

Instrumentation and methodology for comprehensive and quantitative inorganic nanoparticle measurements in real systems

A. Gundlach-Graham¹, L. Hendriks¹, B. Ramkorun-Schmidt², A. Praetorius³, F. von der Kammer³, R. Kägi⁴, B. Hattendorf¹, D. Günther^{1*}

¹Department of Chemistry and Applied Biosciences, ETH Zurich, ²BAM Federal Institute for Materials Research and Testing, ³Department of Environmental Geosciences, University of Vienna, ⁴Eawag

As more anthropogenic nanoparticles are included in consumer products and manufacturing processes, the transport of these particles into non-target biological and environmental systems is unavoidable. In the past decade, numerous researchers have sought to understand the fate and transport of nanoparticles within organisms and in other complex systems, such as wastewater processing, surface water, and soils. Clearly, understanding the speciation and presence of nanoparticles is vital to assess routes of exposure and potential human- and eco-toxicity of these particles. However, analytical measurements of the concentration and speciation of nanomaterials in real systems are still required to verify the relevance of many lab-scale nanoparticle exposure studies and of computer models of nanomaterial fate and transport. Importantly, the assessment of nanomaterials in real systems is lagging because most currently available analytical methods for nanoparticle detection have insufficient specificity and sensitivity.

Anthropogenic nanomaterials in biological or environmental systems are difficult to detect because they are small (hundreds to millions of atoms), dilute in terms of total mass concentration, and are present in complex matrices that may even contain native (naturally occurring) nanoparticles. Here, I will discuss an emerging method called single-particle inductively coupled plasma time-of-flight mass spectrometry (sp-ICP-TOFMS), which offers potential to provide high-throughput and sensitive determination of inorganic nanoparticles in real systems. In sp-ICP-TOFMS, a dilute nanoparticle-containing solution is introduced into a plasma that is hot enough to fully break down the nanoparticles into their component atoms and ionize those atoms. When measured by TOF mass spectrometry, the ion cloud from each nanoparticle produces a brief and intense transient signal at the mass channels specific to the elements present in the particle. The structure and frequency of these “single-particle” [1] events carries information about the nanoparticles in a sample, including the elemental and isotopic composition of particles, particle-number concentrations, and particle-mass distributions. Importantly, sp-ICP-TOFMS presents a direct route to measure very low (i.e. environmentally relevant) concentrations of diverse inorganic nanoparticles because the measured analytical signal does not depend on bulk concentration, but just the mass of analyte atoms present in each particle.

Here, I will present an overview of nanoparticle detection by sp-ICP-TOFMS, highlighting both the advantages and limitations of the instrumentation and current methodologies. I will emphasize our recent developments in sample introduction and calibration strategies to facilitate the high-throughput simultaneous quantification of diverse, multi-elemental nanoparticles from environmental samples. Additionally, I will explain how elemental “fingerprints” can be used to distinguish anthropogenic particles against a natural nanoparticle background.

[1] Degueldre, C.; Favarger, P. Y., *Colloids and Surfaces A*, **2003**, 217, 137-142.