Annual Report

Institute of Hydrochemistry

Chair for Analytical Chemistry

2010

Institute of Hydrochemistry
Chair for Analytical Chemistry
Technische Universität München
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Editor: Dr. Thomas Baumann

Editorial

Dear coworkers, friends and colleagues,

the institute made it's way through 2010 like a cruise ship in rough sea and is vitally going to celebrate it's 60th anniversary in 2011. With a crew of 50 highly motivated people, two thirds working on their PhD or habilitation, we were able to maintain a high standard of research.

Research funding covered research topics from exhaust aftertreatment and soot aerosols over microorganisms (bacteria, viruses), toxins in food and air, laser assisted in situ gas analysis for biogas monitoring, to safety issues with geothermal wells and process studies in silicon micromodels which mimic the pore space in soil. It's like a bunch of wild flowers: diverse and therefore attractive. And Analytical Chemistry serves as the ribbon holding this bouquet together.

I would like to highlight our new brand-new Raman microscope, the second system at the institute, which is used interdisciplinarily for the characterization of aerosols, nanoparticles, biofilms, and processes in soil. Also, the microarray technology is now widely adopted as a versatile tool for fast screening of water and dairy products for all kinds of substances and found a new home within a strong consortium of a leading manufacturer of monitoring systems and diary industry. PCR was successfully implemented onto the chip and we are expecting great interest in the microbiology community.

Looking ahead, we will see a number of reconstruction and renovation measures at the institute, but luckily it's only the building which is growing old and there are no signs of aging in the group. It‘s still an enormous pleasure to me, to see how the various groups are adapting and improving their main research topics to the current needs backed up by the accumulated expertise. For instance, my group started 35 years ago with aerosol analysis. Nowadays, the old publications find new readers in the field of nanoparticle research.

Finally, I would like to thank all funding agencies, reviewers, coworkers and our circle of friends for their continuous support and critical comments.

All the best for the year 2011!

Reinhard Niessner
Head of the Institute

We had so many group pictures over the past years, therefore here's the view some kilometers south of the institute...

C. Helmbrecht, R.Niessner, T. Baumann, D. Knopp, C. Haisch, and M. Seidel are not on this picture

1 Research

1.1 Hydrogeology and Hydrochemistry (Head: PD Dr. T. Baumann)

1.1.1 Gas Composition and Hydrogeochemistry of the Malm Aquifer

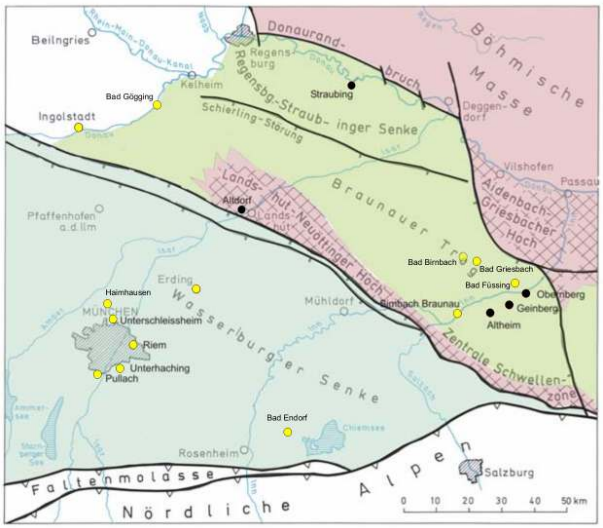
Funding: BMU (Federal Ministry for the Environment)
Cooperation: FU Berlin; LIAG Hannover; LfU Bayern; Erdwerk GmbH, München; HydroConsult GmbH, Augsburg

The Malm aquifer is one of the most important deep groundwater aquifers, and is extensively used for deep geothermal exploration in the Bavarian Molasse Basin. In the Munich area several new geothermal projects were realized in the last decade, and new deep wells were drilled. For an optimized development and implementation of a geothermal power plant, it is important to know the hydrochemical characteristics of the thermal water and the hydrogeochemical processes which are occuring during production and reinjection of the thermal water.

Processes which endanger the stability and safety of the drilled well, for example the occurrence of H_2S in the gas phase, are of particular importance. H_2S is not just a health hazard, but also causes corrosion to the steel pipes and other materials. With the help of isotopic measurements, the origin and occurrence of H_2S was revealed.

A first hypothesis – the impregnation of thermal water by sour gas – seemed to be supported by exceptionally high H_2S concentrations. However, a gas reservoir was nowhere to be found.

The isotopic signatures of ^{34}S at five geothermal sites vary from +2.5 to +9.7 ‰ for δ^{34}S-sulfide and +8,5 to +20,8 ‰ for δ^{34}S-sulfate. The enrichment of the heavy isotope leads to two processes: thermophilic reduction of sulfate in the presence of hydrocarbons, mainly CH_4, which occurs at elevated temperatures in the Basin centre, and bacterial reduction of sulfate, which happens at lower temperatures at the Basin margin. An impregnation with sour gas can be excluded for now.



Location of the geothermal wells

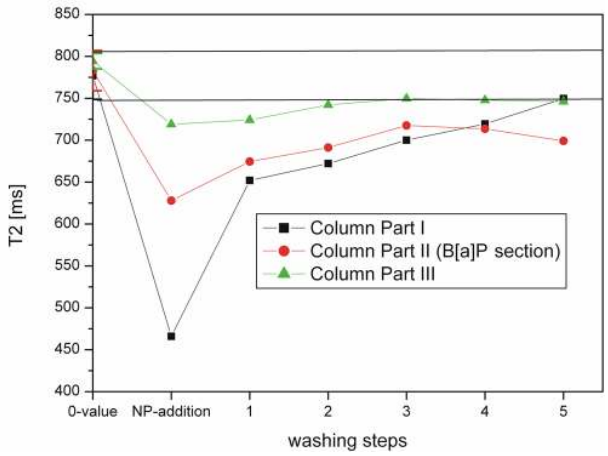
The isotopic composition of water (^{18}O, ^{2}H) is close to the Global Meteoric Water Line, with a tendency to lower δ^2H values, caused by the continental effect. The large deviation observed at one site, indicates mixing with formation waters.

The $\delta^{18}O/\delta^{2}HO$ ratio also indicates an evaporation temperature of about 4.6 °C for the waters in the central Molasse Basin, which puts them into the pleistocene age (roughly 10000 years)
(*C. Mayr*)

1.1.2 Visualization and Quantification of Processes at Biogeochemical Interfaces with Magnetic Resonance Imaging

Funding: DFG (German Research Foundation)
Cooperation: Partners in the Priority Program SPP1315

MRI is a very powerful technique to visualize processes in soil. As biogeochemical interfaces in the soil serve as initial "reactive filters" there is a need to visualize processes especially at the interfaces. Therefore in this work MRI-active nanoparticles conjugated to antibodies specific to organic pollutants, which we like to observe, were prepared and fully characterized. Besides, NMR relaxometric column experiments, as preliminary stage for MRI experiments, with silica gel as model matrix for porous media were performed. There, it was shown, that layers of grains with bound B[a]P can be detected with the help of paramagnetic antibody-coupled MRI-active nanoparticles.



T2 times of water in a silica gel column indicates the location of a B[a]P contamination in the presence of MNPs

MRI-active magnetite (Fe_3O_4) nanoparticles (MNPs) coated with dicarboxypoly-ethylene glycol were synthesized and coupled to the monoclonal antibody 22F12 directed against benzo[a]pyrene (B[a]P), which was developed at our institute. The nanoparticle synthesis is based on former work about the preparation of magnetic nanoparticles for immunomagnetic separation of *E. coli* and developed further. The surface of the MNPs was first coated with (3-aminopropyl)triethoxysilane by a silanization reaction to introduce amino groups. Then, the PEG diacid was coupled covalently to these amino groups forming a peptide bond. The remaining reactive carboxy groups of the polyethylene diacid were then used to link the antibody to the MNPs again with a peptide bond.

The as prepared antibody-coupled MNPs against B[a]P (AbMNPs) were percolated through a column filled with silica gel with one layer of B[a]P. The column was washed several times to get rid of the nonspecifically bound AbMNPs. By measuring the T2 values of water protons within the different sections of the column with NMR relaxometry after every washing step one can detect the BaP layer, where the T2 value is significantly lower (700 ms) than the starting value (775 ms).
(*M. Rieger*)

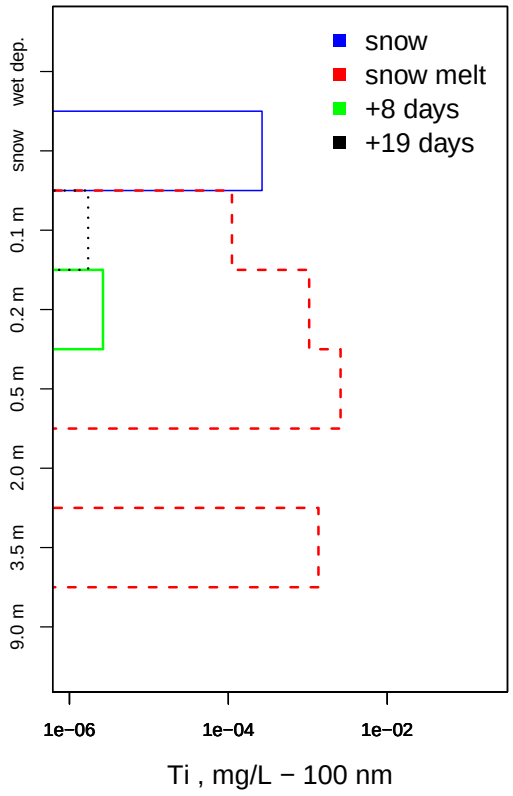
1.1.3 Nanoparticles at the Interface between Atmosphere and Hydrosphere

Funding: IWC

The emissions of engineered nanoparticles are increasing and there are reports of adverse effects on aquatic ecosystems and possible health issues. Aquifers and soils are the primary filter systems to remove engineered nanoparticles. These effects are used e.g., for bank filtration. Recent flooding events, on the other hand, show the limited capacity of this filter. Dissolved organic matter (DOM), present in surface water and top soil in larger quantities, has a stabilizing effect on most nanoparticles. Thus, a transport of engineered nanoparticles through the soil seems likely.

The monitoring programme at field lab in the unsaturated zone located in the Munich gravel plain, shows, that transport of particles is mainly driven by extreme climatic events. Nanoparticles deposited during dry periods may accumulate on the plant leaves and on the top soil. Heavy rainfall after a dry period will mobilize the nanoparticles. Through cracks in the top soil, preferential flow can transport the (surface modified) particles to the groundwater. During winter, particles are deposited on the snow cover. Sublimation of snow may lead to relatively high concentrations in the remaining snow. Cracks in the top soil caused by freezing ease the transport of nanoparticles together with the melting snow. During winter, however, aging and masking of the nanoparticles should be different.

Transport of unaltered, dispersed nanoparticles in intact soil columns is very limited. Filtration efficiencies are on the order of 98.5 % for a sand column which was 10 cm long. This is in contradiction to field observations and underlines the importance of preferential flow and masking for nanoparticle transport.
(*S. Huckele*)



Vertical transport of Ti particles in the vadoze zone after a snow melt event

1.1.4 Development of A New Strategy for a Hydraulic Barrier at a Multiple Contaminated Site

Funding: Mitteldeutsche Sanierungs- und Entsorgungs GmbH
Cooperation: LAF, Magdeburg; GICON, Dresden; Quadriga, Berlin

The groundwater contaminations in the Bitterfeld-Wolfen area are treated in the framework of an ecological super fund project. There are numerous groundwater wells to ensure an appropriate groundwater level in the City of Bitterfeld and to prevent the propagation of contaminants into the surroundings. While the injection of CO_2-enriched water into the pumping cones has been successfully prevented well aging at one site, the specific yield of the wells decreased despite of CO_2-augmentation at another site.

Pump with incrustations and SEM image of the incrustations

At this site, the mixing of groundwater with pH-values between 4 and 13 and high concentrations of VOC caused the development of organic carbon coatings. Therefore, a new strategy had to be developed to maintain the effectiveness of the hydraulic barrier.

A literature survey showed, that there are no case studies for in situ remediation methods applicable to the specific site. As an active groundwater barrier had to be maintained continuously, any full-scale research and development project to implement an in situ treatment was considered too risky.

Therefore, the focus of development was put to passive hydraulic barrier systems with easy access for maintenance. The design of the hydraulic barrier had to prevent mixing in the aquifer, both horizontally and vertically. Hydrochemical simulations were run to assess the potential for inorganic precipitations. Since data to simulate organic precipitations is scarce, further research is needed for the prediction of the long-term behaviour of the barrier system.
(*T. Baumann*)

1.1.5 Cybutryn in Marinas of a Lake in Bavaria

Funding: IWC
Cooperation: LfU Bayern; Otto-von-Taube-Gymnasium, Gauting

Cybutryn is a highly effective biocide, which is commonly used in antifouling paints to prevent the growth of autotrophic organisms called "fouling", on boats. From the boats it is continuously released to the surrounding water. Today it is the most frequently detected antifouling biocide worldwide, and environmental assessment is difficult. Its occurrence in freshwater is hardly investigated. In Germany it was detected in marinas in concentrations between 20 ng/L and 50 ng/L and sediment concentrations between 8 and 36 μg/kg, dry weight.

In this study which was performed as a Seminar thesis in the framework of TUM-Kolleg, a cooperation between the Otto-von-Taube Gymnasium and TUM, the Cybutryn concentrations in marinas of a lake with mainly recreational use during one boating season were measured and interpreted. Further, concentrations of Cybutryn in the lake sediment were measured to discuss possible accumulation effects.

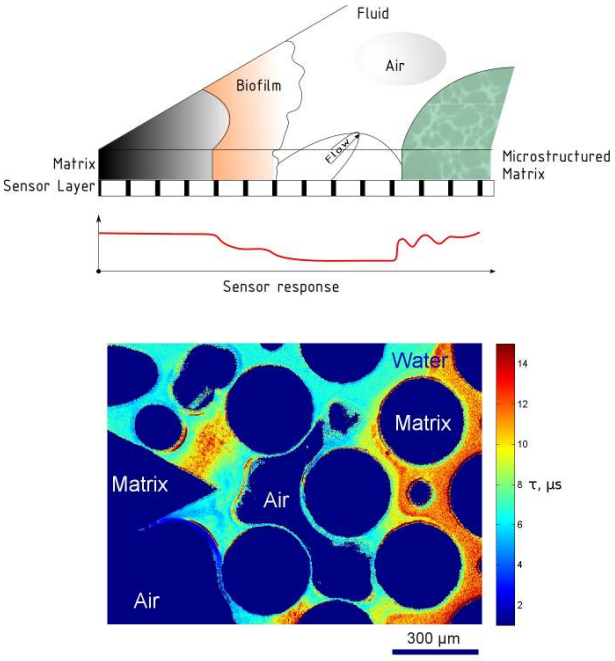
Spring sampling campaign at Lake Starnberg

The concentrations measured in Lake Starnberg were generally lower than the concentrations measured in marine harbors and also lower than the majority of concentrations reported for other freshwater environments. The shape of the harbor had a strong influence on water concentrations. In open harbors with high water exchange rates the concentrations were lower than in closed harbors. Accumulation in the sediment is dependent on the sediment properties and independent from the shape of the harbor. In sand and clayey sands lower concentrations were measured than in clay sediments. Due to the seasonal use of Cybutryn the concentrations changed over the year, beginning with low concentrations before season starts, peak concentrations after the alighting of the vessels followed by slowly declining concentrations, depending mostly on the rate of water exchange. A significant decline is expected after season, when the boats are removed from the lake. The concentrations measured in September were lower than expected, except for a very protected harbor. This was due to a flooding that raised the mean water level by about 0,5 meters and diluted the Cybutryn. Constant concentrations at the outflow of Lake Starnberg suggest that Cybutryn is distributed evenly in the water body. As particularly the concentrations in May (after the start of the boating season) are exceeding the environmental standard, suggested by the German Expert Group on Water Quality (LAWA), with a calculated fraction of only 3 % of all boats painted with Cybutryn containing paints, a higher fraction could easily lead to concentrations that might cause environmental damage.
(*E. Heuer*)

1.1.6 In situ Analysis of Pore Scale Processes at Biogeochemical Interfaces

Funding: DFG (German Research Foundation)
Cooperation: T. Mayr, University of Graz; Partners in the Priority Programme SPP 1315

Biogeochemical interfaces (BGI) in soil control the fate of organic chemicals and the functionality of soil as a filter to protect groundwater resources. In contrast to batch systems the processes within soil are depending on the spatial position/access of the reactants. To understand and quantify the processes at BGI, the concentration gradients at the interfaces have to be measured and the spatial and temporal dynamics of the BGI themselves have to be monitored.



Schematic of the micromodel setup and false color image showing the concentration of O_2 around an air bubble

Micromodels are microfluidic systems which mimic the pore structure of soils and aquifers. They allow the visualization of the spatial development of BGI under varying environmental conditions with single interface resolution. In this project, the micromodel technique is extended with chemically sensitive sensor layers. The sensor dyes (PtTFPP and Macrolex Yellow or Ir(Cs)2(acac)) are dissolved in a polymer (PS) layer and attached to the micromodel. Fluorescent particles are used to measure the local flow velocity at the interfaces. Together this allows a fast mapping and quantification of sum parameters (oxygen concentration, pH, Cl^-). The image shows a false color image of the luminescence decay times of sensor particles in a micromodel which contains oxygen-free water and air bubbles. Lower decay times indicate higher O_2-concentrations. The image is part of a time series with a temporal resolution of 10 s that gives access to the dissolution rates of the air bubbles.

Raman microscopy is used to measure the concentration of hexadecane and phenanthrene, possible degradation products, and changes of the BGI with high spatial and temporal resolution ($<2\,\mu$m, <1 s) as a function of the geometry of the interface, the composition and the flow rate of the fluid, the presence of a biofilm, the presence of nonaqueous phases.

These innovative measurements are non-destructive and, apart from the visualization of local flow velocities, do not require tracers in the fluid flow. The time series data of the spatial features and concentration gradients at BGI is a keystone for quantification of the processes at BGI and provides a link between projects on the molecular level (AFM), pore scale visualizations (CLSM, μCT) and projects on the dm-scale.
(*C. Metz*)

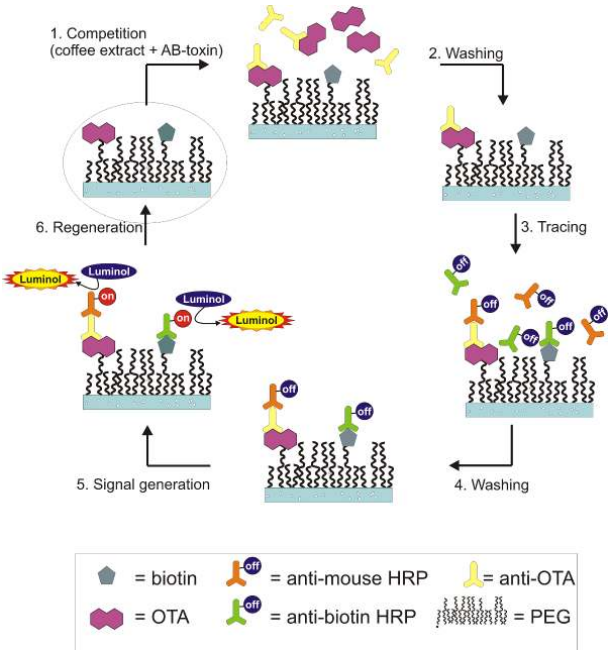
1.2 Bioanalytics (Head: Prof. Dr. D. Knopp)

1.2.1 Hapten Microarray-based Screening of Mycotoxins in Food Samples

Funding: BMBF (Federal Ministry for Education and Research)
Cooperation: Eurofins Analytik GmbH; Wiertz-Eggert-Jörissen, Hamburg; Ring Engineering Ltd., Azur, Israel

Since occurence of mycotoxins in different food has been the issue of health concerns for decades worldwide, a high number of analytical methods and screening tests for their control has been developed. In the future, multi-mycotoxin methods (multiple analytes determined in a single run) will have the edge over other methods.

As an example, ochratoxin A (OTA) is a fungal mycotoxin that poses considerable health risks to humans and to domestic animals because of its high nephrotoxicity, teratogenicity, immunosuppression, and carcinogenicity. For this reason, the European Commission has adopted regulations concerning the maximum permissible OTA amount in diverse raw foodstuffs and crops prone to contamination destined for human consumption. Well established methods for OTA analysis traditionally make use of TLC or HPLC and a suitable detection method such as FD, UV, or MS. Alternatively, simple membrane based formats, e.g. flow-through immunoassay and immunochromatographic assay are rapid, easy to use, and suitable for testing in the field. Another noticable trend is the above mentioned simultaneous measurement of multiple mycotoxins. Therefore, in this project, the previously developed Munich Chip Reader 3 (MCR 3) and namely developed biochips are tested for the determination of mycotoxins.



Schematic representation of the Ochratoxin A analysis of green coffee samples

Several peptide-mycotoxin conjugates and a peptide-biotin conjugate (as a positive control) were successfully synthesized and covalently immobilized on a derivatized glass chip. A proof-of-principle investigation was performed to study the reusability of the biochip with spiked green coffee extracts and minimal sample preparation. Though a lower limit of quantification (LOQ) for OTA in the lower ppb range was achieved, additional efforts are necessary to decrease the LOQ further. Other measures are devoted to limiting matrix effects, i.e., first of all the unspecific loss of chemiluminescence signal, because it leads to overestimation of contamination values. Further experiments have to be performed which are focussed on the detailed evaluation of performance characteristics according to well accepted guidelines of official authorities.
(*J. Sauceda-Friebe*)

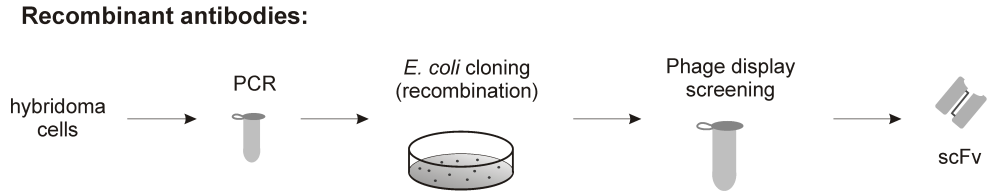
1.2.2 Recombinant Antibodies Directed Against the Polycylic Aromatic Hydrocarbon Benzo[a]pyrene

Funding: BMBF (Federal Ministry for Education and Research)
Cooperation: Martin-Luther University Halle-Wittenberg; Quo data GmbH, Dresden; University of Guelph, Canada

Polycyclic aromatic hydrocarbons (PAHs) are formed as a result of incomplete combustion of organic compounds. In the European Council Directive 98/83/EC concerning the quality of water intended for human consumption (drinking water directive) a limit value of 10 ppt was set for benzo[a]pyrene (B[a]P) which is the lowest of all threshold levels set for individual chemical parameters in this directive. Sensitive and reliable analytical methods are needed to evaluate the presence of B[a]P at very low concentration in several matrices.

In the past, we reported on the development of a highly sensitive indirect competitive ELISA for the detection of B[a]P in potable water. Fourteen monoclonal antibodies were generated in mice using novel B[a]P derivatives. With the best antibody (clone 22F12) an LOD of 24 ppt was obtained. Thus there is a need for antibodies with a higher affinity to B[a]P to reach the limit value of 10 ng/L.

In this project, the properties of monoclonal B[a]P antibodies will be further optimized using genetic engineering. For that purpose in the first step additional high affine monoclonal antibodies were produced. The screening was carried out using different methods, including direct /indirect microtiter plate ELISA tests and a new chip based method. Ten of the most sensitive clones were chosen to create a monoclonal antibody library. Antibody genes were amplified by PCR and expressed as single chain Fv (scFv). The major advantage of these antibody fragments is that they are smaller in size and therefore easier to manipulate genetically and express in bacterial systems. Up to the present, recombinant antibodies were prepared for only a few environmental chemicals, mainly pesticides. The recombinant antibodies prepared in this project, will initially be tested using surface plasmon resonance on specially prepared chips and newly synthesized PAH-derivative conjugates.



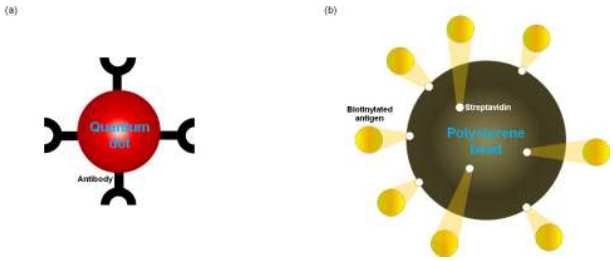
Preparation of recombinant antibodies.

(*X.Y.Z. Karsunke, M. Pschenitza*)

1.2.3 Microparticle-Based Assay of Small Analytes Using Flow Cytometric Detection Quantum Dot(QD)/Antibody Probes

Funding: DAAD (German Academic Exchange Service), IWC, and Gwangju Institute of Science and Technology, Republic of Korea

Suspension assays (bead-based assays) using encoded microparticles have become important to flow cytometry because of the ease of antibody/antigen conjugation and the possibility that particles can be used to detect targets too small (e.g. chemicals) to generate a significant scattered light signal. Encoded beads are already in use commercially, mainly for assays that require multiplexing in small sample volumes. They have been shown to have sensitivities comparable to both ELISAs and microarrays. For evaluation, optical detection methods (combination of light scattering and fluorescence) have emerged as the standard for flow cytometry. A new generation of fluorescent labels, colloidal semiconductor nanocrystals (also referred to as quantum dots (QDs) have attracted a great deal of interest in the biosensing community after Nie et al. and Alivisatos et al. described their first description in a biological context in 1998. One possible application area is assay labelling, which is studied in this project. In detail, QD/antibody (QD/Ab) detection probe and a bead/B[a]P capture probes were prepared and used for the immunological recognition of the polycyclic aromatic hydrocarbon compound B[a]P. Commercially available QDs were bioconjugated with monoclonal anti-B[a]P antibody 22F12 to obtain detection probe. Different capture probes were prepared by using streptavidin coated magnetic beads or polystyrene beads and biotinylated B[a]P-derivative. Flow cytometric analysis is performed with a Cell Lab Quanta SC. For evaluation, the electronic volume and side-scattered light are used to obtain information about particle size, i.e., to differentiate between single beads and OD/Ab/B[a]P/bead aggregates. (QD) fluorescence is used to quantify fluorescently labeled aggregates and for calculation of the B[a]P concentration in unknown samples.



Schematic drawing of (a) QD/Ab detection probe and (b) bead/B[a]P capture probe.

(*Hye-Weon Yu*)

1.2.4 Development of Quantitative Immunochemical Column Tests for Rapid On-site Screening

Funding: DAAD (German Academic Exchange Service)
Cooperation: Department of Common and Inorganic Chemistry, Chemistry Institute, Saratov State University, Saratov, Russia

Nowadays one of the trends in food and environmental analysis is the development of cost-effective test formats, which allow a rapid answer about presence or absence of a contaminant in a sample. If possible, such tests should be applicable on-site to screen many samples in a short time. Most popular are antibody-based tests as they are characterized by high sensitivity and specificity. The lateral-flow immunoassay (LFIA) format, also known as immunological dipstick or immunochromatographic assay, is by far the most common, because it can be manufactured very cost-efficiently and can be used by untrained personnel. This non-instrumental technique combines the chromatographic principle and immunochemical recognition of analyte. Another principle was used for the gel-based column immunoassay technique, which allows to combine preconcentration by an immunoaffinity support and visible detection of the analyte by an enzymatic reporter. To our experience, the sensitivity can be tuned over a larger range compared to LFIA and interfering (coloured) compounds can be easily removed.

Immunochemical test columns and handheld reader.

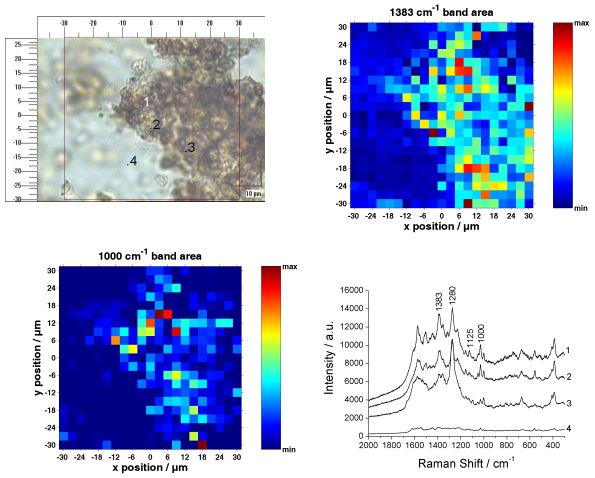
In this project, the development of a quantitative immunochemical column test for the polyaromatic hydrocarbon compound benzo[a]pyrene in food supplements using 3 different support materials for the immobilization of antibodies and a commercially available handheld photometer (Senova GmbH) was investigated.
(*I. Yu. Goryacheva, N. Beloglazova, A. Proydakova*)

1.3 Applied Laser Spectroscopy (Head: Dr. C. Haisch)

1.3.1 Label-Free In Situ Chemical Imaging of Biofilms by Surface-Enhanced Raman Scattering (SERS)

Funding: DFG (German Research Foundation)
Cooperation: Institute of Water Quality Control, TUM (Prof. Horn)

Biofilms, being communities of microorganisms embedded in a matrix of extracellular polymeric substances (EPS), represent the predominant mode of microbial life on Earth. Depending on the type of biofilm and microorganisms involved, up to 90 % of the particulate fraction of the biofilm can be EPS (biopolymers such as polysaccharides, proteins, nucleic acids, lipids, and humic-like substances). Information on physico-chemical properties of the EPS matrix is relevant in various fields, such as medicine, industry and technological processes. Therefore, the establishment of a rapid nondestructive analytical tool that can provide us with detailed chemical information, high spatial resolution, sensitivity, and reproducibility is desired. Raman microscopy (RM) is a nondestructive analytical technique which is based on the effect of inelastic light scattering by molecules. RM provides whole-organism fingerprints for biological samples with spatial resolution in the μm range. Low water background makes RM beneficial for in situ studies of biofilms, since water is the major component of the biofilm matrix. Although RM provides us with chemical information about biofilm constituents and their distribution in biofilm matrix, the Raman efficiency (typically 10^{-6} - 10^{-8}) and therefore the sensitivity of RM are limited.



SERS-Mapping of biofilm

Surface-enhanced Raman scattering (SERS) in combination with RM is a promising technique for the chemical characterization of biological systems. It yields highly informative spectra, can be applied directly in aqueous environment, and has high sensitivity in comparison with normal Raman spectroscopy. SERS can operate if the analyte molecules are attached to, or in the immediate proximity of metallic (Ag, Au, or Cu) substrate with nanometer-roughened surface. The total enhancement factor is in the range of 10^3 - 10^6 (under certain conditions up to $\approx 10^{14}$).

For the first time we applied SERS for in situ, label-free chemical imaging of biomatrices as complex as multispecies heterotrophic biofilms. For SERS measurements we employed hydroxylamine hydrochloride reduced silver colloids that can be reproducibly synthesized at room temperature, resulting in a relatively monodisperse hydrogel with silver particles of 20 - 30 nm diameter. Good SERS measurement reproducibility, along with a significant enhancement of Raman signals by SERS ($>10^4$) and highly informative SERS signature, enables rapid SERS imaging (1 s for a single spectrum) of the biofilm matrices starting from their initial growth phase. Altogether, this indicates the potential of SERS for biofilm analysis, including the detection of different constituents and the determination of their distribution in a biofilm even at low biomass concentration.

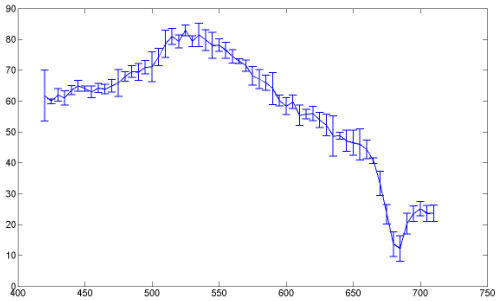
(*N. P. Ivleva*)

1.3.2 Application of the Wide-Wavelength Photoacoustic Aerosol Spectrometer

Funding: IWC

The photoacoustic (PA) process is based on a light–matter interaction. The absorbed photon energy is transformed into a local heating followed by an expansion resulting in the generation of a sound wave. Usually modulated continuous wave (cw) light is employed for this kind of spectroscopy. The disadvantage of this method is the limited number of available wavelengths and the very narrow tuning range defined by the laser diode technology.

Our new Photoacoustic Aerosol Spectrometer is based on a Nd:YAG–OPO system as light source. The signal wave with a tuning range of 410 - 710 nm, the idler wave 710 - 2600 nm and the 355-nm pump beam are passed through three individual photoacoustic cells. Inside this cells the light is interacting with the aerosols and a sound signal is generated which is detected by microphones. The amplified microphone signals, the pulse energy of the laser beams and the particle number density measured by a condensation particle counter are digitized and stored simultaneously for each wavelength selected for the scan. A Labview program is used to handle the measurement process and the data storage. This PA spectrometer is using 5-ns short laser pulses with a high intensity in the range of 200 MW/cm^2 ensuring the broad tuning range in comparison of systems using low intensity cw light sources.



PA absorption spectra of gold particles as aerosol

Amongst others, soot particles were used to test the performance of the spectrometer. These particles are well characterized: the optical absorption spectrum can be described by an exponential function defined by the so called Angstrom coefficient. Our measurements of the soot absorption spectrum fit to the published numbers with a correlation of better than 99 % which underlines the usability of the spectrometer as a device for spectral absorption measurements. Improvements of the beam quality, reducing the noise generated by scattered light, increased the sensitivity of the system by more than two decades to a level of 10^{-5} m^{-1}.

Another performance test was done with gold nanoparticles which are used for Surface-enhanced Raman spectroscopy (SERS). The absorption of these particles with a typical diameter of 10 nm fits well to the results measured with a UV-vis spectrometer in the liquid phase.

(*P. Menzenbach*)

1.3.3 Label-Free In Situ Microarray Detection of Microorganisms in Water and Aerosol Based on Surface-Enhanced Raman Scattering

Funding: IWC

We developed a label-free in situ detection principle of microorganisms on a microarray chip using Surface-enhanced Raman scattering (SERS). The microarray is situated in a flow-through system, to eliminate the risk of contamination of the sample as well as of the operator by potentially hazardous samples, and integrated to a Raman microscope for the SERS measurements (see Fig.). SERS enables the enhancement of low Raman signals and hence allows obtaining fingerprint spectra of different biological systems with high sensitivity.

A variety of metal structures (Ag, Au and Cu) are used to induce the SERS effect. We have optimized SERS particles for the specific application on bacteria, which reveal enhancement factors up to 10^8 with the test analyte crystal violet, in comparison to normal Raman. This large enhancement makes SERS a suitable tool for the characterization and quantification of different bacteria. High resolution mapping of bacteria distribution for quantification experiments and single bacteria imaging have successfully been carried out. Raman spectra are collected in a given raster distributed over different areas. A fixed area of 600 μm $\times$ 600 μm is scanned in 25-μm steps for quantification. From the spectrum of each spot, it is deduced whether an analyte is bound at this position (hit) or not (no hit). A higher number of hits corresponds to a higher analyte concentration. For single cell SERS imaging, an area of 20 μm $\times$ 20 μm is scanned in 0.5-μm steps resulting in a one-to-one imaging of single bacteria cells. The total assay time of microorganism recognition is 30 min and requires a total reactant volume of 1.5 mL to analyze cells in a wet environment. A quantitative analysis on a microarray surface takes additional 90 min.

Microarray flow cell consisting of immuno-complexes and SERS substrates. A) Prior to the antigen addition. B) The antigens are added by a syringe pump and remain in the flow-cell bound to the antibodies. For SERS detection metal colloids are brought in contact to the analytes. C) A laser beam is exposed to the analytes and metal nanoparticles induce SERS enhancement in the presence of Raman active compounds.

This new method offers the advantages of reduced assay times, simple handling and lower reactant volumes compared to methods where the target molecules need to be labelled. It enables a label-free readout for in situ microorganism detection in aqueous environment and is promising as a complementary method for drinking water analysis. Currently, we are studying its application on living bacteria using silver and gold nanoparticles as SERS media.

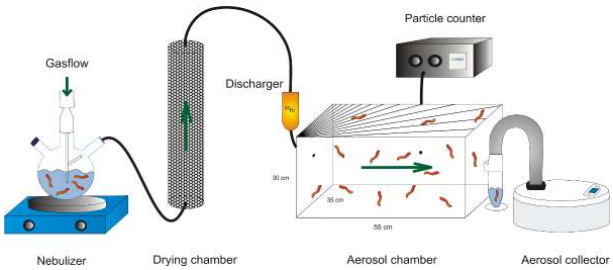
Our preliminary results indicate highly promising perspectives for such a SERS tool for characterization of microorganisms. As the detection is carried out in aqueous environment, a non-destructive analysis is possible. The synthesized particles can also be used for a variety of other SERS applications. The method can provide us with new information about the binding between antigen and antibody in the future, which again can give us a better knowledge on biological activities in microorganisms. To further optimize the method, in vitro agglomeration of the SERS substrates will be carried out.

(*M. Knauer*)

1.3.4 Label-Free in situ Microarray-Detection of Bioaerosols by Means of Surface-Enhanced Raman Scattering (SERS)

Funding: IWC

Bacterial contamination of indoor air is a serious threat to human health. Pathogenic germs can be transferred from the liquid to the aerosol phase for instance when the water forms an aerosol like in showers, air conditioners, or spas. Existing analytical instruments for the assessment of indoor air quality assessment and contamination monitoring are mostly time consuming as they generally require for a cultivation step. The need for a rapid, sensitive and selective detection method of bioaerosols is evident.



Experimental setup

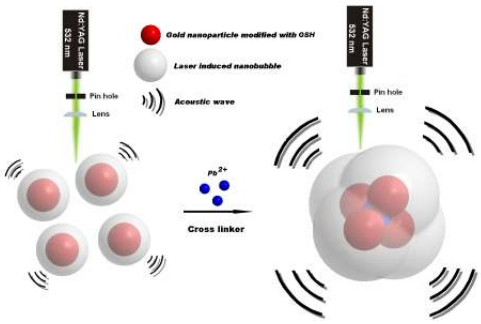
We are developing a new immunoassay microarray flow-through system for the surface-enhanced Raman scattering (SERS) measurements of bioaerosols. This system is constructed to ideally support the non-destructive in situ analysis of different microorganisms in aerosol environment. The bioaerosols are collected in buffer solution by a portable air sampler, by means of coriolis force. After an immobilization of desired antibodies to an activated PEG-coated surface, this platform is placed in a flow cell through which the contaminated liquid sample is flushed. Finally, SERS media is added and the liquidized aerosol sample is quantified spectroscopically.

(*K. Schwarzmeier, M. Knauer*)

1.3.5 Laser-induced Nanobubbles as an Analytical Tool

Funding: IWC, China Scholarship Council

Gold nanoparticles (GNP) have attracted enormous attention for biosensor and bioassay in the past decades. A common sensing mechanism is based on aggregation caused by binding between target and receptor-conjugated GNP, which leads to a colour change of GNP suspension. The colour change can be noticed by naked eyes or can be detected by a UV-vis spectrometer. In this work we present a more sensitive tool to monitor GNP aggregation. This tool is based of measurement of PA signal generated by laser-induced nanobubbles (PA-LINB). We found the amplitude of PA-LINB is strongly dependent on the GNP size, which can be used for detecting GNP aggregation. Furthermore, Pb^{2+} is widely considered as one of highly toxic heavy metal ions. The contamination of drinking water with lead poses a serious threat to global health, as it can damage the nervous system and causes brain disorders, particularly to children. The maximum contamination level of lead in drinking water is defined by U.S. Environmental Protection Agency (EPA) to 75 nM. Hence a method to improve colorimetric detection of Pb^{2+} has been developed based on PA-LINB, which can combine the advantages of colorimetric arrays and the high sensitivity of PA-LINA in detecting aggregation. The limit of detection of Pb^{2+} is as low as 8 nM.



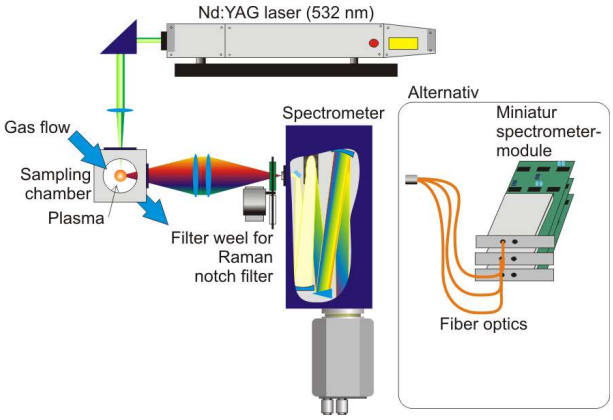
Sensor principle

(*X.J. Liu*)

1.3.6 Detection of Biogas Compounds Using Laser Induced Breakdown Spectroscopy and Raman Spectroscopy

Funding: EU (European Union)
Cooperation: Italian Agency for New Technologies, Energy and Sustainable Economic Development, Italy; MTU Onsite Energy, Germany; Ansaldo Fuel Cells, Italy; TUBITAK Marmara Research Centre, Turkey; University of Genoa - DICAT department, Italy; Royal Institute of Technology KTH, Sweden; OVM-ICCPET Institute, Romania; Joint Research Centre JRC, Belgium

As a part of research and development of renewable energy fuel cells are getting important. Within a project funded by the European Union the use of biogas as energy source for high temperature fuel cells should be explored. Especially Molten Carbonate Fuel Cells (MCFC) are quite promising regarding their efficiency and environmental aspects. These cells gain energy by transformation of hydrogen which is produced by reformation of the main component of biogas methane. But the reactions on the anode and cathode of the fuel cells, which mainly influence the performance of the cell, are very sensitive to some compounds included in biogas depending on its source. Sulfur components, halogenated hydrocarbons and siloxanes impact the reactions in the cell and reduce efficiency and lifetime. Hence the cleaning of the biogas before using it for MCFCs and a continuous monitoring of the biogas composition are very important. The different aspects of the project like cleaning strategies, impact of compounds on cell performance and analysis of the biogas composition are handled by different groups. We are responsible for the detection of corrosive compounds in the biogas. The requirements for the detection device are high since monitoring should be continuously to indentify problems in the cleaning and to avoid damages of the expensive fuel cells. Furthermore biogas can contain a wide range of substances which are agressive even in very low concentrations. Regarding these aspects, two analysis methods based on laser spectroscopy are chosen to develop a new analysis device.



Experimental setup.

The new device is based on laser induced breakdown spectroscopy (LIBS) and on Raman spectroscopy. LIBS enables the detection of the elemental composition by a laser induced plasma. Raman spectroscopy gives information about the molecular composition. To combine both methods, an especial spectroscope is used, which has two different light entrances and thus can detect LIBS and Raman signals on one single detector. The sample gas is flushed through a gas cell in which the laser is focused from one side, while the light signal is detected rectangular and transmitted by an optical fiber to the spectrometer.

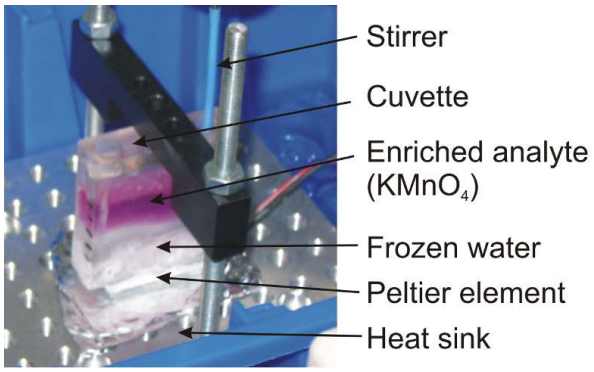
The big advantage of the combination of LIBS and Raman spectroscopy is the possibility to get elemental and molecular information about the biogas sample with high temporal resolution. Furthermore, both methods can be used in a wide range regarding the diversity of compounds and their varying concentrations.
(*A. Okroy*)

1.4 Laser-based Separation (Head: Dr. C. Helmbrecht)

1.4.1 Enrichment of Hydrocolloids by Directional Freezing of Water

Funding: IWC

Particles in the size regime of several nanometers (nanoparticles) have exceptional properties which make them favorable for the improvement of products such as coatings, foodstuff, and cosmetics. Use and disposal of such refined products lead to the ubiquitous presence of engineered nanoparticles in the environment. Due to the very low concentrations of engineered particles in environmental samples the in-situ detection and discrimination of these particles remains a challenging task for chemical analysis.



Experimental setup

The directional freezing of water is a new technique for the enrichment of water-suspended particles, e.g. hydrocolloids. A batch system was designed for the enrichment of an approx. 15 mL sample. The bottom part of the sample compartment was attached to a cooling device with a surface temperature below the freezing point of the liquid. By variation of the freezing conditions the overhead liquid volume can be adjusted and was typically 3 mL resulting in a theoretical enrichment of factor of 5. The influence of particle size, concentration and freezing conditions on the enrichment of nanoparticles in the overhead liquid was characterized for silver, gold and polystyrene nanoparticle suspensions in the size range between 6 nm and 200 nm.

In any enrichment technique, the grade of deterioration of the colloidal sample due to the enrichment process needs to be minimal in order to prevent instability or agglomeration of the sample. The influence of the enrichment process of both directional freezing and centrifugation was quantified by the analysis of particle size and particle size distribution. The fast and precise in-situ determination of the particle size distribution was performed by asymmetric flow-field flow fractionation (AF^4) coupled with slot-out-let technique. A procedure was developed for low concentrated nanoparticles in the size range between approx. 1 and 300 nm. The size distributions determined by AF^4 were compared to distributions obtained from digital processing of TEM images.

Results show that directional freezing is a gentle technique for the enrichment of low-concentrated nanoparticle dispersions. The laboratory-scale enrichment system is capable of an 8-fold enrichment with a 70 % recovery rate within one hour. Higher enrichment can be achieved by sequential freezing of the same sample.
(*C. Helmbrecht*)

1.4.2 Synthesis of Monodisperse Cubical and Cylindrical Calcium Carbonate Particles – A Reference For Particle Shape?

Funding: IWC

The determination of particle size is based on the approximation of spherical particles. The calibration of common measurement techniques, e.g. light scattering, with size standards of different shapes could improve the characterization of real world samples which are mostly irregular.

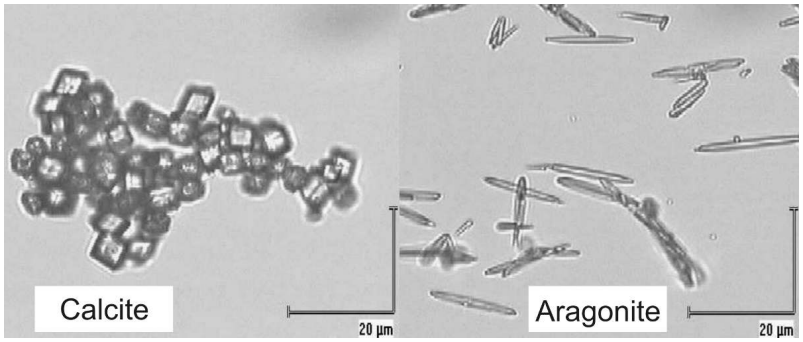
Contrary to spherical particle dispersions only few particle systems with irregular but well defined morphology are known which can be synthesized with a monodisperse size distribution. In many cases, the synthesis procedure to gain monodisperse particles is tedious and time consuming with low yield.

Calcite, Aragonite and Vaterite are the modifications of calcium carbonate and are extensively described in literature. The variety of modifications is advantageous for the synthesis of $CaCO_3$ particles of arbitrary shape, however, a thorough control of the reaction is crucial. Within this project, several approaches were tested, developed and optimized to synthesize monodisperse calcium carbonate particles of cubical and needle-like shape in the size range of 1 μm.

The calcium carbonate particles are synthesized by precipitation from salt solutions. Different salts, salt concentrations and additives are tested. The precipitation in the presence of buffer systems at constant pH improved the reproducibility of particle size and size distribution. The edge length of cubical particles was typically 4.5 μm and the relative standard deviation was better than 25 %. Nitrilotriacetic acid (NTA) and Ethylenediaminetetraacetic acid (EDTA) were used as complexing agents to mask Ca^{2+} in solution. In both cases the controlled destruction of the complex was tested in several buffers. In that way, the Ca^{2+} concentration increase slow and very homogeneous over the reaction volume, favoring monodisperse needle-like particles with length between 10 μm and 20 μm (standard deviations between 25 % and 40 %, dependent on the complexing agent and buffer).

The size and morphology of the particles was determined by SEM and optical microscopy images. With digital image processing, particle dimensions were extracted from the microscope images to create particle size distributions. The $CaCO_3$ modifications of dried bulk samples deposited on a filter were determined by FT-IR spectroscopy. Raman microspectroscopy (RM) allowed the modification analysis of single particles due to its lateral resolution of a few micrometers.

Based on the particle analysis the reaction parameters are optimized according to monodispersivity and purity of chemical morphology.



TEM images of $CaCO_3$ particles

(*C. Helmbrecht, N. P. Ivleva*)

1.4.3 Photophoretic Separation of Hydrocolloids

Funding: DFG (German Research Foundation)

The key parameter of common techniques for the characterization and separation of particles suspended in liquids is the hydrodynamic diameter. A separation of dispersions according to the chemical properties of the particles could be essential for the clarification of processes in chemistry, pharmacy, life science or biology.

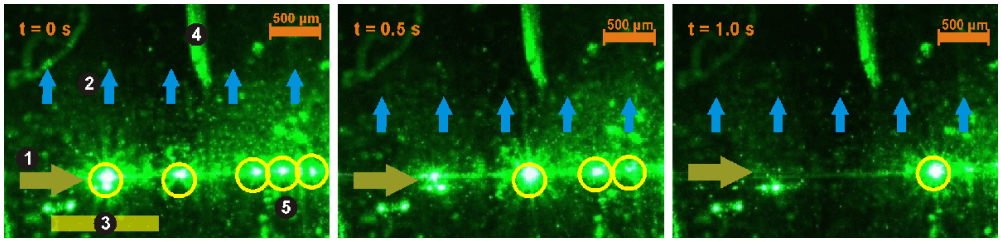
As chemical information can be determined from the analysis of refractive index and light absorption, optical techniques are beneficial for particle analysis. The characterization and separation of suspension mixtures due to their optical properties can be achieved by the application of light-induced forces.

Light as flux of photons can exert forces on media due to momentum exchange and is termed radiation pressure. If the masses involved are rather small, e.g microparticles, and the photon flux is high, e.g. from a laser, the radiation pressure causes migration of the microparticles in the laser beam. In the case of transparent particles this phenomenon is called photophoresis (direct photophoresis).

A laser beam perpendicular to the flow direction of a liquid containing particles causes a lateral displacement of the particles, the photophoretic displacement. Due to the photophoretic displacement, the particles are moved in different flow regimes. The magnitude of the photophoretic displacement is dependent on the intrinsic particle properties and can be applied for the separation of polydisperse samples.

For the separation of samples a bench-top device based on cross-flow configuration is currently being developed. The particle flow is perpendicular to the focussed laser beam. Separation of a polydisperse sample can be achieved by optimizing the photophoretic displacement of a fraction by variation of laser power and flow velocity of the bulk flow.

Photophoresis is a gentle and contact-free separation technique for polydisperse dispersions. As the separation is dependent on intrinsic particle parameters, no auxiliary information, e.g. staining, is needed for distinction of irregularly shaped particles, bacteria or cells.



Time sequence of separation in a cross flow, 1 = laser beam, 2 = bulk flow, 3 = colloid beam, 4 = separator, dispersion (left), separated particles (right), 5 = particle migrating in the beam.

(*C. Helmbrecht*)

1.5 Bioseparation and Microarray Technology (Head: Dr. M. Seidel)

1.5.1 Flow-Through Microarray Chip for Routine Quality Control of Food – Further Developments

Funding: Bayerische Forschungsstiftung (Bavarian Research Foundation
Cooperation: GWK Präzisionstechnik GmbH (München)

Aim of the project is the production of analytical microarray chips for routine laboratories in combination with a fluidic system and a data evaluation software enabling for fast and fully automated processing of immunoassays in routine laboratories. This technique is dedicated for the parallel determination of multiple analytes in complex matrices such as antibiotics in raw milk. In order to realize the project, the design of the regenerable flow-through microarray chip and the fluidic system was finalized. A new electronic hardware for a robust analysis was implemented and a new software for the fluidic processing and data analyis was launched on the stand-alone platform MCR 3 (Munich Chip Reader 3rd generation). The goal regarding the new device control was first of all an user-friendly, easy and safe handling of the MCR 3 platform for using in routine laboratories. Thus, a high grade of automatization in sample analysis and data evalution was realized. Also, facile programming of immunoassays had to be ensured enabling for flexible assay designs depending on the desired application. Using the new software, we could transfer and optimize the assay steps established for the quantification of antibiotic contaminants in food samples.

Image of the MCR3

For commercial applications the robustness of the enclosed microarray chips regarding long-term stability is crucial. Basic requirements for the production of regenerable microarray chips are first of all stable signals and second the possibility to ship them without any loss of quality. Therefore the study of shelf life for antibiotic microarrays was an important part in this project. In order to find the best conditions for shelf life, several storage types like preserving the microarray chips in the refrigerator, freezer or after freeze drying at RT were examined.

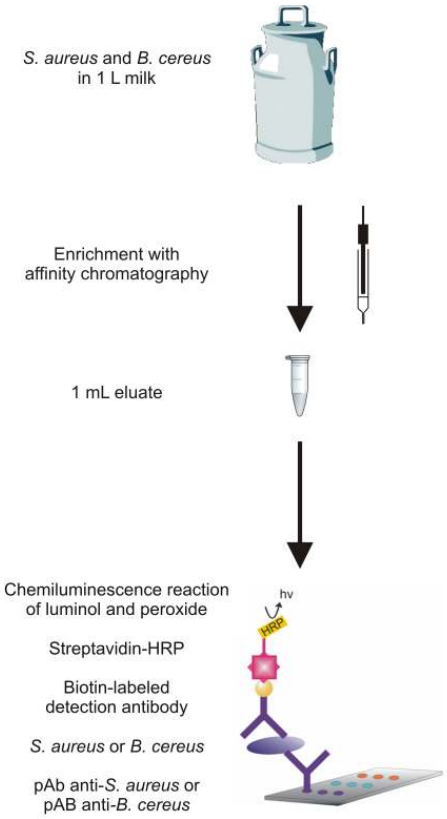
The realization of the new software and the stable antibiotic microarrays represent a further step of the MCR 3 platform on its way of becoming a demanded tool for cost-effective rapid and parallel quantification of various analytes without time-consuming sample pretreatment.

(*K. Wutz, A. Szkola*)

1.5.2 Detection of *Staphylococcus aureus* and *Bacillus cereus* in Milk Products After Enrichment With Bioaffinity Columns

Funding: Forschungskreis der Ernährungsindustrie (Research Foundation of the German Food Industry, FEI)
Cooperation: Chair for Hygiene and Technology of Milk, LMU München; Institute for Food Chemistry, University Hamburg; Chair for Fluid Mechanics, Friedrich-Alexander-University Erlangen-Nürnberg

The primary aims in the production of food are quality management and consumer protection which lead to an increase of efficiency and competing power in food industry. These aims are only possible with the development of reliable, easy and fast methods of analysis. Because of the high automatization in food industry the analytical systems should be integrated locally and be able to measure different analytes. In dairy industry the fast identification of microorganisms is very essential. For milk and dairy products *Staphylococcus aureus* as indicator for hygiene and *Bacillus cereus* as indicator for decayed food play an important role.



Schematic of the workflow

In routine analysis cultivation methods are often in use but the time between sampling and the result is with more than 24 - 48 h too long because dairy products have a very short storability. By the development and combination of new analytical techniques the risks could be estimated in a shorter time. In this work a multiplex antibody microarray with stopped-flow principle will be developed for the analysis of different microorganisms in one experiment.

Antibody microarrays have a limit of detection of 10^3 - 10^5 cells/mL. To increase the sensitivity of the analysis system, a previous enrichment step is needed. In this work bioaffinity chromatography is used to concentrate microorganisms from 1 L of milk. At the same time matrix components are removed. For affinity ligands antibodies and aptamers are tested which capture the microorganisms. After elution the concentrate is heat inactivated and measured with a chemiluminescence based microarray platform with sandwich immunoassay. The final aim is to concentrate microorganisms from 1 L to 1 mL within 1 h. As a result it will be possible to detect 10^4 cells per liter by microarrays.

The support material of the bioaffinity column consists of a monolith with a pore size of $20 \pm 4\,\mu$m, which was developed for the special purpose to enrich microorganisms in water. Now it is adapted for the use in the milk analysis.

The surface of the monolithic material is designed to have a minimal attachment of the milk components. Therefore the surface is coated with DAPEG and with this method antibodies have already been immobilized on the column. For that anti-HRP has been used as a test antibody. With a standard BCA-test for the detection of proteine concentrations the maximum amount of anti-HRP on the monolithic column was quantified to be $7{,}4 \pm 1{,}3$ mg/g. First enrichment experiments showed that the selective capture of microorganisms with affinity chromatography is possible. The next experiments will be done with heat inactivated *S. aureus* and *B. cereus* to optimize the parameters.
(*S. Ott*)

1.5.3 AquaSens: Rapid Enrichment and Quantification of Microorganisms in Water

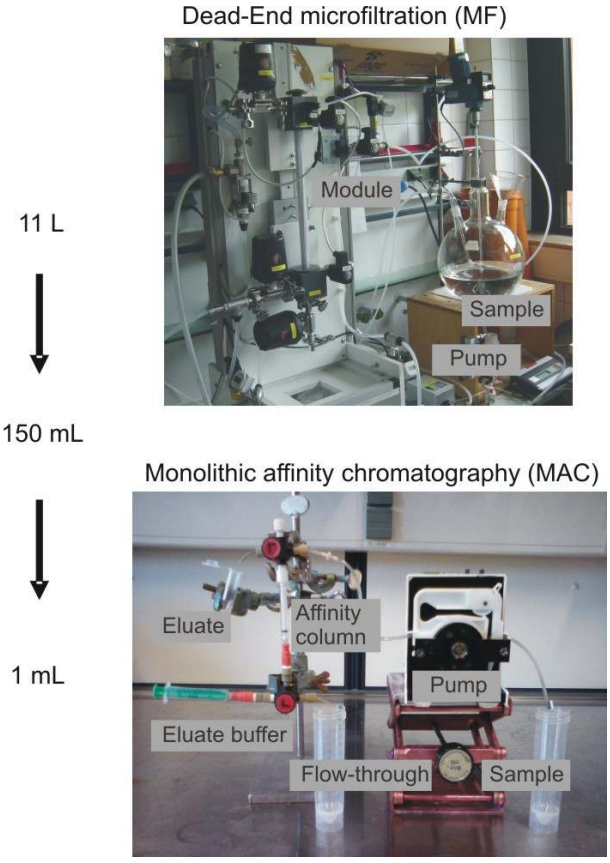
Funding: BMBF (Federal Ministry of Education and Research)
Cooperation: Siemens AG, München; FRIZ Biochem Gesellschaft für Bioanalytik mbH, München; Inge AG, Greifenberg; IWW Rheinisch-Westfälisches Institut für Wasserforschung GmbH, Mülheim a.d. Ruhr; Technologiezentrum Wasser, Karlsruhe

The fast and sensitive detection of microorganisms for health and safety reasons is very important in many fields - especially in the quality control of tap water. A high amount of people has just a limited quantity of safe tap water. Waterborne diseases and death are the consequences of pathogens in tap water. Therefore a rapid, quantitative and multianalyte detection system is needed. *E. coli* serves as hygiene indicator for this system. There must not be 1 cell in 100 mL of tap water. To reach this LOD the water sample has to be enriched.

The combination of a primary enrichment with microfiltration and a selective further enrichment with monolithic affinity chromatography is required for the detection of microorganisms with microarrays. The final experiments for the combined enrichment have been done together with the IWW in Mülheim a.d. Ruhr.

They have developed an automated dead-end microfiltration system. The corresponding microfiltration module was designed by Inge AG and had a surface of 0.15 m^2. The support material of the column designed by the IWC consists of a monolithic polymer with a pore size of $20 \pm 4\,\mu$m, which was developed for the enrichment of microorganisms in water. The capture process is of electrostatic nature. PmB, an antibiotic against Gram-negative bacteria was immobilized on the column for additional capture of the bacteria to the column.

To test this combination, 10^8 *E. coli* cells in 11 L of tap water were filtered by dead-end microfiltration. A concentrate of 150 mL was obtained. It was then acidified to pH 4 and pumped over the monolithic column. After the capture process, 200 μL of the elution buffer (pH 8.2) were sucked through the column from the opposite direction. After 5 min resting time, 800 μL of the elution buffer were added to the column to obtain 1 mL of eluate.

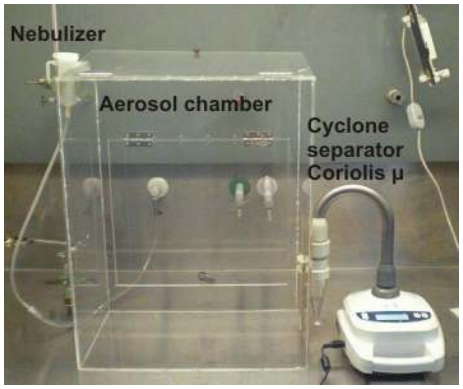


The recovery of the monolithic column alone was between 75.0 ± 4.7 % and 94.3 ± 13.1 %, detected with the flow cytometer. The recovery of the combined enrichment process was between 6.2 % and 70.3 %, which indicates a high variability by using dead-end microfiltration in combination with MAC. The recovery of the combined system was detected with by Colilert-18, DAPI-dye and antibody microarrays. The microarray analysis was comparable with the flow cytometry. (*S. Ott*)

1.5.4 Detection of *L. pneumophila* in Bioaerosols by Means of Antibody Microarrays

Funding: IWC

Legionella spp. infections are a growing problem for the public health care system. Legionella can be found ubiquitous in natural and artificial water systems. Infections are mainly caused by the transmission of contaminated aerosols, which can originate from showers, cooling towers or air conditioning systems among others. Thus, the monitoring of bioaerosols concerning Legionella is of high importance and the quantitative detection is an analytical challenge, which is not solved yet. The currently used standard method for the detection of Legionella is the determination of the colony number in a selective medium. This method is very sensitive but labor-intensive and time-consuming (10 days). To enable a fast and early intervention in case of contamination, a rapid, sensitive and multi-analyte quantification method is necessary, as the genus Legionella has many species and serogroups. Serogroup 1 of *L. pneumophila* is responsible for Legionnaires' disease which has a mortality rate in the order of 10 to 15 %. The microarray technology is a fast and parallel quantification of different bacteria and it is possible to discriminate rapidly between pathogenic and non-pathogenic contaminations.



Setup for bioaerosol production and sampling

The aim of this work was to develop a method for the detection of heat-inactivated *L. pneumophila* Serogroup 1 and living *E. coli* in bioaerosols. Bioaerosol was produced with a nebulizer, which is commonly used for the therapy of respiratory diseases. For collecting the airborne microorganisms the cyclone separator Coriolis μ, a device particularly designed for bioaerosol sampling, was utilized. For the microarray measurements a chemiluminescence readout system was used. Antibodies against the bacteria were immobilized on polyethylene glycol modified glass surfaces and served as selective capture molecules.

The bioaerosol was released to a plastic chamber and the bacteria from the aerosol could subsequently be collected in the liquid phase using the Coriolis μ with a recovery of $32{,}2 \pm 6{,}5\,\%$ for *E. coli* and $23{,}5 \pm 4{,}4\,\%$ for *L. pneumophila*. The measurements were carried out with microarrays and additionally with flow cytometry as reference method. The recoveries obtained with microarrays were in good agreement with the results of the flow cytometry.

The key parameter for bioaerosol measurements is the number of cells that can be detected per volume of air. The detection limit for aerosols can be derived from the sampling interval, the flow rate of the sampler, the sampling volume, the sampling efficiency and the detection limit of the detection method in the liquid phase. For the used setup and the microarray detection the achieved detection limit was about $7 \cdot 10^3\,\mathrm{cells/m^3}$ using the maximum sampling flow rate (300 L/min) and a sampling interval of 10 min.

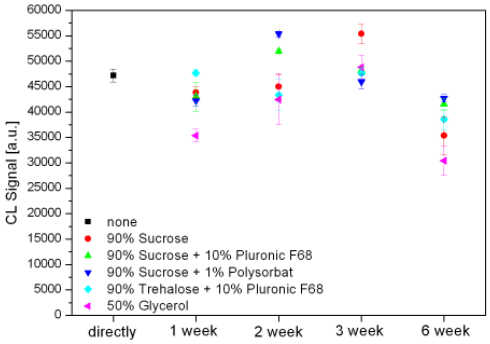
In further experiments a matrix rich in microorganisms was simulated for the quantification of L. pneumophila. This mixed bioaerosol contained *L. pneumophila* with about 1 % *E. coli*. The microarray measurements showed that the measurement of mixed bioaerosols was possible and reproducible results could be obtained. Especially for the measurement of mixed bioaerosols the microarray technique showed the advantages of selectivity and the possibility to analyze different analytes in one sample.
(*V. Langer G. Hartmann*)

1.5.5 Development of an Antibody Microarray for the Detection of Biotoxins

Funding: IWC
Cooperation: Robert-Koch-Institute (Dr. Dorner)

The biological agents, who arguably pose the greatest threat for humans in case of a bioterroristic attack, are smallpox, plague and airborne anthrax as well as intoxication with botulinum neurotoxins (BoNT). Wein and Liu published a mathematical model, which shows the devastating consequences in a cow-to-consumers supply chain of a deliberate release of botulinum toxin. Devoid of any control, the mean number of people who consume the contaminated milk is 568 000.

Also other high molecular-weight proteotoxins such as ricin and staphylococcal enterotoxin B (SEB) are regarded as potential biological warfare agents, because of their availability, stability, ease of preparation and high toxicity. To prevent contamination of water and food, and thus to ensure the safety of society, a rapid and sensitive method for the simultaneous detection of as many bioterroristic agents as possible is required. The microarray-technology particularly being a multiplex detection system is suitable for these applications.



Different additives for the long-term stability of antibody microarrays

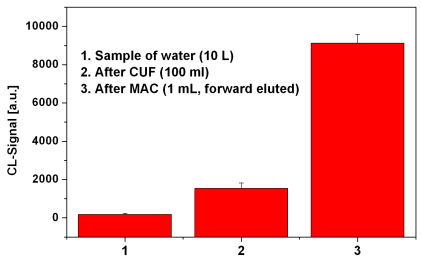
The aim of the work is the development of a multi-analyte immunoassay for the detection of proteinogenic biotoxins. The quantification of antigens will be implemented using a sandwich immunoassay. Therefore capturing antibodies are immobilized covalently on polyethylene glycol substrates, which capture the toxins out of liquid samples like water, milk or juice. Antigen-specific detection antibodies are used which are detected by an enzyme-catalyzed chemiluminescence reaction (CL). The CL signal is recorded by a CCD camera. As capturing or detection antibodies, both monoclonal and polyclonal antibodies could be used. The measurements are carried out on the MCR 3 platform.

Using antibody microarrays for multiplex analysis it is essential, that the chips are storable and transportable. Until now antibody microarrays could only be used one-time, as so far there is no possibility to regenerate these chips without any loss of the signal intensity. So in this work, it was especially important to analyze the shelf life of antibody-microarrays. To find the optimal conditions for long term stability, different filling solutions and storage types were tested. Antibody-microarrays filled with sugar solutions like sucrose or trehalose and stored in the refrigerator showed the best results. Storage over 3 weeks was possible without any loss of chemiluminescence signals. With these results an antibody microarray on the MCR 3 platform will be established for the quantification of the three biotoxins BoNT, SEB, and ricin. The quantitative results will be compared with the suspension array, which is developed at the RKI by using the Luminex platform.
(*A. Szkola*)

1.5.6 Combined System for Enrichment and Detection of Microorganisms in Drinking Water

Funding: DFG (German Research Foundation)

Monitoring the microbial quality of drinking water is of high importance in the health care system as safe drinking water is a basic requirement for maintaining human health. Pathogenic bacteria, which are relevant concerning drinking water quality, include e.g. *E. coli* O157:H7, *Salmonella typhimurium*, *Campylobacter jejuni* and *Legionella pneumophila*. Also the quantification of the indicator organism *E. coli* was in the focus. Most of the currently used detection methods for bacteria are quite time consuming, which prevents a fast and early intervention after a contamination event. Therefore a rapid, sensitive and especially multi-analyte detection method is essential. The microarray technology is a promising method for the detection of bacteria as a fast and parallel quantification of different analytes is possible in one experiment. In order to reach the required sensitivity, bioanalytical detection systems need to be combined with a previous enrichment step to enrich bacteria from 10 - 100 L water samples to a 1 mL concentrate.



Increased CL-signals on antibody microarrays by the enrichment of *L. pneumophila* with cross-flow ultrafiltration (CUF) and monolithic affinity chromatography (MAC)

The aim of this project was a combination of a primary mechanical enrichment, followed by a affinity separation method and a subsequent microarray detection to obtain a system which can be used for water monitoring. The first enrichment step is carried out with a computer controlled cross-flow filtration system using a hollow fibre membrane module, a peristaltic pump and valves arranged in a system that allows circulation. The tangential flow of the sample avoids intense fouling on the filter module. Using microfiltration membranes the enrichment took 15 min for 10 L of water. Ultrafiltration membranes have a lower permeability and the enrichment took 23 min. The second enrichment step is done with monolithic affinity chromatography. The support material of the column consists of a monolithic polymer with a pore size of $20 \pm 4\,\mu$m, which was developed for the rapid and selective enrichment of microorganisms with a high concentration factor. The microorganisms were captured electrostatically using an acidified sample at pH 3. Matrix components were separated to minimize interferences by the multiplexed bioanalysis. The enriched microorganisms were obtained by elution with 1 mL of carbonate buffer (pH 8.2) in 10 min. The detection of bacterial cells is performed using antibody microarrays on an automated chemiluminescence readout system. The spotted antibodies against the relevant bacteria serve as selective capture molecules. They are immobilized on polyethylene glycol-modified glass surfaces. For the bacteria recognition a second antibody is used, allowing the formation of a sandwich immunoassay. The detection is realized by means of a horseradish peroxidase-catalyzed chemiluminescence reaction. A quantitative result was obtained after 67 min, so that the combined analyis strategy took 1 h and 40 min.

Finally, after a combination of enrichment and detection living *E. coli* cells and heat-inactivated *L. pneumophila* could be quantified with detection limits of $4 \cdot 10^5$ cells/mL and $1 \cdot 10^3$ cells/mL, respectively, by means of a stopped-flow microarray chemiluminescence immunoassay. By combining cross-flow ultrafiltration, monolithic affinity chromatography and microarray analysis 10^8 *L. pneumophila* could easily detected in 10 L of water. An amplifiction of CL signals on the antibody microarray with a factor of 9 was achieved with cross-flow ultrafiltration and by a factor of 54 by combining CUF and MAC.

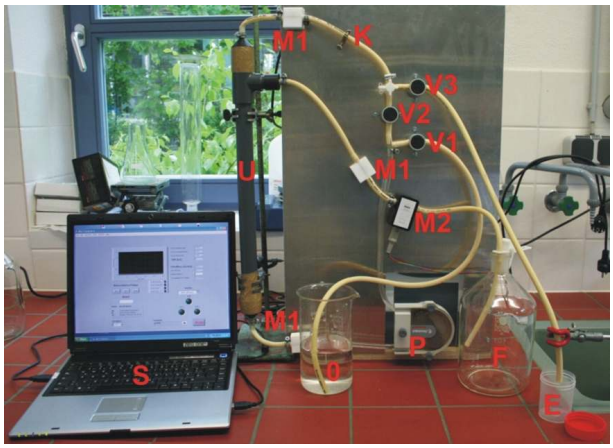
(*V. Langer, M. Rieger, L. Pei, S. Ott*)

1.5.7 Pathogenic Viruses in Water – Detection, Transport and Elimination

Funding: DFG (German Research Foundation)
Cooperation: Centre of Infectiology and Infection Prevention of the University of Bonn, Federal Environment Agency, Berlin; Institute of Groundwater Ecology at the Helmholtz Zentrum, München; Institut für Siedlungswasserwirtschaft und Abfalltechnik of the Leibniz University, Hannover

Viruses are one of the most dangerous contaminants in water. Mainly enteroviruses (Polioviruses, Coxsackie virus A and B, ECHO virus), Norwalk or Norwalk-like viruses, Rotaviruses, Hepatitis E and A virus and Adenovirus belong to the health-relevant water-associated viruses. In order to avoid the outbreak of water-borne diseases caused by such viruses, it is necessary to have a system for monitoring samples quickly and sensitively.

Detecting water-borne viruses is much more complex than the detection of other microorganisms. Many viruses are only poorly cultivable and when these cultivation methods are possible, it takes a lot of time until getting results. Furthermore, viruses are able to cause diseases in very low concentrations. So in this project a system, which combines the enrichment of viruses out of 30 m^3 water with the detection and quantification, will be developed. For first experiments, the bacteriophage MS2 will be used, representative for RNA phages. Afterwards phiX174 will serve as a model system for somatic phages. The system should consist of a 2-stage cross-flow ultrafiltration (CUF) combined with electrostatic enrichment by means of monolithic columns. The following quantification can be done by quantitative cell assays, as well as by bioanalytic methods like DNA microarray or quantitative PCR. The cross-flow filtration should be able to enrich viruses from large volumes (30 m^3) to a volume of about 10 L in the first and 50 - 100 mL in a second step. With monolithic columns based on porous polymers a further enrichment will be possible. The resulting small volumes of about 1 mL can then be utilized for detection. With the combination of these methods monitoring of drinking water should be able within hours.



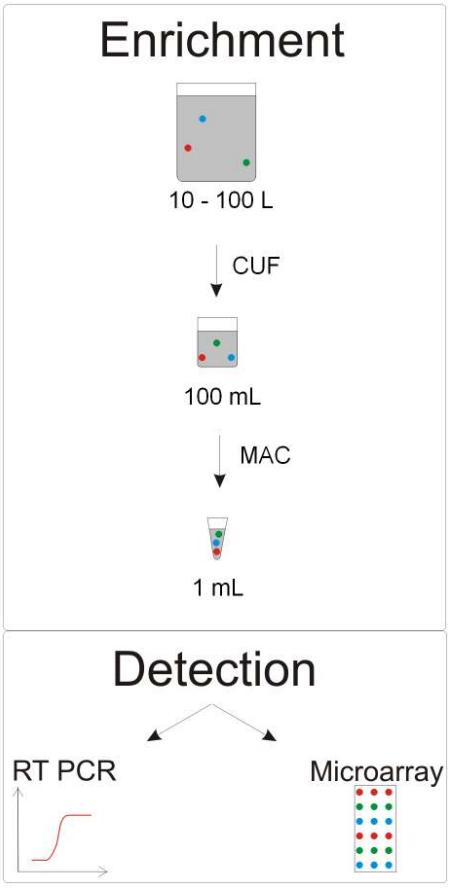
Setup or the cross-flow ultrafiltration unit.

A testing device of the small CUF unit 2 is already constructed. There, optimal conditions for the filtration, elution and cleaning are determined with bacteriophage MS2 as a model virus. A plaque-assay for MS2 based on *E.coli* was established in order to determine the recovery rates of the enrichment steps. It was also shown, that the quantification with PCR is working. So, the recovery of MS2 (spiked in 20 L drinking water; $2 \cdot 10^8$ PFU) enriched with the CUF unit 2 was $30 \pm 9\%$ (n = 4). For the enrichment of MS2 by means of monolithic columns, 10 mL drinking water was enriched to a final volume of 1 mL with a velocity of 10 mL/min. Here, we found higher recovery rates ($139 \pm 19\%$; n =3) than for glass wool filtration ($41 \pm 6\%$; n = 3). (*M. Rieger, L. Pei*)

1.5.8 PATH$_2$OGENSCAN: Microbial Water Quality Monitoring by Means of Rapid Enrichment Methods and DNA Microarrays

Funding: BMBF (Federal Minitry of Education and Research); MOST (Ministry of Science and Technology, Israel)
Cooperation: State Health Department, Stuttgart (LGA); Water Technology Center, Karlsruhe (TZW); GWK Präzisionstechnik GmbH, Munich; Technion, Israel

Quality control of water is very important for the public health. Therefore rapid analytical detection and quantification methods are needed for monitoring of different kinds of water, for example surface water, sewage water or drinking water. Pathogenic organisms and particularly viruses are able to cause diseases in very low concentrations. Thus, the aim of this project is the rapid, user-friendly and precise quantification of waterborne pathoges and indicator organisms (Norovirus, Adenovirus, Rotavirus, bacteriophages MS2 and ΦX174, *E. coli*, *E. faecalis*, *L. pneumophila*, Cryptosporidium und Giardia). An automated detection and quantification system for these relevant pathogens is needed, because cultivation methods are problematical. They are time-consuming and many viruses are poorly or not cultivable.



Concept for rapid analysis of microorganisms in water

Therefore, we are developing a DNA microarray for multiplex analysis. Depending on the water sample, different enrichment methods are tested and compared in cooperation with TZW and LGA, for example glasswool filtration, crossflow filtration, cation-coated filters or monolithic chromatography. The organisms should be concentrated and matrix must be removed before analyzing with the DNA microarray. The nucleic acid of the pre-enriched organisms must be isolated, before amplification in a PCR reaction. Labeled primers will be used to separate the double-strands and to generate a chemiluminescence signal on the flow-through DNA microarray platform.

In our institute, we are developing a crossflow ultrafiltration system (CUF) to enrich the water sample from about 10 - 100 L to a volume of 100 mL. For bacteriophage MS2 the enrichment in 20 L of drinking water is possible in 33 min with a stable recovery rate of 30 ± 9 %. The following step is the monolithic affinity chromatography (MAC) for further enrichment to a volume of 1 mL. Therefore first experiments have been done to enrich 10 mL of tap water spiked with MS2 to a volume of 1 mL. 84 ± 6 % of the phages were adsorbed at the surface and all of them (recovery was 139 ± 19 %) could be eluted with an extraction buffer containing 3 % beef extract and 0.5 M glycine at pH 9.5. The last step is the analysis with quantitative reverse transcription PCR and DNA microarray. The working range for the PCR combined with an isolation method for RNA is $9{\cdot}10^3$ - $9{\cdot}10^8$ PFU/mL. It could already be shown, that the combination of the monolithic enrichment and quantification with PCR is working. For the microarray detection a limit of detection of $1 \cdot 10^5$ PFU/mL was achieved.

In the next time, we plan further optimization work on all process steps to increase the sensitivity of this analysis system. Furthermore the analysis platform MCR3 should be adapted for measuring the DNA microarrays at stringent conditions by heating the flow cell and the tubes.
(*M. Rieger, L. Pei, S. Prell*)

1.5.9 Validation of the Munich Chip Reader (MCR 3) for the Analysis of Antibiotics in Raw Milk Samples

Funding: BayStMELF (Bavarian State Ministry for Nutrition, Agriculture and Forestry)
Cooperation: Chair of Hygiene and Technology of Milk (LMU München), Milchprüfring Bayern e.V. (Wolnzach), MUVA (Kempten)

The Munich Chip Reader, 3rd generation (MCR 3), has been developed as standalone platform enabling fast and cost-effective analysis of multiple analytes in various food and liquid matrices. In this context, the quality control of raw milk regarding antibiotic residues is an actual topic of food safety due to the associated risks for human health.

Aim of the project is bridging the gap between common insensitive and time consuming microbiological methods (inhibition tests) on the one hand, and cost-intensive methods using mass spectrometry (HPLC-MS) on the other hand. The realization lead to the development of automated chemiluminescence immunoassays performed using regenerable flow-through microarray chips (CL-MIA) based on PEG-ylated glass surfaces. Different antibiotic derivatives are directly coupled to epoxy-activated PEG chips allowing for multiplexed analysis of currently 14 antibiotic residues in raw milk without sample pretreatment. Experiments were successfully carried out obtaining the working ranges of all 14 respective antibiotics including the corresponding MRL values.

For validation of the established method the precision and reproducibility had to be proved in a service routine laboratory. In cooperation with the Milchprüfring Bayern e.V. and the MUVA Kempten we have characterized and validated the MCR 3 platform by comparing the results with BRT Inhibitor Tests and HPLC-MS measurements and we have found a good accuracy of the method as shown in the table.

Detected Antibiotics	MRL [µg/L]	BRT [µg/L]	MCR 3 [µg/L]	HPLC-MS [µg/L]
Penicillin G	4	≥ 4	3,8	3,9
Penicillin G	4	≥ 4	6	4,3
Penicillin G	4	≥ 40	22	29,5
Penicillin G	4	≥ 800	833	976
Penicillin G, Neomycin B	4, 1.500	≥ 16	15, 56	14,9
Cloxacillin	30	≥ 30	25	21,1
Cloxacillin	30	≥ 30	37	34,1
Cloxacillin	30	≥ 60	102	105
Cloxacillin	30	≥ 300	265	281
Cloxacillin	30	≥ 300	200	274

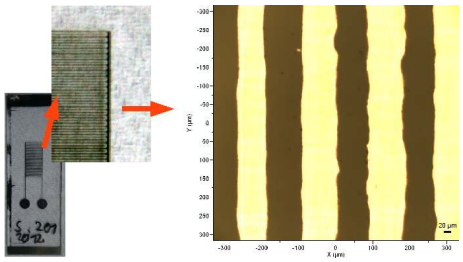
To summarize, the new microarray biosensor system offers the potential of inexpensive identification and quantification of antibiotics and will aid the food industry to ensure quality and safety of milk.
(*K. Kloth, K. Wutz*)

1.6 Aerosol Research (Head: Prof. Dr. R. Niessner)

1.6.1 Soot Conductivity as a Sensor Principle

Funding: Audi AG
Cooperation: Abgaszentrum der Automobilindustrie (ADA), Weissach

Atmospheric aerosol particles form a class of air pollutants of great concern to air quality. They are of central importance for atmospheric chemistry and physics, climate and public health. Especially in urban area, soot particles emitted by diesel engines account for a major fraction of air pollutants. Present and future emission limits require that these particles are efficiently removed from diesel engine exhaust. Diesel particulate filters (DPF) used for this purpose must be regenerated periodically by oxidation. Since the DPF can be damaged by thermal and mechanical forces its functionality needs to be monitored. Therefore an on-board soot sensor must be introduced into the post DPF exhaust gas stream. Many different principles for soot detection are currently under development. A promising principle is the detection by a sensor measuring the electrical conductivity of soot particles deposited between two electrodes. Since the exhaust of a diesel engine is a mixture of many different substances in the gas, liquid and solid phase, with changing compositions, it is vital to investigate all possible influences on the sensor signal.



Interdigital electrodes on a glass slide produced by lithography

In order to achieve a reliable on-board diagnostic for DPF systems a deeper understanding of the mechanisms which lead to a conductivity signal must be obtained. In this study different factors like density and temperature are investigated. Additionally, inorganic impurities in the soot composition that may lead to deposition of particles with different conductive properties need to be considered. However, the main focus of this work is the investigation of structural properties of soot and their influence on the conductivity.

Different carbonaceous materials (Printex XE2, Printex 30, special black, spark-discharge soot and graphite powder) are pressed to a pellet and investigated by a four-point conductivity measurement. This method allows us to determine the conductivity in dependence of the density. Additionally, graphite powder is mixed with SiO_2, TiO_2 and Fe_3O_4. This allows us to interpret the influence of less conductive particles being mixed with soot. For structural analysis Raman microspectroscopy is applied. We use the newly developed multi-wavelength Raman microspectroscopy to characterize the structure and to correlate the structural with conductivity data. Additionally, a five-band fitting procedure is applied to gain additional parameters concerning the graphitic and amorphous content of soot and related carbonaceous samples.

Moreover, a thermophoretic precipitator has been developed to deposit a soot layer on a glass surface. This glass surface is modified by lithography with interdigital electrodes. This combines the conductivity measurement principle with a controlled and size independent precipitation. However, it is still crucial to test this sensor principle with an independent and reliable method. Therefore a test vehicle will be equipped with the AVL Micro Soot Sensor to validate this promising approach for an on-board particle sensor.
(*J. Schmid, B. Grob*)

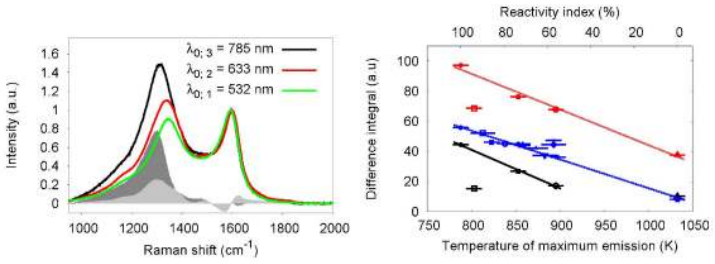
1.6.2 Multi-Wavelength Raman Microspectroscopy for Rapid Prediction of Soot Oxidation Reactivity

Funding: IWC
Cooperation: Daimler AG, MAN SE

The reduction of soot nanoparticles emitted by diesel engines is a pressing theme. To meet the present and future emission limits, soot particles must be removed from the engine exhaust. Diesel particulate filters, which have been applied for this purpose need to be regenerated by gasification of the deposited soot. The efficiency of this regeneration step is strongly affected by the oxidation reactivity of the deposited soot particles. In particular, the formation of highly reactive soot would make it possible to reduce energy consumption at the regeneration step (due to shorter combustion times and lower temperatures).

Experiments concerning the reactivity of soot are done by Temperature Programmed Oxidation (TPO). High Resolution Transmission Electron Microscopy (HRTEM) is usually applied for investigation of soot structure. However, TPO and HRTEM measurements are very time and cost consuming. On the other hand, one can obtain detailed information about the reactivity of soot by measuring the structure with Raman Microspectroscopy.

Raman spectra show peaks at 1580 cm^{-1} (G or "Graphite" peak) and 1350 cm^{-1} (D or "Defect" peak), but the D and G peaks exhibit strongly varying relative intensities and widths.



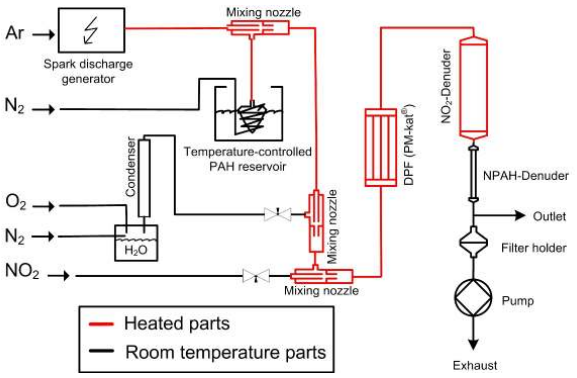
Raman spectra of soot at different emission temperatures

In order to obtain detailed structural information Multi-wavelength Raman microspectroscopy (MWRM) analysis for characterization of soot structure and reactivity was developed. This new method is based on the dispersive character of carbon D mode in Raman spectra (i.e. red shift and increase in intensity at higher excitation wavelength, λ_0). The approach was proven by investigating various diesel soot samples and related carbonaceous materials at different λ_0 (785 nm, 633 nm, 532 nm and 514 nm). In order to compare the behavior of the D mode for various samples and to derive a single parameter characterizing the soot structure, the difference of integrals for pairs of spectra collected at different λ_0 was calculated. MWRM analysis revealed substantial differences in the structural ordering which decreases from graphite, over Printex XE2 and various diesel soot samples, to spark discharge soot. To obtain the relation between structure and reactivity of soot, MWRM analysis was combined with temperature-programmed oxidation (TPO). TPO allowed us to characterize the oxidation behavior of soot in terms of the maximum emission ($CO + CO_2$) temperature and reactivity index. The latter was calculated by introducing the reactivity limits: spark discharge soot containing a large amount of disorder represents the upper limit, whereas the lower limit is given by graphite powder with high structural order. The comparison of MWRM (viz., the observed Raman difference integrals) and TPO data revealed a linear correlation between soot structure and oxidation reactivity. Thus we demonstrated for the first time the potential of MWRM for a robust and rapid prediction of diesel soot reactivity based on the structure-reactivity correlation.
(*J. Schmid, B. Grob, N. P. Ivleva*)

1.6.3 Nitro-PAH Formation in Diesel Particulate Filters

Funding: DFG (German Research Foundation)

The progressive regulations on diesel exhaust pollutant emissions led to the development of diesel particulate filters (DPF) to reduce the amount of emitted soot particles. These filters mainly consist of ceramic monoliths with alternating flow channels (so called "closed structure" design) which are closed at the ends to force the exhaust gas through this porous structure. Another filter setup is the "open structure" where the soot gets trapped while the exhaust passes some metallic mesh structures. Both systems need a regeneration procedure which oxidizes the trapped soot to prevent the filter from plugging. This regeneration can be achieved with elevated temperatures (> 500 °C) or at moderate temperatures (230 °C - 350 °C) with the aid of some oxidants like O_2 or NO_2. The superior oxidation potential of NO_2 in comparison with O_2 as well as the presence of NO_x in the exhaust gas (which can be converted to NO_2 with help of an oxidation catalyst) led to its favoured use during DPF regeneration. But there are valid assumptions that this technology is capable of increasing the mutagenic potential of diesel exhaust, for example by nitration of polycyclic aromatic hydrocarbons (PAH) during continuous regeneration with NO_2. This nitration would lead to the much more toxic nitrated polycyclic aromatic hydrocarbons (NPAH).



Setup of the DPF simulation system

The aim of our study is to investigate this possible nitration reaction. Our first published experiments showed the nitration of pyrene and benzo[a]pyrene (B[a]P) at various conditions relevant for diesel exhaust, leading to the corresponding NPAH (1-nitropyrene and 6-nitro-B[a]P). During the investigation of the nitration at higher temperatures we found that the PAH as well as the PAH desorbed into the gas phase. These results proved the necessity of further investigation on the gas phase reaction taking place between NO_2 and PAH. Therefore a new simulation system was built, which allowed the controlled heating of all relevant parts and mixing chambers to simulate real diesel exhaust pipe conditions.

Before starting this investigation another problem in sample generation had to be solved. Our previous results showed, that a NO_2-scrubbing device is needed to avoid nitration of unreacted PAH passing the DPF and being collected on a sampling filter afterwards. These PAH would be nitrated on the sampling filter causing positive artefacts if the excess of NO_2 wouldn't be removed prior to filtration. The method of choice was to use annular denuders coated with potassium iodide. For the new simulation system a greater capacity and better efficiency of these denuders was required. So we built new heatable denuders and optimized the heat stability, capacity and efficiency of the coating.

Also the gaseous PAH and NPAH should be quantified before passing the soot layer of the sampling filter to avoid adsorption. So with the use of XAD4 coated annular denuders in front of the sampling filter a better estimation of the gas/particle fractionation of PAH and NPAH can be determined.

With this new improved simulation system (figure) we are now able to investigate and differentiate particle as well as gas phase nitration of PAH inside different DPF-structures.

(*M. Carrara, J.-C. Wolf*)

1.6.4 Characterization of Internally Mixed Soot Aerosols by Raman Microspectroscopy

Funding: DFG (German Research Foundation), RFBR (Russian Foundation of Basic Research)
Cooperation: Institute of Nuclear Physics, Moscow State University

In order to evaluate the effect of transport emissions on the environment and to define the resultant limitations, it is necessary to determine the specific characteristics of particle emission of different vehicles and different fuels. Therefore it is crucial to develop a method for the characterization of soot composition, structure and reactivity in accordance with the current requirements.

Nowadays, the most widely used techniques for black carbon (BC) monitoring are based on thermal and optical methods. The measurements of total carbon (TC) amount are usually in fairly good agreement, whereas the measurements of elemental carbon (EC) amount result in extensive deviations. Among others, metal contaminations of multicomponent aerosols produced by diesel and gas turbine engines due to fuel additives, oil contaminations, or corrosion can cause these deviations. These contaminations may catalyze the oxidation of soot particles, leading to significant changes in their physical, thermochemical and optical properties.

Quartz fiber filter loaded with soot doped with iron compounds (left) and same filter with residues of iron oxides after burning the filter in oxygen stream (right).

In the experiments, which were conducted so far, emphasis was placed on soot internally mixed with iron compounds. Iron is the dominant relevant metal components that can be found in real soot as in the soot emission of ships.

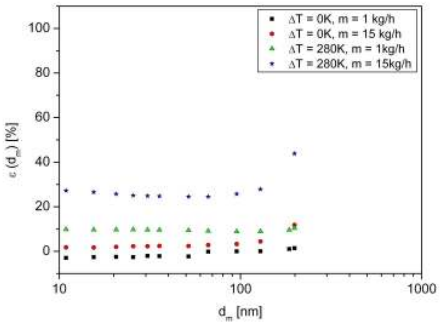
In order to investigate the influence of metal compounds on soot properties, a test bench including a burner unit was built up. Propane is used as fuel gas and burned in an oxygen stream. The flame can be additionally fed with a nitrogen stream charged with iron compounds. The synthesized iron-doped soot was collected on quartz fiber filters. Scanning electron microscopy verified the existence of iron on the filters. Raman analysis at λ_0 of 633 nm revealed signals in the lower shift range from 200 to 800 cm^{-1} in addition to the characteristic bands of soot at 1334 and 1600 cm^{-1}. Burning of the filter samples in an oxygen stream revealed an orange residue which was characterized by Raman Microspectroscopy to be iron oxide.
(*H. Bladt, N. P. Ivleva*)

1.6.5 Analysis of Deposition Mechanisms on the Gas Side Surface of Exhaust Gas Heat Exchangers

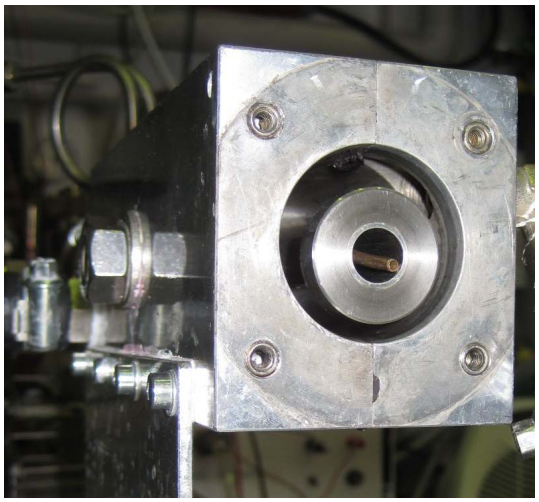
Funding: FVV (Association for Combution Engine Research)
Cooperation: Institute for Internal Combustion Engines, TUM

The combustion process in diesel engines is a source for hazardous environmental pollutants such as nitrogen oxides (NO_x) or particulate matter (soot). Cooled exhaust gas recirculation (EGR) is a very effective method to reduce NO_x emissions of diesel engines. However, due to particulate matter and other components present in diesel exhaust gas, EGR heat exchangers are very prone to fouling.

Different mechanisms for particle deposition in EGR heat exchanger fouling are known, like diffusion, impaction, interception and thermophoresis, the latter usually being assumed to be of greatest influence for deposit build-up.



Increase of deposition efficiency for increasing temperature gradient within the cooler and increasing gas mass flow. Deposition efficiency is not dependent on particle size for particles < 200 nm



Front view of opened heat exchanger with soot sampling capillary in the center

Various model cooler experiments were performed using a model aerosol that either contained only soot particles from a spark discharge generator (GfG) or GfG soot with HC, water and H_2SO_4 vapor added.

Particle concentrations and sizes were varied and measured using differential mobility analyzer, scanning mobility particle sizer and Faraday cup electrometer. By using a new measurement setup at the model test bench, it was possible determine the soot concentration in the center axis of the flow through the tubed model cooler.

Dry soot aerosol became deposited due to thermal forces under corresponding temperature and flow conditions. However, aerosol containing HC or H_2SO_4 vapor showed a higher potential for deposit build-up. Nuclei present in the exhaust gas condense on the cooled wall and build up a sticky layer where soot particles are firmly attached. Additionally, condensation creates a concentration gradient which leads to an enhanced particle transport to the wall, the process being known as diffusiophoresis. We found that this mechanism has a major contribution to EGR heat exchanger fouling, as diesel exhaust always contains condensable components, e.g. water vapor.

Additionally, samples of soot deposited in the model heat exchanger used at the engine test bench of the Institute for Internal Combustion Engines were analyzed to gain information on organic carbon, sulfate and calcium contents. With these results it was possible to draw further conclusions on the influence of diffusiophoresis on the deposit build-up.

Besides the experimental work, theoretical predictions for different mechanisms were determined. For diffusion, thermophoresis and diffusiophoresis calculations were performed and the results compared to the experimental data. Good agreement was found for some of the theories, for others large deviations occurred. At this point, further work is necessary and in progress. (*G. Hörnig*)

2 Publications of Present Members of the IWC

2.1 Journal articles (reviewed)

T. Baumann, L. Toops and R. Niessner; Colloid Dispersion on the Pore-Scale. Water Res. 44 (2010) 1246-1254

M. Carrara, J.C. Wolf and R. Niessner; Nitro - PAH Formation Studied by Interacting Artificially PAH - coated Soot Aerosol with NO_2 in the Temperature Range of 295 - 523 K. Atmos. Environ. 44 (2010) 3878-3885

M. G. Gonzalez, X. Liu, R. Niessner and C. Haisch; Lead Ion Detection in Turbid Media by Pulsed Photoacoustic Spectrometry based on Dissolution of Gold Nanoparticles, Sensors & Actuators B 150 (2010) 770-773

M. G. Gonzalez, X. Liu, R. Niessner and C. Haisch; Strong Size - Dependent Photoacoustic Effect on Gold Nanoparticles by Laser - induced Nanobubbles. Appl. Physics Letters 96 (2010) 174104/1-174104/3

C. Haisch, K. Eilert-Zell; M. Vogel, P. Menzenbach and R. Niessner; Combined Optoacoustic/Ultrasound System for Tomographic Absorption Measurements: Possi - bilities and Limitation. ABC 397 (2010) 1503-1510

C. Haisch, L. Opilik, M. Hays and R. Niessner; Photothermophoresis as a New Tool for Aerosol Characterizations. Journal of Physics: Conference Series 214 (2010) 012011, 6 pages

N. Ivleva, M. Wagner, A. Szkola, H. Horn, R. Niessner and C. Haisch; Label - free In Situ SERS Imaging of Biofilms. J. Phys. Chem. B 114 (2010) 10184-10194

N. Ivleva, M. Wagner, H. Horn, R. Niessner and C. Haisch; Raman Microscopy and SERS for In Situ Analysis of Biofilms. Journal of Biophotonics 3 (2010) 548-556

M. Knauer, N. Ivleva, R. Niessner and C. Haisch; Optimized SERS Colloids for the Characterization of Microorganisms. Anal. Sci. 26 (2010) 761-766

M. Knauer, N. Ivleva, X. Liu, R. Niessner and C. Haisch; Surface - enhanced Raman Scattering - based Label - free Microarray Readout for the Detection of Microorganism. Analytical Chemistry 82 (2010) 2766-2772

M. Kumke, A. Kupstat, D. Knopp and R. Niessner; Novel Intramolecular Energy Transfer (ET) Probe for the Detection of Benzo [a] pyrene Metabolites in a Homogeneous Competitive Fluorescence Immunoassay. J. Phys. Chem. B 114 (2010) 1666-1673

Z. Lin, J.-M. Lin, R. Niessner and D. Knopp; Double - codified Gold Nanoparticle Based Automated High – throughput Chemiluminescence Immunoassay for 2,4 - Dinitrotoluene. Anal. Methods 2 (2010) 824-830

X. Liu, M. Knauer, N. Ivleva, R. Niessner and C. Haisch; Synthesis of Core Shell SERS Tags for Bioimaging. Anal. Chem. 82 (2010) 441-446

E. Maiolini, D. Knopp, R. Niessner, S. Eremin, L. Bolleli, E. Ferri and S. Girotti; Chemiluminescent ELISA for BTEX Determination in Water and Soil. Anal. Sci. 26 (2010) 773-777

R. Niessner; Quantitative Determination of Phosgene Doses by Reflectometric Badge Readout. ABC 397 (2010) 2285-2288

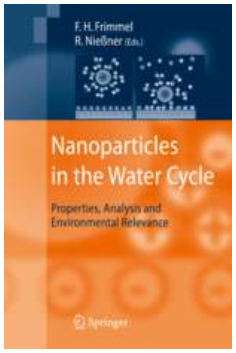
R. Niessner, J. Broekaert, M. Bron, J. Einax, H. Emons, C. Haisch, C. Huber, N. Jakubowski, D. Knopp, J. Popp and M. Schäferling; Trendbericht Analytische Chemie 2008/2009. Nachrichten aus der Chemie 58 (2010) 223-235

G. Pappert, M. Rieger, R. Niessner and M. Seidel; Immunomagnetic Nanoparticle - based Sandwich CL-ELISA for the Enrichment and Quantification of E. coli. Microchim. Acta 168 (2010) 1-8

D. Tang, Y.Yu, R. Niessner, M. Miro and D. Knopp; Magnetic Bead - based Fluorescence Immunoassay for Aflatoxin B1 in Food using Biofunctionalized Rhodamine B - doped Silica Nanoparticles. Analyst 135 (2010) 2661-2667

C. J. Werth, C. Zhang, M. Brusseau, M. Oostrom, and T. Baumann; A review of non-invasive imaging methods and applications in contaminant hydrogeology research, J. Contam. Hydrol. 113 (2010) 1-24.

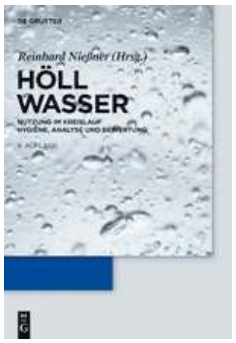
2.2 Monographs



T. Baumann, Nanoparticles in Groundwater - Occurrence and Applications, In: F. H. Frimmel, R. Niessner, Nanoparticles in the Water Cycle, Springer, Berlin (2010) 23-34.

F. H. Frimmel and R. Niessner (Eds.); Nanoparticles in the Water Cycle. Springer, Heidelberg (2010) 239 pages

R. Niessner, Nanoparticles Acting as Condensation Nuclei – Water Droplet Formation and Incorporation. In: F. H. Frimmel, R. Niessner, Nanoparticles in the Water Cycle, Springer, Berlin (2010) 13-21.



R. Niessner (Ed.); Höll: Wasser. de Gruyter, Berlin (2010) 1019 pages

K. Botzenhart, M. Seidel, M.; Wasservirologie, In: R. Niessner, Höll - Wasser, de Gruyter, Berlin (2010) 412-426.

S. Carlson, M. Seidel; Mikrobiologie des Wassers, In: R. Niessner, Höll - Wasser, de-Gruyter, Berlin (2010) 305-409.

H. H. Dieter, H. Höring, T. Baumann, Befund und Bewertung, In: R. Niessner, Höll - Wasser, de Gruyter, Berlin (2010) 713-808.

2.3 Conference Presentations

2.3.1 Oral Presentations

T. Baumann, Quantification of colloid transport at the pore scale in micromodels, Institute of Analytical Chemistry and Food Chemistry, 15.6.2010, TU Graz (invited).

M. Carrara, J. Wolf, R. Niessner, Laboratory Investigation of Post – Combustion NPAH Formation, Intern. Aerosol Conference, 29.8.-3.9.2010, Helsinki, Finland

C. Helmbrecht, R. Niessner, Continuous Characterization And Separation of Colloidal Mixtures by Photophoresis, Particles 2010, 22.-25.5. 2010, Orlando, USA

S. Huckele, R. Niessner, T. Baumann, Screening von Nanopartikeln in der ungesättigten Zone, FH-DGG Tagung 2010, 12.-16.5.2010, Tübingen.

N. P. Ivleva, C. Haisch, R. Niessner, T. Baumann, Towards In Situ Studies of Processes at Biogeochemical Interfaces by Raman Microspectroscopy, SPP 1315 Biogeochemical Interfaces in Soil, 04.-05.10.2010, Dornburg, Germany

N. P. Ivleva, Raman Microscopy in Environmental Analysis, Horiba Raman User Meeting 2010, 03.-04.5.2010, Munich, Germany (invited)

N. P. Ivleva, Raman Spectroscopy in Environmental Matrices, Analytica 2010, 23.-26.3.2010, Munich, Germany (invited)

M. Knauer, M. E. Schuster, J. Schmid, D. Su, R. Schlögl, R. Niessner, N. P. Ivleva, Soot Structure-Reactivity Correlations: Combined Studies with Raman Microspectroscopy, High-Resolution Transmission Electron Microscopy, and Temperature-Programmed Oxidation, International Aerosol Conference 2010, 29.8.-3.9.2010, Helsinki, Finland

C. Mayr, R. Niessner, T. Baumann, Untersuchung der Isotopen ^{34}S, ^{18}O und ^{2}H im Thermalwasser des Malmaquifers im Grossraum München, FH-DGG Tagung 2010, 12.-16.5.2010, Tübingen.

R. Niessner, Laser oder Antikörper – Zwei Freunde des Analytikers, GDCh – Vortrag an der Universität Hamburg, 17.6.2010, Hamburg (invited)

R. Niessner, Laser oder Antikörper – Zwei Freunde des Analytikers, GDCh – Vortrag an der TH Darmstadt, 4.5.2010, Darmstadt (invited)

R. Niessner, Chemiluminescence & Microarray Technology: A Strong Partnership for Analysts, XIV. International Symposium on Luminescence Spectrometry, 13. – 16.7.2010, Prague, Czech Republic (invited)

R. Niessner, Mikroarray – Technologie: Möglichkeiten und Herausforderungen zur Überwachung von Lebensmitteln, 15. Heiligenstädter Kolloquium, 27. - 29.9.2010, Bad Heiligenstadt (invited)

R. Niessner, Microarray – Technology: A Way to Exonerate Classical Analysis, ISEAC 36, Intern, Symp. On Environ. Anal. Chem., 5.-9.10.2010, Rome, Italy (invited)

R. Niessner, M. Carrara and J.-C. Wolf, Laboratory Investigation on Nitro-PAH Formation in the Temperature Range of 298 - 423 K, AAAR 29 th Annual Conference, 25. – 29.10.2010, Portland, USA

R. Niessner, Microarray Technology as Future Tool to Exonerate Classical Chemical Analysis Merck-Symposium, 3.9.2010, Darmstadt (invited)

M. Seidel, Rapid Microbiological Water Monitoring Based on Polymeric Imprinting Enrichment Coupled to Spectral Inspection and Microarray Technology. German-Israel Cooperation in Water Technology Research, 11th Status Seminar, 11.-13.10.2010, Darmstadt.

M. Seidel, Flow-through Chemiluinescence DNA Microarrays for the Quantification of Bacteria and Viruses in Water Samples. XIV. International Symposium on Luminescence Spectrometry, 13.-16.7.2010, Prague, Czech Rebublic.

M. Seidel, K. Kloth, C. Baumgartner, R. Diertrich, T. Westermair, E. Märtlbauer, R. Niessner, Characterization and Validation of a New Microarray Analysis Platform

for Parallel and Rapid Detection of Various Antibiotics in Raw Milk. 6th International Symposium on Hormone and Veterinary Drug Residue Analysis, 1.-4.6.2010, Ghent, Belgium.

M. Seidel, Kombination von Anreicherungstechniken und Mikroarrays zur schnellen Multiplex-Analyse von Mikroorganismen. 12. Vortragstreffen des Hochschullehrer-Nachwuchses bei der DECHEMA, 14.-26.2.2010, Dresden.

M. Seidel, S.C. Donhauser, K. Kloth, A. Wolter, R. Niessner, Flow-through Chemiluminescence Microarrays for the Rapid Quantification of Pathogens and Antibiotics in Liquid Samples. Rapid Methods Europe 2010, 25.1.-27.1.2010, Noordwijkerhoot, The Netherlands.

2.3.2 Poster Presentations

C. Helmbrecht and R. Niessner, Characterization of Optical Particle Properties by Photophoretic Velocimetry (PPV), Wasser 2010, 10.-12.5.2010, Bayreuth.

G. Hörnig and R. Niessner, Investigation of Mechanisms Involved in Particle Deposition in EGR Coolers, IAC 2010, 29.08. - 03.09.2010, Helsinki, Finland

N. P. Ivleva, M. Wagner, H. Horn, R. Niessner, C. Haisch, Raman Microscopy and Surface-Enhanced Raman Scattering for In Situ Biofilm Characterization, BIOFILM 4, 01.-03.9.2010, Winchester, UK

N. P. Ivleva, M. Wagner, A. Szkola, H. Horn, R. Niessner, C. Haisch, In situ Imaging der Biofilmmatrix mittels oberflächenverstärkter Raman-Streuung (SERS), Wasser 2010, 10.-12.5.2010, Bayreuth.

M. Knauer, N. P. Ivleva, M. Hübner, R. Niessner, C. Haisch, Label-free in situ Microarray Detection of Microorganisms in Water based on Surface-Enhanced Raman Scattering (SERS), Wasser 2010, 10.-12.5.2010, Bayreuth.

V. Langer, G. Pappert, R. Niessner, M. Seidel: Schnelle Anreicherung von Mikroorganismen mittels Immunomagnetischer Separation und Detektion mittels Sandwich-ELISA und Mikroarray. Wasser 2010, 10.-12.5.2010, Bayreuth

C. Mayr, R. Niessner, T. Baumann, Geothermie im Voralpenland - Eine Herausforderung für die Wasserchemie, Wasser 2010, 10.-12.5.2010, Bayreuth

C. Mayr, R. Niessner, T. Baumann, Die möglichen Auswirkungen von Schwefelwasserstoff im Tiefengrundwasser des Malm auf die Geothermie, Der Geothermiekongress 2010, 17.-19.11.2010, Karlsruhe.

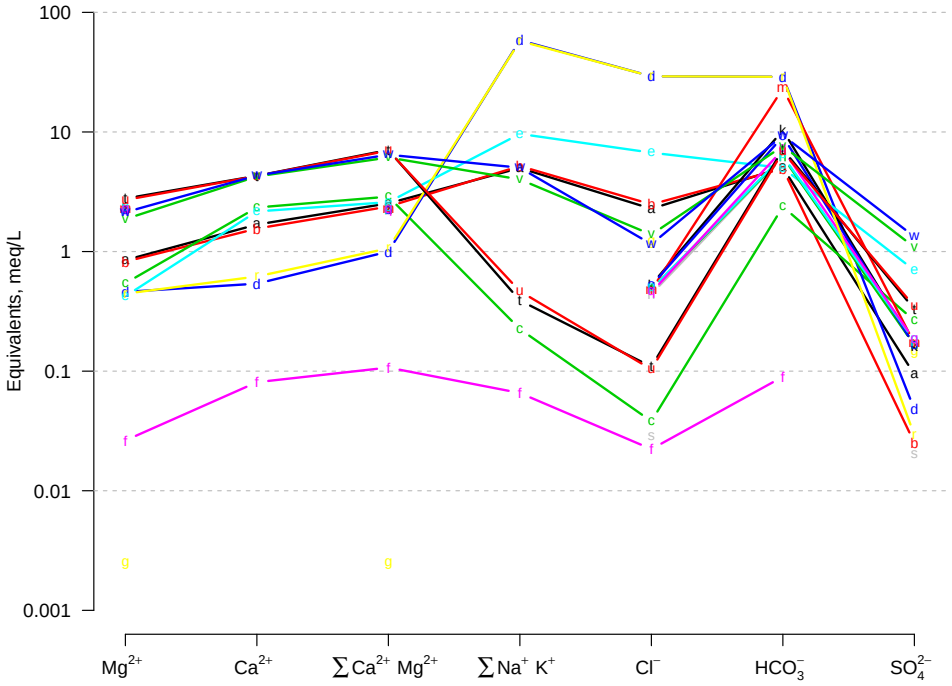
R. Niessner, J. Schmid, M. Knauer and N. Ivleva, Study of Soot and Reactivity based on the Dispersive Character of D Mode in Raman Spectra, AAAR 29 th Annual Conference, 25.-29.10.2010, Portland, USA

M. Seidel, S. Ott, C. Peskoller, R. Nießner, Entwicklung eines geschlossenen Verbundverfahrens zur schnellen und selektiven Anreicherung von Mikroorganismen in Umweltwasserproben. Wasser 2010, 10.-12.5.2010, Bayreuth

J. Schmid, M. Knauer, B. Grob, R. Niessner, N. P. Ivleva, Analysis of Soot Structure and Reactivity Based on the Dispersive Character of D Mode in Raman Spectra, International Aerosol Conference 2010, 29.08.-03.09.2010, Helsinki, Finland.

2.4 Hydrochemical and Hydrogeological Consulting

The hydrochemical analyses in 2010 cover a large part of natural and contaminated groundwaters. The hydrochemical variability, both, with respect to the major ion ratios (see figure) and with regard to the concentration of major constituents, trace elements and organic contaminants was high.



Mineralisation control analyses Bad Abbach, Bad Aibling, Bad Birnbach, Bad Füssing, Bad Griesbach, Bad Gögging, Bad Rodach, Bad Tölz, Bad Wiessee, Bad Wimpfen, Bad Wörishofen, Bayreuth, Beresniki (Ukraine), Erding, Hölle, Kondrau, Lipik (Croatia), Memmingen, Neumarkt i. d. Opf., Sibyllenbad, Straubing, Utting, Weißenstadt

Hydrogeological and hydrochemical expertises (mineral water, spa water) Bad Reichenhall, Bad Tölz, Bad Wörishofen, Kondrau

Deep Hydrogeothermal Energy Exploration Aschheim, Dürrnhaar, Erding, Kirchstockach, Oberhaching, Pullach, Sauerlach

2.5 Bachelor Theses

Michael Bauhofer: Ochratoxin A Determination in Green Coffee Samples by Means of the MCR 3 (Munich Chip Reader 3) Platform

Irma Dreier: Serological Diagnosis of Antiphospholipid Syndrom by Microarray Analysis

Sandra Ertl: Hydrochemistry of the Malm Aquifer in the Western Molasse Basin; Geothermal Well Bad Wörishofen GT 2

Eva Hahn: Development of Synthesis Specifications for the Controlled Preparation of Spherical and Cubical CaCO3-Particles

Manuela Hollering: Methods for Entrance Monitoring at Landfill Sites

Maria Hübner: Development of Substrates for Surface-Enhanced Raman Scattering as a Label-Free Microarray Readout Method for the Detection of Escherichia Coli Bacteria

Stephanie Huber: Development of a DNA Microarray for the Detection of Bacteriophage MS2

Viola Kirchner: Detection of Biogas Components Using Spectroscopic and Chromatographic Methods

Bettina Kiwull: Fouling of Exhaust Gas Coolers Analysis of Soot Particle Deposition Depending on Particle Size and Temperature

Patrick Köllner: Optimization of Surface-Enhanced Raman Scattering (SERS)-Based Readout System

Jens Kück: Analysis of the Kinetics of Performance Reference Compounds for the Passive Sampling of Polycyclic Aromatic Hydrocarbons in Air with PDMS (TWISTER)

Susanne Mayer: Visualization and Quantification of Processes at Biogeochemical Interfaces with Magnetic Resonance Imaging

Martina Nentwig: Surface-Enhanced Raman Scattering (SERS) on Airborne Microorganisms

Constantin Pröll: Synthesis of $CaCO_3$-Particles in the Presence of Buffers and Ca^{+2} Complexing Agents in Aqueous Solutions and Emulsions

Julia Rieb: Incidence and Dynamics of Catecholamines in Mesofauna of Surface and Groundwater

Josef Schachtner: Determination of the Cross Reactivity of Monoclonal B[a]P Antibodies Against the 16 EPA Polycyclic Aromatic Hydrocarbons

Andrea Schmidt: Hydrochemistry of the Malm Aquifer

Qin Xin: Detection of E.Coli and Legionella Pneumophila Using Antibody Microarrays

2.6 MSc and Diploma Theses

Cand. geol. Felix Grimmeisen: The Hydrogeological Relevance of the Middle-Turon in der Freihöls-Bodenwöhr Basin (Oberpfalz)

BSc Georg Hartmann: Quantification of *E. Coli* and *Legionella Pneumophila* in Bioaerosols

BSc Christiane Kiske: On-line SPE-LC-UV Analysis of the Contrast Medium Iomeprol in Whole Blood and Plasma Samples

Cand. geol.. Klaus Mayer: Hydrogeology of the Dogger Sandstone in the Middle Franconian Alb

BSc Michael Pschenitza: Screening and Characterization of Hybridoma Cell Supernatants and Cleansed Monoclonal Benzo[a]pyrene Antibodies

Cand. Dipl.-Ing. (FH) Patrick Scharnagl: Holographic Laser Spectroscopy for Particle Characterization

BSc Sebastian Schmitt: Sediment Concentrations and Toxicity of Endocrine Disruptors

BSc chem. Susanna Vazac: Development of an Immuno Analytical Method for Mycotoxin Detection in Wheat

BSc chem. Jan-Christoph Wolf: Benzo[a]pyrene Analysis in Exhaust Gas Measurement Technology

2.7 PhD Theses

MSc chem. Matteo Carrara: Formation of Nitrated Polycyclic Aromatic Hydrocarbons in Diesel Particulate Filters: Laboratory Experiments and Test-Bench Measurements

Dipl.-Chem. Markus Knauer: Struktur-Reaktivitäts-Korrelation von Dieselruß und Charakterisierung von PAHs und Carbonylen im Abgas von Biokraftstoffen

Dipl.-Met. Carsten Kykal: Einsatz der Photo-Thermophorese zur Aerosolcharakterisierung

Apothekerin Carolin Müller: Immunoanalytische Detektion von Beta2-Glykoprotein I-Autoantikörpern beim Antiphospholipid-Syndrom

Dipl.-Biotech. Gerhard Pappert: Immunomagnetische Anreicherung von Mikroorganismen und ihre bioanalytische Quantifizierung

Dipl.-Chem. Caroline Peskoller: Entwicklung eines schnellen und selektiven Anreicherungssystems für Bakterien in Trinkwasser mittels Querstromfiltration und Affinitätschromatographie

3 Teaching, Colloquia, and Other Activities

3.1 Classes

3.1.1 Chemistry (B.Sc. and M.Sc.)

- Hydrogeological, Hydrochemical and Environmental Analysis Seminar (Hydrogeologisches, Hydrochemisches und Umweltanalytisches Seminar); Niessner, Baumann
- Graduate Course in Analytical Chemistry: Lecture in Organic Trace Analysis-Physical and Chemical Separation Methods (Nebenfach Analytische Chemie: Vorlesung Organische Spurenanalytik-Physikalisch-chemische Trennmethoden); Niessner
- Graduate Course in Analytical Chemistry: Lecture in Organic Trace Analysis-Applications of Selective Receptors (Nebenfach Analytische Chemie: Vorlesung Organische Spurenanalytik-Nutzung selektiver Rezeptoren); Niessner, Seidel
- Graduate Course in Analytical Chemistry: Lab in Organic Trace Analysis (Nebenfach Analytische Chemie: Kurspraktikum Organische Spurenanalytik); Niessner, Seidel

- Graduate Course in Analytical Chemistry: Research Lab in Organic Trace Analysis (Nebenfach Analytische Chemie: Forschungspraktikum Organische Spurenanalytik); Niessner, Seidel
- Trace Analysis Techniques (Spurenanalytische Techniken); Niessner

3.1.2 Chemical Engineering (Diplom)

- Aerosol Characterisation (Aerosolcharakterisierung); Niessner
- Environmental Measurement Technologies Lab (Praktikum Umweltmesstechik); Niessner, Haisch
- Gas Measurement Technologies/Chemical Sensors (Gasmesstechnik/Chemische Sensoren); Niessner

3.1.3 Pharmacy

- Instrumental Analytical Chemistry, (Instrumentelle Analytische Chemie); Haisch

  Lectureship at Ludwig-Maximilians-Universität München

3.1.4 Geosciences (B.Sc. and M.Sc.)

- Analytical Chemistry I: Instrumental Analysis for Geoscientists (Analytische Chemie I: Instrumentelle Analytik für Geowissenschaftler); Niessner
- Analytical Chemistry II - Organic Trace Analysis for Geoscientists (Chemische Analytik II - Organische Spurenanalytik für Geowissenschaftler); Niessner
- Applied Hydrogeology (Angewandte Hydrogeologie); Baumann
- Contaminant Hydrogeology (Transport von Schadstoffen im Grundwasser); Baumann
- Remediation Design (Erkundung und Sanierung von Grundwasserschadensfällen); Baumann
- Technical Hydrogeology (Technische Hydrogeologie); Baumann
- Regional Hydrogeology (Regionale Hydrogeologie); Baumann
- Fluidflow in Porous Media Lab (Hydrogeologisches Laborpraktikum); Baumann, Haisch, Niessner
- Numerical Methods Lab (Hydrogeologische Modellierung II); Baumann
- Hydrogeological Field Lab (Hydrogeologische Feldmethoden); Baumann, Haisch
- Hydrogeological Mapping (Hydrogeologische Kartierung); Baumann, Haisch
- Hydrogeological, Hydrochemical and Environmental Analysis Seminar (Hydrogeologisches, Hydrochemisches und Umweltanalytisches Seminar); Baumann, Niessner
- Hydrogeological and Hydrochemical Field Trips (Hydrogeologische und Hydrochemische Exkursion); Baumann, Niessner

- Water Chemistry I (Wasserchemie I); Niessner
- Water Chemistry II - Hydrocolloids, Micellar Systems and Photochemical Transformations (Wasserchemie II - Hydrokolloide, micellare Systeme und photochemische Umsetzung); Niessner
- Hydrochemical Lab (Hydrochemisches Praktikum); Knopp, Baumann

3.1.5 Biosciences (B.Sc. and M.Sc.)

- Biochemical Analysis (Biochemische Analytik); Görg, Gierl, Knopp, Nitz, Parlar, Schwab, Seidel
- Analytical Chemistry - Separation Techniques, Chemical and Biochemical Sensors (Analytische Chemie - Trenntechniken, chemische und biochemische Sensoren); Knopp
- Bioanalytics I: Immunological Procedures; Sensor Technologies (Bioanalytik I: Immunologische Verfahren; Sensortechniken); Knopp
- Biochemical and Molecular Biological Methods for Environmental Analysis (Biochemische und molekularbiologische Verfahren in der Umweltanalytik); Knopp
- Biochemical and Molecular Biological Procedures for Envrionmental Analysis II - Enzymatic Methods, DNA Probes (Biochemische und molekularbiologische Verfahren in der Umweltanalytik II - enzymatische Verfahren, DNA-Sonden); Knopp

3.1.6 ERASMUS Docent Mobility

- Immunoextraction and molecularly imprinted solid-phase extraction (MISPE); Master Course of Analytical Sample Preparation, (University of Palma, Mallorca, Spain) 30.03.-01.04.2009, Knopp

3.2 Institute Colloquia

Prof. Dr. P. Haring Bolivar, Institut für Höchstfrequenztechnik und Quantenelektronik, Universität Siegen: Towards High Sensitivity THz Biomolecular Sensors (26.01.2010)

Dr. Dietmar Krautwurst, Hans–Dieter–Belitz–Institut / Deutsche Forschungsanstalt für Lebensmittel-chemie, Freising: Human Olfactory Receptor Families and their Odorants (02.02.2010)

Prof. Dr. Maximilian Fleischer, Siemens AG, München: Chemical Sensing Principles & their Applications (22.02.2010)

Prof. Dr. Hendrik Emons, Joint Research Centre European Commission, Geel/Belgium: Needs, Possibilities and Current Limitations to Reliably Detect and Quantify Genetically Modified Organisms (25.02.2010)

Dr. Wolf-Dieter Hergeth, Wacker Chemie AG, München: Industrial Polymerization Monitoring and Polymer Analytics (15.03.2010)

Prof. Dr. Ingo Klimant, Institut für Analytische Chemie und Lebensmittelchemie, TU Graz: Novel High Performance Materials for Optical Sensors (01.04.2010)

Prof. Dr. Sebastian Schlücker, Universität Osnabrück, Fachbereich Physik Biophotonik: Biomedical Applications of Raman and SERS Microscopy (08.04.2010)

Prof. Dr. Ruey-an Doong, National Tsing Hua University, Hsinchu: Nanostructured Materials for Environmental and Energy Applications (13.04.2010)

Prof. Dr. Sue-min Chang, National Chiao Tung University, Hsinchu: Surface Modification of TiO_2 for Highly Photocatalytic Activities (14.04.2010)

PD Dr. Gertrud Morlock, University of Hohenheim, Institute of Food Chemistry, Stuttgart: Miniaturized Planar Chromatography Using Office Peripherals (18.05.2010)

Dr. Uli Rant, Walter Schottky Institut, Technische Universität München: Electrically Switchable DNA Layers for the Label-Free Detection and Size-Analysis of DNA and Protein Targets on a Chip (10.06.2010)

Prof. Dr. Dieter Trau, Division of Bioengineering and Department of Chemical & Biomolecular Engineering, National University of Singapore: Smart Capsules, Random Beads and Pinball Fluidics for Bioanalytics (14.06.2010)

Prof. Dr. Eva Stöger, Universität für Bodenkultur Wien, Department für Angewandte Genetik und Zellbiologie: Plantibody Production - Opportunities and Bottlenecks (29.07.2010)

Prof. Dr. Luisa Torsi, Aldo Moro University, Chemistry Department, Bari/ Italy: A Perspective View on Organic Field-Effect Transistor Sensors (01.09.2010)

Dr. Ulrich Rothbauer, LMU Biocenter Martinsried-Planegg: Connecting Biochemistry and Cell Biology with Nanobodie (04.10.2010)

Prof. Dr. Peter H. Seeberger, Max-Planck-Institute of Colloids and Interfaces Potsdam-Golm, Department of Biomolecular Systems: Carbohydrates on Surfaces and Particles – Diagnostic Applications

Dr. Nenad Gajovic-Eichelmann, Fraunhofer IBMT, Potsdam-Golm: New Materials for Molecular Recognition and Bioanalytical Applications (05.11.2010)

PD Dr. Phillipe Schmitt-Kopplin, Helmholtz Zentrum München: Unraveling Chemical Space with High Resolution Analytical Techniques in Environment and Health (22.11.2010)

Dr. Ursula Fittschen, Universität Hamburg, Institut für Anorganische und Angewandte Chemie: Ink Jet Technology for X – Ray Fluorescence Analysis (07.12.2010)

Dr. Katja Heister, Technische Universität München, Department für Ökologie und Ökosystemmanagement, Wissenschaftszentrum Weihenstephan für Ernährung: Characterisation of Model Compounds of Artificial Soils by Using NanoSIMS (10.12.2010)

3.3 External Tasks and Memberships

Prof. Dr. Reinhard Niessner

University Grants Committee Hong Kong	Member
Ad hoc Committee on Theme-based Research	Member
Search Committee Hydrochemistry (Karlsruhe Institute of Technology)	Member
Search Committee Environmental Chemistry (Vienna University)	Member
Search Committee Environmental Analytical Chemistry (Antwerp University)	Member
Bayer. Fachausschuss für Kurorte, Erholungsorte und Heilbrunnen	Member
DECHEMA Commission "Chemische Grundlagen und Anwendungen der Sensortechnik"	Member
Heinrich-Emanuel-Merck-Award Committee	Jury Head
Analytical Chemistry	Associated Editor
Analytical and Bioanalytical Chemistry	Advisory Board Member
Analytical Sciences	Advisory Board Member
Annual Review of Einvironmental Chemistry	Editorial Comittee Member
Intern. J. Environ. Analytical Chemistry	Advisory Board Member
Microchimica Acta	Advisory Board Member
Fresenius' Environmental Bulletin	Advisory Board Member

PD Dr. Thomas Baumann

Bayer. Fachausschuss für Kurorte, Erholungsorte und Heilbrunnen	Member
VBEW AA Grundwasserschutz	Member

Prof. Dr. Dietmar Knopp

Ecotoxicology and Environmental Safety	Editorial Board Member
Chromatographia	Editorial Board Member
International Journal of Environmental Research and Public Health	Editorial Board Member

Dr. Michael Seidel

KRdL-3/7/04, "Luftgetragene Mikroorganismen und Viren", im VDI/DIN	Member
DECHEMA ad hoc Arbeitsgruppe Biosicherheit	Chair

4 Equipment

4.1 Hydrogeology

Two pilot scale tanks with flow lengths of up to 10 m allow transport experiments in a controlled environment while preserving almost natural conditions. Apart from studies on the transport behaviour of contaminants and colloids, these facilities are used for testing sensor prototypes and serve as a test bed for numerical models.

4.2 Environmental Analytical Chemistry

4.2.1 Dioxin Laboratory

3 High security labs with locks,
separate activated carbon filter and high-performance particle filter systems

4.2.2 Aerosol Research

1 Aerosol chamber (1 m^3)
1 Aerosol flow tube (10 L)
1 Ozone analyzer (UV absorption)
1 NO/NO_2 analyser (Chemiluminescence)
2 Aerodynamic particle sizers (0.5-25 μm)
1 Berner impactor (9 stages, 50 nm - 16 μm)
1 Electrical low-pressure impactor (12 stages, 30 nm - 10 μm)
2 Low-Volume filter samplers (PM 10, PM2.5)
1 High-Volume filter sampler (PM 2.5)
2 Differential mobility particle sizer systems (10-1000 nm)
2 Diffusion batteries (5-300 nm)
5 Condensation nucleus counters
3 Electrostatic classifiers (10-1000 nm)
2 Spark-discharge soot aerosol generators (polydisperse ultrafine carbon aerosol)
1 Berglund-Liu aerosol generator (monodisperse aerosols, 0.8-50 μm)
1 Floating bed aerosol generator (powder dispersion)
1 Rotating brush aerosol generator (powder dispersion)

4.2.3 Bioanalytics

Bioseparation:
Crossflow Filter (Inge AG)
Crossflow Filter (Spectrum Laboratories, Inc)
Pressure and Flowrate controlled Crossflow Filtration System (IWC)
Molecular Biology:
1 Biacore X100, General Electric
1 Real-time PCR (Light Cycler 480, Roche) Microarray Technology:
3 Chemiluminescence Microarray Reader (PASA, IWC)
3 Chemiluminescence Microarray Reader (MCR 3, IWC)
1 Ink-Jet Microdispenser (Nanoplotter, GeSim)
2 Contact Microarrayer (BioOdyssee Caligrapher, BioRad)
Microbiology:
1 Flow Cytometer (Cell Lab Quanta SC, Beckman Coulter)
1 Water Microbiology (Colilert-18 and Quanti-Tray 2000, IDEXX)
1 Clean bench (Haerasafe KS, Kendro)
1 Microbiological Incubator (BD 53, Binder)
1 Autoclave (Century 2100, Prestige Medical)
1 Autoclave (SHP Steriltechnik)
Standard Lab Equipment:
1 Lyophilizer (Alpha 1-4 LSC, Christ)
1 Washer Disinfector (DS 500 Lab, International Steel CO.SPA)
1 Ultrapure Water System (Direct-Q 3 UV, Millipore)

1 Refrigerated Centrifuge (Universal 320R, Hettich)
1 Climatic chamber (Memmert HCP 108)
2 Fluorescence reader systems, time-resolving
3 Photometric reader systems
1 384-channel washer, Biotek
1 Turbidometer (WTW GmbH)
1 Nanophotometer (Implen GmbH)

4.2.4 Chromatography and Particle Separation

3 GCs with FID, NPD, ECD, TEA, and AED
1 Orbitrap-based benchtop MS, Exactive/HCD-System, Thermo Fischer
1 High-resolution GC/MS, VG Autospec
1 Asymmetrical Field-flow-fractionation system
1 SFE-System with modifier, Suprex
2 Concentrators for dynamic headspace analysis
1 High-speed counter-current-distribution chromatographie system
4 HPLC, UV/VIS array detector, programmable fluorescence detector
1 Capillary electrophoresis system
1 Ion chromatograph, Dionex 4500 i
1 Ion chromatograph, Dionex BioLC (Photodiode Array Detector, Electrochemical Detector)
1 LC system, ECONO
1 Preparative HPLC
1 Zetaphoremeter, SEPHY

4.2.5 Elemental Analysis

1 TXRF, Atomika EXTRA II a
1 Flame-Photometer, Eppendorf ELEX 6361
2 AAS systems with flame atomization, electrothermal atomization, hydrid system,
Perkin-Elmer PE 3300, ELAN 4100
1 ICP-MS, Perkin-Elmer ELAN 6100

4.2.6 Laser

3 He/Ne-laser
6 Nd-YAG-laser
1 CO_2-laser
3 Dye-laser (tuneable with frequency doubler)
5 N_2-laser
8 Diode-lasers (600-1670 nm; up to 2 W CW)
1 Laser-diode-array with 10 diodes (0.8 μm - 1.8 μm)
1 Laserdiode with external resonator
1 Optical parameter oscillator (410 nm - 2.1 μm)

4.2.7 Optoelectronics/Spectrometer

1 Rowland spectrometer
2 Echelle spectrometer
1 FTIR-Spectrometer, Perkin Elmer 1600
1 Fluorescence spectrometer, Perkin Elmer LS-50
1 Fluorescence spectrometer, Shimadzu RF 540
1 Fluorescence spectrometer, Shimadzu RF 5301 PC
1 UV/VIS spectrometer, Beckman DU 650
1 Boxcar integrator
4 Digital storage oscilloscopes (400 MHz, 500 MHz)
3 Optical multichannel analysators with monochromators, time-resolving
3 Intensified CCD cameras
1 Wavemeter

4.2.8 SEM/Microscopy/Raman-Microscopy

1 SEM/EDX system
1 Polarisation microscope for phase analysis
1 Fluorescence microscope
1 Image analysis software for automated image processing
1 Inert gas glovebox
1 Laser Raman microscope, Renishaw (514 nm, 633 nm, 780 nm)

4.2.9 Sum Parameters

2 Coulostat for C quantification, Coulomat 702
1 DOC analysator, UNOR 6 N
1 TOC analysator, TOCOR 2
1 AOX/TOX, Sigma

5 Staff 2010

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