

# **Annual Report**

# Institute of Hydrochemistry

# **Chair for Analytical Chemistry**

2008

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Editor: Dr. Thomas Baumann

## Editorial



Dear coworkers, friends and colleagues,

the year 2008 offered a new experience with respect to teaching and research: Now that the transition from Diploma programs to Bachelor programs is almost complete, the request for Bachelor theses comes in waves. When the first wave hit the institute in March 2008, we had to supervise 25 BSc theses simultaneously. Quite a challenge, not only regarding the limited space. Together with 22 PhD students every desk and every lab space was more than busy. Fortuntately, all BSc students finished their theses successfully after two or three months, thus giving the PhD students a little room for their research.

The funding situation in 2008 reflects the diversity of the institute: From biodiesel to microarray development and from geothermal energy to photophoretic separation. While some colleagues of mine already suspect that I might become fuzzy with so many diverse topics, I can reassure them, that there is common denominator to all projects: Analytical Chemistry.

My personal highlight in 2008 was the first commercial application of the Munich Chip Reader 3 for routine analysis in a laboratory of the dairy industry. The heart of the MCR 3 automated biochip platform is an exchangeable, regenerable immunochip which is able to detect 13 antibiotics in milk simultaneously and within 6 minutes. The chip can be used for up to 50 analyses in sequence, thus substituting old-fashioned, time consuming inhibition tests. Today, various groups at IWC work independently on the creation of new biochip applications for this platform (e.g. rapid screening for microorganisms or toxins).

To understand my enthusiasm one should know about the beginning of this development 10 years ago. At that time a joint research project with a MITI institute in Japan was the nucleus. It took significant financial expenses, several PhD students, and the help of a small, but highly proficient precision engineering company (GWK, Munich) to make this idea come true.

It is our mission to keep our standards in research and teaching high, this is reflected in the quality of published papers. The productive working atmosphere at the institute is driven by the enthusiasm of each individual member, so what do we have to fear?

The economic crisis. We realize a tendency to postpone project decisions. Our industrial partners become more and more cautions about potential financial risks. Even students feel unsure about an academic career in Germany. The outlook for 2009 therefore is short: We will simply do our best.

Let me express my sincere thanks to all members of the institute, our partner institutes and organisations, the funding organisations, the reviewers of our proposals and publications, and our "Freundeskreis" for continuous support.

All the best for the year 2009!

Reinhard Niessner Head of the Institute



Head of the Institute and Group Leaders 2008

C. Haisch, D. Knopp, M. Seidel, T. Baumann, R.Nießner

## 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 Cooperation: FU Berlin, GGA Hannover, LfU Bayern, Erdwerk GmbH, HydroConsult

The Malm aquifer beneath the Molasse Basin is one of the targets for the exploration of geothermal energy. With temperatures up to 150 °C and pumping rates exceeding 50-80 L/s, the geothermal energy can be used in central heating facilities and geothermal power plants. Currently, there are almost a dozen new exploration projects, each offering new insights into the geology, fault and carst systems, hydraulic and hydrogeochemical settings of the Malm aquifer. This joint research project aims at a better understanding of the Malm aquifer and the processes occuring in deep geothermal aquifers in order to allow a better prediction of the geothermal potential and possible risks.

Our part is to collect, evaluate and model the hydrochemical composition of the Malm groundwater. This data is vital to the long term operation of the geothermal wells. It also serves as a benchmark for the geological and hydrogeological models.

A first screening of the gas composition indicates that the concentration of hydrogen sulfide in the gas phase is related to the overall gas concentration. Concentrations of up to 2 vol-% in the gas phase have been measured but the majority of the samples is the lower vol-% range (see Figure). Under reservoir conditions (p > 100 bar) all gases are dissolved. Degassing is driven by the least soluble gas, usually methane, and takes place in the production well only.

The origin of  $H_2S$  is still unclear: Isotopic measurements of <sup>34</sup>S in SO<sub>4</sub><sup>2-</sup> and  $H_2S$  suggest a thermal reduction (starting at 120-140 °C) of sulfate. As the temperatures of the thermal water are well below 120 °C, the thermal water likely has to be flowing from the South where the Malm aquifer reaches deeper. The concurrent occurrence of sulfate and sulfide and high salt concentrations in some of the geothermal waters indicate mixing with groundwater seeping from the overlying stratum.



 $\mathsf{H}_2\mathsf{S}$  concentrations in the gas phase of the groundwaters in the Malm-aquifer

A monitoring will be performed to assess the hydrochemical variation of the thermal water and to quantify the effects of varying geothermal load in winter and summer. A detailed investigation of the sulfur species including isotopic measurements is necessary to gain insight into the hydrochemical and hydrodynamic processes.

(C. Mayr)

#### 1.1.2 Colloids Within the Inn River

#### Funding: IWC

Colloids and nanoparticles in surface waters are tracers for the hydrodynamics in the river, for the geological setting and the weathering situation in the catchment area, and for anthropogenic influences.

The size ditribution of the fines transported in a river is mainly affected by the flow velocity and turbulences in the river. Larger particles will settle in lakes, as well as upstream of weirs and dams. Downstream of weirs and powerplants an increase of larger particles is likely because of erosion in the river bed. Short term effects on the particle size distribution include anthropogenic input, like effluents of sewage treatment plants, and heavy rainfall or droughts.

The mineralogical composition reflects the geology and the weathering situation in the (sub-)catchment area. The stability of the fines is also controlled by the geological



Colloid size distribution and selected particles along the Inn River

setting. While carbonates are likely to precipitate or dissolve due to changes of the carbonate equilibrium, clay minerals are much more stable. This mainly affects the theoretical transport distance of the fines.

In a joint project involving four Bachelor theses, the particles in the Inn River where studied. The sampling started at the origin of the river in the Swiss alps. Samples were taken at each tributary and at each significant change of the flow conditions (dams and weirs). The samples were filtered and analyzed to obtain the particle size distribution, the elemental composition of the filtered particles, the mineralogical composition and the number of algae.

The results showed the effects of the tributaries coming

from the North (limestone) adding carbonate particles, while the main tributaries coming from the South were dominated by clay particles and other silicates. Snow melt in some subcatchment areas led to a significant decrease of the total dissolved salts. There was a significant decrease of freshwater algae from the origin to the mouth indicating decreasing river water quality.

Anthropogenic effects include an increase of the concentration of organic matter and of certain metal ions (e.g. lead, antimony). Also effects of road de-icing were obvious on the subcatchment area scale.

(M. Reitzel, M. Stoiber, M. Ueckert, K. Wallgren)

#### 1.1.3 Nanoparticles at the Interface between Atmosphere and Hydrosphere

#### Funding: Gottlieb Daimler- and Carl Benz Foundation

Nanoparticles in aquatic environments might be ecotoxic. Nevertheless, synthetic nanoparticles are used in many different applications, including nanopesticides and construction materials. Currently, there are few applications, mostly in the field of soil remediation, where nanoparticles are directly injected into a subsurface environment Instead, a significant pathway might be the release of nanoparticles into the air, for instance due to weathering processes or during the application of pesticides, followed by transport through the air and a deposition on the ground surface. Only under favorable conditions nanoparticles will be filtered in the soil. During heavy rain or melting snow nanoparticles will likely bypass the top soil layer and critical concentrations of nanoparticles in groundwater might occur. Significant mass transfer rates have been measured in a similar immission situation for PAHs and PCBs associated to soot particles.

Despite of the importance of the interface between atmosphere and hydrosphere, there is a lack of data with regard to the immission situation and the processes at this interface.

This project aims at a survey and quantification of the immission situation for nanoparticles, its spatial and temporal variation, and at a monitoring of the transport processes of deposited nanoparticles from soil surface to groundwater. The effects of nanoparticle aging have to be measured to derive the long-term stability and mobility. The data generated in this project will set the ground for an assessment of this ubiquitous large scale process.

The Institute of Hydrochemistry hosts a unique field laboratory which provides access to soil, unsaturated zone, and groundwater of a glacial sand and gravel aquifer. In combination with wet-only and dry-only samplers the immission of nanoparticles can be quantified and their transport through the soil will be observed.

Aerosol samples, soil samples, seeping water samples, and groundwater samples will be collected and analyzed to trace different particles through the soil and unsaturated zone to the groundwater. Particles will be immission monitoring



Setup of the vadoze zone laboratory

separated by ultrafiltration and asymmetrical flow field-flow fractionation (AF4). Analysis will be performed by SEM/EDX, Raman microscopy, and AF4/ICP-MS.

Tracer tests will be run with particles of different sizes and surface functionalities at the field lab and in a tank setup. The particle properties controlling mobility and stability will be measured for stock particles and particles in a natural environment.

Finally the transport of aged nanoparticles will be compared with stock nanoparticles using micromodels and column tests. This will help to assess a change of transport properties at different stages.

(S. Huckele)

#### 1.1.4 Stabilization of Colloids in Multiphase Systems

### Funding: DFG

Colloids and nanoparticles are not only enhancing the transport of contaminants which are otherwise immobile but also potential hazardous materials themselves. The mobility of colloids and nanoparticles in shallow aquifers is controlled by colloid-colloid, colloid-interface interactions and the stability of the colloids.



Effect of humic acid on the dispersivity of colloids

Conventional transport investigations (spatial resolution 0.01 to 100 m, temporal resolution minutes to days) give integrated results of the overall transport processes. There is little chance to quantify single processes unambiguously. In contrast, micromodel experiments offer a spatial resultion in the  $\mu$ m range and a temporal resolution down to milliseconds but limited heterogeneity. These experiments, therefore, are best for the quantification of single-particle/single-interface processes.

Processes on the pore scale are relevant for the transport of nanoparticles in particular. While some industrial researchers argue that synthetic nanoparticles are only stable in their stabilizing solutions, thus the environmental impact will be negligible, experimental data shows that humic substances are stabilizing synthetic nanoparticles. When colloids and nanoparticles are passing through the soil, interactions with humic substances are likely. The stabilization effects the size of the aggregates. Therefore, colloid dispersion can be used to measure the effects of stabilization of colloids. In the presence of humic acid in the solution aggregation should be reduced and colloid dispersion should increase. Experimental data shows an increase of the dispersivity by a factor of 3 and supports this hypotheses. Therefore, transport of synthetic

nanoparticles has to be studied in all environments to assess the immission situation and potential health effects. (*L. Toops*)

#### 1.1.5 Development of a Strategy to Decrease Well Aging at a Multiple Contamimated Site

#### Funding: MDSE

The Bitterfeld-Wolfen area is known for lignite mining and its chemical industry, but also for its contaminations of groundwater and soil. There are about 5000 contamination sites spread over an area of  $10 \text{ km}^2$ . These contaminations are far too complex to be treated individually.

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. Recent investigations show massive incrustations in some of those wells,

pumps, draining pipes. The incrustations impair the proper operation of the wells and also increase the costs for the hydraulic barrier.

To prevent the incrustations and to increase the reliability of the hydraulic barrier system, a field test was carried out at one of the most affected wells. Water enriched with carbon dioxide was augmented into the pumping cone of the well through two injection wells at a rate of 5% of the withdrawal rate.

As a consequence of the augmentation of the contaminated groundwater the pH-level dropped from pH 9.5 to pH 7. At pH 7 the organic carbon did flocculate rapidly under steady state conditions but the aggregates where easily dissolved by stirring. This is in contrast to the formation of aggregates at pH 9 and higher. Here, the flocculation took more time, but the aggregates were stable.

During the pilot test the specific yield of the well was constant as long as the pumping rate was constant. Sudden increases of the pumping rate caused a stepwise decrease of the specific yield. The filter cake that was building up due to sudden changes of the flow velocity was successfully decreased by injecting water into the well. Therefore, high pressure injection should be an appropri-



Incrustations in a pipe caused ba precipitation of organic material and carbonates

ate measure to remove this filter cake completely. The back pressure of the pump was constant, indicating that the addition of carbon dioxide prevents precipitation in the pipe system. Without the addition of carbon dioxide a complet incrustation in the pipe system was observed (see image).

(S. Lauber, C. Muhr)

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

#### 1.2.1 Hapten Microarray-based Screening of Mycotoxins in Food Samples

#### Funding: BMBF

Cooperation: Eurofins Analytik GmbH, Wiertz-Eggert-Jörissen, Hamburg, and Ring Engineering Ltd., Azur, Israel

Mycotoxins are fungal toxic secondary metabolites that can be found as contaminants of important crops for human consumption such as corn, wheat, nuts and dried fruit. In particular, the isocoumarin-like aflatoxins (B1, B2, G1 and G2) and ochratoxin A pose considerable risks due to their adverse and toxic effects in animals and humans. Therefore it is crucial to develop accurate and efficient toxin screening and quantitation methods that comply with the tight legislation enforced not only by the European Union, but also by most countries around the world.

In this project, the previously developed Munich Chip Reader 3 (MCR3) and the biochips will be tested for the determination of aflatoxins and ochratoxin A content



Schematic of the Aflatoxin biochip

in relevant food matrices such as peanuts and almonds. First, the tolerance towards matrix effects of new generated mouse monoclonal antiaflatoxin antibodies was assayed by means of a classic indirect competitive immunoassay format on polystyrene microtiter plates. Next, analyses on the MCR3 platform were performed, based on well-known CLIA principles: the toxin contained in a liquid sample competes with the toxin covalently immobilized on a PEGylated glass chip by means of a 4-residue peptide linker for the binding of a specific antibody in a flow through assay. The antibody bound to the immobilized toxin is recognized by the a secondary horseradish peroxidase labelled anti-mouse antibody and allows for the determination of toxin content in the original sample. In parallel experiments, the platform was used for the first time to generate calibration curves of both ochratoxin A and aflatoxin B2 spiked sampes. The obtained  $IC_{50}$  values for both calibration curves were in the  $\mu g/L$  concentration range. Next, the determination of mycotoxins in natural contaminated food samples was started.

Further, to save time and costs for the analysis, a modification of the conventional competitive indirect ELISA is investigated. In detail, a monoclonal

anti-aflatoxin B2 antibody was directly conjugated to horseradish peroxidase (HRP) in order to avoid the use of a secondary labelled antibody and analogous incubation step. This ELISA is compared to a conventional indirect ELISA using the same monoclonal anti-aflatoxin B2 antibody and secondary goat-anti mouse HRP-labelled antibody. Assays are run both an microtiter plates (ELISA) and glass chips (CLIA). (*C. Cervino, J. Sauceda, S. Ott*)

#### 1.2.2 Highly Efficient Hybridoma Screening Technique Based on Antibody Microarrays

#### Funding: IWC

A key step for the generation of hapten specific Mabs ist the screening of hundreds to thousands of possible candidates for high-affinity hapten specific Mabs. Therefore the de facto standard method, the indirect ELISA screening on microplates, is still mostly used.

The aim of this work was to transfer the direct ELISA format for screening cell supernatants to a microarray format. Therefore, the antibodies in the cell supernatants had to be immobilized covalently on a glass surface. The necessary surface chemistry for this application had already been developed and



Principle of the hybridoma cell screening

could be successfully used without any modification. Different possibilities for the immobilisation of antibodies in cell supernatant were tested and optimized. The chemiluminescence flow-through immunoassay with the format of a direct non-competitive ELISA was done semi-automatically with the Munich Chip Reader (MCR) 2. The data evaluation was done with the software Sip 0.4 (Karsunke Softwarebüro, Wolnzach). The software recognises spots automatically and sums up the signal intensities of a square with given side length (inputted as the number of pixels) around the spot. The new method might allow improvements in the initial cell cultivation step of the fused cells, as only nanoliter volumes of supernatant per clone are required. Consequently, hybridoma screening can be carried out earlier after the cell fusion. (*M. Rieger, C. Cervino*)

#### 1.2.3 New Nanometer-sized Particles for Bioanalytical Applications

Funding: Alexander von Humboldt-Foundation

The emerging research field of nanotechnology, the process to generate and manipulate nanomaterials, provides exitingly new possibilities for advanced development of new analytical tools for bioanalytical applications. For example, the synthesis of new labels could lead to more sensitive membrane-based immunoassay formats such as flow-through assays and lateral flow tests. These methods do not require any special equipment and can be performed as on-site screening tests. For successful development, the label is very important because immunochromatographic tests are basically designed for visual inspection. Gold nanoparticles have been extensively employed due to their inherent advantages, such as easy preparation and good biocompatibility. In this project, e.g. new gold-nanoparticles-integrated magnetic microspheres for labelling of primary antibodies are designed and used for the fast screening of aflatoxins in food, as a model.

(D. Tang)



Antibody-labelled gold-nanoparticle-integrated magnetic microsphere

## 1.2.4 New Non-instrumental Immunochemically-Based Field Tests for Monitoring of Polycyclic Aromatic Hydrocarbons (PAHs) in Aqueous Samples

#### Funding: DAAD

Cooperation: Department of Common and Inorganic Chemistry, Chemistry Faculty, Saratov State University, Saratov, Russia; Laboratory of Food Analysis, Faculty of Pharmaceutical Sciences, Ghent University, Belgium



Dose response test series with different concentrations of BaP

Currently, ELISAs performed in a microtiter plate or test tubes are the most common techniques used for immunoassays. They are rapid and simple to perform and the instrumentation is portable for use in the field. However, with the demand on even shorter analysis time and more user-friendly field assays, other formats are being explored. Ideally, they should require only low-cost instrumentation and do not need a power supply. As a disadvantage, the sensitivity required to monitor the set limit values, especially for environmental pollutants, is often not reached predominantly and tests are prone to matrix effects.

PAHs belong to the set of persistent organic pollutants which represent a hazard to humans and to the whole ecosystem. Usually, they occur as complex mixtures, not as single compounds. Benzo[a]pyrene (BaP) is on the priority list published by the U.S. Environmental Agency. 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 BaP, which is the lowest of all limit values set for individual chemical parameters in this directive.

In this project, a gel-based immunoassay, performed in test columns (Bond Elut cartridges), was developed for highly sensitive and reliable detection of BaP in water samples. It combines preconcentration and detection of the target analyte using anti-PAH antibodies and horseradish peroxidase-BaP tracer conjugate in one single cartridge. Water sample preparation, such as extraction, centrifugation, or filtering was found to be unnecessary. No interference by higher water-soluble PAHs at 4000-fold excess compared to BaP was observed. The assay was configured as a qualitative test (positive/negative) at a cut-off level of 5 ppt, however, this level can be adapted to the required analyte concentration by rather simple adjustment of the anti-PAH antibody concentration of the test zone. The additional gel layer (control zone) which was introduced into the column can be used to indicate the validity of the test. (*I. Yu. Goryacheva, E. Basova*)

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

#### 1.3.1 Photophoretic Characterization and Separation of Colloids

#### Funding: DFG

Photophoresis (PP) and photothermophoresis (PTP) are two closely related effects, which occur when particles get illuminated by intense light. Transfer of momentum from scattered photons (PP) and locally inhomogeneous heating, resulting in locally increased impingement rates of the surrounding molecules, generate driving forces, which move fine particles either towards or away from the light source.

To characterize aerosols, a system was developed that automatically records velocities induced by photophoretic forces and performs a statistical evaluation to describe the particle ensemble properties. It allowed a continuous monitoring of photophoretic velocities of a large number of particles in a short time, where each particle is separately measured. By using a differential mobility analyzer, a preselection of particles with approximately the same aerodynamic diameter from a polydisperse aerosol can be done. Information on the size dependency of the photophoretic velocities for different materials can be gained and the differentiation of particles of the same aerodynamic

size but different optical and thermal conductivity properties becomes possible. Different evaluation procedures are currently compared, to assess their capability to resolve minute differences in the optothermal properties of particles.

In an aqueous system transparent and spherical hydrocolloids were used as calibration standards. Here, the predominant effect is direct photophoresis. For the separation of particles a flow cell was developed, which consists of two chambers, containing the sample colloids and pure water, respectively (see Fig.). Both chambers are connected over a small opening. The bulk flow was applied perpendicular to the laser beam. The laser beam with Gaussian intensity profile was focused in the middle of the flow cell at the position of the opening. When a particle is in the proximity of the laser beam, it gets centered in the beam by the optical forces and starts to migrate in the direction of propagation of the beam. Due to the counteraction of friction force and photophoretic force, the particle leaves the beam, resulting in a distance termed retention distance from its origin. The figure shows an



Schmatic of the photophoretic separation cell and an example of the separation of  $1\mu m$  and  $4.8\mu m$  PS particles

image sequence of photophoretic separation of a particle mixture of polystyrene particles with 1  $\mu$ m and 4.8  $\mu$ m in diameter. When the photophoretic force is strong, as for the 4.8  $\mu$ m particles (bright green spots), the particle is transported over the 400  $\mu$ m long opening in the chamber containing pure water. The trajectories of the smaller particles (red, 1  $\mu$ m) remain nearly undisturbed and follow the bulk flow. In that way, particles with different sizes or refractive indices can be discriminated and enriched by their different retention distances. Techniques on the basis of light induced forces are excellent techniques for contact-free sample handling with high resolution characterization and separation of particles, cells and bacteria.

(L. Opilik, M. Oster, C. Kykal, C. Helmbrecht)

#### 1.3.2 Surface Enhanced Raman Scattering for a Label-free Readout of Antibody-based Microarrays

#### Funding: IWC

Raman Spectroscopy (RS), as vibrational spectroscopy, provides highly specific information and is, compared to IR spectroscopy, more appropriate for analyzing biological molecules in aqueous samples. All biologically relevant molecules such as proteins, nucleic acids, carbohydrates, and lipids exhibit distinct Raman spectral features by yielding molecular fingerprints. However, conventional RS is hampered for biomolecular characterization by its limited sensitivity. With Surface Enhanced Raman Scattering (SERS) signal enhancement occurs in the presence of metal colloids and allows detection down to the single molecule level. Increased sensitivity, compared to conventional RS, is reached by interactions between metal and analyte through electromagnetic and/or chemical enhancement. We are investigating on a label-free detection principle of microorganisms on microarray, using SERS.





Miroscopic image of microorganisms and corresponding Raman spectrum

SERS offers the advantages of reduced assay times, simpler handling and lower reactant volumes compared to methods where the target molecules are labelled. The microarray immunosensor is a multiplex flow-through system which utilises a platform where the recognition takes place. This chip is based on immobilized antibodies connected to an amino-modified surface by micro-printing or microstructuring processes. The amount of reagents needed for SERS detection is very low and an inexpensive chip production in larger scale is possible. The major difference between the used microarray system and most immunoassays is that the microarray system offers a flow-through implementation of the reagents whereas the immunoassays are mostly carried out stationary in microtiter plates. It has been proven that microarrays are able to reach lower LODs and IC50 values which is probably caused by lower diffusion times within flat flow cells. For signal enhancement, silver and gold nanoparticles in the size range of 20 nm to 100 nm have been used. These monodisperse colloid sols were prepared in a reproducible way and possess a shelf life of over five weeks. Enhancement factors in the range of  $10^3$ - $10^6$  have been reached. Total assav time is below five minutes and total reactants volume is below 3 mL. Integration into an automatic fluidic system is planned. (M. Rye-Johnsen, L. Xiangjiang)

#### 1.3.3 Analysis of biofilm matrix by Raman Microscopy and Surface Enhanced Raman Scattering (SERS)

#### Funding: DFG

#### Cooperation: Prof. Horn, TUM

Biofilms present a ubiquitous form of microbial life in natural environment and can occur at solid–liquid, solid–air, liquid–liquid, and liquid–air interfaces. They are structured communities of microorganisms, which are embedded in a matrix formed by extracellular polymeric substances (EPS, such as polysaccharides, proteins, nucleic acids and lipids). Detailed information about chemical composition and structure of the EPS matrix is relevant e.g. for the optimization of biocides, of antifouling strategies and for biological wastewater treatment. Raman Microscopy (RM) is a nondestructive spectroscopic analytical technique which is based on the effect of inelastic light scattering by molecules. RM provides "whole-organism fingerprints" for the characterization and identification of different biological systems with spatial resolution of optical microscope. RM requires no or limited sample preparation. Raman spectra are characterized by a high specificity, generally revealing sharper and clearer bands than IR spectra, and low water background.

The study of multispecies biofilms showed that RM provides detailed chemical information about different constituents of a complex biofilm matrix, and can correlate variations of the chemical composition to different structural appearances within the EPS matrix. The results of the RM analysis of biofilms are in good agreement with data obtained by Confocal Laser Scanning Microscopy (CLSM) that was applied to study the distribution of microorganisms and EPS glycoconjugates in biofilm matrix. However, the sensitivity of RM is limited. Thus, collection times of minutes are needed to record spectra with a high signal-to-noise ratio, even when applying high laser power.

The Raman effect can be dramatically enhanced if a molecule is attached or in the immediate proximity to metallic substrate (usually Ag or Au). This technique is known as SERS. We obtained reproducible SERS spectra from different constituents (aggregates and protozoa) of



SERS-Spectra of biofilm

multispecies biofilm. The use of colloidal silver nanoparticles for in situ SERS measurements by RM allowed us to achieve an enhancement factor of up to 2 orders of magnitude (see Figure). Comparison of normal Raman (NR) and SERS spectra, both obtained with an excitation wavelength of 633 nm, revealed significant differences in the positions and the relative intensities of the bands. The SERS spectra are characterized by higher number of discriminable peaks. The good reproducibility of the SERS spectra obtained from different biofilm constituents suggests a great potential of SERS for a detailed and sensitive chemical characterization of different biofilm components and the analysis of their relative abundance in the biofilm matrix.

Thus, RM and SERS can be efficient tools for a label-free chemical analysis of biofilms. Moreover, the combination of RM/SERS with CLSM can provide new know-ledge about the complex structure/function-correlations in biofilms matrix. (*N. P. Ivleva*)

#### 1.3.4 Application of Microchannel Systems for Parallel Research on Biofilm Prevention by Surface Modification

#### Funding: Stipend by Tokyo University (Prof. Kitamori)

Biofilms are agglomerations of bacteria in a polysaccharide matrix. They predominantly develop at interfaces in contact with water. They are responsible for adverse effects like biofouling or corrosion. Manifold approaches to prevent or control biofilm growth on surfaces and in pipes exist. Disinfection with chlorine is the common method for drinking water systems. Other methods include the modification of surfaces with hydrophilic or hydrophobic substances or even with substances that act as disinfectants. This way, the prevention of initial attachment of biofilm is attempted. Surface modification methods exist to a vast amount, and no unified theory on the mechanism of biofilm adhesion exists due to the variability of bacteria.



Response of biofilm growth to the hydrophobicity of the surface

Therefore, multiple experiments have to be carried out, if possible under identical conditions, to optimize the surface modification method for one existing biofilm bacteria mix.

In microchannel systems, parallelization of experiments can be done in large numbers, and numerous experiments can be carried out simultaneously under identical condition. They are versatile flow channels where flow and outer conditions can easily be controlled. Due to their size, reagent consumption in microchannels is minimal, limiting cost and amount of waste solution.

A biofilm mix from wastewater treatment plant activated sludge was introduced in four parallel microchannels simultaneously and grown under identical conditions. The surfaces of the four microchannels were modified with different chemicals to vary the surface contact angle and check the relation to biofilm growth. After one month growth, biofilm was removed with pressure plugs and the

surface coverage was determined before and after the plugs, as seen in the figure. As can be seen, biofilm growth was directly related to contact angle, but surface coverage with biofilm was reduced to similar levels by the applied pressure plugs. (*T. Roßteuscher*)

## 1.4 Aerosol Research (Head: Prof. Dr. R. Nießner

#### 1.4.1 Structure-Reactivity Correlations of Soot, Studied by Raman Microspectroscopy and Temperature Programmed Oxidation

#### Funding: DFG

Cooperation: Prof. Schlögl, Fritz-Haber-Institute of the Max-Planck-Society, Berlin

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 used for this purpose must be regenerated periodically by oxidation and this regeneration step is strongly depending on the reactivity and thereby the structure of the deposited soot.

The reactivity of soot is determined by Temperature Programmed Oxidation (TPO). For investigation of soot structure High Resolution Transmission Electron Microscopy (HRTEM) is applied. But, TPO and HRTEM measurements are very time and cost

consuming and therefore it is necessary to establish a rapid analytical tool for the determination of the structure and reactivity of soot.

Raman Microscopy (RM) provides fingerprint spectra and has been applied for the structural characterization of different soot samples. The spectra show peaks at ca. 1580 cm<sup>-1</sup> (G or "Graphite" peak) and 1350 cm<sup>-1</sup> (D or "Defect" peak), but the D and G peaks exhibit strongly varying relative intensities and widths. For quantitative spectral analysis we applied a five-band fitting procedure with combination of four Lorentzian-shaped bands (G, D1, D2, D4 at ca. 1580, 1350, 1620 and 1200 cm<sup>-1</sup>) and one Gaussian-shaped band (D3 at ca. 1500 cm<sup>-1</sup>). For validation of RM structural analysis, HRTEM and EELS were applied.

For GfG soot the two observed Raman peaks became narrowed during oxidation, whereas the spectra of EURO VI and



Raman spectra of soot

EURO IV soot remained largely unchanged. The different behaviour of GfG soot on one hand and EURO VI and EURO IV soot on the other hand can be explained by differences in their structure. For GfG soot the relative intensity of D3 band is decreasing rapidly during the TPO, suggesting a rapid preferential oxidation of highly reactive amorphous carbon. The decrease of the D1 band width indicates a decrease of chemical heterogeneity and an increase of structural order upon oxidation. The slight changes for EURO VI soot compared to EURO IV soot suggest a more disordered and hence more reactive structure for EURO VI soot than for EURO IV soot. The Raman spectroscopic parameters are in good agreement with the results of HRTEM and EELS data and suggest that differences in the oxidation behaviour determined by TPO are associated with the different nanostructures.

(M. Knauer, N. P. Ivleva)

#### 1.4.2 Characterization of Soot Reactivity by Temperature Programmed Oxidation and Raman Microspectroscopy

#### Funding: FVV

#### Cooperation: Prof. Pischinger, Institute of Combustion Engines, RWTH Aachen

Soot particles emitted by diesel engines account for a major fraction of air pollutants in urban area. A wide range of particle trapping systems and exhaust aftertreatment technologies have been proposed and are currently under development. Continuously regenerating traps or diesel particulate filters which have been applied for this purpose have to be regenerated periodically by oxidation and gasification of the deposited soot. The behaviour of this regeneration step is strongly influenced by the structure and reactivity of the deposited soot particles. Especially the production of highly reactive soot would make it possible to perform this regeneration step at relatively low temperatures. Therefore a rapid analytical tool for the determination of soot reactivity is needed.



Temperature dependency of the mass conversion rates of soot

Raman Microspectroscopy (RM) can be applied to get detailed information about the reactivity of soot. A correlation between the structure of soot and Raman spectroscopic parameters has already been reported and discussed in literature.

RM and TPO combined with FTIR gas analysis have been used to determine structural changes and reactivity of different carbonaceous samples upon oxidation by  $O_2$ (5% in  $N_2$ ) up to 873 K in a diesel exhaust aftertreatment model system. As reference for reactivity limits, we used spark discharge generated soot (GfG) as upper limit (65% mass conversion) and a commercially available graphite powder (Graphite) for determination of a lower limit (1-2% mc). Investigations on real diesel soot samples (EURO IV and VI), taken from the undiluted raw exhaust of heavy duty test engines have also been performed. It was found that the real diesel soot samples show mass conversions of 15-20%.

The Raman spectroscopic parameters indicate a decrease of structural order from Graphite over the real diesel soot samples to GfG soot and are in good agreement with the oxidation behaviour of soot during the TPO. We are now planning to investigate a set of diesel soot samples, generated under different engine conditions and to analyse the reactivities of those soot samples by RM and TPO. Overall, RM provides information about changes in structural order of graphitic and amorphous carbon fractions during oxidation and can be used to analyze oxidation readiness of soot.

(M. Knauer, J. Schmid, N. P. Ivleva)

## 1.4.3 Emissions of PAHs, Nitro-PAHs and Carbonyl-compounds During the Combustion of Biofuels and Biofuel Mixtures

#### Funding: Fachagentur Nachwachsende Rohstoffe

Cooperation: Prof. Schramm, Institute of Ecological Chemistry, Helmholtz Zentrum München; Prof. Hausberger, Institute of Combustion Engines, TU Graz; Prof. Geringer, Institute of Combustion Engines, TU Vienna

There is a lower limit of supplied fossil fuels, originated from underground, which can be applied as petrol. Also an enhancement in the greenhouse effect, hence earth atmosphere heating, implies that alternative energy sources are needed. Due to the increasing use of biofuels and fuel mixtures, the possibility of partially substituting fossil fuels has arisen. Though, up to now there is just little knowledge about in which extent the addition of biofuels to fossile fuels will change the emission rates of PAHs, nitro-PAHs and carbonyl compounds during engine combustion.

To get more detailed information on the emission rates of the different engine exhaust components, samples were taken after dilution tunnels at vehicle roller testbenches in Graz and Vienna during defined test cycles. Heavy duty vehicles as well as passenger cars have been used during this study. To determine differences in the emission rates, fossile diesel, biodiesel and vegetable oil as well as mixtures with different amounts of biofuels in fossile fuel were investigated.

Particle bound PAHs and nitro-PAHs were sampled on quartzfiber filters, which were extracted and cleaned up for quantification by HPLC-FD in laboratory afterwards. The gaseous carbonyl compounds were collected with gas washing bottles using a solution of dinitrophenylhydrazine in acetonitrile and were detected by HPLC-UV.

The measurements show differences in the concentration of PAHs and carbonyl compounds between the different types of fuel investigated in this study. Exhaust samples obtained from the pure biodiesel cyclic measurements show slightly increased values of PAHs. Fossile diesel and the fuel mixtures of fossile diesel, biodiesel and vegetable oil, on the other hand, show very similar values among each other of PAHs and carbonyl compounds. Differences are also recognized when pure vegetable oil is directly compared to fossile diesel. In this case, even higher values are found of PAHs- and carbonyl compounds- concentrations than those obtained when operating with fossil diesel alone.



Photograph of the measurement setup at the roller test bench

Within the nitro-PAH category, the largest fraction of compounds is made by the mutagenic acting 1-nitro pyrene and the mono-nitronaphthalene. The concentrations of these compounds are within the range of few  $ng/m^3$ . Other analyzed nitro-PAH concentrations are partially below the limit of detection. No significant difference of nitro-PAHs was found between the different fuels.

Overall, we found that the combustion of vegetable oil can lead to a higher emission of PAHs and carbonyl compounds. The addition of biodiesel did not have that strong effect. Next step would be to investigate samples taken at the tractor motor testbench in Graz to confirm these results.

#### 1.4.4 Nitro-PAH Formation in Diesel Exhaust

#### Funding: DFG

Diesel particulate matter is widely considered as a possible human carcinogen. It represents a complex mixture of organic and inorganic materials where the inorganic part mainly consists of fine soot particles produced during the high temperature combustion of fuel. Several classes of organic components such as polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs (nitro-PAHs) and aliphatic hydrocarbons can adsorb on the soot surface. PAHs are often already present in the fuel and they may survive the combustion process while others can be formed de-novo. On the other

hand, nitro-PAHs are formed during the combustion via electrophilic substitution in presence of NO<sub>2</sub>. Nitro-PAHs have been found to account for over 50% of the total vapor- and particle-phase direct mutagenicity of ambient air and particulate matter; the carcinogenic character of diesel soot is mainly attributed to nitro-PAHs

Diesel particulate filters (DPF) have evolved into a promising technology to reduce harmful diesel emissions. They are typically ceramic monoliths produced with alternating flow channels, which are closed at the ends to force the exhaust flow to pass through the porous wall of the honeycomb filtration media. The solid particles are deposit in the pores. This kind of filters became plugged soon by the soot that they trap and this leads to an increase of the backpressure that compromises the correct engine running. Therefore, it is necessary to regenerate the filters periodically at elevated exhaust temperature. Often, the exhaust gas is first passed through a diesel oxidation catalyst designed to convert NO to  $NO_2$  which is used to assist the filter regeneration by enhanced soot oxidation. Considerable amount of PAHs may reside on the soot particles and the filter structure could support the nitration chemistry leading to a post-combustion formation of nitro-PAHs. Heterogeneous gas-particle degradation of PAHs has already been studied and real DPFs have already been tested with respect to nitro-PAH formation. Nevertheless, information on the nitration kinetic with a focus on reaction products and under conditions relevant for Diesel after-treatment systems are still missed.

Our experiments deal with the interaction of artificially pyrene-coated spark discharge particles with NO<sub>2</sub>. The obtained sub-monolayer pyrene coating was selected to simulate the adsorption conditions of volatile PAHs in a Diesel exhaust tailpipe system. The heterogeneous reactions of adsorbed pyrene with

 $NO_2$  have been investigated over a wide range of conditions comprehensive of Diesel exhaust relevant specifications. 1-nitropyrene has been found as the main nitration product. Its production is linearly correlated with the reaction time. By increasing the  $NO_2$  concentrations, the produced 1-NPYR is also increased linearly.

In particular, after 60 min, production of 1-NPYR as been noticed at the lowest concentration used of 60 ppmv NO<sub>2</sub>. For a reaction time of 30 min 1-NPYR production was starting at 450 ppmv NO<sub>2</sub>. Such residence times and concentrations are comparable to the conditions of DPF when the regeneration is started by the artificial increase of the NO<sub>2</sub> concentration. We demonstrate that under such conditions production of 1-NPYR and other nitro-PAHs is possible. Looking for the effects of temperature, we found the highest 1-NPYR production at 100 °C. At higher temperature, the 1-NPYR amount found on the aerosol particles is comparable to the reaction at 20 °C. Probably at high temperature newly formed 1-NPYR sublimates into the gas phase and it is no more detectable on the particles.





#### 1.4.5 Analysis of Soot Deposition Mechanisms on the Gas Side Surface of Heat Exchangers Used in Exhaust Gas Recirculation

#### Funding: FVV

Vehicles with diesel engines become more and more popular due to their low fuel consumption and dynamic handling. However, diesel engines account for the production of a major fraction of air pollutants such as nitrogen oxides  $(NO_x)$  or particulate matter (soot). A method used for the reduction of  $NO_x$  emissions by lowering the combustion temperature is exhaust gas recirculation (EGR). One can differentiate between uncooled and cooled EGR, with the latter requiring the use of heat exchangers but being more effective. However, the use of EGR leads to an increase in soot particle production. The deposition of soot contained in the diesel engine exhaust gas is a

major problem for the use of heat exchangers in cooled EGR since the deposits cause decreasing heat transfer efficiencies and increasing pressure losses.

To establish a better understanding for the deposition mechanisms involved in EGR coolers, a test bench was constructed at the IWC. With this test bench it is possible to simulate real diesel exhaust by generating a model aerosol with similar size distributions. Measurements at constant temperature and pressure conditions are conductable with the construction.

The deposition efficiency of a heat exchanger provided by a diesel car manufacturer was experimentally determined. Additionally it was possible to exchange the inlet nozzle of the cooler for two different inlet cones to study the influence of the inlet geometry on particle deposition. For the experiments gas temperatures, temperature differences and pressure conditions for dry and humid soot aerosol were varied.



Photograph of the EGR test bench

The experiments show that soot is collected inside the

heat exchanger, especially on the front plate at the cooler's inlet. Depending on the temperature and pressure conditions overall deposition efficiencies between 2% and 35% were found.

The mechanisms of sedimentation and diffusion do not greatly influence deposition. Thermophoresis due to a temperature difference in the system is playing a minor role in the transport of soot particles to the walls as deposition also occurs when no temperature difference is present. The main fraction of particles is assumed to become impacted and stick onto the front plate by the mechanism of interception, thus building up a soot layer that possibly enhances further deposition. (*G. Hörnig*)

#### 1.4.6 Fe-C Reactions in Soot Particles in the Context of Toxicity and Climate

#### Funding: IWC and Central Washington University, Ellensburg, WA

Atmospheric aerosols play a variety of important roles in the environment, two of which include detrimentally impacting human health and modulating global climate. Anthropogenic aerosols emitted by the combustion of fossil fuels and other organic materials are particularly important, as they can (i) induce physiological disorders in cardiovascular and respiratory systems, carcinogenicity and even mutagenicity and (ii) absorb solar radiation, thus increasing atmospheric temperatures. The ultrafine size fraction of ambient particles (ultrafine particles, UFP, diameter < 100 nm) has recently been identified as being far more potent in their adverse health effects than



Photograph of the spark discharge particle generator

their larger counterpart because they can reach deep into the alveolar region of the lung, and through an intricate relationship with particle surface functional groups, they then traverse cell membranes and translocate to sensitive target organs where they cause oxidative stress that ultimately ends in cell death. The surface chemical aspect of UFP reactivity has generally been correlated with chemical constituents that are able to catalyze the production of highly oxidizing reactive oxygen species (ROS, i.e.,  $OH \cdot$ ,  $HO_2^{-}/O_2^{--}$ ,  $H_2O_2$ ) which induce oxidative stress and for which the two main chemical groups identified as culprits are aromatic hydrocarbons and trace metals.

Of particular interest in the present study is the effect of iron, as (i) it is the most abundant transition metal present in ambient UFP, stemming from engine wear, lube oil additives, and in Europe also from fuel additives, (ii) it can partake in fast and reversible redox processes thus acting as efficient catalysts for electron transfers, (iii) it plays a central role in producing the most powerful oxidant, hydroxyl radical,  $OH \cdot$ , in the Fenton reaction,  $Fe(II) + H_2O_2 \longrightarrow Fe(III) + OH \cdot + OH^-$ , and (iv) recent evidence form exposure studies confirms that iron and carbon act synergistically in producing ROS.

Iron containing soot particles will be generated with a modified spark discharge generator, and to mimic distinct ageing processes that soot particles undergo after production and emission from an internal combustion engine, particles will be subjected to a range of temperatures. Biologic and atmospheric particle reactivity will be investigated in relation to particle size, surface area, surface charge, bulk and surface iron content and speciation, elemental and organic carbon content, soot structure and degree of oxidation. Results from this study will also increase

understanding of iron-nanoparticle relationships in other areas, such as the enhanced toxicity observed in carbon nanotubes containing iron from fabrication related catalytic residues and the correlation observed over remote oceans between combustion emissions and iron solubility. Increased iron solubility may lead to an enhancement of biologically available iron to the vast areas of the open ocean where phytoplankton are iron-limited, and this, in turn, increases productivity and affects the biogeochemical cycling of C and S which play important roles in the modulation of global climate. (U. Jaeger, A. Johansen)

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

#### 1.5.1 Antibody Microarrays for the Quantification of Living E. coli Bacteria

#### Funding: IWC

The microbiological purity of drinking water is one of the most important requirements for the maintenance of human health. This is why very strict limits are defined; according to the Drinking Water Ordinance there must not be  $E.\ coli$  or coliform bacteria detectable in 100 mL of drinking water. The currently used methods for monitoring and quality control of drinking water are labour intensive and time

consuming. Therefore fast, sensitive, automatable and particularly multianalyte test systems are of high interest. Only in this way are fast and early interventions possible after a contamination event. Concerning the monitoring of drinking water E. coli is of particular importance as an index germ for the potential presence of pathogenic microorganisms. A method for the quantification of living E. coli bacteria using antibody microarrays is to be developed. The aim here is the quantification by means of the enzymes  $\beta$ -galactosidase and  $\beta$ -glucuronidase, which are to be obtained from *E. coli* by cell lysis. The principle of the applied method is based on an Enzyme-linked Immunosorbent Assay (ELISA), which is transferred to a microarray platform. The antibody microarrays are produced on polyethylene glycol modified glass surfaces. The enzyme-specific immobilized antibodies serve as capture macromolecule. For the enzyme recognition step, enzyme-specific antibodies are used, which are detected by a horseradish peroxidase catalyzed chemiluminescence reaction. The generated chemiluminescence reaction is recorded by a CCD camera.

Different Sandwich ELISA systems were tested on the microarray platform and potential systems for further studies were determined, whereas until now the experi-

ments have been performed with commercially available  $\beta$ -galactosidase solutions. In this context the use of both monoclonal and polyclonal enzyme-specific antibodies was tested.

(V. Langer)



Schematic of the antibody microarray

## 1.5.2 Development of an Epoxy-based Monolith Used for the Bioseparation of Bacterial Cells

#### Funding: IWC

Monoliths have become an interesting alternative to columns packed with beads since their introduction as a separation material in the late 1980s. They overcome the limitations of chromatography beads and have been successfully employed for separation involving large biological molecules such as proteins, plasmid DNA, and viruses. Polymeric monoliths consist of a solid continuous phase permeated by a continuous network of through-pores and can be distinguished depending on their shape, backbone material, porosity or pore size. Despite their differences they all are characterized by low mass transfer.

An epoxy-based monolith has been developed for use as hydrophilic support in bioseparation. This monolith is produced by a self-polymerization of polyglycerol-3glycidyl-ether at room temperature within in one hour. The self-polymerization was



SEM image of the epoxy-based monolith and packed monolithic column

initiated with the Lewis acid  $BF_3$ , which activated the epoxy groups for a nucleophilic attack. By adding pore forming agents, a coherent network of pores was formed during the polymerization process by phase separation. One receives a highly cross-linked structure that provides useful mechanical properties. The porosity and pore diameter can be controlled by varying the composition of the porogen. The resulting monolith contains epoxy and hydroxy groups, which can be used directly for ligand immobilization. The diol groups on the material generate a hydrophilic surface and, in addition they tend to support with low specific binding for many biological agents.

An epoxy-based monolith with a high porosity (79%) and large pore size  $(22 \ \mu m)$  is prepared and used in affinity separation of bacterial cells. These features allow the free passage of bacterial cells  $(1 \times 3 \ \mu m)$  through the column.

As affinity ligand the peptide antibiotic Polymyxin B (PmB) was used, which was covalently immobilized with the carbonyldiimidazole (CDI) method. PmB is a cationic cyclic decapeptide, which is known to interact with the negatively charged cell walls of gram-negative bacteria. This adsorption activity depends on the pH value and ionic strength of the sample. The efficiency of the monolithic affinity column was studied with *E. coli* spiked in water. Bacterial cells were concentrated on the column at pH 4 and eluted by changing the pH value without impairing viability of bacteria. It was observed a sharp and effective elution profile of the *E. coli* cells. An amount of  $97\pm3\%$  of captured cells were recovered in only 200  $\mu$ L elution volume. The capacity of the affinity monolith was  $4 \cdot 10^9 E$ . *coli* cells and was nearly independent of the flow rate up to 10 mL/min. Thereby, it is possible to separate and enrich gram-negative bacterial cells, such as *E. coli*, with high flow rates (10 mL/min) and low backpressure (<1 bar) in a volume as low as 200  $\mu$ L compatible for RT-PCR, microarray formats, and biosensors.

(C. Peskoller)

#### 1.5.3 Development of Multifunctional Antibody-coupled Nanoparticles

#### Funding: DFG

#### Cooperation: DFG SPP 1315

In recent years, the environmental analyst's attention is turned more and more on polycyclic aromatic hydrocarbons (PAHs). This is a group of hydrophobic organic compounds, which enrich themselves ubiquitary in the environment. The most important representative is benzo[a]pyrene (BaP). PAHs are mainly generated during an incomplete combustion and due to their mutagenic and carcinogenic effects, they offer a huge harmful potential for humans and animals. Hence, the development of new methods to detect PAHs, especially BaP, attracts more and more interest in the research. One challenge is the detection of PAH in soil by means of Magnetic Resonance Imaging (MRI) and antibodies, which are coupled to nanoparticles containing gadolinium (Gd). In doing so, these nanoparticles can be used for time-resolved visualization.

In a feasibility study, several magnetite nanoparticles were successfully synthesized using a precipitation reaction of  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$ , initialized by

a 25%  $\rm NH_3$  solution. The reaction took place in an aqueous solution of dicarboxy-polyethylene glycol, therefore the nanoparticles were coated by polymer and equipped with free reactive carboxy groups. After a magnetic purification, the nanoparticles were coupled with the ligand L-Lys-mono-amide-DOTA and the anti-BaP antibody with the EDC/NHS method.

This step was followed by a further magnetic purification and the complexation of the  $\mathrm{Gd}^{3+}$  ions by the DOTA (1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid). After the final magnetic purification, the modified nanoparticles were distinguished by means of UV-Vis spectroscopy and SEM measurements. In the UV-Vis spectrum, the typically asymptotical decrease of the absorbance curve in the range of higher wavelengths was visible. The SEM pictures showed on the one hand, that the average particle size was 200 nm and on the other hand they showed the agglomeration of the particles. Tests showed that the last fact did not have any

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SEM image of the Gd-nanoparticles

negative impact on the particle properties. The presence of iron and gadolinium could be shown with EDX measurements. By the presence of Gd it was evident, that the DOTA coupling and the following complexation of the  $\mathrm{Gd}^{3+}$  ions must have been successful. The quantification of the iron and gadolinium content was achieved by ICP-MS. Here, recovery rates of 24% (Fe) and 100% (Gd) were obtained. The antibody concentration of the nanoparticles suspension was determined via a Bradford test. Here, the recovery rate was also 100%. By means of column tests, it could be shown, that anti-BaP-antibody-coupled nanoparticles bond specifically to BaP contaminated column material and were retained.

(R. Plapperer)

#### 1.5.4 Development of an Enrichment System and Antibody Microarrays for the Detection of Microorganisms in Drinking Water

#### Funding: DFG

Crossflow microfiltration (CFM) offers the possibility to concentrate bacterial organisms in a single process using size-exclusion-based filtration and combining then to bioanalytical methods. We developed a rugged, automated CFM system for onsite concentration of large volumes of environmental water samples. A hollow fiber

membrane module was used. The efficiency of the CFM system was studied for *E. coli* spiked in a 10 L tap water sample. In the experiments the recovery rates and viability of microorganisms were analyzed depending on the TMP. The crossflow experiments of spiked tap water samples have shown no filtrate flow decline at a TMP between 40 and 100 mbar. The recovery rates of the cells were above TMP = 50 mbar constant with a rate of 90%. It was possible to concentrate with the setup 10 L of tap water with a permeate flow of 700 mL/min in 15 min (200-fold enrichment) to 50 mL. A high and consistent recovery of  $91.3 \pm 5.4\%$  living cells was found in the concentration range 0.01 and 100 cfu/mL. The work shows that the crossflow filtration is an efficient, fast and consistent enrichment method with high recovery rates. It is possible to combine this method online with other systems, like immunomagnetic separation process for a further concentration to a volume of 1 mL. These volumes are compatible to rapid analyzing systems like FCM, immunoassays, biosensors and analytical microarrays. Also the combination with real-time PCR could be possible.

A mulitplexed chemiluminescence sandwich immunoassay on antibody microarray platforms were developed for the rapid and parallel detection of the pathogenic germs E. coli O157:H7, Salmonella typhimurium and Legionella pneumophila. All steps of the sandwich immunoassay were performed in the flow cell of our flow-through chemiluminescence microarray readout system. For capturing cells out of water samples speciesspecific polyclonal antibodies were used which were immobilized covalently on poly(ethylene glycol)-modified glass substrates. The applied microarray surface chemistry provides for highly uniform and reproducible surfaces. Bacteria captured by the arrayed antibodies were detected via specific secondary antibodies labeled with biotin and streptavidin marked with horseradish peroxidase. After addition of luminol and hydrogen peroxide chemiluminescence signals were generated where cells had been bound. Chemiluminescence signals were recorded by a charge-coupled device (CCD) camera integrated in the microarray readout system. The overall assay time was 13 min, enabling a fast sample analysis. In multianalyte experiments the limit of detection for S. typhimurium in buffer was  $3 \cdot 10^6$  cells/mL, whereas *E. coli* O157:H7 could be detected down to

 $3 \cdot 10^3$  cells/mL. For *L. pneumophila* a LOD of  $1 \cdot 10^5$  cells/mL was achieved. Quantification of samples containing all three bacteria were possible in a wide concentration range covering at least two orders of magnitude with good recoveries. (*C. Peskoller, A. Wolter*)



방법 문화 전 것으로 한다.	pAb L. pneumophila			
	pAb Salmonella			
	pAb <i>E. coli</i> O157:H7			
	pAb <i>E. coli</i>			
	pAb <i>E. coli</i>			
	negative control			
	positive control			



Setup of the CFM system and a calibration curve and image of heat-killed *E. coli O157:H7* on the antibody microarray

#### 1.5.5 Detection of Antibiotics in Milk with the Munich Chip Reader 3 (MCR 3)

Funding: Forschungskreis der Ernährungsindustrie AiF FV 197ZN II Cooperation: Prof. Märtlbauer, Institute for Hygiene and Technology of Milk, LMU Munich

A novel automated chemiluminescence (CL) read-out system for analytical flowthrough microarrays based on multiplexed immunoassays has been developed. The Microarray Chip Reader (MCR 3, built-up by GWK Präzionstechnik GmbH) is designed as a stand-alone platform, which is able to quantify multiple analytes in complex matrices of food, water, or other liquid samples for field analysis or for routine analytical laboratories. All important components of the CL microarray platform are combined for a fully automated multiplexed immunonalysis: the enclosed flow-through microarray chip, the fluidic system and the software module enable automated calibration and determination of analyte concentrations during a whole working day. The detection of

antibiotics in milk is one example demonstrating the power of these technique. There is a lack on quantitative multi-residue detection-methods for routine analysis although the EU has defined maximum residue levels (MRLs) for a number of antibacterial reagents. Therefore, an automated multianalyte detection instrument is needed quantifying simultaneously antibiotics within some minutes. Also a regenerable microarray chip is required to avoid changing the chip between the measurements. PEG-ylated chip surfaces are used because of their known durability against chemical treatment. The chip consists on two channels for parallel measurement and regeneration. The microarray chip is designed for parallel analysis of 13 different antibiotics in milk applying an indirect competitive microarray immunoassay. Microspotted antibiotics are directly coupled to epoxylated PEG surfaces. The simultaneous determination of sulfamethazine, sulfadiazine, streptomycin, cloxacillin, ampicillin, penicillin G, cephapirin, neomycin B, gentamycin,



erythromycin A, tylosin, enrofloxacin and tetracycline on one single immunochip is possible by a CL-MIA within six minutes. The produced multi-use hapten microarray with the robust and chemical-resistent epoxy-PEG surface is applicable for more than 50 successive measurements with a good reproducibility. (*K. Kloth*)

#### 1.5.6 Validation of the MCR 3 System for the Detection of Antibiotics in Milk

#### Funding: BayStMELF

Cooperation: Milchprüfring Bayern e.V., Institute for Hygiene and Technology of Milk, LMU Munich, MUVA Kempten

The regenerable hapten microarrays based on PEG-ylated surfaces can be used for the parallel analysis of 13 different antibiotics in milk within 6 minutes. Microspotted antibiotic derivatives like sulfonamides,  $\beta$ -lactams, aminoglycosides, fluorquinolones and polyketides are directly coupled to epoxy-activated PEG chips without further use of linking agents. Using the MCR 3 platform, this antigen solid phase was stable for at least 50 consecutive analyses. Calibration experiments were successfully carried out obtaining the working ranges of all 13 respecting antibiotics including the corresponding MRL values.



Response of the MCR 3 chip to a milk sample containing cloxacillin

The practical applicability was tested in a service routine laboratory, yielding an excellent precision of the method. First measurements with real samples of raw milk (fat content:  $\geq 4\%$ ) were accomplished at the Bayerische Milchprüfring e.V. (MPR, Wolnzach) in order to test the developed immunochip on the MCR 3 platform and to compare the results with commercially available microbiological inhibitor tests, which are used in the central testing laboratories to control milk of dairy tankers. These test systems are time consuming (2-3h) and give information only about a detection range of single antibiotic classes like  $\beta$ -lactams. The microarray image shows two different CCD exposures of microarrays detecting 13 different antibiotics and the reference substance DNPEDA with 5 replicates in each row. Blank milk and a positivetested milk sample containing cloxacillin were measured on the same biochip after one regeneration cycle. The concentration of cloxacillin was high enough to reduce the signal intensity to background level. The signal intensities

of all other analytes were unchanged and reproducible. The concentration of cloxacillin in this sample was estimated to be about 370  $\mu$ g/L which is far above the MRL of 30  $\mu$ g/L. This value agrees with the semiquantitative result obtained by a microbial inhibitor test (cloxacillin: > 220  $\mu$ g/L).

Overall, the new microarray system offers the potential of identification and quantification of antibiotics and will aid the food industry to maintain quality and safety of milk. In cooperation with the LMU Munich (Prof. E. Märtlbauer), the Milchprüfring Bayern e.V. and the MUVA (Kempten) we are currently engaged in the validation and the evaluation of the MCR 3 platform. In this context, the IWC is responsible for the microarray chip production.

(K. Kloth)

#### 1.5.7 AQUASens: Development of a CMOS-based Platform for the Detection of Microorganisms in Water

#### Funding: BMBF

Cooperation: Siemens AG, FRIZ Biochem Gesellschaft für Bioanalytik mbH, Inge AG, IWW Rheinisch-Westfälisches Institut für Wasserforschung GmbH, Technologiezentrum Wasser Karlsruhe

The AQUASens project aims to develop a rapid online detection system for pathogenic microorganisms in water. The setup consists of an immunomagnetic separation (IMS) for pre-selection and pre-concentration, a PCR amplification step, and a chemiluminescence-based microarray readout for quantification.

IMS is particularly well suited for human cell separation. The interconnection between microfiltration and microarray analysis is a new task. The IMS has to handle of large sample volumes and separate the enriched bacterials from interfering matrix components. The application The use The use in order to concentrate cells with maximum selectivity.

Superparamagnetic beads bind via coupled antibodies to relevent target cells that are retained on a column in the presence on an external magnetic field and can be eluted. After a suitable sample preparation, it is possible to concentrate a sample volume of 50 mL containing up to  $10^7 \ E. \ coli$  cells down to an elution volume of 1 mL within a separation time of 10 min and without loss of sample material. Separated living *E. coli* cells are quantified with Colilert 18 and Flow Cytometry. The next step is the connection to qPCR or DNA microarrays.

For the quantification on DNA microarrays, we have developed a new hybrization assay on DNA microarrays. The so-called stopped-PCR strategy amplifies target DNA which is strongly dependent on the applied gene copies. The quantification is carried out by a flow-through chemiluminescence microarray readout system. The DNA microarrays are based on a poly(ethylene glycol)-modified glass substrate. The probes on the surface are 18 or 25 nucleotides long and the quantified PCR product 60 nucleotides. The amplification is stopped after 25 cycles, at this point amplification was in the middle of the logarithmical phase and the spread between different DNA starting concentrations reaches a maximum. A conjugate of streptavidin and horseradish peroxidase (HRP) binds to the biotinylated strands on the microarray surface and catalyzes the reaction of luminol and hydrogen peroxide.



Recovery of E. coli cells after IMS



Dose-response curve (n=6) for uidA of E. coli

The generated light emission was recorded by a sensitive CCD chip. The detection limit for the gene uidA (beta-galactosidase) of *E. coli* was  $1.1 \cdot 10^5$  copies/mL. This system allows for a sensitive detection and quantification of *E. coli* in a concentration range from  $10^6$  to  $10^9$  copies/mL

(G. Pappert, S. Donhauser, M. Seidel)

#### 1.5.8 Development of a Flow-Through Multichannel Microarray Chip for Parallel Detection of Bacteria

#### Funding: IWC

The aim of this work was to develop a multi-channel flow-through chemiluminescence microarray readout system for the parallel detection of microorganisms. A disposable chip made of plastic was devised as a base support for the non-competitive immunoassay.

A black chip made of acrylonitrile but adiene styrene copolymer was used. Antibodies were spotted into the channels of the chip via a contact printer and got adsorbed to the chip surface. The enzyme peroxidase acted as analyte and in addition generated the desired chemilum inescent signal after adding luminol and hydrogen peroxide. This signal was collected by the CCD camera. For the calibration of POD, a linear range of 0.024  $\mu$ g/mL to 0.743  $\mu$ g/mL and a limit of detection of 1.8 ng/mL was assessed. The overall assay time was 11 min and 10 s.



Photograph of the ABS chip

In order to demonstrate the feasibility of the developed system, heat inactivated pathogenic bacteria were measured. Polyclonal antibodies against the pathogenic bacteria E. coli O157:H7, Salmonella typhimurium and Legionella pneumophila were immobilized on the ABS chip to use them as a specific interceptor for the bacteria. In single experiments the LODs varied from  $1.8 \cdot 10^4$  cells/mL for E. coli O157:H7,  $7.9\cdot 10^4$  cells/mL for Legionella pneumophila to  $2 \cdot 10^7$  cells/mL for Salmonella typhimurium. The overall assay time for measurement and calibration was 18 min, enabling a very fast sample analysis. Calculated cross reactivities were in the range of 2% for E. coli 0157:H7 and Salmonella typhimurium. Determination of recovery rates was effected by spiking PBS samples with all three pathogenic bacteria. The recovery rates were between 77% and 130% with errors between 7% and 27%.

Errors in a range of 20% are often observed in ELISAs. In the case of *Salmonella typhimurium* the error of the recovery rate was 80%. This high value is explained as a consequence of the high slope of the calibration curve for *Salmonella typhimurium*. Nevertheless, it could be shown that the parallel detection of bacteria is possible.

Clear advantages of the ABS-chips compared to glass slides were the shorter assay time and the lower reagent consumption. One further advantage of the ABS chip was the simple and fast immobilization of antibodies by adsorption. (X, Y.Z. Karsunke)

## 2 Publications of Present Members of the IWC

### 2.1 Journal articles (reviewed)

- C. Adelhelm, R. Niessner, U. Poeschl and T. Letzel; Analysis of Large Oxygenated and Nitrated PAHs Formed Under Simulated Diesel Engine Exhaust Conditions (by Compound Fingerprints with SPE/LC-API-MS). Anal. Bioanal. Chem. 391 (2008) 2599-2608
- S. Baumgartner, I. Fuertler-Leitzenberger, E. Drs, A. Molinelli, R. Krska, U. Immer, K. Schmitt, M. Bremer, W. Haasnoot, C. Danks, V. Romkies, P. Reece, P. Wilson, M. Kiening, M. Weller, R. Niessner, E. Corsini and S. Mendonca; European Survey for Hidden Allergens in Foos: A. Care Study with Peanut and Hazelnut. ACS Symposium Series 1001 (2008) 370-381
- N.V. Beloglazova, I.Y. Goryacheva, D.A. Mikhirev, S. De Saeger, R. Niessner and D. Knopp; New Immunochemically-based Field Test for Monitoring Benzo[a]pyrene in Aqueous Samples. Analytical Sciences 24 (2008) 1613-1617.
- C. Cervino, S. Asam, D. Knopp, M. Rychlik and R. Niessner; Use of Isotope-Labeled Aflatoxins for LC-MS/MS Stable Isotope Dilution Analysis of Foods. J. Agric. Food Chem. 56 (2008) 1873-1879
- C. Cervino, E. Weber, D. Knopp and R. Niessner; Comparison of Hybridoma Screening Methods for the Efficient Detection of High-affinity Hapten-specific Monoclonal Antibodies. J. Immunol. Methods 329 (2008) 184-193.
- C. Haisch; Quantitative Analysis in Medicine Using Photoacoustic Tomography. Analytical and Bioanalytical Chemistry 393 (2008) 473-479
- C. Haisch, C. Kykal and R. Niessner; Photophoretic Velocimetry for the Characterization of Aerosols. Anal. Chem. 80 (2008) 1546-1551
- A. Held, A. Zerrath, U. McKeon, T. Fehrenbach, R. Niessner, C. Plass-Dülmer, H. Berresheim and U. Pöschl; Aerosol Size Distributions Measured in Urban, Rural and High-alpine Air with an Electrical Low Pressure Impactor (ELPI). Atmospheric Environment 42 (2008) 8502-8512
- C. Helmbrecht, R. Niessner and C. Haisch; Characterization of Cells and Bacteria by Photophoretic Velocimetry. Proc. SPIE 6859, 685913-685913-7 (2008)
- N. P. Ivleva, M. Wagner, H. Horn, R. Niessner and C. Haisch; In Situ SERS Analysis of Biofilm. Anal. Chem. 80 (2008) 8538-8544
- M. Knauer, M. Carrara, D. Rothe, R. Niessner and N. P. Ivleva; Changes in Structure and Reactivity of Soot During Oxidation and Gasification by Oxygen, Studied by Raman Microscopy and Temperature Programmed Oxidation. Aerosol Science & Technology 43 (2008) 1-8
- J.J. Liu, J.M. Lin and D. Knopp; Using a Circular Groove Surrounded Inlet to Generate Monodisperse Droplets Inside a Microfluidic Chip in a Gravity-driven Manner. J. Micromech. Microeng. 18 (2008) 095014
- N. Nestle, A. Wunderlich and T. Baumann; MRI Studies of Flow and Dislocation of Model NAPL in Saturated and Unsaturated Sediments. Europ. J. Soil Sci. 59 (2008) 559-571

- R. Niessner, J. Broekaert, J. Einax, H. Emons, C. Haisch, C. Huber, N. Jakubowski, D. Knopp, J. Popp, F. Scheller and W. Schuhmann; Analytische Chemie 2006/2007. Nachrichten aus der Chemie 56 (2008) 418-427
- M. Rampfl, S. Mair, F. Mayer, F. Sedlbauer, K. Breuer and R. Niessner; Determination of Primary, Secondary, and Tertiary Amines in Air by Direct or Diffusion Sampling Followed by Determination with Liquid Chromatography and Tandem Mass Septerometry. ES & T 42 (2008) 5217-5222
- M. Seidel and R. Niessner; Automated Analytical Microarrays: A Critical Review. Analytical and Bioanalytical Chemistry 391 (2008) 1521-1544
- P. Stolper, S. Fabel, M. Weller, D. Knopp and R. Niessner; Whole-cell Luminescence Based Flow-through Biosensor for Toxicity Testing. Anal. Bioanal. Chem., 390 (2008) 1181-1187
- Z. Sun, W. Schuessler, M. Sengl, R. Niessner and D. Knopp; Selective Trace Analysis of Diclofenac in Surface and Wastewater Samples Using Solid-phase Extraction with a New Molecularly Imprinted Polymer. Anal. Chim. Acta 620 (2008) 73-81
- A. Wolter, R. Niessner and M. Seidel; Detection of Escherichia coli 0157: H7, Salmonella typhimurium, and Legionella pneumophila in Water Using a Flow-Through Chemiluminescence Microarray Readout System. Anal. Chem. 80 (2008) 5854-5863
- I. Yu Goryacheva, N.V. Beloglazova, S.S. Eremin, D.A. Mikhirev, R. Niessner and D. Knopp (2008); Gel-based Immunoassay for Non-instrumental Detection of Pyrene in Water Samples. Talanta 75 (2008) 517-522
- K. Zell, M. Vogel, P. Menzenbach, R. Niessner and C. Haisch; First Practical Experiences with the Optoacoustic/Ultrasound System OPUS. Proc. SPIE 6856, 6850 S (2008)

## 2.2 Conference Presentations

#### 2.2.1 Oral Presentations

- T. Baumann and R. Niessner, Hydrochemie und Gaszusammensetzung des Tiefengrundwassers aus dem Malmaquifer im Voralpenland, FH-DGG Tagung, 21.5.-24.5. 2008, Göttingen.
- T. Baumann, Colloids in Groundwater and at Contaminated Sites, Analytica Conference, 1.4.-3.4.2008, München.
- T. Baumann, Colloids in Groundwater From Field Scale to Pore Scale, ESR Christchurch Science Centre, 25.11.2008, Christchurch/NZL (invited)
- C. Cervino, J.C. Sauceda, R. Niessner and D. Knopp, Mycotoxin Analysis by Automated Flow-through Immunoassay with Chemoluminescence Readout. XIII International Symposium on Luminescence Spectrometry, 07.-11.09.2008, Bologna, Italy.
- S. Donhauser, R.Niessner, M. Seidel, Rapid Automated Chemiluminescence Oligonucleotide Microarray for the Detection of Human Pathogens in Liquids e.g. Drinking water, 13. International Symposium on Luminescence Spectrometry, 7.-11.9.2008, Bologna, Italy.
- L. Toops, R. Niessner and T. Baumann, Colloid Dispersion in Groundwater The Pore Scale Perspective, FH-DGG Tagung, 21.5.-24.5.2008, Göttingen.

- C. Haisch, Optoacoustics in Medicine: Chances and Limitations, Seminar Series of the Laser Research Center of the University Clinic, Ludwig Maximilian Universität, 17.11.2008 Munich, Germany (invited)
- C. Haisch, Optical and Optothermal Methods for the Characterization of Aerosols and Colloids, Seminar Series of the Institute for Quantum Electronics, ETH Zu:rich, 29.09.2008 Zurich, Switzerland (invited)
- C. Haisch, New developments in Photoacoustic Spectroscopy for the Simultaneous Quantification of Gases and Particles, 5. International Exhaust Gas and Particulate Emissions Forum, 19.-20.02. 2008, Ludwigsburg, (invited, awarded: Best Talk of the Conference)
- D. Knopp, Immunoanalysis in Environmental and Food Chemistry. 35th International Symposium on Environmental Analytical Chemistry, (ISEAC), 22.-26.06.2008, Gdansk, Poland (invited)
- D. Knopp, Immunologische Methoden in der Umwelt- und Lebensmittelanalytik: Stand und Perspektiven. Institut für Analytische Chemie und Lebensmittelchemie der Universität Wien, 20.11.2008, Wien, Austria (invited).
- D. Knopp, New Immunoarray-based Tool for Assessment of Aflatoxins in Food and Feed samples. 2nd Sino-German workshop on separation and analysis of complex samples, 23.-28.9.2008, Shanghai and Fuzhou, China.
- R. Niessner, Laser Light or Antibody Two Good Friends to Analysts. ISRANALYT-ICA 2008, 23.1.2008, TelAviv, Israel (invited)
- R. Niessner, C. Kykal and C. Haisch, Photophoresis as a New Diagnostic Tool for Aerosol Studies. European Aerosol Conference, 24.-29.8.2008, Thessaloniki, Greece
- R. Niessner, N. P. Ivleva and M. Knauer, Changes in Structure and Reactivity of Soot during Oxidation, Studied by Raman Microscopy and Temperature Programmed Oxidation. European Aerosol Conference, 24.-29.8.2008, Thessaloniki, Greece
- R. Niessner, Microarray Platforms and their Photonic Readout Status & Trends. XIII Intern. Symp. On Luminescence spectrometry, 7.-11.9.2008, Bologna, Italy (invited)
- R. Niessner, Analytical Chemistry. Laser Light or Antibody Two Good Friends to Analysts. 2008 Intern. Chemical Conference Taipei: Analytical Chemistry, 2.-5.10.2008, Kaohsiung, Taiwan (invited)
- R. Niessner, Microarray Platforms and their Photonic Readout Status & Trends. 3.10.2008, Tsing Hua University Hsinchu, Taiwan (invited)

#### 2.2.2 Poster Presentations

- M. Carrara and R. Niessner, Diesel Particulate Aftertreatment: A source for Nitro-PAHs? European Aerosol Conference, 24.-29.8.2008, Thessaloniki, Greece
- C. Cervino, J.C. Sauceda, D. Knopp and R. Niessner; Hapten Microarrays for Mycotoxin Food Analysis. 10. Statusseminar Chip Technologien. 31.1.-1.2. 2008, Frankfurt a.M.
- S. Donhauser, R. Niessner, M. Seidel, Rapid Automated Chemiluminescence Oligonucleotide Microarray for the Detection of Human Pathogens in Liquids, e.g. Drinking Water, 10. Statusseminar Chiptechnologien, 31.1-1.2.2008, Frankfurt a.M.

- C. Haisch and R. Niessner, Engine Exhaust and Atmospheric Aerosol Characterization by a Single Photoacoustic Instrument. European Aerosol Conference, 24.-29.8.2008, Thessaloniki, Greece
- K. Kloth, A. Didier, R. Dietrich, R. Märtlbauer, R. Niessner, M. Seidel, Development of a Regenerable Hapten Microarray for the Rapid Parallel Detection of Antibiotics in Milk, 10. Statusseminar Chiptechnologien, 31.1-1.2.2008, Frankfurt a.M.
- C. Peskoller, M. Seidel, R. Niessner, Anreicherung von Mikroorganismen in Trinkwasser durch Crossflow-Filtration, Wasser 2008, 28.-30.4. 2008, Trier.
- M. Seidel, A. Wolter, C. Peskoller, G. Pappert, R. Niessner, Antikörper-Mikroarrays als immunoanalytische Plattform f
  ür die schnelle Quantifizierung von Mikroorganismen im Trinkwasser, Wasser 2008, 28.-30.4. 2008, Trier.
- M. Schneider, A. Schubert, T. Baumann, F. Böhm, U. Steiner, C. Mayr and C. Kofahl, Vorstellung eines aktuellen Forschungsvorhabens zur Charakterisierung tiefer Grundwasserfliesssysteme für geothermale Energie am Beispiel des Malmaquifers im süddeutschen Molassebecken, Geothermiekongress 2008, 11.-13.11.2008, Karlsruhe.
- A. Wolter, C. Peskoller, R. Niessner, M. Seidel, A New Concept for the Detection of Microorganisms in Drinking Water, 10. Statusseminar Chiptechnologien, 31.1-1.2.2008, Frankfurt a.M.
- G. Pappert, R. Niessner, M. Seidel, Antibody Screening with Automated Whole-cell Chemiluminescence Microarrays for the Detection of Human Pathogens in Liquids, e.g. Drinking Water, 10. Statusseminar Chiptechnologien, 31.1-1.2.2008, Frankfurt a.M.

#### 2.2.3 Organisation of Scientific Meetings

T. Baumann: Gordon Research Conference Flow & Transport in Permeable Media, 11.-17.7.2008, Oxford (Session Chair)

## 2.3 Patents

C. Peskoller, M. Weller and R. Niessner; Synthetic Resins based on Epoxides. PCT/EP 2008/003566

## 2.4 Hydrogeological Consulting

The hydrochemical analyses in 2008 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, Bayreuth, Bad Birnbach, Bad Endorf, Bad Füssing, Bad Griesbach, Bad Gögging, Hölle, Kondrau, Neumarkt i. d. Opf., Bad Rodach, Sibyllenbad, Straubing, Utting, Bad Wiessee, Bad Wimpfen, Bad Wörishofen
- Hydrogeological and hydrochemical expertises (mineral water, spa water) Bad Abbach, Bad Gögging, Bitterfeld, Kondrau, Sibyllenbad, Bad Tölz, St. Petersburg, Weißenstadt
- Deep Hydrogeothermal Energy Exploration Altdorf, Aschheim, Dürrnhaar, Erding, Garching, Munich, Poing, Pullach, Sauerlach

#### 2.5 Bachelor Theses

- Adelaida Arreaza: Labor<br/>versuche zur Sanierung einer Grundwasserkontamination mit NaOH durc<br/>h ${\rm CO}_2\mbox{-}{\rm Injektion}$
- Victor Bretzler: Quantitative Analyse mit Photoakustischer Spektroskopie
- Andreas Brunner: Charakterisierung der optischen Eigenschaften von Kolloiden mittels photoakustischer Spektroskopie
- Dominik Bucher: Charakterisierung von unbeschichteten und beschichteten Polystyrol-Latex-Partikeln durch Photo-Thermophorese
- Katrin Deller: Erste Versuche zur Verknüpfung der immunomagnetischen Separation mit der Mikroarray-Technologie zur Detektion von Mikroorganismen im Wasser
- Alexandra Dieter: Kinetische Untersuchungen zur Oxidationsfähigkeit verschiedener Russarten während der Behandlung mit Sauerstoff bei hohen Temperaturen
- Gabriel Fischer: Optimization of a Parallel Microarray-based Analytical Method for the Screening of Mycotoxins
- Franziska Glüer: Estimation of the Potential of Shallow Geothermal Energy in Poland
- Florian Golling: Synthese von Monolithen für die Affinitätschromatographie zur Separation von Bakterien
- Florian Huber: Detektion von E. coli über real-time PCR und Mikroarrays
- Jessica Huber: Schrittweise Entwicklung einer immunanalytischen Methode zur Bestimmung von Aflatoxin in Erdnüssen
- Stefan Huber: Validierung des Microarray Chip Readers 3 (MCR3) zur Quantifizierung von Antibiotika in Milch
- Alexander Kawase: Herstellung von monolithischen Proanthocyanidin-Affinitätssäulen zur Separation von Bakterien in Wasser
- Christian Münchmeyer: Analyse von Biofilmmatrix mittels Raman-Mikroskopie und oberflächenverstärkte Raman-Streuung (SERS)
- Patrick Neubert: Funktionalisierung von CMOS-basierten Immunosensoren mit Antikörpern
- Manuela Philipp: Charakterisierung eines mikrofluidischen Aufbaus zur Trennung von Partikeln mittels optischer Kräfte
- Felix G. Quitterer: Sorption und Desorption von transgenen Cry-Proteinen an homoionisierten Tonmineralien
- Maximilian Reitzel: Untersuchung der Schwebstofffracht im Inn Geologische Aspekte
- Sebastian Schmitt: Einfluß der Pufferzusammensetzung und Art der Protinzugabe auf die Extraktionseffizienz von Cry Proteinen aus Böden
- Monika Stoiber: Untersuchung der Schwebstofffracht im Inn Hydrochemische Aspekte
- Katharina Titze: Untersuchung des Verhaltens von strukturierten Aerosolpartikeln durch Photo-Thermophorese
- Martina Ueckert: Untersuchung der Schwebstofffracht im Inn Biologische Aspekte
- Susanna Vasac: Schrittweise Entwicklung einer immunanalytischen Methode zur Bestimmung von Aflatoxin in Mandeln

Katarina Wallgren: Untersuchung der Schwebstofffracht im Inn – Anthropogene Effekte

Sebastian Walter: Quantifying Sorption of Acidic Compounds on Peat

## 2.6 MSc and Diploma Theses

- Susanne Heinrich: MRI-aktive Gadoliniumpartikel: Entwicklung und Kopplung an Antikörper (Schriftliche Hausarbeit zur Zulassung zur Ersten Staatsprüfung für das Lehramt an Gymnasien)
- Cand. ing. Gabriele Hörnig: Fouling in Abgaswärmetauschern Aufbau eines Modellprüfstands und Charakterisierung des Ruß-Abscheidevermögens der gasseitigen Oberfläche verschiedener AGR-Wärmetauscher
- Cand. chem. Xaver Y. Z. Karsunke: Entwicklung eines Mehrkanal-Mikroarray-Chips zur parallelen Detektion von Mikroorganismen
- Cand. geol. Steffen Lauber: Entwicklung einer Methode zur Erhöhung der Standzeiten von Sanierungsbrunnen im ÖGP Bitterfeld/Wolfen Hydrochemische Aspekte
- Cand. geol. Christina Mayr: Mikroskalige Visualisierung des Transports von Aktivkohlekolloiden in einenm porösen Medium und deren Wechselwirkungen an reaktiven und nicht-reaktiven Grenzflächen (Univ. Hamburg)
- Cand. geol. Claudia Muhr: Entwicklung einer Methode zur Erhöhung der Standzeiten von Sanierungsbrunnen im ÖGP Bitterfeld/Wolfen Geohydraulische Aspekte
- BSc Richard Plapperer: Entwicklung von multifunktionellen Antikörper-gekoppelten Nanopartikeln als MRI-aktive Substanzen
- BSc Martin Rieger: Entwicklung eines automatischen Verfahrens zum Hochdurchsatzhybridomascreening für die Generierung haptenspezifischer monoklonaler Antikörper
- BSc Maria Rye-Johnsen: Development of a Regenerable Hapten-Microarray for the Rapid Parallel Detection of Antibiotics in Milk
- Cand. geol. Natascha Torres: Untersuchung einer Nickelanomalie im Grundwasser

## 2.7 PhD Theses

Leb.-Chem. Michael Rampfl: Entwicklung und Validierung eines neuen analytischen Verfahrens zur qualitativen und quantitativen Bestimmung von gasförmigen Amin-Emissionen aus Materialien und Werkstoffen für den Innenraum

## 3 Teaching, Colloquia, and Other Activities

## 3.1 Classes

- 3.1.1 Chemistry (B.Sc. and M.Sc.)
  - Analytical Chemistry Physical and Chemical Separation Methods (Analytische Chemie Physikalisch-chemische Trennmethoden); Niessner
  - 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
- Hydrogeological, Hydrochemical and Environmental Analytics 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
- Water Chemistry Lab II (Wasserchemisches Praktikum II); Niessner, Haisch, Knopp, Seidel

#### 3.1.2 Chemical Engineering (Diplom)

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

#### 3.1.3 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
- Introduction to Hydrogeology (Ringvorlesung Geowissenschaften); Baumann
- 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 Analytics 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

#### 3.1.4 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

#### 3.1.5 ERASMUS Docent Mobility

• Bioanalytical Methods in Environmental and Food Chemistry (Gdansk University of Food Technology, Poland) 22.-26.6.2008; Knopp

#### 3.2 Institute Colloquia

- PD Dr. Birgit Kanngießer, Technische Universität Berlin:  $\mu$ -elemental Imaging (14.1. 2008)
- Prof. Dr. William Shotyk, Institute of Environmental Geochemistry, Universität Heidelberg: Pathways of Lead and Antimony from the Atmosphere to the Hydrosphere (15.1.2008)
- Dr. Petra S. Dittrich, Dept. Miniaturization, ISAS Dortmund: Lab-on-Chip Technology for Analytics and Cell Biology (20.1.2008)
- Dr.-Ing. Thomas Kleine-Ostmann, Phys.-Techn. Bundesanstalt Braunschweig: Terahertz Spectroscopy: Potentials & Needs (12.2.2008)
- Prof. Dr. Wolfgang Parak, Philipps-Universität Marburg: Inorganic Colloidal Nanoparticles – from Synthesis to Biological Applications (15.2.2008)
- Dr. Peter Miethe, Forschungszentrum für Medizintechnik und Biotechnologie, Bad Langensalza. Development of Fast Immunoassays for Highly Toxic Substances and Contaminants (4.3.2008)
- Dr. Wlad Kusnezow, Deutsches Krebsforschungszentrum Heidelberg: From Current Antibody Arrays to Future Diagnostic Assays: Physicochemical Basics, Technological Development and Perspectives (11.3.2008)
- Dr. Daniel Razansky, Institute for Biological and Medical Imaging, Technical University Munich and Helmholtz Center Munich: Macroscopic and Mesoscopic Molecular Imaging of Living Tissues (17.4.2008)
- Prof. Dr. W. Lindner, Department of Analytical Chemistry and Food Chemistry, University of Vienna, Austria: Chromatographic Enantiomer Separations, a Mature Technique or Still a Challenge to be Mastered? (25.4.2008)
- Prof. Dr. E. James Davis, University of Washington: Principles and Applications of Electrodynamic Aerosol Balances (28.5.2008)
- Dr. Michael Schäferling, Institut für Analytische Chemie, Universität Regensburg: Luminescence Lifetime Imaging and Time-resolved Fluorimetry for (Bio)Analytical Applications (11.6.2008)
- Dr. Florian Einsiedl, National University of Ireland, Galway: When Microbes Meet Sulfate: Insights into Stable Isotope Fractionation During Bacterial Sulfate Reduction (18.6.2008)
- Prof. Dr. Asit K. Ray, Department of Chemical Engineering, University of Kentucky:, Tailoring of Nano-size Progeny Droplets Emitted by Columbic Explosions (2.7.2008)
- Prof. Dr. Diana S. Aga, Associate Professor, Chemistry Department University at Buffalo: Analytical Challenges in Investigating the Fate and Transport of Pharmacentricals in the Environment (8.7.2008)
- Prof. Dr. Detlev Belder, Institut für Analytische Chemie, Universität Leipzig: Chemical Reactions and Analysis on a Chip (16.7.2008)
- Dr. Oliver Trapp, Max-Planck-Institut für Kohlenforschung, Mülheim a.d.R.: New Routes in the High-Throughput Screening of Catalysts (29.7.2008)
- Prof. Dr. Patrick Wagner, Universität Hasselt, Belgien: Biosensing with Molecular Imprints and Diamond-based Platform Materials (2.9.2008)

- Dr. Michael Hays, US EPA: Advancing the Characterization of Carbonaceous Source Aerosols (24.9.2008)
- Dr. Beate Strehlitz, Helmholtz-Zentrum für Umweltforschung, Leipzig: DNA-Aptamers - New Bioreceptors for Biosensors (25.9.2008)
- Dr. Barbara Navé, BASF AG, Limburger Hof: Entdeckung moderner Pflanzenschutzmittel (31.10.2008)
- Dr. Markus Ammann, Paul-Scherer-Institut, Villigen/Schweiz: Mechanisms and Kinetics of Heterogeneous Reachtions of Nitrogen Oxides with Tropospheric Aerosol Particles (6.11.2008)
- Prof. Dr. Alfred P. Weber, Institut für Mechanische Verfahrenstechnik, TU Clausthal: Contact Charging of Bouncing Aerosol Nanoparticles (10.11.2008)
- Dr. Thole Züchner, Universität Leipzig: New Methods for Proteome Analysis: Ultrasensitive Protein Detection Using Time Resolved Fluorescence (19.11.2008)
- Dr. Olga Popovicheva, Moscow State University: Transport-emitted Particles and Oxidation (01.12.2008)
- Dr. Ute Resch-Genger, BAM Berlin: From Functional Chromophores to Fluorescence Standards: Fluorescence Spectroscopy at BAM (8.12.2008)
- Prof. Dr. Alois Jungbauer, University of Natural Resources and Applied Life Sciences, Wien: Monoliths for the Ultrafast Separation of Large Biomolecular Assemblies (16.12.2008)

## 3.3 External Tasks and Memberships

#### Prof. Dr. Reinhard Niessner

Bayer. Fachausschuß für Kurorte, Erholungsorte	Member		
und Heilbrunnen			
DECHEMA Commission "Chemische Grundlagen	Member		
und Anwendungen der Sensortechnik"			
DFG-Senatskommission für Wasserforschung	Member		
Heinrich-Emanuel-Merck-Award Committee	Jury Head		
Analytical Chemistry	Associated Editor		
Analytical and Bioanalytical Chemistry	Advisory Board Member		
Microchimica Acta	Advisory Board Member		
Fresenius' Environmental Bulletin	Advisory Board Member		
Analytical Sciences	Advisory Board Member		
Analyst (until 4/2008)	Advisory Board Member		

#### PD Dr. Thomas Baumann

Bayer.	Fachausschuß	für	Kurorte,	Erholungsorte	Member
und Hei	lbrunnen				
VBGW	AK Grundwass	sers	chutz		Member
DIN NA	119-01-02-05	UA	Elution		Member

#### Prof. Dr. Dietmar Knopp

Ecotoxicology and Environmental SafetyEditorial Board MemberChromatographiaEditorial Board MemberInternational Journal of Environmental ResearchEditorial Board Memberand Public HealthEditorial Board Member

#### Dr. Michael Seidel

KRdL-3/7/04, "Luftgetragene Mikroorganismen Member und Viren", im VDI/DIN 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.

Additionally three landfill monitoring sites, one municipal solid waste landfill, one MSWI bottom ash landfill, and one mixed waste landfill are run by the institute.

## 4.2 Environmental Analytical Chemistry

#### 4.2.1 Laser

- 3 He/Ne-laser
- 6 Nd-YAG-laser
- $1 \text{ CO}_2$ -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  $\mu \mathrm{m}$  1.8  $\mu \mathrm{m})$
- 1 Laser<br/>diode with external resonator
- 1 Optical parameter oscillator (410 nm 2.1  $\mu \rm{m})$

#### 4.2.2 Optoelectronics/Spectrometer

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

#### 4.2.3 Chromatography

3 GCs with FID, NPD, ECD, TEA and AED 1 High-resolution GC/MS, VG Autospec

1 LC-Orthogonal-ESI-TOF-MS, Micromass

- 1 Lyophilizer
- 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
- $3~\mathrm{HPLC},~\mathrm{UV}/\mathrm{VIS}$  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

#### 4.2.4 Dioxin Laboratory

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

#### 4.2.5 Bioanalytics

#### Bioseparation:

- Crossflow Filter (Inge AG)
- Crossflow Filter (Spectrum Laboratories, Inc)
- Pressure and Flowrate controlled Crossflow Filtration System (IWC) Molecular Biology:
- 1 Real-time PCR (Light Cycler 480, Roche) Microarray Technology:
- 3 Chemiluminescence Microarray Reader (PASA, IWC)
- 1 Chemiluminescence Microarray Reader (MCR 3, IWC)
- 1 Ink-Jet Microdispenser (Nanoplotter, GeSim)
- 1 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)
- 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 Chip spotter system, GeSIM
- 1 384-channel washer, Biotek

#### 4.2.6 Element Analytics

- 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

#### 4.2.7 SEM/Microscopy/Colloid Sizer

- 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)
- 1 Zetaphoremeter, SEPHY

#### 4.2.8 Sum Parameters

- 2 Coulo<br/>stat for C quantification, Coulomat702
- 1 DOC analysator, UNOR 6 N
- 1 TOC analysator, TOCOR 2 1 AOX/TOX, Sigma
- 1 11017/ 1 017, Bigilia

#### 4.2.9 Aerosol Research

- 1 Aerosol chamber (1  $\mathrm{m}^3)$
- 1 Aerosol flow tube (10 L) 1 Ozone analyzer (UV absorption)
- 1 Ozone analyzer (OV absorption) 1 NO/NO<sub>2</sub> analyser (Chemiluminescence)
- 2 Aerodynamic particle sizers  $(0.5-25 \ \mu m)$
- 1 Berner impactor (9 stages, 50 nm 16  $\mu$ m)
- 1 Electrical low-pressure impactor (12 stages, 30 nm 10  $\mu$ m)
- 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)
- $2~{\rm Spark}\mbox{-discharge soot aerosol generators}$  (polydisperse ultrafine carbon aerosol)
- 1 Berglund-Liu aerosol generator (monodisperse aerosols, 0.8-50  $\mu \rm{m})$
- 1 Floating bed aerosol generator (powder dispersion)
- 1 Rotating brush aerosol generator (powder dispersion)

## 5 Staff 2008

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