Metrohm

Application Work AW US6-0186-012014

Determination of Inorganic Arsenic and Selenium species in Tap Water with Gradient Ion Chromatography-Inductively Coupled Plasma-Mass Spectrometry (IC-ICPMS)

Branch

Water, Wastewater, Environmental protection, Public health

Keywords

IC-ICP-MS; Arsenic; Selenium; 850; Agilent 7700; Metrosep Anion Dual 3

Summary

Simultaneous analysis of arsenic and selenium species in tap water was done by IC-ICP-MS. High pressure gradient IC using Metrosep Dual 3 column was employed to achieve ideal separation of As(III), As(V), Se(IV) and Se(VI) prior to injection into an ICP-MS Agilent 7700 instrument. The IC and ICP/MS was synchronized using remote signal. The MagIC Net software controls the sample loading and determination and gradient program while data handling and manipulation is done with the Agilent Chem Station software.

Samples

- No sample preparation required for tap water samples.
- Spiked tap water samples were prepared by spiking with 0.5ppb arsenic and selenium standard.

Instruments

ProfIC Cation HP-Gradient	2.850.1220
Professional Sample Processor: Pump	2.858.0020
Remote box	6.2148.010
Cable for MagIC Net/Chemstation sync	6.2141.380
Metrosep Anion Dual 3	6.1006.120
Metrosep RP 2 Guard	6.1011.030
ICP-MS Agilent 7700	

Reagents

- Ammonium nitrate 99.999% trace metals basis – Sigma Aldrich
- Ammonium hydroxide solution 28% NH_3 in H2O, ≥99.99% trace metals basis – Sigma Aldrich
- Methanol CHROMASOLV®, for HPLC, ≥99.9%
- Arsenic (III), 1000 mg/L solution in 2% HCl, SPEX CertiPrep
- Arsenic (V), 1000 mg/L in H_2O, SPEX CertiPrep®
- Assurance Grade Selenium (+VI) Speciation Standard, SPEX CertiPrep®
- Assurance Grade Selenium (+IV) Speciation Standard, SPEX CertiPrep®
- Nitric acid, w(HNO_3) = 65 %, suprapur, CAS 7697-37-2
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

IC Solutions

Eluent A	5mM NH_4NO_3
Eluent B	50mM NH_4NO_3 + 2% Methanol, pH: 8.7

Standard solutions

As (III), As (V), Se(IV) and Se(VI) calibration and check standards were prepared from commercially (NIST traceable) certified reference standards.

(ppb)*	Std. 1	Std. 2	Std. 3	Std. 4
As(III)	0.1	0.5	1	2.5
As(V)	0.1	0.5	1	2.5
Se(IV)	0.2	0.5	1	2.5
Se(VI)	0.2	0.5	1	2.5

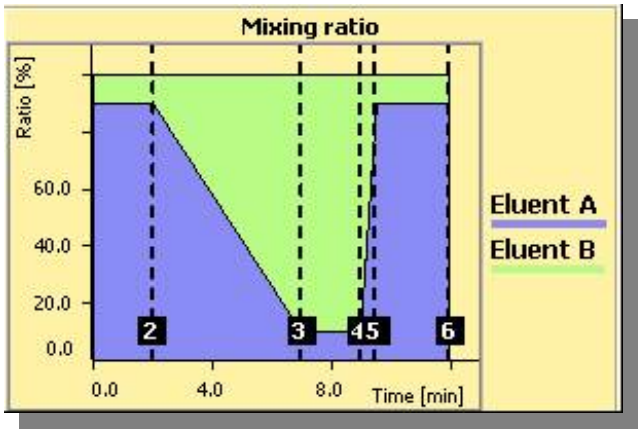
- - parts per billion

IC Parameters

Flow	1.0 mL/min
Injection Volume	100 µL
Recording time	12 min
Temperature column	Off

Gradient Program (Ion Chromatography)

Time (Min)	Eluent A (%)	Eluent B (%)	Curve	Flow
Start	90	10		1.0
2.0	90	10	Linear	1.0
7.0	10	90	Linear	1.0
9.0	10	90	Linear	1.0
9.5	90	10	Linear	1.0
12.0	90	10	Linear	1.0



Agilent ICPMS Parameters

RF power	1450W
Plasma gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	1.12 L min^{-1}
Sampling depth	6.8mm
Spray chamber temperature	5 °C
Ion lens setting Optimized for best sensitivity using	10mgL^{-1} Li, Ce, Y and Tl in 2% (w/w) HNO_3 solution

Data Acquisition Parameters

Monitoring masses	As - 75 amu, Se – 79amu
Acquisition mode	Spectrum and time resolved analysis

Results

	As(III) Conc. [ppb]	As(V) Conc. [ppb]	Se(IV) Conc. [ppb]	Se(VI) Conc. [ppb]
Tap Water				
Mean (N=12)	0.042	0.054	0.206	0.242
Standard Deviation	0.005	0.008	0.024	0.027
RSD %	12.989	15.098	11.428	11.129
Spiked Tap Water				
Mean (N=12)	0.546	0.584	0.627	0.725
Standard Deviation	0.018	0.020	0.050	0.080
RSD %	3.267	3.354	7.970	11.009
Spike Recovery %	**100.815**	**106.025**	**84.275**	**96.492**

Calculations

The data calculations were generated automatically by the Agilent Chem Station software.

Comments

Arsenic, a metallic element found naturally in the environment in ores and soil, may exist in both organic and inorganic forms. Inorganic arsenic, whether naturally occurring or introduced anthropogenically, usually exists as either arsenate [As5+] (fully oxidized) or arsenite [As3+] (partially reduced).

Inorganic arsenic is associated with excess skin, lung, liver, bladder, and kidney cancers in humans following chronic exposure. Both arsenate and arsenite are genotoxic, capable of inducing chromosome aberrations and sister chromatid exchange in rodent and human cells. In this regard, arsenite is approximately an order of magnitude more potent than arsenate .Both forms of inorganic arsenic compromise pulmonary alveolar macrophage function at non-cytotoxic concentrations, with arsenite more potent than arsenate .Both forms of inorganic arsenic produce tumors following intra-tracheal instillation to the lungs of hamsters[4].

The low spike recovery may be due to Se(IV) oxidizing to Se(VI). Standards should be kept refrigerated and limited from exposure to air prior to use.

Arsenic (III) is very unstable and rapidly oxidizes to arsenic (V). Keep standard refrigerated and closed off from air.

A 100µL sample loop gave good detection for all species, increasing the injection volume to 250µL could provide lower detection levels.

Appendix (List)

- Chromatograms
- Calibrations
- Instrument Flow Schematic

References

1. Laura Hinojosa Reyes *et al*, **Simultaneous determination of arsenic and selenium species in fish tissues using microwave-assisted enzymatic extraction and ion chromatography–inductively coupled plasma mass spectrometry**, *Talanta Vol. 78 (2009) 983–990.*
2. Jorgel. Guzman Már *et al,* **Simultaneous Extraction of Arsenic and Selenium Species From Rice Products by Microwave-Assisted Enzymatic Extraction and Analysis by Ion Chromatography-Inductively Coupled Plasma-Mass Spectrometry**, *J. Agric. Food Chem. 2009, 57, 3005–3013.*
3. EPA Method 6800: **Elemental and speciated isotope dilution mass spectrometry**
4. Dr. C.J.Saranko et el, **Fact Report for toxicity of Arsenite and Arsenate**, *Florida Dept. of Health, November 6th 1998*

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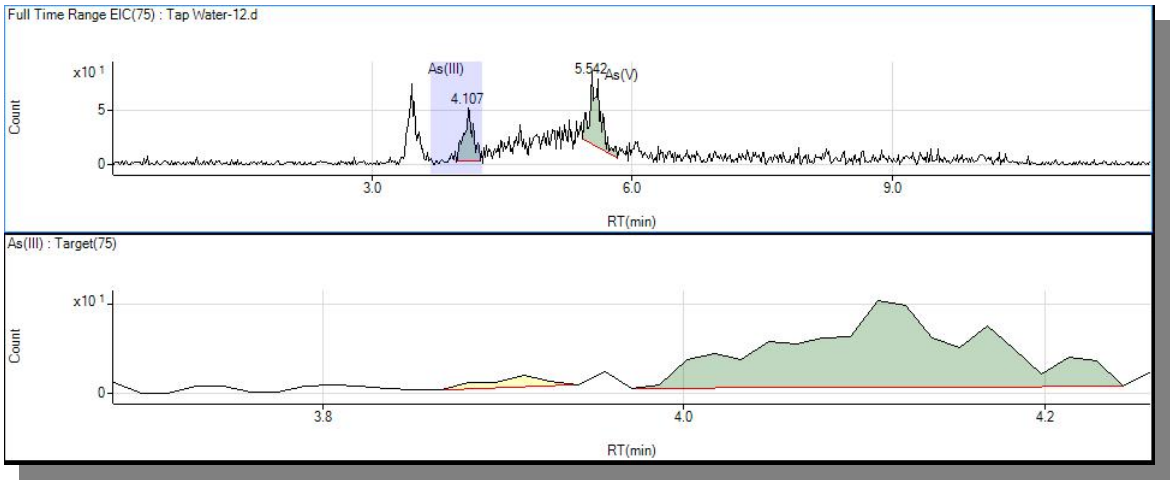
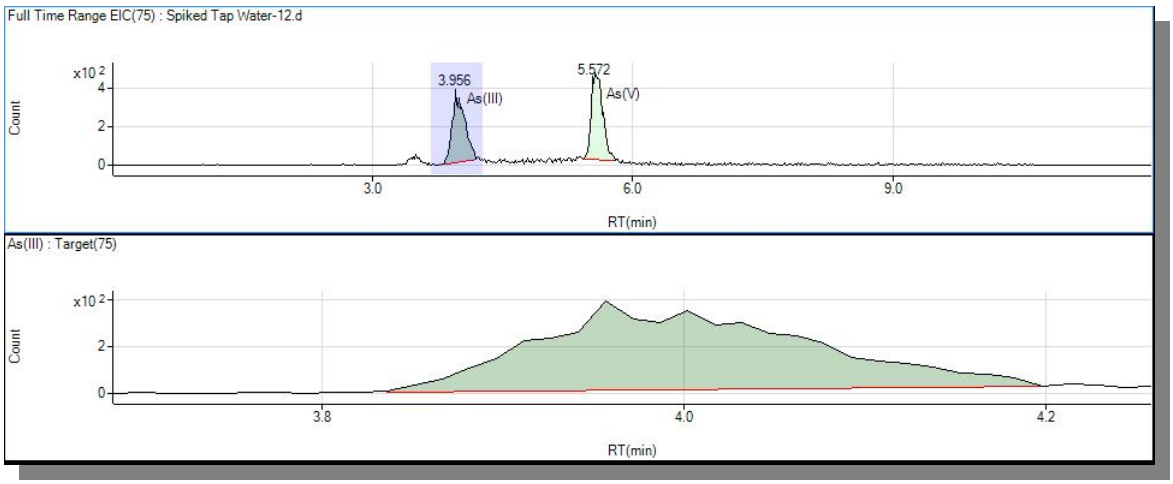
Appendix

Chromatograms

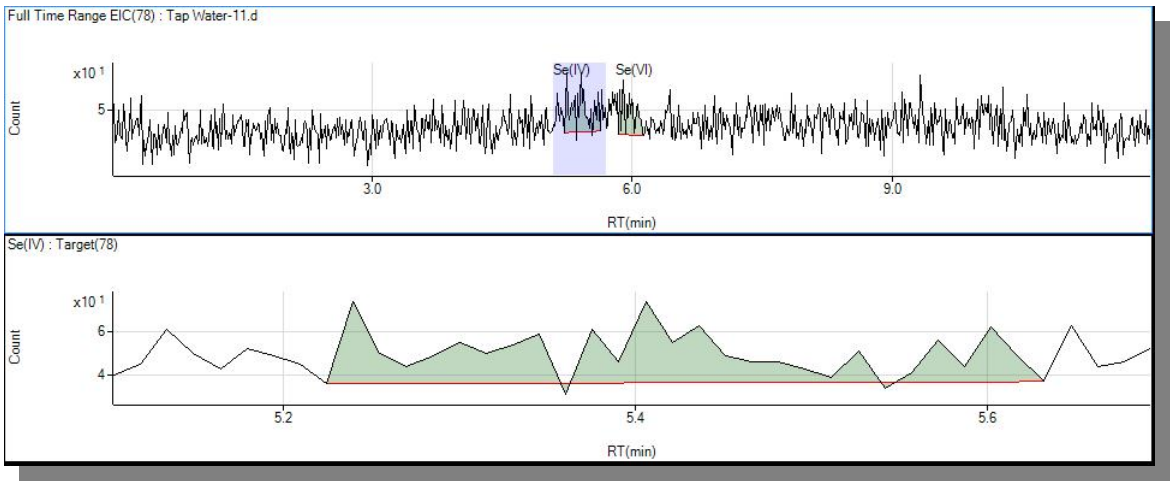
Chromatogram of As(III) and As(V) Species in Tap Water.



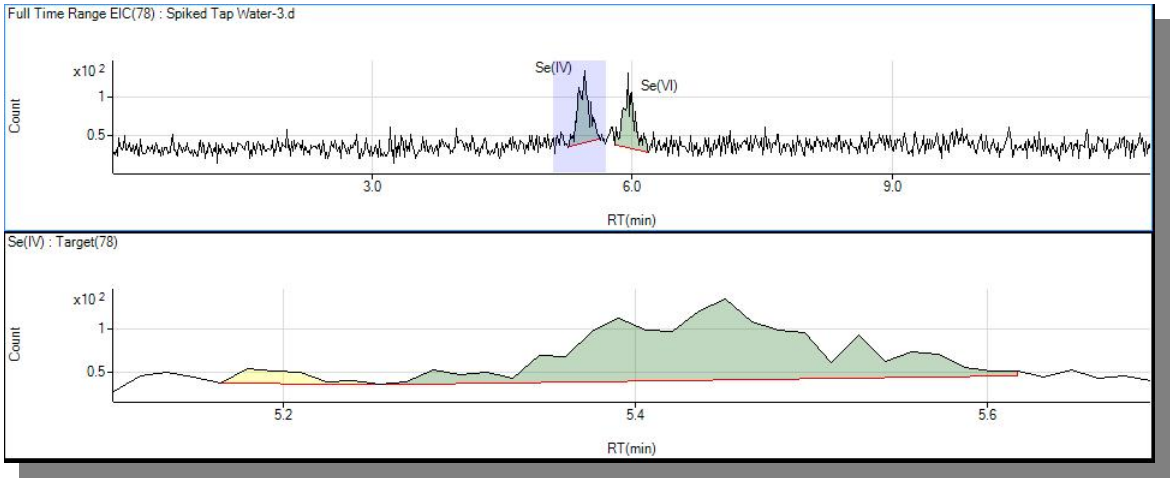
Chromatogram of As(III) and As(V) Species in Tap Water spiked with 0.5ppb As(III) and As(V).



Chromatogram of Se(IV) and Se(VI) Species in Tap Water.

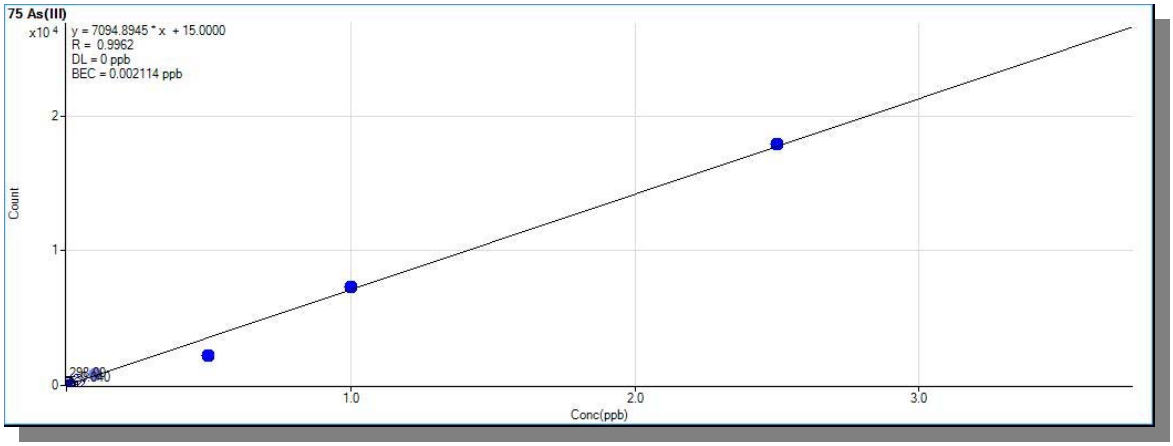


Chromatogram of Se(IV) and Se(VI) Species in Tap Water spiked with 0.5ppb Se(IV) and Se(VI).

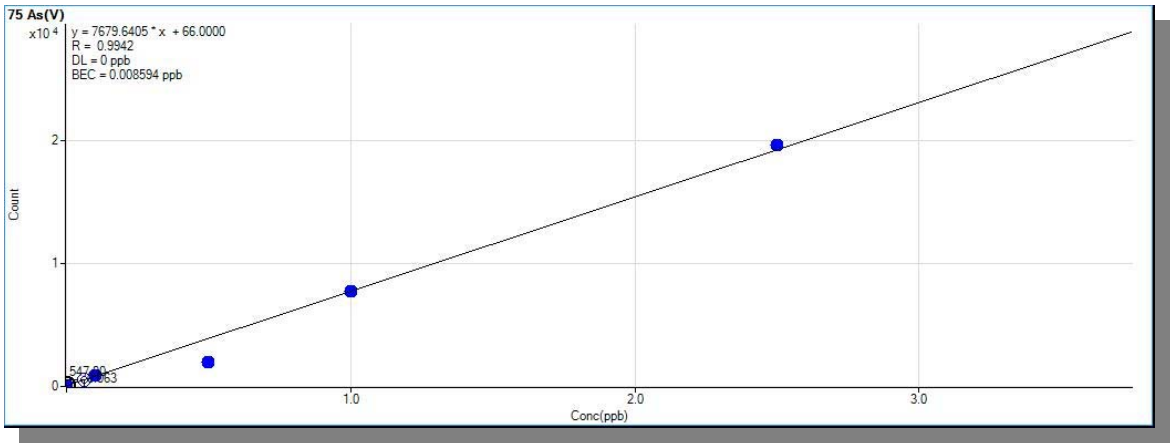


Calibration

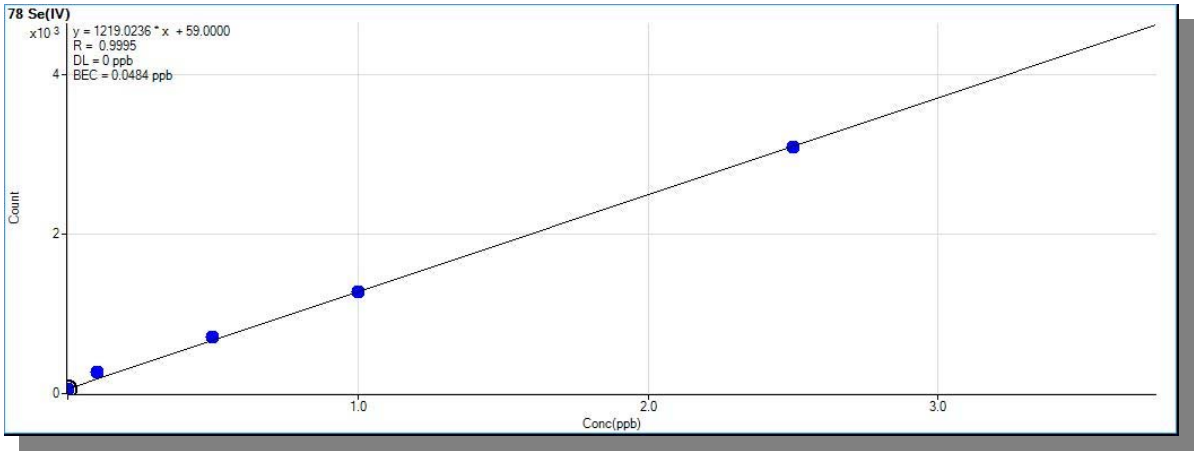
Arsenic(III) calibration curve



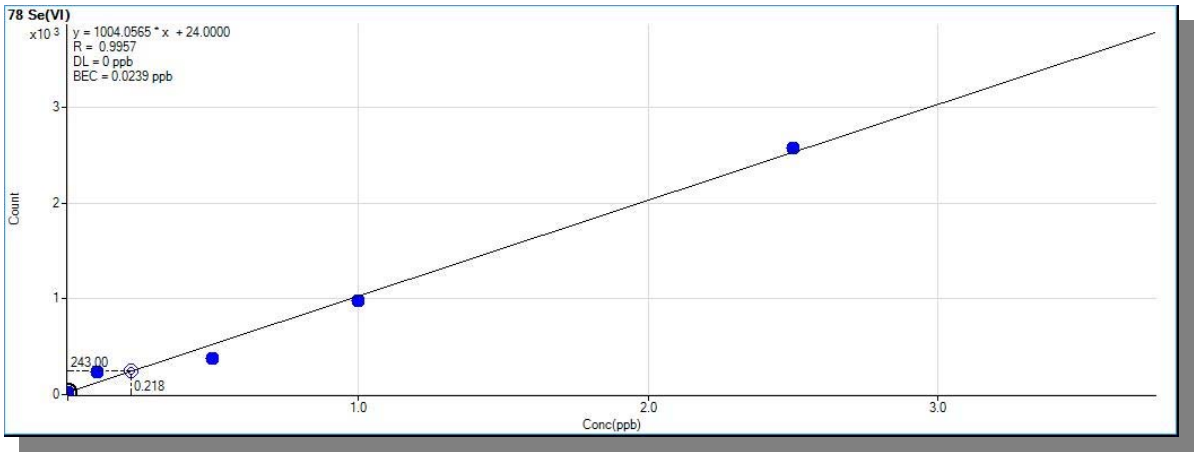
Arsenic (V) calibration curve



Selenium (IV) calibration curve



Selenium (VI) calibration curve



Instrument Flow Schematic

The diagram gives a general description of the flow path of an Ion Chromatography Inductively Couple Plasma-Mass Spectrometer.