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The WCAS Analytical Digest

WEST COAST ANALYTICAL SERVICE, INC.

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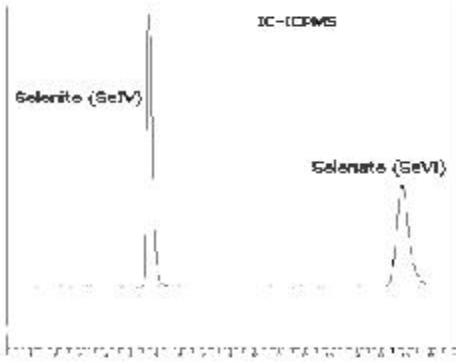
Selenium Speciation

Selenium (Se) is both an essential nutrient as well as a toxic chemical. This dual effect has been recognized for many naturally occurring chemicals. Trace amounts are beneficial, while larger amounts are harmful. Of course the toxicity of selenium depends greatly on the chemical form or species.

Selenium is used in food supplements, photographic processes, and electronics. It is regulated by both the EPA and the FDA. It is also on the California Prop. 65 list as the disulfide; however, no "safe harbor limit" has been established. Traditional tests for trace Se include hydride generation-atomic absorption (HG-AA) and graphite furnace atomic absorption (GFAA). Modern techniques include ICPMS and ICPMS-DRC.



Selenium has 6 naturally occurring isotopes, four of which are commonly used in ICPMS: 77 (7.6%), 78 (23.8%), 80 (49.7%), and 82 (9.2%). The major isotope ^{80}Se is isobaric with the $^{40}Ar_2^+$ from the argon plasma. DRC is needed to reduce this interference. Normally the ^{82}Se has a slightly better signal to noise than either the ^{77}Se or ^{78}Se in normal ICPMS or ^{80}Se in DRC. Interferences include $^{40}Ar^{37}Cl^+$ on ^{77}Se and Br^+ on ^{80}Se and ^{82}Se. These interferences can easily be removed in either of two ways: (1) using hydride generation to introduce the sample into the ICPMS or (2) using the DRC to remove the interfering ions from the plasma. Both methods are very efficient, so much so that sea water can be analyzed without any interference. Detection limits for Se are generally 2 µg/L; with hydride or DRC the detection limit is generally 0.5 µg/L.

Selenium can exist in various ionic and covalent, organic and inorganic forms. Some of the more chemically important forms are listed to the right. Various forms of liquid chromatography (HPLC) have been used to separate these ions and compounds. The chromatogram to the left shows the ion chromatographic separation of selenite and selenate ions at 1 µg/mL using a Hamilton PRP X-100 column with 10 mM ammonium nitrate and phosphate at pH 6.3. The ^{82}Se isotope was monitored.

Acrylamide

Acrylamide is used primarily to make polyacrylamide. It is sometimes used to clarify water, acting as a coagulant. EPA has set a limit on residual acrylamide of 0.5 µg/L in drinking water when used in this manner as has the World Health Organization.

In California, the current Prop. 65 No Significant Risk Level (NSRL) is 0.2 µg/day. However, recently Swedish researchers reported finding very high levels of acrylamide in fried foods (potato chips, median 1200 µg/kg; french fries, 450 µg/kg) and baked foods (cereal and breads, 100-200 µg/kg).

There are a few analytical alternatives for trace analysis of acrylamide monomer. Both HPLC (liquid chromatography) and GC (gas chromatography) based techniques can be used to determine trace amounts of acrylamide. The Swedish group used LC-MS-MS for their analysis. However, such equipment is not commonly available.

EPA 8316 uses HPLC with UV detection at 195 nm giving a detection limit of ~10 µg/L in water. But this short wavelength is not very selective for acrylamide, i.e. interferences are likely, and the sensitivity is not adequate for water or Prop. 65 levels. EPA 8032 uses GC-ECD after bromination of the acrylamide. This method is much more selective for acrylamide, and detection limits are much lower, 0.03 µg/L. However, in foods, the acrylamide may suffer from interferences and poor extraction efficiency.

One modification that has been tried at WCAS is an isotope dilution technique coupled with GCMS. Acrylamide-d_3 is added as an isotope dilution standard prior to a modified EPA 8032 extraction followed by GCMS analysis. Please give Jack Northington a call if you have any questions or would like a quote for testing.

Selenium Species

Inorganic forms

Selenite (SeO_3^{-2}) and selenate (SeO_4^{-2}), and selenocyanate ($SeCN^-$), the disulfide (SeS_2, antidandruff), the oxide (SeO_2), various selenides (e.g. PbSe).

Organic forms

Seleno-amino acids (selenomethionine), selenoproteins

Quick Quotes

There is nothing noble in being superior to some other man. The true nobility is in being superior to your previous self.

Hindustani proverb

Skillful pilots gain their reputation from storms and tempests.

Epicurus

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WCAS Laboratory Tidbits

For more information on any of the following call 562-948-2225 and ask for the person mentioned or Eric Lindsay.

The 2002 AAPS Annual Meeting and Exposition will be held in Toronto Canada from November 10-14. Several of us will be at booth # 364 to talk to you about our latest methods, capabilities, and on going projects we are working on for you. I'm sure we will have a give away also so stop on by and say hello!

If we missed you at the AAPS National Biotechnology Conference in San Diego give Eric Lindsay a call and he will send you our new handout concerning our biotechnology capabilities.

Water Treatment Chemicals such as sodium hypochlorite, hydrofluosilicic acid, aluminum sulfate, cationic polymer, ferric chloride, calcium oxide, and others are coming under scrutiny by most water treatment facilities. **Purity and activity of most chemicals should not be assumed** as these impurities could cause unwanted chemical reactions. WCAS is testing these chemicals to assure that specifications for each chemical are met. Most of the testing required in the individual monographs is wet chemistry which we have extensive experience in. Give Eric Lindsay a call for a quote.

Organic Chemical Screens are requested quite frequently. As you may have seen in a previous Analytical Digest we had an article about Residual Solvents in pharmaceuticals and raw materials. We have now added to our web site a page concerning screening for organic chemicals. The main focus of this page is concerning the differences between volatiles, semivolatiles, and nonvolatile organics. Since each "type" of organic requires a separate analysis we need to know what you are looking for. Give Louis Albanese a call if you have any questions.

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DEHP Interlaboratory Study

In February 2002, WCAS participated in an international interlaboratory study to measure various phthalates in three types of PVC. The study was conducted by the Institute for Interlaboratory Studies (IIS), and 20 laboratories participated. WCAS was the only lab in the US to participate. Our GCMS technique was used to test for 11 different phthalate esters. The samples included a transparent PVC with 17% phthalate, a yellow toy containing 0.7%, and an orange bulk PVC containing about 1%. The results from the study can be viewed at the IIS web site.

The results for DEHP are summarized below. The study included 10 other phthalate esters as well as total phthalates. Our results showed no false positives or false negatives, and all results were within one standard deviation of the mean.

DEHP Wt%

Sample	Study Mean ± SD	WCAS Results
210	16.8 ± 1	17.1
211	0.0104 ± 0.007	0.0054
212	0.28 ± 0.14	0.29

Lead in Chocolate

Lead (Pb) has been an environmental concern for many years. The concern has most recently focused on drinking water, plumbing fixtures, calcium based supplements and antacids, PVC plastics, brass keys, and now Chocolate. KNBC News in Los Angeles reported the story several weeks ago.

The California legislation known as Proposition 65 has set a “safe harbor” limit for lead at 0.5 ug/day. The concern over Pb in chocolate is articulated in a Fact Sheet published by the American Environmental Safety Institute. AESI proposes a limit of 0.02 ug/g Pb in chocolate. The fact sheet can be found at http://www.wcas.com/tech/FactSheet.PDF.

EPA 5035 with Tekmar 3100 and SOLATek 72

WCAS announces the installation of a new Tekmar 3100 Sample Concentrator and a SOLAtek 72 multi-matrix autosampler for performing purge and trap volatile organics analysis (VOA). In addition to traditional purge and trap sample extraction by EPA 5030, this system complies with the requirements for EPA 5035, closed-system purge and trap, designed to minimize the loss of volatile organic compounds during analysis.

The traditional EPA 5030 calls for weighing aliquots of soil or solids prior to purge and trap. During this operation the majority of very volatile compounds like trichloroethylene can be lost. EPA 5035 uses sealed sample vials, sealed after sampling and never opened prior to analysis. All operations are done by penetrating a septum of the vial keeping the sample sealed and preserving the volatile organic compounds. The range for EPA 5035 is 0.5 to 200 µg/kg.

What happens if the sample contains more than 200 µg/kg? Well, you only have one chance on an individual sample. Samples should be screened to protect the purge and trap system from contamination by high level samples. A portion of the sample is screened for volatile organics by either headspace analysis or methanol extraction. So you need at least duplicate or triplicate samples.