



Trace Selenium Speciation Capabilities

34	78.96
958 494	-2,4,6
4.80	Se
[Ar]3d ¹⁰ 4s ² p ⁴	
Selenium	

While selenium is an essential micro-nutrient in most animals, it can also be toxic to aquatic organisms and birds in higher concentrations. Selenium toxicity in humans is rare, but possible at high enough concentrations. Selenium is a naturally occurring element which can be found almost anywhere on Earth, including in seawater, rocks, minerals, and soils. The highest concentrations of selenium are often found within organic shales, petroleum formations (oil sands, coal, crude oil), and phosphate deposits. Selenium may exist within these deposits and formations in a number of different forms including organic selenium (selenium incorporated within a complex organic molecule), elemental selenium, or selenium bound to minerals (such as iron or manganese). When these selenium-rich formations are disturbed and exposed to air during mining operations, selenium in the mined products or surrounding rock or soil formations is oxidized to the highly soluble forms of selenate (SeO_4^{2-} , Se(VI)) or selenite (SeO_3^{2-} , Se(IV)). These soluble forms of selenium then enter the ecosystem with runoff during normal rainfall events. In a soluble form, selenium can be absorbed or ingested by aquatic organisms or birds.

Regulation of Selenium in Discharges

Recent studies on the toxic effects of selenium (e.g. "Draft Aquatic Life Water Quality Criteria for Selenium – 2004", EPA 822D04001, November 2004) have prompted many



States to reduce the allowable selenium concentrations in their water quality criteria standards. In some cases, NPDES permits are now being issued having discharge limits below 5 ug/L total recoverable selenium. To help define the nature and extent of selenium present in discharges or outfalls, many industries are interested in determining the concentration of selenium species rather than just total recoverable selenium. Selenite is more soluble, more toxic, and more reactive than selenate. The uptake of the two species into aquatic organisms or other life occurs by different pathways, and therefore has much different toxicological effects. A discharge permit, which is written to require the analysis of total recoverable selenium in the effluent, may not be

adequately addressing EPA's concern about selenium. Elemental selenium, which is not soluble and presents a much lower toxicological risk, may be present in the effluents

being monitored. By understanding the speciation of selenium in the discharge (soluble vs. non-soluble, selenate vs. selenite), industries can work with the regulatory agencies to develop a discharge permit which takes into consideration the chemistry of the regulated source. If treatment systems are required to be installed, understanding the selenium chemistry will also aid with the proper selection of selenium treatment or control systems.

Clean Sampling

Analysis of ultra trace levels of selenium and selenium species require the use of clean sampling techniques as well as preparation and analytical methods which are specific to ultra trace (sub parts per billion) metals analysis. Use of standard sampling containers and traditional analytical methods such as GFAA (graphite furnace atomic absorption), ICP (inductively coupled plasma spectroscopy), or ICP-MS (inductively coupled plasma-mass spectroscopy) will often result in false positives and inaccurate results due to sample contamination and analytical interferences.

The initial sample collection event is perhaps the most important step in obtaining a representative sample of the source water. Sampling staff need to be trained on clean sampling techniques (EPA Method 1669), and be equipped with clothing, gloves, and sampling containers appropriate for trace metals sampling. CH2MHILL's Applied Sciences Laboratory (ASL) in Corvallis, Oregon can provide the sampling materials, training, and sample collection staff to assure that samples are collected with minimal risk of sample contamination.

Selenium Speciation Analysis



There are currently no standardized or federally published methods for selenium speciation analysis. However, ASL's scientific experts have developed a new proprietary method for speciating selenium. When samples are first received from the customer, the samples

are handled, prepared and analyzed in the trace metals laboratory. This space is segregated from other laboratory spaces and the room air is filtered to minimize any risk of sample contamination. Samples are then analyzed by pumping a portion of sample through an ion chromatography (IC) column which is connected to an ICP-MS instrument. The ICP-MS subsequently detects each species of selenium (Se VI or Se IV) as it exits the IC column. This analytical approach is sometimes called IC-ICP-MS. To eliminate analytical interferences and improve detection limits, the ICP-MS system is equipped with a Collision Cell (also known as DRC). The Collision Cell reduces the chance of reporting false selenium concentrations due to interfering compounds. ASL's current reporting limits for the determination of selenate (Se (VI)) and selenite (Se(IV)) by selenium speciation are 0.25 ug/L.

Contacts

For more information on this and other services CH2M HILL's ASL can provide, please contact:

ASL Customer Service

(asl@ch2m.com)

541-768-3120



CH2MHILL
Applied Sciences Laboratory