

# An update on method development to analyze nanoparticles in complex samples

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Due to the increasing demand on analytical methods for nanomaterials in complex samples several research projects have been initiated during the last five years. The main tasks of these projects were to develop and verify analytical concepts which provide us with reliable quantification data on nanomaterial in complex samples. Complex samples of interest were e.g. of environmental origin (e.g. surface water) or consumer and food products. Major challenges for the analysis of nanoparticles in complex samples are interferences between target analyte, which is the nanoparticle and matrix constituents, generally low concentrations and low contrast of the target analyte compared to the matrix, alteration of the target analyte during sample preparation and the difficulty in quantification of the amount of nanoparticles. Considerable advances have been made in terms of developing generic concepts including quality criteria for method development. Recently, Wagner et al. (2015) published the first tested generic sample preparation scheme for separation, characterization, and quantification of ENPs in complex food matrices which defines quantitative quality criteria. This novel generic sample preparation scheme and the applied quality criteria are of pivotal relevance for standardized method development for ENPs in food and consumer products. Besides progress in sample preparation analytical techniques have been further developed which enable us to quantify the amount of nanomaterial, determine their particle size distribution and their origin (Praetorius et al. 2015).

We will present here three case studies which depict **i)** the generic sample preparation concepts with its benefits and limits, **ii)** quantification of single particles in aqueous media using ICP-MS analysis and **iii)** a new analytical concepts for nanomaterials based on single particle ICP-MS.

In our experimental case study we challenged the generic sample preparation approach and selected a real food sample and a cosmetic sample (sample 1: a powdered tomato soup which contains SiO<sub>2</sub> particles as anti-caking agent (E551), and sample 2: a sunscreen which contains TiO<sub>2</sub> as UV-filter and Fe-oxides as pigment). Following sample preparation, the extracted particles were analyzed by asymmetric flow field flow fractionation (AF<sup>4</sup>) online coupled to multi-angle light scattering (MALS) and inductively coupled plasma mass spectrometry (ICP-MS). As the most prominent result, it was found that an adapted generic sample preparation scheme in combination with the AF<sup>4</sup>-MALS-ICPMS analysis was applicable for both matrices. For SiO<sub>2</sub> in tomato soup, complete matrix removal and Si mass recovery > 90% were achieved using acid digestion supported by heat (90°C) and hydrogen peroxide as oxidation agent. The static light scattering signal was used for the first time as a fingerprint to identify the type of particles present in the food matrix. For TiO<sub>2</sub> in sunscreen, ENPs could be isolated by a combination of combustion and solvent washing followed by magnetic separation of TiO<sub>2</sub> and Fe-oxides. Recoveries were sufficiently high to perform FFF-MALS-ICPMS analysis indicating complete separation of TiO<sub>2</sub> and Fe-oxides ENPs.

The quantification of single Ag nanoparticles (AgNP) which were released from solid materials (e.g. polypropylene and polyethylen) into a fluid (water and water with 20% ethanol) was studied by single particle ICPMS (sp-ICPMS, Laborda et al. 2011). Sp-ICPMS assumes spherical particles with a known stoichiometry. Based on this assumption both particle concentration and size can be determined. State of the art concepts previously used to study the migration behavior of organic compounds were thereby

transferred to the migration of nanoparticles from products such as food containers to food simulants. Total migration rates of Ag and specific Ag migration of AgNPs and dissolved Ag were determined. Specific AgNPs migration rates were up to a factor of 1000 below dissolved Ag migration rates. We demonstrated that released Ag (particulate and dissolved) is significantly attached to the surfaces of the migration test beakers (between 10 and 50% of total released silver). Therefore, the specific migration rates determined in state-of-the-art migration tests do not fully reflect the NPs behavior.

Quantification of engineered titanium dioxide nanoparticles (TiO<sub>2</sub> NPs) in soil and surface water is required in order to estimate the expected release into the environment during their application e.g. for UV-filter in sunscreen. The detection of engineered TiO<sub>2</sub> is a challenging task because of high natural background concentrations. Several analytical approaches previously described in v.d. Kammer et al. (2012) have been tested in a field study at the Old Danube Lake (Vienna, Austria). During summer the lake is intensively used as bathing area which makes it very suitable for a field investigation to study the release of TiO<sub>2</sub> from sunscreen in surface water. We here present analytical results of a two-year sampling campaign where we determined the distribution of Ti in water column and sediment samples as well as the variation of elemental ratios which could potentially be used to identify the release of engineered materials. However, there was no clear increase in Ti concentration in the water column which could be attributed to the application of TiO<sub>2</sub> containing sunscreens. Sp-ICPMS data suggested an increase in particle number concentration of TiO<sub>2</sub>. Complementary electron microscopy studies indicated the presence of single TiO<sub>2</sub> particles which might be originated from sunscreens. However, it was not possible to quantitatively discriminate engineered and natural particles from each other. As reported in Praetorius et al. (2015) the quantification and identification of natural CeO<sub>2</sub> containing particles and engineered CeO<sub>2</sub> particles might be possible using sp-ICPMS. Natural CeO<sub>2</sub> containing particles are characterized by a heterogeneous elemental composition and shape. Engineered CeO<sub>2</sub> NPs have a known stoichiometry and do not contain (or only traces of) other elements. On the basis of this assumption we expect pulse signals of natural Ce-containing particles to be low and to not represent the true size of the particle detected by the mass detector of the ICP-MS. In contrast, engineered CeO<sub>2</sub> NPs will appear as a spike which is significantly higher than the background signal.

*Acknowledgment* – The NanoDefine project is supported by the European Commission under the Environment (including climate change) Theme of the 7<sup>th</sup> Framework Program for Research and Technological Development.

## References

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