CASE STUDY

ICP-Mass Spectrometry

Colorado School of Mines Uses a NexION 300Q ICP-MS to Obtain a Better Understanding of the Environmental Impact of Engineered Nanomaterials

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There is an unprecedented amount of scientific research going on today dedicated to the study of a world so small, we cannot see it even with a conventional microscope. That world is the field of nanotechnology – the realm of atoms and nanostructures. But what actually is nanotechnology? The National Nanotechnology Initiative (NNI) defines nanotechnology as the study of materials with dimensions <100 nm, where unique properties enable novel applications to be carried out. For example, gases, liquids, and solids can exhibit unusual physical, chemical, and biological properties at the nanoscale level, differing in critical ways from the properties of the bulk materials. Nanomaterials occur in nature, such as clay minerals and humic acids, but they can also be produced by human activity such as diesel emissions, or welding fumes. In addition, nanomaterials

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can be specifically engineered to exhibit unique optical, electrical, physical, or chemical characteristics. Depending on their chemical and physical characteristics, these engineered nanomaterials (ENMs) can be made to exhibit greater physical strength, enhanced magnetic properties, better conduction of heat or electricity, greater chemical reactivity, or improved optical properties.

Engineered Nanomaterials

Most ENMs can be divided into two main categories - carbon-based, such as nanotubes, which are used to improve material strength, or metal-containing ones such as silver (Ag), gold (Au), or titanium (Ti) nanoparticles (NP), which are incorporated into a product matrix like a solar cell. For these applications, the ENMs are typically bound to the matrix of the material, and as a result, are less likely to be released into the environment. However, many of the metal-containing ENMs are used in dispersive applications where they are intentionally released from the product. For example, fabrics containing silver nanoparticles used to kill bacteria release silver at varying rates during the washing cycle, depending on the type of fabric and the washing conditions. It is therefore clear that the use of ENMs in consumer, industrial, and healthcare products is growing rapidly, with an estimated 1000 commercially-available products being used today for many diverse and varied applications.

Environmental Impact

The unique properties of ENMs have also created intense interest in the environmental behavior of these materials. Due to the increase in use of nanotechnology-based products, nanoparticles are more likely to enter the environment. Different ENPs will have different properties and will therefore behave very differently when they enter the environment. So in order to ensure the continued development of nanotechnology products, there is clearly a need to evaluate the risks posed by these engineered nanoparticles, which will require proper tools to carry out exposure assessment studies to better understand how they interact with soil, sediment, and water systems.

Colorado School of Mines

One of the leading academic research groups involved with the study of the impact of ENPs on the environment is the Colorado School of Mines (CSM), based in Golden, Colorado. Founded in 1874, two years before Colorado officially became a state, Mines' early academic programs primarily focused on geology, mineralogy, mining engineering and metallurgy, with an emphasis on gold and silver and the assaying of these minerals. As the institution grew, it has expanded its role to focus specifically on understanding the Earth, harnessing energy and sustaining the environment. Today, CSM has achieved global recognition by developing a curriculum and research program geared towards responsible stewardship of the Earth and its resources.

Characterization of Engineered Nanoparticles

The major research into nanoparticles at CSM is being carried out by Dr. James Ranville, an associate professor in the Department of Chemistry and Geochemistry. Under his guidance, Dr. Ranville's laboratory is focused primarily on environmental geochemistry, with a particular emphasis on carrying out research into the characterization of nanoparticles in various environmental processes. Some of his other studies include an understanding of arsenic and uranium contamination in ground waters, and the aquatic toxicity of cadmium (Cd), copper (Cu), and zinc (Zn) in streams impacted by the mining industry.

Current analytical approaches to assess the impact of nanoparticles on the environment include a combination of computer modeling to predict life cycles and direct analytical measurement techniques. Prediction of environmental concentrations of ENPs through modeling is based on knowledge of how they are emitted into the environment, together with their eventual fate and behavior, which requires validation through measurement of actual environmental concentrations. For ENPs that are only recently being introduced into the environment, extremely sensitive methods are required. Although the direct measurement approach is not hampered by the underlying assumptions of exposure modeling, it is very important to assure that direct observations are representative in time and space for the regional setting in which the observation was made. This was emphasized by Dr. Ranville when he explained,

> *"ENPs differ from most conventional dissolved chemicals in terms of their heterogeneous distributions. Therefore, when it comes to environmental health studies (EHS), it is not only important to determine their concentrations, but also other metrics like shape, size distribution, and chemical composition, which require extremely sophisticated techniques."*

Many analytical techniques are available for nanometrology, only some of which can be successfully applied to nano-EHS studies. Traditional methods for assessing particle concentration and particle size distributions include: electron microscopy, chromatography, field flow fractionation, centrifugation, laser light scattering, ultrafiltration and UV spectroscopy. Difficulties generally arise due to a lack of sensitivity for characterizing and quantifying particles at environmentally relevant concentrations (low µg/L). Furthermore, the lack of specificity of these techniques is problematic for complex environmental matrices that may contain natural NPs having polydispersed particle distributions, as well as having heterogeneous compositions.

Role of ICP-MS

An integral part of Dr. Ranville's research in the area of nanoparticle sensitivity and specificity has involved the use of ICP mass spectrometry (ICP-MS). Because of its trace element capability, and extremely low detection limits, the technique is ideally suited to the characterization of ENPs, containing elements such as Ag, Au, Ti and Fe, which have been integrated into larger products such as consumer goods, foods, pesticides, pharmaceuticals, and personal care products. The ubiquitous use of goods containing these nanomaterials will inevitably lead to environmental releases, which may be studied and quantified using state-of-the-art ICP-MS technology, such as PerkinElmer's NexION® 300Q system, which Dr. Ranville's lab acquired recently.

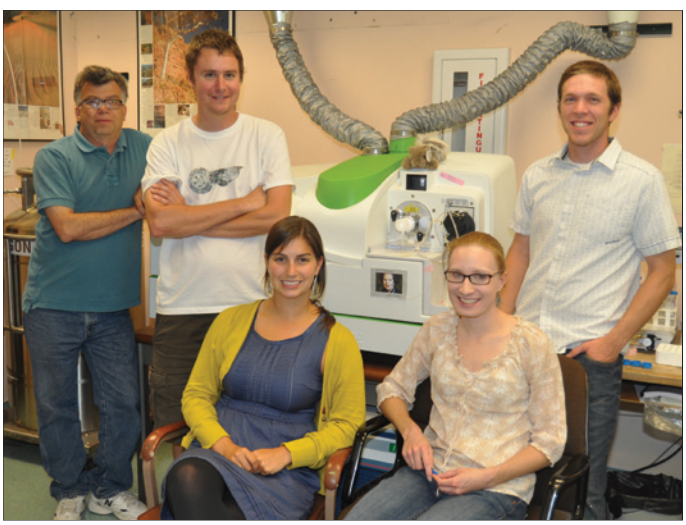

Figure 1. Dr. Jim Ranville *(far left)* and his graduate students *(left to right)*: Rob Reed, Denise Mitrano, Val Stucker, Evan Gray; and sitting on top of the NexION 300Q is Jerry the Plasma Squirrel.

Single Particle ICP-MS Studies

One area in particular that his team is focusing on is single particle (SP) ICP-MS, which is a novel technique for detecting and sizing metallic nanoparticles at environmentally relevant concentrations. While this method is still in its infancy, it has shown a great deal of promise in several applications, including determining concentrations of silver nanoparticles in complex matrices, such as wastewater effluent. The method involves introducing NP-containing samples, at very dilute concentration, into the ICP-MS and collecting time-resolved data. Very short integration times on the order of 5-10 ms are used in order to detect individual particles as pulses of ions after they are ionized by the plasma. Observed pulse number is related to the nanoparticle concentration by the nebulization efficiency and the total number of NPs in the sample, while the mass, and thus the size of the NP is related to the pulse intensity. The principles of characterizing nanoparticles using SP-ICP-MS are shown in Figure 2.

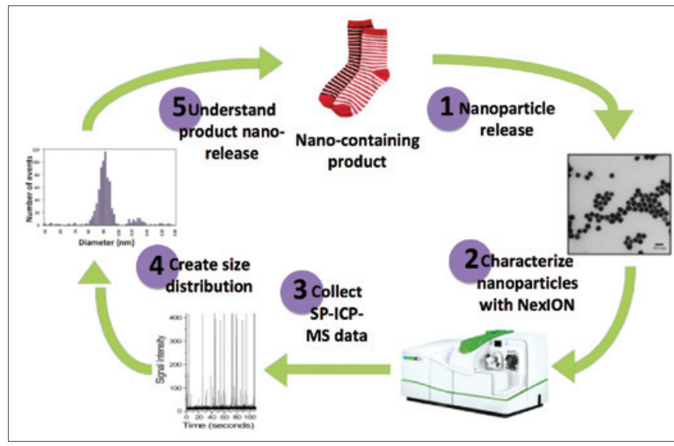

Figure 2. Principles of characterizing nanoparticles using single particle ICP-MS analysis with the NexION 300Q system.

In this example, nano-Ag imbedded in athletic socks, which is used as a bactericide, has been shown to release during simulated wash cycles.[1] By collecting and analyzing a simple aqueous solution with the NexION 300Q ICP-MS,[2] and collecting data using the SP-ICP-MS technique,[3] the size, concentration, and associated dissolved material can be quantified – all important parameters in environmental and biological modeling. Once the raw data is collected, the dissolved content is at low signal intensity, with nanoparticles creating pulses above this background where the height of the pulse relates to the mass of analyte and the number of pulses correlates to the concentration of NP in the samples. The size distribution of particles in the sample can be calculated using well-understood SP-ICP-MS theory.[4] A histogram of nanoparticle diameter versus number of events (NP number) can then be created in order to visualize the NP distribution in the sample, in addition to calculating the concentration of both NP and dissolved fractions of the NP released from the products.[5] In this way, scientists can have a better understanding of how nanomaterials will behave in the environment at realistic concentrations.

Optimized Measurement Protocol

However, it should be emphasized that for this approach to work effectively at low concentrations, the speed of data acquisition and the response time of the ICP-MS detector must be fast enough to capture the time-resolved nanoparticles pulses, which typically last only a few milliseconds or less. This is emphasized in Figure 3, which shows a real-world example of the time-resolved analysis of 30 nm gold particles using the NexION 300 ICP-MS. It can be seen that the gold nanoparticle has been fully resolved and characterized with 3-4 data points in <1 millisecond, showing the benefit of very fast data acquisition rate and short dwell times of the NexION 300 system for this kind of work.

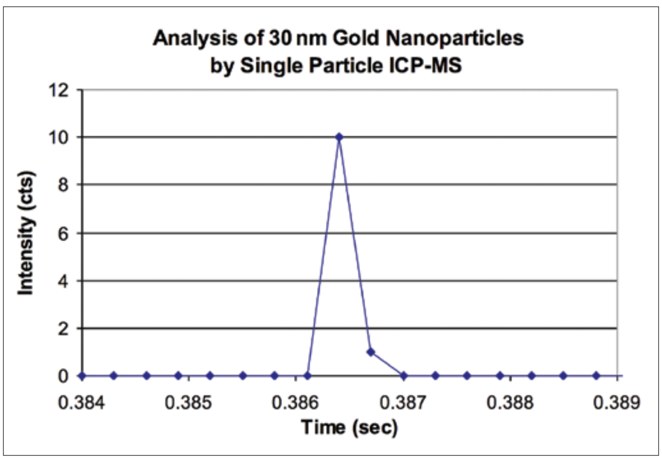

Figure 3. Time-resolved analysis of 30 nm gold nanoparticles using the NexION ICP-MS, showing the pulse is fully characterized in less than 1 ms.

Dr. Ranville and his team have published a number of papers and articles on this very exciting area of research, some of which are referenced at the end of this article. His PhD students play a very important role on the diverse range of nanoparticle studies they have carried out. Of particular mention is Denise Mitrano, who is examining NPs in wastewaters, the likely major route of environmental exposure to NPs released from consumer products. Rob Reed is looking at the release of NPs from various types of products, including the release of carbon nanotubes, which can be analyzed by ICP-MS due to the residual catalysis metals present in the tubes. And Evan Gray is examining tissues to determine the potential for bioaccumulation of NPs.

Dr. Ranville has been a long-time user of PerkinElmer equipment over the years ever since he joined the CSM faculty in 1994. That year, he acquired an Optima™ 3000 ICP-OES, which was followed by an ELAN® 6000 ICP-MS in 2001 and an Optima 5300 ICP-OES in 2004. The department's trace element capabilities got an upgrade last year when they acquired a NexION 300Q ICP-MS. Dr. Ranville summed up his impressions of the instrument when he commented:

"The NexION 300Q ICP-MS gives us extended capabilities for nanoparticle analysis. As we work with PerkinElmer to develop new ways to detect and quantify nanomaterials, the flexibility of the data acquisition measurement protocol allows us to collect transient data with a very short duty cycle, which will be a major improvement over our existing technology for single particle ICP-MS studies. This is a very significant development for nanometrology, particularly as we move forward into multielement characterization."

There is no question that Dr. Ranville's work is on the cutting edge of what can be achieved with an ICP-MS system. We are honored that they chose the NexION technology for this extremely complex analysis. We are also very hopeful that they will continue to publish their work, as it's very important to have a better understanding of how engineered nanoparticles, particularly those used in consumer product applications, interact with the environment. If they continue to push these boundaries and generate high-quality data, it is only a matter of time before single particle ICP-MS becomes a routine analytical technique.

We'd like to conclude by quoting from CSM's mission statement web page, which clearly encompasses Dr. Ranville's work:

"Mines' well-defined and focused mission is achieved by the creation, integration and exchange of knowledge in engineering, the natural sciences, the social sciences, the humanities, business, and their union, to create processes and products to enhance the quality of life of the world's inhabitants. Mines is consequently committed to serving the people of Colorado, the nation, and the global community by promoting stewardship of the Earth, advancements in energy and sustaining the environment."

There is no doubt that the work being carried out by Dr. James Ranville and his team at the Department of Chemistry and Geochemistry fully embraces the School's mission by making the environment a safer place. We are so happy that PerkinElmer and the NexION 300Q ICP-MS are helping them achieve that goal.

Further Reading

- The National Nanotechnology Initiative (NNI): http://www.nano.gov/
- An Overview of the Capabilities of Field-Flow-Fractionation Coupled with ICP-MS to Separate, Detect and Quantitate Engineered Nanoparticles: J. Ranville, K. Neubauer, R. Thomas; submitted to and accepted by Spectroscopy Magazine, publication date, Summer, 2012.
- An Introduction to Flow Field Flow Fractionation and Coupling to ICP-MS: J. Ranville, D. Mitrano. K. Neubauer; PerkinElmer, Inc. White Paper.
- Determining Transport Efficiency for the Purpose of Counting and Sizing Nanoparticles via Single Particle Inductively Coupled Plasma Mass Spectrometry: H.E. Pace, J. Rogers, C. Jarolimek, V.A. Coleman, C.P. Higgins, and J.F. Ranville; Analytical Chemistry, 83 (24), pp 9361–9369, (2011).
- Detection of Nanoparticulate Silver Using Single Particle Inductively Coupled Plasma Mass Spectrometry: D.M. Mitrano, E.K. Leshner, A. Bednar, J. Monserud, C.P. Higgins, and J.F. Ranville; Environmental Toxicology and Chemistry, Vol. 31, No. 1, pp. 115–121, (2012).
- Silver Nanoparticle Characterization Using Single Particle ICP-MS (SP-ICP-MS) and Asymmetrical Flow Field Flow Fractionation ICP-MS: D.M. Mitrano, A. Barber, A. Bednar, P. Westerhoff, C.P. Higgins, and J.F. Ranville; Journal of Analytical Atomic Spectrometry, 27, 1131-1142, (2012).
- Overcoming Challenges in Analysis of Polydisperse Metal-containing Nanoparticles by Single Particle Inductively Coupled Plasma Mass Spectrometry: R.B. Reed, C.P. Higgins, P. Westerhoff, S. Tadjiki, J.F. Ranville; submitted and accepted by Journal of Analytical Atomic Spectrometry, 27, 1093-1100, (2012).

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