurement uncertainty is important to improve the detection power, as discussed in section 2.1.1. Yet, there are cases for which a higher accuracy and precision on the signal does not provide any further insights. For instance, in the analysis of isomers, should chloroparaffins of different chain lengths be banned as toxic persistent organic pollutants or not.<sup>[50]</sup> Any elemental and/or molecular determination of isomers, *e.g.* by means of mass spectrometry, would not directly distinguish one from the other, especially if these occur as mixtures and undergo extensive fragmentation in the source, *e.g.* electron impact. The enhancement of the figures of merit, *e.g.* mass resolution, would improve the quality of the signal, *e.g.* better peak attribution, better sensitivity, *etc.* but would not offer unambiguous insights on the structure and specific compound.

Either one obtains additional dimensions of analysis to be able to distinguish one isomer from another, by means of *external* data (*e.g.* fusing data with NMR, diffraction, *etc.*) or by means of multiplexing the *internal* data stream, such as collecting inline the collisional cross section as done with ion mobility cells. A fundamental is thus identified, which is not quantitative, as in the previous sections, but is binary: the information is accessed or not.

The community has adopted the term ‘*Bounty Rule*’ to refer to this rule of thumb: “*never trade analytical dimensions for precision or accuracy*”. Historically, the Bounty was a sailing cargo vessel whose part of the crew, following a mutiny and turmoil, were set adrift in the Pacific for several years. At that time technology had made significant progress to determine the longitude with high accuracy, while this did not allow the accurate positioning of a ship. With the introduction of triangulation (further dimensions!), it became easier to spot the position of a ship even under modest precision.

The modification of commercial instrumentation can open new horizons on measurement capabilities. For instance, in collaboration with international partners an ion trap instrument was modified to carry out ion mobility measurements. These modifications permit to determine the collisional cross-section with a mobility resolution of 100,<sup>[51]</sup> and with that obtain hints on the structure. In fact, the aerodynamic cross section of two homologues with different structure may be very different, and with that their ion mobility. This adds one new dimension to the one of collecting a mass spectrum.

Furthermore, many compounds comprise numerous isotopologues whose isotopic patterns can partition using field-asymmetric ion mobility spectrometry (FAIMS) spectra in a manner dependent on the ion geometry and buffer gas composition. Kaszycki *et al.*<sup>[52]</sup> showed that the resulting multidimensional matrix of isotopic shifts is specific to isomers, providing a fundamentally new approach to the characterization of chemical structure.

Combination with flexible sample introduction techniques, *e.g.* X-ray laser,<sup>[40,44,53a,b]</sup> or ionization, *e.g.* CAM<sup>[54]</sup> opens new dimensions on the chemistry during the measurement itself. This is a substantial change of approach from state-of-the-art. Traditionally, off-line sample preparation was opposed to *in situ* direct microanalysis. The possibility to chemically manipulate the analyte during the analysis makes the execution of the analysis much more tunable.

Here a further benefit emerges that new analytical dimensions help one tune and extract additional information.

#### 2.2 Digitally Overcoming the Limits

While the various discussed limits are often extremely complex on an experimental way, digital techniques have opened new ways. Although chemometrics is a 50 years-old discipline, its practical deployment at the fingertip of every analytical scientist is a very recent outcome, not as the consequence of new methods, rather because of the cheap availability of remarkable computational power in every laptop.



While the coverage of this field is an extensive task, beyond the scope of this paper, a few examples can highlight the impact and benefits for analytical research.

### 2.2.1 Data Compression Methods

Everybody is familiar with algorithms for the compression of images (jpg) or audio (mp3) for the sake of portability of data files. Similar methods can be applied to analytical signals upon data collection. This is not only important to reduce the data load (to oppose the increasing data deluge) and CO<sub>2</sub> footprint of measurements (data storage needs power), but also to shrink the so-called time-to-insight (TOI). Time-consuming data collection procedures are not only inefficient, but can impede the obtainment of crucial kinetic information, when the *chemical time scale* is faster than the acquisition time scale (thus causing spectral skew).

In an attempt to overcome such limitation, undersampled data obtained in probing shots are processed by a self-written code to retrieve the entire signal (Fig. 8).

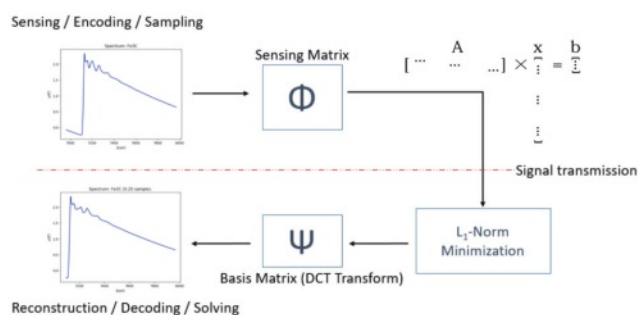


Fig. 8. Compressed sensing procedure to capture an analytical signal by undersampling, and then reconstructing the full signal.

### 2.2.2 Data Kernel Methods

A number of fundamental limits have been discussed above. While some of them are physical barriers associated with the existing measurement fundamentals, the obtainment of the associated insight may not be necessarily precluded. In fact, statistical and chemometrical processing of the available primary data, can help to extract information on a meta-level, with a given confidence.

For instance, the range of commercial techniques for high-resolution gas-chromatography mass spectrometry (GC-MS) has grown with the introduction of Orbitrap FT-MS. Progress with quantitation performance in the analysis of persistent organic pollutants (POP) was reported,<sup>[55]</sup> by averaging of time-domain *transients*, from a number of replicates. Compared to a standard single GC-FTMS experiment replicate, sensitivity improvement of up to 1 order of magnitude was demonstrated. Concomitantly, the increased flexibility in ion signal detection allowed the attainment of ultrahigh-mass resolution approaching  $m/\Delta m \sim 700\,000$  at  $m/z = 200$  Th (Thomson is the unit of mass-to-charge). This makes for a  $\Delta m \sim 0.3$  mTh, which is impressive if one thinks that 0.5 mTh is the mass of an electron. This indicates that mass spectrometry may have overcome a limit to weigh electrons besides ions!

Another example is given in microanalysis of porous materials (Fig. 9). The 3D reconstruction of distribution of elements in a CZTS layer used for photovoltaics was investigated (Fig. 9). As a fundamental limit given by the Poisson criterion, the reduction of the spot size degrades the detection power. The former is important to improve the spatial resolution. In granular samples with a high porosity, it is important to have a small spot size to capture the effective fabric. This tradeoff was overcome by means of a combination of experimental data and computational analysis. The kernel was the collected  $10 \times 10 \times 10$  3D-matrix of data with

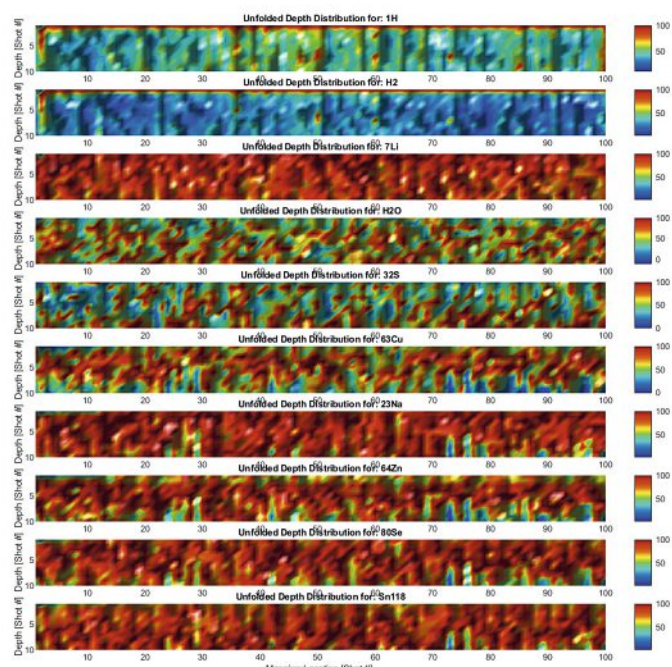


Fig. 9. 3D Mapping of elemental distributions in a porous photovoltaic material 'CZTS', obtained with soft X-ray laser ablation mass spectrometry. The enriched surface hydrogen concentration is visualized.

a 1  $\mu\text{m}$  step size. This database served as a predictor to compute distribution volumes of each element, such that the covariance between data was matched. A threshold was set at 5% (p-value) to remove any low level signal that would give overfitting. The result is a 3D chemical tomography that not only gives the lateral and depth distribution of the analytes in the layered material, including hydrogen, rather it also shows voids associated to the granular structure, crevices and porosity.

We published recently<sup>[56]</sup> a similar example for the analysis of novel CoNCN water-oxidation catalysts.

### 2.3 Prototyping Instrumentation Overcoming the Limits

The discussion so far was focused on methods for data collection and on data processing. Obviously, the instrumental process of data generation by means of analytical devices is also very important. While mainly addressed by instrumentation manufacturers, the potential for exploring different architectures is not to be underestimated. A few examples are given to show how the research efforts of the analytical science laboratory at Empa aim to a holistic innovation.

Direct material microanalysis can be lengthy if carried out with classical wet chemistry methods. Often the semi-quantitative information obtained by fast methods such as laser ablation spectrometries (optical emission spectrometry or also mass spectrometry) is advantageous. The extraction of a dry aerosol and transportation to the inductively coupled plasma mass spectrometry (ICP-MS) is a critical step that could cause fractional loss of analytes. An original set of components has been developed to optimize the transport.<sup>[57]</sup> The recording of sharp transients improved the depth resolution and signal-to-noise ratio, which required fast detection units, such as time-of-flight. Alternative concepts such as the HCT coil discussed above in section 2.1.4 would serve to fill this gap.

#### 2.3.1 24/7 Life Cycle Kinetics

Many advanced studies in materials science are carried out at synchrotron beamlines. Beamlines have unique capabilities, such as coherence, tunability, or sensitivity to difficult analytes such as hydrogen, and so forth. While the scientific possibilities are

very advanced, the flexibility and accessibility are not comparable to instrumentation in the home laboratory. The access to beamtime shifts is not only short and discontinuous. It hinders 24/7 life cycle assessments, poses pressure on the TOI, and limits the creativity because one is bound to carry out the experiments that were approved in the proposal, regardless of the first results. This is a substantially different work model than one has in the lab, where agile trial-and-error following the path of incremental discoveries and validating produces innovation. Furthermore, getting beamtime is often difficult for groups not using it routinely. Finally, the beforehand disclosure of a tentative research idea is not always encouraging to one's reputation (in case of failure or a crazy idea) or compliant with the confidentiality requirements (e.g. drug discovery).

While beamlines work and operate on consolidated engineering, alternative approaches are not excluded *a priori*. Our lab has developed two alternative architectures for tabletop X-ray lasers. One is based on a high-power chirped pulse amplification lasers (Nobel Prize in Physics by Mourou and Strickland, 2018) while the other is based on a high-voltage discharge source. The systems have been recently reviewed elsewhere.<sup>[45]</sup>

### 2.3.2 Transient Kinetics

Be it for fast kinetic phenomena or for the sample introduction of ultrasmall injections (e.g. biofluids in personalized medicine, quasi-non-destructive sampling of economic materials or cultural heritage artwork, realtime process monitoring, etc.) the detection of fast transient signals is challenging. Especially if multiple analytes have to be collected from the tiny sampling, the sensitivity is known to suffer the Poisson limit of counting statistics. Methods that are able to collect full-band (chemical imaging) analytical signals are thus necessary. These methods would of course benefit from sophisticated computational data processing.

Ultrafast photoelectron and photoion spectroscopy (as well as their combination known as 'coincidence spectroscopy') based on photoionization with pico/femtosecond pulses, utilizes detectors based on different electron multipliers such as microchannel plates or single-channel electron multipliers. These detectors have a few important limitations such as fast-signal distortion (low pass operation), mutually exclusive positive or negative mode, dead time, and requirement of trigger. A high-pass induction detector, based on a hollow-cored toroidal coil, was developed that overcomes the above-mentioned limitations. The frequency-dispersive response and linearity of different configurations were analyzed. It is shown that the response is enhanced for ultrafast electron signals, dependent on construction parameters, thus offering response flexibility by design. Kinetic energy distributions of pseudospark-induced electron pulses are characterized in order to validate the capabilities in real applications. Currently, the device is being tested for inductively coupled plasma (ICP) mass spectrometry, in a partnership with a large instrument manufacturer.

### 3. Conclusions

Understanding chemical kinetics is a key to a rational materials design of future energy storage and conversion devices. In this article, we give a short overview on the pertinent scientific as well as technical questions, with particular emphasis on the chemical imaging of the underlying processes. We aim to make clear that progress in materials science is closely linked to improvement in analytical developments. Specifically, we address challenges in hydrogen storage, hydrogen production and conversion, and chemical engineering of processes relevant to the latter. Application of the methods of chemical imaging is not limited to the corresponding time- and space-dependent phenomena in these topics, but new insights will have immediate scientific, technical and societal impact. Furthermore, we describe the limitations of analytical methods relevant for imaging of chemical transformations and show

new ways to improve them. In detail, the relation time and space as is crucial for chemical kinetics has its counterpart in analytical concepts, e.g. the limited detection power at nano-scale is inherently linked to the study of interfaces as well as are matrix effects, because an interface ('nano') is defined by at least two larger regions ('matrix'). Elucidating the time-dependence of processes at such interfaces is practically limited by the imaging resolution, in particular for ultrafast phenomena. Here, much hope lies in new technical developments. We highlight a few contributions from our group. Realistically, though, one needs to make compromises. However, with the digital revolution, new ideas were brought forward such as digital reconstruction of undersampled processes as a result of the technical limitations. In addition, we highlight some practical aspects: long-term measurements (24/7 cycling) are equally demanding, as are non-targeted analyses, in which the number of possibilities grows exponentially.

### Acknowledgements

The authors acknowledge Dr. Norbert Heeb, Adrian Wichser, Matthias Trottmann, Dr. Pavel Trtik (Paul Scherrer Institute). Dr. Jens Jacobsen (Waters Corp.) is credited for the term 'Bounty Rule'.

Received: February 1, 2022

- [1] M. F. Ashby, D. Cebon, *MRS Bull.* **2005**, *30*, 995.
- [2] H. S. Park, O.-H. Kwon, J. S. Baskin, B. Barwick, A. H. Zewail, *Nano Lett.* **2009**, *9*, 3954, <https://doi.org/10.1021/nl9032704>
- [3] P. J. Hall, E. J. Bain, *Ener. Policy* **2008**, *36*, 4352, <https://doi.org/10.1016/j.enpol.2008.09.037>.
- [4] M. Matsuo, A. Remhof, P. Martelli, R. Caputo, M. Ernst, Y. Miura, T. Sato, H. Oguchi, H. Maekawa, H. Takamura, *J. Am. Chem. Soc.* **2009**, *131*, 16389, <https://doi.org/10.1021/ja907249p>.
- [5] J. H. Baricuatro, S. Kwon, Y.-G. Kim, K. D. Cummins, S. Naserifar, W. A. Goddard III, *ACS Catal.* **2021**, *11*, 3173, <https://doi.org/10.1021/acscatal.0c05564>
- [6] T. L. Ward, T. Dao, *J. Membr. Sci.* **1999**, *153*, 211, [https://doi.org/10.1016/S0376-7388\(98\)00256-7](https://doi.org/10.1016/S0376-7388(98)00256-7).
- [7] P. Sherwood, D. Briggs, M. Seah, 'Practical Surface Analysis', in 'Auger and X-ray Photoelectron Spectroscopy 1', **1990**, pp. 555.
- [8] A. Züttel, A. Remhof, A. Borgschulte, O. Friedrichs, *Phil. Trans. Royal Soc. A* **2010**, *368*, 3329, <https://doi.org/10.1098/rsta.2010.0113>.
- [9] Q. Lai, Y. Sun, T. Wang, P. Modi, C. Cazorla, U. B. Demirci, J. R. Ares Fernandez, F. Leardini, K. F. Aguey-Zinsou, *Adv. Sust. Syst.* **2019**, *3*, 1900043, <https://doi.org/10.1002/adsu.201900043>.
- [10] M. Paskevicius, L. H. Jepsen, P. Schouwink, R. Cerný, D. B. Ravnsbæk, Y. Filinchuk, M. Dornheim, F. Besenbacher, T. R. Jensen, *Chem. Soc. Rev.* **2017**, *46*, 1565, <https://doi.org/10.1039/C6CS00705H>.
- [11] Q. Lai, Y. Sun, T. Wang, P. Modi, C. Cazorla, U. B. Demirci, J. R. Ares Fernandez, F. Leardini, K. F. Aguey-Zinsou, *Adv. Sust. Syst.* **2019**, *3*, <https://doi.org/10.1002/adsu.201900043>.
- [12] A. Borgschulte, J. Terreni, B. Fumey, O. Sambalova, E. Billeter, *Front. Ener. Res.* **2022**, *9*, <https://doi.org/10.3389/fenrg.2021.784082>.
- [13] a) M. Paskevicius, L. H. Jepsen, P. Schouwink, R. Cerný, D. B. Ravnsbæk, Y. Filinchuk, M. Dornheim, F. Besenbacher, T. R. Jensen, *Chem. Soc. Rev.* **2017**, *46*, 1565, <https://doi.org/10.1039/c6cs00705h>; b) T. J. Frankcombe, *Chem. Rev.* **2012**, *112*, 2164, <https://doi.org/10.1021/cr2001838>.
- [14] A. Borgschulte, PhD Thesis, Technical University of Braunschweig, **2002**.
- [15] A. Borgschulte, R. Westerwaal, J. Rector, B. Dam, R. Griessen, J. Schoenes, *Phys. Rev. B* **2004**, *70*, 155414, <https://doi.org/10.1103/PhysRevB.70.155414>.
- [16] J. Karst, F. Sterl, H. Linnenbank, T. Weiss, M. Hentschel, H. Giessen, *Sci. Adv.* **2020**, *6*, eaaz0566, <https://doi.org/10.1126/sciadv.aaz0566>.
- [17] a) M. Fanfoni, M. Tomellini, *Il Nuovo Cimento D* **1998**, *20*, 1171, <https://doi.org/10.1007/BF03185527>; b) M. Avrami, *J. Chem. Phys.* **1939**, *7*, 1103, <https://doi.org/10.1063/1.1750631>; c) M. Avrami, *J. Chem. Phys.* **1940**, *8*, 212; d) M. Avrami, *J. Chem. Phys.* **1941**, *9*, 177, <https://doi.org/10.1063/1.1750872>.
- [18] T. Förde, J. Maehlen, V. Yartys, M. Lototsky, H. Uchida, *Int. J. Hydro. Ener.* **2007**, *32*, 1041, <https://doi.org/10.1016/j.ijhydene.2006.07.015>.
- [19] A. Remhof, S. J. van der Molen, A. Antosik, A. Dobrowolska, N. J. Koeman, R. Griessen, *Phys. Rev. B* **2002**, *66*, <https://doi.org/10.1103/PhysRevB.66.020101>.
- [20] P.-C. Chang, Y.-Y. Chang, W.-H. Wang, F.-Y. Lo, W.-C. Lin, *Commun. Chem.* **2019**, *2*, <https://doi.org/10.1038/s42004-019-0189-1>.

- [21] A. Borgschulte, R. Gremaud, Z. Lodziana, A. Zuttel, *Phys. Chem. Chem. Phys.* **2010**, *12*, 5061, <https://doi.org/10.1039/c000229a>.
- [22] A. T. Bell, *Science* **2003**, *299*, 1688, <https://doi.org/10.1126/science.1083671>.
- [23] J. Terreni, O. Sambalova, A. Borgschulte, S. Rudic, S. F. Parker, A. J. Ramirez-Cuesta, *Catalysts* **2020**, *10*, <https://doi.org/10.3390/catal10040433>.
- [24] M. Kim, M. Bertram, M. Pollmann, A. von Oertzen, A. S. Mikhailov, H. H. Rotermund, G. Ertl, *Science* **2001**, *292*, 1357, <https://doi.org/10.1126/science.1059478>.
- [25] Y. Suchorski, J. Zeininger, S. Buhr, M. Raab, M. Stöger-Pollach, J. Bernardi, H. Grönbeck, G. Rupprechter, *Science* **2021**, *372*, 1314, doi: 10.1126/science.abf8107.
- [26] A. Fernández, G. M. Arzac, U. F. Vogt, F. Hosoglu, A. Borgschulte, M. C. Jiménez de Haro, O. Montes, A. Züttel, *Appl. Catal. B: Environ.* **2016**, *180*, 336, <https://doi.org/10.1016/j.apcatb.2015.06.040>.
- [27] B. Fumey, S. Stoller, R. Fricker, R. Weber, V. Dorer, U. F. Vogt, *Int. J. Hydro. Ener.* **2016**, *41*, 7494, <https://doi.org/10.1016/j.ijhydene.2016.03.134>.
- [28] W. Karim, C. Spreafico, A. Kleibert, J. Gobrecht, J. VandeVondele, Y. Ekinici, J. A. van Bokhoven, *Nature* **2017**, *541*, 68, <https://doi.org/10.1038/nature20782>.
- [29] a) P. Boillat, E. H. Lehmann, P. Trtik, M. Cochet, *Curr. Opin. Electrochem.* **2017**, *5*, 3, <https://doi.org/10.1016/j.coelec.2017.07.012>; b) I. Martens, L. G. Melo, M. M. West, D. P. Wilkinson, D. Bizzotto, A. P. Hitchcock, *ACS Catal.* **2020**, *10*, 8285, <https://doi.org/10.1088/2515-7655/abf43d>.
- [30] A. Borgschulte, O. Sambalova, E. Billeter, A. Sterzi, J. Niggli, B. Welte, A. Heel, R. Holzner, *Adv. Sci.* **2021**, *8*, 2101764, <https://doi.org/10.1002/adv.202101764>.
- [31] L. S. Bouchard, S. R. Burt, M. S. Anwar, K. V. Kovtunov, I. V. Koptuyg, A. Pines, *Science* **2008**, *319*, 442, <https://doi.org/10.1126/science.1151787>.
- [32] A. Borgschulte, R. Delmelle, R. B. Duarte, A. Heel, P. Boillat, E. Lehmann, *Phys. Chem. Chem. Phys.* **2016**, *18*, 17217, <https://doi.org/10.1039/c5cp07686b>.
- [33] J. Ulpts, W. Dreher, L. Kiewidt, M. Schubert, J. Thöming, *Catal. Today* **2016**, *273*, 91, <https://doi.org/10.1016/j.cattod.2016.02.062>.
- [34] J. Terreni, E. Billeter, O. Sambalova, X. Liu, M. Trottmann, A. Sterzi, H. Geerlings, P. Trtik, A. Kaestner, A. Borgschulte, *Phys. Chem. Chem. Phys.* **2020**, *22*, 22979, <https://doi.org/10.1039/d0cp03414b>.
- [35] B. Fumey, A. Borgschulte, S. Stoller, R. Fricker, R. Knechtle, A. Kaestner, P. Trtik, L. Baldini, *Int. J. Heat Mass Transf.* **2022**, *182*, <https://doi.org/10.1016/j.ijheatmasstransfer.2021.121967>.
- [36] L. Breiman, *Statist. Sci.* **2001**, *16*, 199, <https://doi.org/10.1214/ss/1009213726>.
- [37] J. Martín, C. E. M. Neira, A. G. Asuero, *Ann. Real Acad. Farm.* **2017**, *83*, 200.
- [38] a) C. J. Li, P. T. Anastas, *Chem. Soc. Rev.* **2012**, *41*, 1413, <https://doi.org/10.1039/c1cs90064a>; b) P. T. Anastas, J. B. Zimmerman, *Chem. US* **2021**, *7*, 2825, <https://doi.org/10.1016/j.chempr.2021.10.025>; c) P. T. Anastas, J. B. Zimmerman, *Green Chem.* **2019**, *21*, 6545, <https://doi.org/10.1039/c9gc01293a>; d) P. T. Anastas, J. C. Warner, 'Green Chemistry: Theory and Practice', Oxford University Press, New York, **1998**, pp. 29; e) P. T. Anastas, D. T. Allen, *ACS Sustain. Chem. Eng.* **2016**, *4*, 5820, <https://doi.org/10.1021/acssuschemeng.6b02484>; f) P. T. Anastas, *Aldrichim. Acta* **2015**, *48*, 3; g) P. T. Anastas, *Crit. Rev. Anal. Chem.* **1999**, *29*, 167; h) P. Anastas, B. X. Han, W. Leitner, M. Poliakoff, *Green Chem.* **2016**, *18*, 12, <https://doi.org/10.1039/c5gc90067k>; i) P. Anastas, *Abstr. Pap. Am. Chem. S.* **2013**, 245.
- [39] J. Miller, J. C. Miller, 'Statistics and chemometrics for analytical chemistry', Pearson education, **2018**.
- [40] D. Bleiner, L. Juha, D. Qu, *J. Anal. At. Spectrom.* **2020**, *35*, 1051, <https://doi.org/10.1039/c9ja00366e>.
- [41] a) D. Qu, D. Bleiner, *J. Anal. At. Spectrom.* **2020**, *35*, 2011, <https://doi.org/10.1039/d0ja00215a>; b) D. Qu, N. Ohannessian, C. Wyder, M. Trottmann, A. Wichser, T. Lippert, D. Bleiner, *Spectrochim. Acta B* **2021**, *181*, <https://doi.org/10.1016/j.sab.2021.106214>.
- [42] J. Rowley, *J. Inf. Sci.* **2007**, *33*, 163, <https://doi.org/10.1177/0165551506070706>.
- [43] T. G. Mayerhofer, J. Popp, *ChemPhysChem* **2019**, *20*, 511, <https://doi.org/10.1002/cphc.201801073>.
- [44] D. Bleiner, M. Ruiz-Lopez, Multiscale lensless imaging with a plasma X-ray laser', Int. Conf. X-ray Lasers 2020, vol. 11886, International Society for Optics and Photonics, **2021**, p. 118860P.
- [45] D. Bleiner, *Spectrochim. Acta B* **2021**, *181*, 105978, <https://doi.org/10.1016/j.sab.2020.105978>.
- [46] M. Nadeem, I. Di Bernardo, X. Wang, M. S. Fuhrer, D. Culcer, *Nano Lett.* **2021**, *21*, 3155, <https://doi.org/10.1021/acs.nanolett.1c00378>.
- [47] D. Bleiner, in 'SPG Mitteilungen', Vol. 66, Swiss Physical Society, Basel, **2022**, p.
- [48] D. Bleiner, Y. Arbelo-pena, 'Detector supplement device for spectroscopy setup', U.S. Patent No. 10,366,863, 30 Jul. **2019**.
- [49] a) Y. Arbelo, D. Bleiner, *Rev. Sci. Instrum.* **2017**, *88*, 024710, <https://doi.org/10.1063/1.4975402>; b) Y. Arbelo, D. Bleiner, *Rapid Commun. Mass Spectrom.* **2019**, *33*, 1196, <https://doi.org/10.1002/rcm.8463>.
- [50] a) N. V. Heeb, S. Iten, L. Schinkel, M. Knobloch, J. Sprengel, P. Lienemann, D. Bleiner, W. Vetter, *Chemosphere* **2020**, *255*, 126959, <https://doi.org/10.1016/j.chemosphere.2020.126959>; b) M. C. Knobloch, F. Mathis, T. Fleischmann, H.-P. E. Kohler, S. Kern, D. Bleiner, N. V. Heeb, *Chemosphere* **2021**, 132939, <https://doi.org/10.1016/j.chemosphere.2021.132939>; c) M. C. Knobloch, L. Schinkel, I. Schilling, H. E. Kohler, P. Lienemann, D. Bleiner, N. V. Heeb, *Chemosphere* **2021**, *262*, 128288, <https://doi.org/10.1016/j.chemosphere.2020.128288>; d) M. C. Knobloch, J. Sprengel, F. Mathis, R. Haag, S. Kern, D. Bleiner, W. Vetter, N. V. Heeb, *Chemosphere* **2021**, 132938, <https://doi.org/10.1016/j.chemosphere.2020.132938>.
- [51] A. A. Shvartsburg, F. Li, K. Tang, R. D. Smith, *Anal. Chem.* **2006**, *78*, 3706, <https://doi.org/10.1021/ac052020v>.
- [52] J. L. Kaszycki, M. A. Baird, A. A. Shvartsburg, *Anal. Chem.* **2018**, *90*, 669, <https://doi.org/10.1021/acs.analchem.7b04610>.
- [53] a) D. Bleiner, *Spectrochim. Acta B* **2020**, <https://doi.org/10.1016/j.sab.2020.105978>; b) D. Bleiner, Y. Arbelo-Pena, L. Masoudnia, M. Ruiz-Lopez, *Physica Scripta* **2014**, T162, <https://doi.org/10.1088/0031-8949/2014/t162/014050>.
- [54] R. K. Marcus, E. D. Hoegg, K. A. Hall, T. J. Williams, D. W. Koppenaal, *Mass. Spectrom. Rev.* **2021**, <https://doi.org/10.1002/mas.21720>.
- [55] K. O. Nagornov, M. Zennegg, A. N. Kozhinov, Y. O. Tsybin, D. Bleiner, *J. Am. Soc. Mass Spectrom.* **2020**, *31*, 257, <https://doi.org/10.1021/jasms.9b00032>.
- [56] a) R. Muller, I. Kuznetsov, Y. Arbelo, M. Trottmann, C. S. Menoni, J. J. Rocca, G. R. Patzke, D. Bleiner, *Anal. Chem.* **2018**, *90*, 9234, <https://doi.org/10.1021/acs.analchem.8b01740>; b) R. J. Muller, J. Lan, K. Lienau, R. More, C. A. Triana, M. Iannuzzi, G. R. Patzke, *Dalton Trans.* **2018**, *47*, 10759, <https://doi.org/10.1039/c8dt01587b>.
- [57] a) D. Bleiner, F. Belloni, D. Doria, A. Lorusso, V. Nassisi, *J. Anal. At. Spectrom.* **2005**, *20*, <https://doi.org/10.1039/b509379c>; b) D. Bleiner, D. Günther, *J. Anal. At. Spectrom.* **2001**, *16*, 449, <https://doi.org/10.1039/b009729m>; c) D. Bleiner, P. Lienemann, H. Vonmont, *Talanta* **2005**, *65*, 1286, <https://doi.org/10.1016/j.talanta.2004.09.004>; d) D. Bleiner, H. Altorfer, *J. Anal. At. Spectrom.* **2005**, *20*, <https://doi.org/10.1039/b505248c>.

#### License and Terms



This is an Open Access article under the terms of the Creative Commons Attribution License CC BY 4.0. The material may not be used for commercial purposes.

The license is subject to the CHIMIA terms and conditions: (<https://chimia.ch/chimia/about>).

The definitive version of this article is the electronic one that can be found at <https://doi.org/10.2533/chimia.2022.192>