Sensitive Nanomaterials-Based Detection System Rapidly Measures Heavy Metals in Liquids

The Pitch

A low-cost, highly sensitive system—using a field-portable instrument—to measure heavy metals in water, saliva, and urine samples has been developed at the Pacific Northwest National Laboratory (PNNL). The device is approximately the size of a lunch box and weighs about 5.5 kg (Figure 1). Sensitivities below 1 ppb in both rat urine and river water with low relative standard deviations have been achieved within a few minutes. The PNNL system has been compared to inductively coupled mass spectrometry, the gold-standard measurement for heavy metals, and has consistently demonstrated comparable performance for detection of toxic heavy metals such as lead and cadmium. The retail price of the new instrument has not yet been determined. However, since its components cost about $12,000 to $15,000, it is anticipated to be considerably less expensive than the typical $100,000 to $150,000 for existing plasma mass spectrometry systems.

Functionalized nanomaterials that serve to preconcentrate the species to be measured for electrochemical detection are a key element of the system. These nanomaterials are of two basic types: a self-assembled monolayer on mesoporous supports (SAMMS®) or functionalized magnetic nanoparticles that provide excellent detection sensitivity at a parts per billion level. SAMMS possess the desired characteristics for metal preconcentration at an electrode surface including (a) high selectivity, (b) high loading capacity, (c) fast sorption kinetics, (d) excellent stability, and (e) the ability to be regenerated. The functionalized magnetic nanoparticles dispersed in solution are designed to have high affinities for target metals while promoting the mass transfer of the metals to the electrode surface and allowing for a refreshable electrode surface.

Although mercury-based electrode materials also have been demonstrated to provide good analytical performance in the electrochemical system, mercury is a toxic material that may be subject to future regulation. In biological samples, use of the nanomaterials avoids using mercury as a preconcentrator. It eliminates the need for sample pretreatment, the use of internal standards, and the use of sonication at the electrode coupled with large sample dilution.

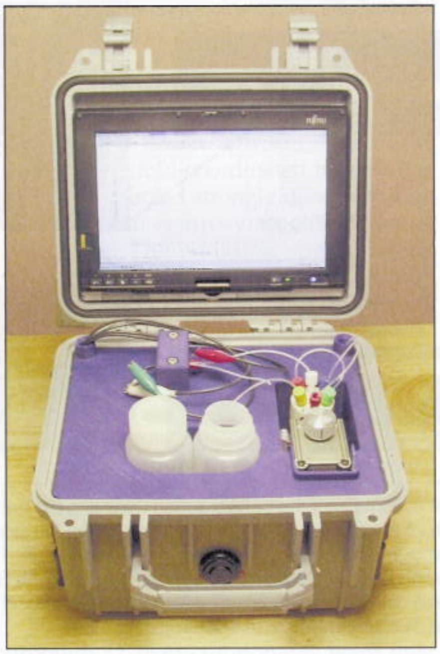

Figure 1. The biomonitoring detection system, developed by the Pacific Northwest National Laboratory, uses two classes of sensors to analyze water, saliva, or urine samples. The system is also being evaluated for use with blood samples. Although small and portable, the system provides detection levels at parts-per-billion.

The Technology

The rapid, portable detection system developed at PNNL is based on combining electrochemical detection with tailored chemistries designed to selectively extract a species of interest from a liquid sample. Chemistries used for SAMMS include SAMMS tailored with thiol (for "soft" heavy metals, e.g., lead), acetamide phosphonic acid (for rare earth metals, e.g., cerium), and iminodiacetic acid ligands (for common transition metals, e.g., mercury). Although functionalization of iron oxide magnetic nanoparticles with dimercaptosuccinic acid (DMSA) is the only one that has been publicly reported, various other tailored chemistries are being explored on the nanoparticles, including acetamide phosphonic acid, glutathione, and quaternary amines.

In the SAMMS approach, the materials are mixed with other materials to form a paste or ink that is used to coat the electrode of the sensor to increase its affinity for the analytes of interest. Examples include: (a) combining the thiol-functionalized SAMMS with carbon paste, (b) forming a paste with iminodiacetic-acid–functionalized SAMMS and carbon nanotubes, and (c) mixing acetamide-phosphonic-acid–functionalized SAMMS with conductive graphite ink to form a screen-printed electrode in a disposable sensor. Each of these alternatives has demonstrated good analytical performance, with the SAMMS/carbon nanotube electrode providing the lowest limits of detection for lead.

In the magnetic nanoparticle approach, the functionalized magnetic nanoparticles are infused into the liquid sample. Because the nanoparticles have a high affinity for heavy metal ions, the analytes are efficiently bound to their surface; and because the nanoparticles are magnetic, they can be immobilized on a magnetic-based electrode prior to voltammetric detection. The DMSA nanoparticles are synthesized by forming a functionalized chemical surface on an iron oxide particle core. Use of an electromagnetic electrode is the most efficient means of collecting the magnetic nanoparticles for subsequent detection due to the ability to readily remove the nanoparticles from the electrode after analysis by turning off the current to the coils.

Opportunities

Pacific Northwest National Laboratory is seeking commercialization partners interested in further developing, licensing, manufacturing, and marketing their electrochemical heavy metals sensor systems. Qualified partners could include both instrument companies and materials suppliers. The SAMMS system is believed to be more appropriate for measuring heavy metals in biological samples (e.g., urine). The magnetic nanoparticles system is believed to be preferred for use in environmental samples such as natural waters. However, the analytical approach can be tailored to the needs of individual partners.

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