



ENVIRONMENTAL NEWS

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LIQUID CHROMATOGRAPHY – OCTOPOLE REACTION CELL - INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY PROJECT # 2 : SPECIATED ARSENIC and SELENIUM

Introduction

As covered in Enviromail Issue #18, ALS Environmental (ALSE) has installed an Agilent 7500c ICP-MS with an Octopole Reaction Cell (ORC), which can be coupled with a High Performance Liquid Chromatograph (HPLC). **Following the completion of extensive validation ALSE is proud to announce the first commercially available NATA accredited metal speciation capability for Arsenic and Selenium in Australia.**

Project 1- Ultra-trace Metals in Saline Waters (NATA accredited – See Enviromail #18)

Project 2 - Determination of Speciated Arsenic and Selenium (As³⁺, As⁵⁺, Se⁴⁺).

Project 3 - Determination of Organo Metallics (eg. Butyl Tin, Methyl Mercury)

This Environmental Mail, the second in the series of three focuses on the determination of speciated Arsenic and Selenium - the concept and the detection levels available.

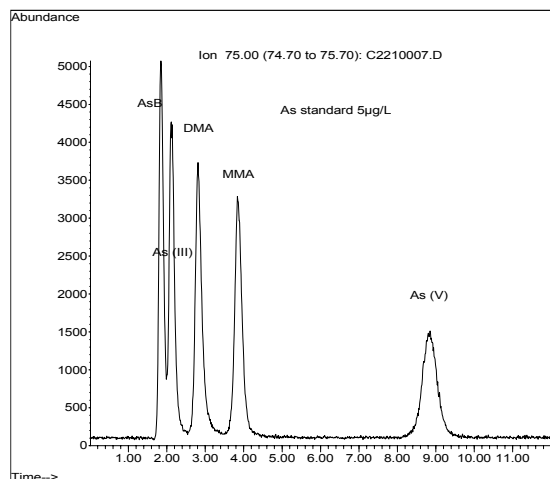
Background on Speciation Requirements

The toxicity of trace metals in the environment can in many cases be dependent upon the chemical form in which they occur. The separation and detection of these species can therefore assist risk-based toxicity assessments as prescribed in ANZECC 2000.

Arsenic can be found in the environment as arsenite [As(III)], arsenate [As (V)], and organoarsenic compounds such as monomethylarsonic acid (MMA), dimethylarsenic acid (DMA) and arsenobetaine (AsB). In descending order of toxicity, As (III) and As (V) are the most toxic, then DMA and MMA, with AsB the least toxic. For Selenium, the (IV) and (VI) valence states are most common, with (IV) the most toxic.

Speciation Analysis

When interfacing Liquid Chromatography (LC) with Inductively Coupled Plasma Mass Spectrometry (ICP/MS), elemental species elute one by one from the LC column directly into the ICP Argon Plasma. Here they are degraded, atomized and ionized with resultant ions transported into a mass spectrometer, where they are detected and quantified. The example chromatogram provides an example of the output from the HPLC/ORC-ICP/MS for Arsenic Speciation. Selenium may also be speciated using the same anion exchange column as arsenic, but with an alternate mobile phase.



Guidelines and LORs

The ANZECC 2000 Guidelines Trigger values for Fresh and Marine Waters are summarised in the following table along with our standard ALSE LORs.

ALS Method Codes: Arsenic in Fresh water (EG032FR) and Saline water (EG032SL).
Selenium in Fresh water (EG033FR) and Saline water (EG033SL).

Forms of Arsenic (Note: Only As(III) and As(V) are reported unless requested otherwise)	LOR Fresh Waters (µg/L)	LOR Saline Waters (µg/L)	ANZECC trigger values (95% level of protection (µg/L) unless stated otherwise)	
			Fresh Waters	Marine Waters
As(III), (Arsenite)	1	2	24	2.3 ⁽¹⁾
As(V), (Arsenate)	1	4	13	4.5 ⁽¹⁾
Se (IV), Selenium	1	2	11	3
AsB, (Arsenobetaine) ⁽²⁾	1	4	N.A.	N.A.
DMA, (Dimethylarsenic Acid) ⁽²⁾	1	4	N.A.	N.A.
MMA, (Monomethylarsonic Acid) ⁽²⁾	1	4	N.A.	N.A.

Notes

⁽¹⁾ Insufficient data is available for derivation of statistically based trigger values in marine waters. 'Low reliability' levels (due to insufficient data) for As (III), As (V) and Se (IV) are tabled as per the guidelines.

⁽²⁾ The presence of Organic forms of Arsenic is determined by this analysis however these are not reported unless specifically requested. No data is available (N.A.) in ANZECC for regulatory limits for these Organo-arsenic species.

Sampling and Storage

It is recommended the water samples be preserved with dilute hydrochloric acid for both arsenic and selenium speciation work. It is also strongly recommended that samples be field filtered prior to acidification using a 0.45µm membrane. Aeration of the sample must be minimized during this filtration process. ALS also recommends the inclusion of trip/field blanks when sampling for these analytes.

For 'mass balance' purposes, it may also be useful to undertake 'Total' (non-speciated) element analysis. This involves the collection of an additional field filtered sample – preserved with nitric acid.

References:

- Australia and New Zealand Guidelines for Fresh and Marine Water Quality – October 2000.
- Elemental Speciation by Chromatographic Separation with ICPMS detection. Journal of Chromatography A, 974 (2002) 1-21, by Claudia A. Ponce de Leon, Maria Montes-Bayon, Joseph A Caruso, Department of Chemistry, University of Cincinnati, Cincinnati OH 45221-172, USA.

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