ABC's spotlight on the nanoworld

Günter Gauglitz¹

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At the Analytica 2016 in Munich, ABC organized a session dedicated entirely to nano. Already 2 years ago, a spotlight on this topic was published in ABC with the focus on carbon nanotubes [1], pointing out that nanomaterials have a large variety of specific properties and numerous applications. The session at the Analytica tried to cover some of these aspects, discussing properties of nanoparticles, their characterization, their use for specific applications, and quite a few techniques taking advantage of these properties.

“Nano” is derived from the Ancient Greek term *νανος*, meaning *dwarf* [2], and was first introduced at the conference of the Union Internationale de Chimie in 1947. In 2000, the National Nanotechnology Initiative (NNI) in the US was instituted, and soon the term *nanotechnology* was introduced, a keyword covering a wide up-coming field of research. Nanoparticles, by definition particles with a diameter of 1 to 100 nanometers, can be synthesized from a variety of materials, such as metals, dendrimers, micellar structures, soot particles, or asbestos. The specific properties come from the surface-to-volume ratio, from the possible porosity, and from potential plasmonic effects. All these can be beneficial on account of their antibacterial activity and their potential use as a carrier for drugs, and because they allow signal enhancement. The drawback is their potential toxicity, not only in themselves, but through their bio-coating, causing undesirable biomolecular interaction processes. From an analytical point of view, such nanoparticles influence extraction and chromatographic

processes and open new fields through signal enhancement; they also can be used, after functionalization, for labeling or as markers in proteomics. Many classic analytical tools have been modified to allow good characterization of such nanoparticles, especially metal nanoparticles, and even new innovative techniques have been developed. All these aspects have been covered in the session at the Analytica.

Functionalization of nanoparticles is an essential approach to optimize their properties for specific applications. In principle, such nanoparticles can be used for protein/peptide separation using monolithic columns. By these means, capillary liquid chromatography has a high potential for such a separation with the advantage of high efficiency, high resolution, and low sample consumption. This is especially the case when coupling these columns with mass spectrometry. Polymer monoliths, silica monoliths, or organic silica hybrid monoliths can be used. The chromatographic performance can be improved through tailored preparation processes, control of porous properties, and increase of the surface area [3]. Regarding the antibacterial properties of nanomaterials, e.g., for food packaging, copper nanoparticles can be embedded in polylactic acid, which combines antibacterial properties of copper nanoparticles with the biodegradability of the polymer matrix. The synthesis, analytical characterization, and performance in real samples related to bioactivity tests allow the preparation of antibacterial systems for novel active food packages [4]. In the case of metal-based pharmaceuticals, in earlier times only the toxicity of elements was determined. However, it soon became apparent that this only allowed an insufficient biochemical or toxicological investigation, especially for living organisms. It is, however, rather important to know the chemical form of a specific element (i.e., the oxidation state in which this species is introduced into the environment or organism). Such speciation analysis can be done with hyphenated systems, combining gas chromatography (GC),

✉ Günter Gauglitz
guenter.gauglitz@uni-tuebingen.de

¹ Institute of Physical and Theoretical Chemistry, Eberhard Karls Universität, Auf der Morgenstelle 18, 72076 Tübingen, Germany

high - performance liquid chromatography (HPLC), and capillary electrophoresis (CE) with various mass spectrometry or spectroscopic methods. Such hyphenated techniques are tools for drug speciation analysis, and allow high elemental selectivity and high sensitivity, especially when targeting metals or metal- containing drugs [5].

Especially silica nanoparticles are suitable for food and consumer products, in case their physicochemical and toxicological properties are known. Differential centrifugal sedimentation, field flow fraction, and scanning or transmission electron microscopy are combined to classify these nanomaterials. Essential is also the particle surface chemical composition, e.g., determined by particle-induced X-ray emission and X-ray photoelectronic spectroscopy. Thus, analytical techniques for particle size distribution and chemical composition allow the characterization of relevant nanomaterials [6]. Nanoparticles are usually present in complex matrices. To really characterize them, micro-extraction techniques such as field- and flow-based separation or solid-phase micro-extraction and liquid-phase microextraction are necessary. The development of new miniaturized units and hybrid extraction media, the evaluation of micro-extraction tools for problem solving in environmental and food fields as well as the use of ionic liquids open new nanotechnological tools to extract information about these nanoparticles [7].

Nanoparticles can be contrast agents for in-vivo bioimaging [8]. Mass spectrometry imaging allows for the direct and simultaneous analysis of the spatial distribution of molecular species from sample surface tissue sections [9]. Such medical diagnostics or food analytics are an upcoming interesting field of analysis. Sometimes, lab-on-chip systems are used, where the possible detection can be done using chromatographic or spectroscopic methods. However, the interesting part is the simultaneous identification and quantification of analytes in such systems using the plasmonic effects of metal-based surfaces or nanoparticles. A combination of lab-on-chip (LOC) with quantitative surface-enhanced Raman spectroscopy (SERS) opens a new field of standardized measurements in microfluidic systems and is a powerful tool in bioanalytics [10].

New strategies, apart from the typical mass spectrometric characterization of these classic analytical methods, are attempted by combining spectroscopic and electrochemical measurements. Using sophisticated structure-extraction methods and such systems, particles can be classified according to size and properties [11]. Bioanalytical applications, however, require well-designed surface properties of nanoparticles. They have to be well-characterized to provide both a stable aqueous colloidal dispersion and the ability to conjugate biomolecules and other ligands on the nanoparticle surface. Photon up-converting particles can be examined well, being excited by near - IR radiation to avoid scattering and auto-fluorescence [12]. Especially, high-resolution electrochemical imaging, combining atomic-force microscopy (AFM) and scanning

electrochemical microscopy (SECM), or these methods combined with the infrared spectroscopy, can be considered as an additional approach to conventional electrochemical methods, biomimetic sensors, and DNA sensing to open the interesting field of nanomedicine for analytics [13].

In summary, understanding of molecular interactions, characterization of properties, and dependence on size or coating determine optimal nano-technological applications in energy, environment, electronics, life science, medicine, and even space. Furthermore, challenges and knowledge about risk and toxicity should influence human progress and survival, opinion of social society, and decisions of policy makers. It is obvious that analytics play an essential part for these topics, which were strengthened by the information on modern analytical possibilities given at the conference session.

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Günter Gauglitz is Senior Professor at the Eberhard Karls University of Tübingen working in analytical and physical chemistry. He was chairman of the GDCh Division of Analytical Chemistry and chaired the Europt(r)ode VIII meeting. For more than 15 years, his main scientific interests have centered on research and development in chemical and biochemical sensors with special focus on the characterization of interfaces of polymers and biomembrane surfaces, spectroscopic

techniques, use of spectral interferometry to monitor changes in optical thickness of thin layers, and effects of Fresnel reflectivity at interfaces. He has been Editor of Analytical and Bioanalytical Chemistry (ABC) since 2002.