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Subject: Selenium Speciation of Las Vegas Wash water
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SUMMARY

Speciation of selenium is one of the key factors controlling its environmental and ecotoxicological processes. Since selenite (IV) is more toxic than selenate (VI), it is desirable to understand the distribution of species present to assess the relative toxicity of selenium present in any environment. SNWA collected water samples for selenium speciation from the Las Vegas Wash and tributaries to the Las Vegas Wash for analysis by the R&D Division. Since selenocyanate has been detected in wastewaters from industrial processes, it was also added as a target analyte in the analytical method. Preserved and unpreserved LV Wash and tributary samples were analyzed by IC-ICP/MS within two days of receipt at our facilities. Additionally, total elemental selenium in each sample was established using ICP/MS. The distribution of the three target arsenic species and comparison with total selenium revealed that selenate is the vastly dominant selenium species in the LV wash and tributaries. The following sections briefly discuss analytical details and results.

MATERIALS AND METHODS

METHOD

Water samples are preserved with 0.1% (v/v) hydrochloric acid (HCl) and analyzed for three selenium species using ion chromatography (IC) separation with a sodium hydroxide eluent and detection using inductively-coupled plasma mass spectrometry (ICPMS) at m/z 82. A small portion of a homogeneous aqueous sample containing particles no larger than 0.45 μ m is injected into an ion chromatograph. The sample merges with the hydroxide stream and is pumped through the ion chromatographic system. Selenate, selenite, and selenocyanate are separated on the basis of their affinity for the active sites of the column packing material. Samples are ionized and detected using online ICP/MS detection with a 99% confidence level at concentrations down to 1.0 μ g/L. Signal correction during detection (Ge m/z 72) is employed to correct for signal drift during analysis.

ANALYTICAL WORKING RANGE

A calibration curve for each analyte of interest is constructed to cover the range of concentrations expected for samples. For this method, the calibration

range for the three selenium species in the matrix of interest is 1.0 to 100.0 $\mu\text{g/L}$

RESULTS

The IC-ICPMS method performed well for the analysis of the three selenium species. Good resolution was achieved in both standards (Figure 1) and LV Wash and tributary sample spikes (Figure 2). Total selenium concentrations as high as 45 $\mu\text{g/L}$ were detected in the Wash and tributaries to the Wash, and speciation established selenate as the predominant species (Table 1). No apparent differences were observed between preserved and unpreserved samples at 2 days post-sampling. Small peaks were observed for a few samples at retention times other than the targets, but the alignment of the selenate concentration with total Se concentration suggests these peaks do not significantly contribute to total Se.

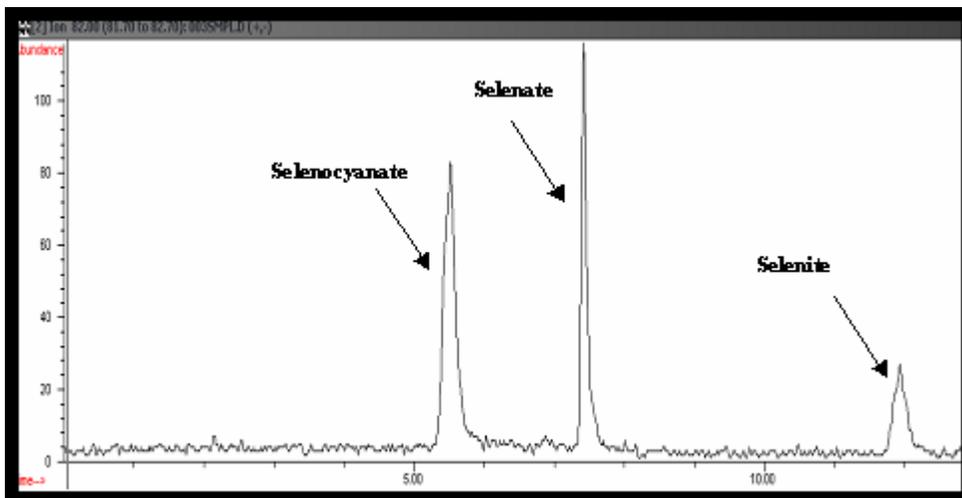


Figure 1. - Chromatogram of Se standards at 5.0 $\mu\text{g/L}$ concentration

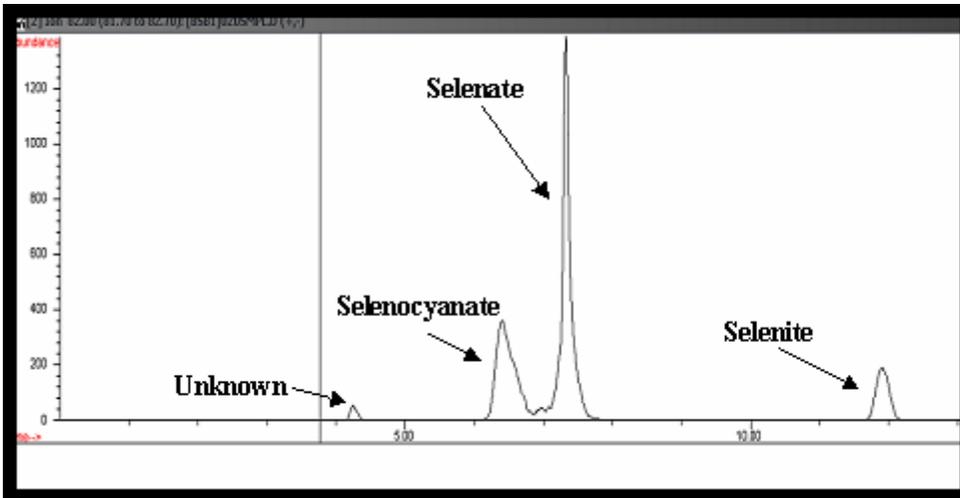


Figure 2. - Chromatogram of a water sample from the LV Wash spiked with 50.0 g/L selenate, selenite and selenocyanate.

Table 1-Results summary for Se species in LV Wash

Sample ID	Preservative	IC-ICPMS Results			ICPMS Mass Balance
		Selenate	Selenocyanate	Selenite	Total Selenium
LW 10.75	Unpreserved	15.51	<1.0	<1.0	13.50
LW 10.75	Unpreserved	14.16	<1.0	<1.0	14.18
MC_1	Unpreserved	22.05	<1.0	<1.0	22.33
DC_1	Unpreserved	14.51	<1.0	<1.0	16.19
WD	Unpreserved	41.56	<1.0	<1.0	46.56
WD-Dup	Unpreserved	46.87	<1.0	<1.0	45.85
LW 0.8	Unpreserved	3.59	<1.0	<1.0	4.96
LW 10.75	Preserved- 0.1% (v/v)HCl	15.29	<1.0	<1.0	13.50
MC_1	Preserved- 0.1% (v/v)HCl	20.49	<1.0	<1.0	20.11
MC_1	Preserved- 0.1% (v/v)HCl	19.03	<1.0	<1.0	20.26
DC_1	Preserved- 0.1% (v/v)HCl	13.75	<1.0	<1.0	14.92
WD	Preserved- 0.1% (v/v)HCl	46.71	<1.0	<1.0	43.53
WD-Dup	Preserved- 0.1% (v/v)HCl	37.59	<1.0	<1.0	41.38
LW 0.8	Preserved- 0.1% (v/v)HCl	3.00	<1.0	<1.0	3.37