Determination of selenite and selenate in environmental waters by ion chromatography-mass spectrometry (IC-MS)

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Abstract

Purpose: To develop a method to determine selenite and selenate in spiked environmental waters by coupling ion chromatography with single quadrupole mass spectrometry (IC-MS)

Methods: Selenite and selenate are separated from other common anions in environmental water by a high-capacity anion exchange column in 20 minutes and are then detected by coupling a conductivity detector (CD) and a single quadrupole mass spectrometer (MS) detector in series. Anion exchange chromatography using eluent generation and suppressed conductivity detection provides chromatographic selectivity, analytes in the ionic form, and compatibility with MS. Electrospray ionization (ESI) is used to introduce the liquid IC stream (after suppression) as a fine spray into the MS source.

Results: The IC-MS method offers significant advantages over IC-CD methods in terms of sensitivity and selectivity. The limits of detection of selenite and selenate using IC-MS were 4 µg/L and 2 µg/L, respectively. This method was applied to wastewater, river water, and lake water samples. The recovery of selenium species in environmental water that was spiked with known standards was 90-105%. The mass spectrometer was operated in selected ion monitoring (SIM) mode, allowing minimal sample cleanup and ensuring sensitive and selective quantification.

Introduction

Selenium is an essential trace mineral for the human body. It is a constituent of selenoproteins that play critical roles in reproduction, thyroid hormone metabolism, DNA synthesis, and protection from oxidative damage and infection. Selenium is also an important element in environmental research due to the narrow window differentiating its presence as an essential trace element and its toxic effect upon exposure. Due to this potential toxicity, there is a regulatory need to reduce selenium contamination of environmental waters. The EPA has set the maximum contaminant level (MCL) for selenium in drinking water at 50 µg/L.[1]

Selenium is often found in the inorganic forms selenite and selenate in environmental samples, and the toxicity of selenium greatly depends on its speciation. Consequently, selenium in environmental samples should be determined not only as total selenium, but also as species-specific when possible. Selenite is more toxic than its selenate form. ICP-MS and ICP-OES are very sensitive techniques. However, they can only determine total selenium concentration. A method by coupling ion chromatography with conductivity detector was developed to determine selenate and selenite species present or formed during bioremediation processes of selenate contaminated drinking, ground, or wastewater. The detector limit is 20 µg/L and 40 µg /L for selenate and selenite, respectively.[2]

We developed a more sensitive method to quantitate selenite and selenate in spiked environmental waters by coupling ion chromatography with mass spectrometry (IC-MS). An Integrion IC system coupled to an economical and simple-to-use single quadrupole MS (ISQ-EC) was used to screen and confirm the presence of selenite and selenate. Anion exchange chromatography using eluent generation and suppressed conductivity detection provided chromatographic selectivity, analytes in the ionic form, and the possibility of downstream MS detection. Electrospray ionization (ESI) was used to introduce the liquid IC stream, after suppression, as a fine spray into the MS source. The HESI-II probe improved the ESI interface by allowing the use of high temperatures and voltage to deliver better desolvation and enhanced sensitivity; thus, a make-up solvent was not needed. The mass spectrometer was operated in selected ion monitoring (SIM) mode, allowing minimum sample cleanup and ensuring sensitive and selective quantification. Isotope labeled chlorate ^{18}O was used as the internal standard to ensure quantitation accuracy. Performance data for the method such as recovery, precision, sensitivity, and calibration range were also reported. Together, these data show that IC-MS can successfully determine the two targeted selenium species in spiked environmental water samples.

Materials and methods

Samples

Environmental water samples were collected from the San Francisco Bay area (Sample #1: Wastewater, Sample #2: Lake water, Sample #3: River water).

Test Method(s)

- Thermo Scientific™ AS-AP Autosampler with sample syringe, 250 µL and 1200 µL buffer line
- Thermo Scientific™ ISQ EC™ single quadrupole mass spectrometer

Figure 1. IC-MS configuration with matrix diversion
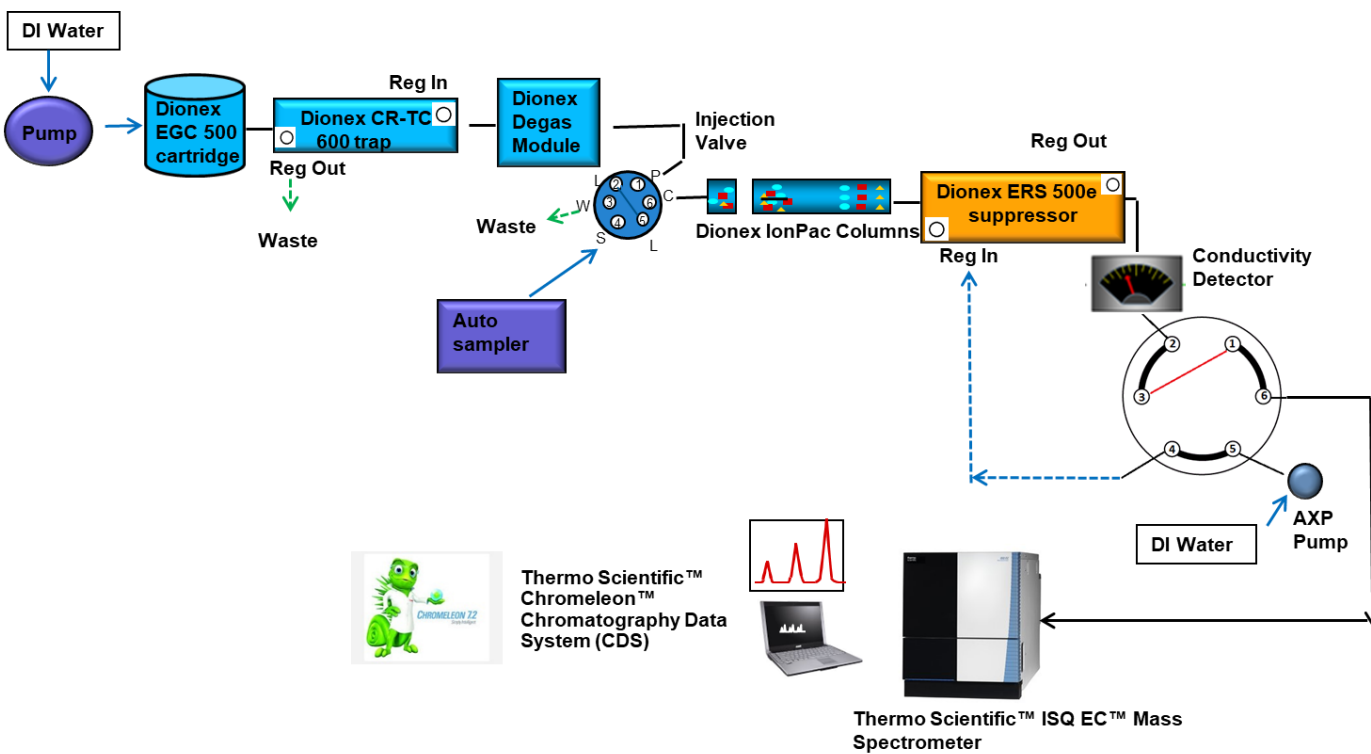
Chromatographic Conditions

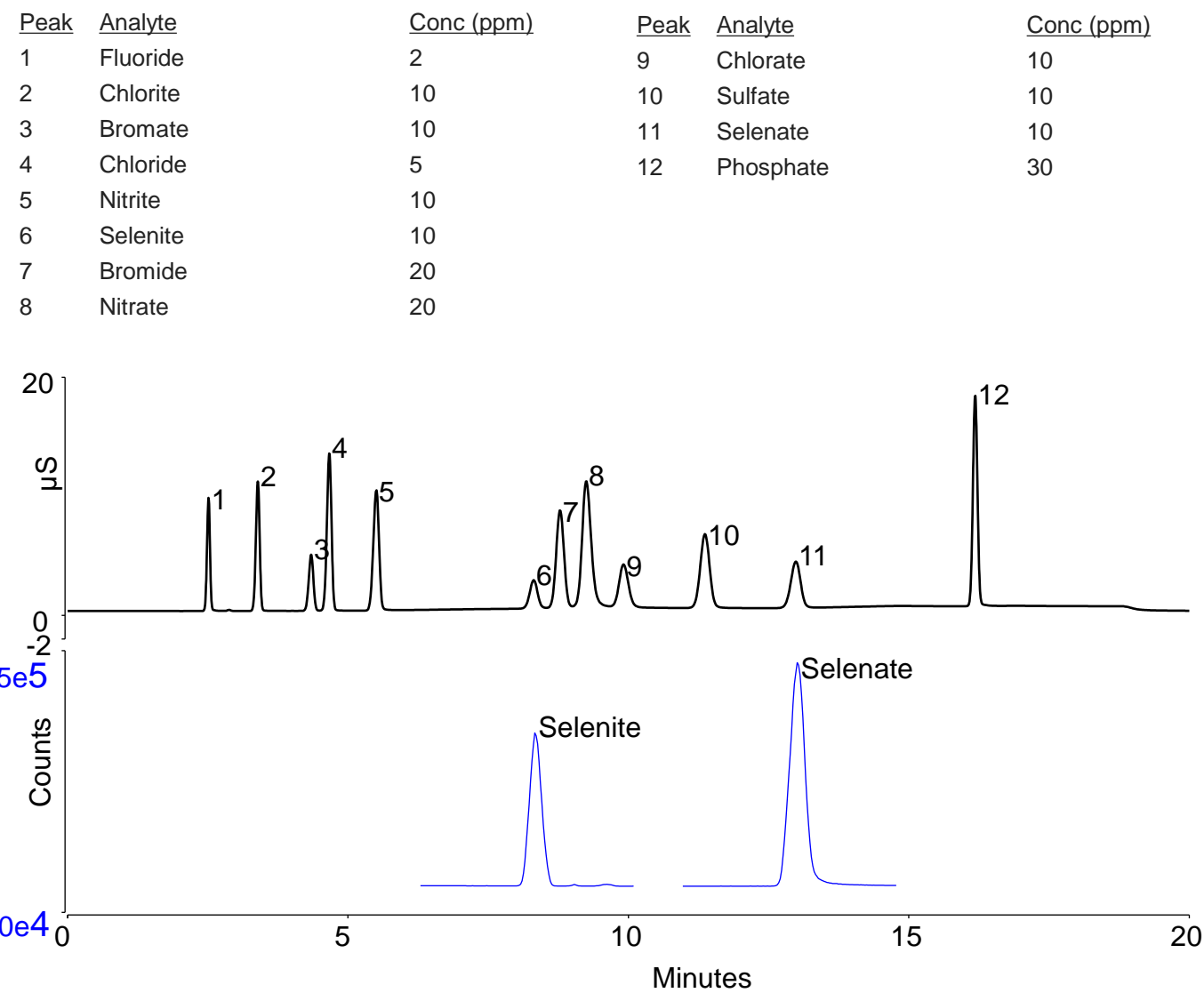|	
Columns	Thermo Scientific™ Dionex™ IonPac™AG11-HC Guard Column, 2 x 50 mm Dionex IonPac AS11-HC Analytical Column, 2 x 250 mm
Eluent	12-20 mM KOH from 0-10 min, 20-50 mM KOH from 10-14 min, 50 mM KOH from 14-16 min, 12 mM KOH from 16-20 min
Eluent source	Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator Cartridge with Thermo Scientific™ Dionex™ CR-ATC 600
Flow rate	0.38 mL/min
Column temperature	30 °C
Injection volume	5 µL
Detection	Suppressed Conductivity, Dionex ADRS 600 Suppressor (2 mm)
Ionization interface	Electrospray ionization (ESI), negative mode
Gas control	Sheath gas pressure: 56.4 psi; aux gas pressure: 5.7 psi; sweep gas pressure: 1 psi
Source voltage	-2500 V
Vaporizer temperature	316 ºC
Ion transfer tube temperature	250 ºC
Run time	20 min

Data Analysis

Data analysis was performed using Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3.1.

Results

Separation

The Dionex IonPac AS11-HC columns are specifically designed to resolve many inorganic anions and organic acid anions from a single sample injection in one gradient run using hydroxide eluents. The Dionex IonPac AS11-HC column is a high-capacity column, allowing the injection of more concentrated samples without overloading and peak broadening. High capacity is a critical factor for the determination of selenite and selenate at the low µg/L concentrations in environmental water samples containing high concentrations of common anions such as chloride, nitrate, and sulfate. Figure 2 shows a separation of common anions, selenite, and selenate within 20 min using the Dionex IonPac AS11-HC column. The top chromatogram displays the CD profiles of all anions. The bottom chromatogram displays the MS profile of selenite and selenate. As Figure 2 shows, selenite and selenate were resolved from common inorganic anions.

Figure 2. Separation of selenite and selenate from common anions

Peak	Analyte	Conc (ppm)	Peak	Analyte	Conc (ppm)
1	Fluoride	2	9	Chlorate	10
2	Chlorite	10	10	Sulfate	10
3	Bromate	10	11	Selenate	10
4	Chloride	5	12	Phosphate	30
5	Nitrite	10			
6	Selenite	10			
7	Bromide	20			
8	Nitrate	20			

Calibration and Limit of Detection (LOD)

Calibration standard mixtures (selenite and selenate) in the range of 10-250 µg/L were prepared in DI water. Potassium chlorate ^{18}O standard was spiked to each calibration standard at 100 µg/L.

The LOD method is based on the signal-to-noise (S/N) ratio, which is determined by comparing a measured signal from a low-concentration standard and establishing the minimum concentration at which the analyte can be reliably detected. A S/N of 3, aligned with the industry standard, is used for estimating the detection limit (LOD). In this study, the baseline noise was first determined by measuring the peak-to-peak noise in a representative 1-min segment of the baseline where no peaks elute. The signal was determined using selenite standard (5 µg/L) and selenate standard (2.5 µg/L). To examine the influence of a high-concentration anion matrix on the measurements, a laboratory synthetic sample matrix (LSSM) was prepared. The LSSM is a solution of common anions prepared at high concentration (250 mg/L chloride, 20 mg/L nitrate, 150 mg/L carbonate, 250 mg/L sulfate). Table 1 shows the calibration and LOD.

Table 1. Calibration and Limit of Detection

	Calibration range(µg/L)	Coefficient of Determination (r^2)	LOD (µg/L) in water	LOQ (µg/L) in LSSM
Selenite	10-250	0.9992	3.93	4.02
Selenate	10-250	0.9994	2.02	1.92

Sample Analysis

Selenite and selenate were not detected in any of the three environmental water samples. Therefore, we spiked selenite and selenate into real environmental waters and created simulated contaminated environmental water samples. Figure 3 shows the chromatographic profiles (MS and CD) of wastewater spiked with the 50 µg/L selenite and selenate mixture.

Figure 3. Sample #1 (Wastewater) spike with 50 µg/L Selenite and 50 µg/L Selenate
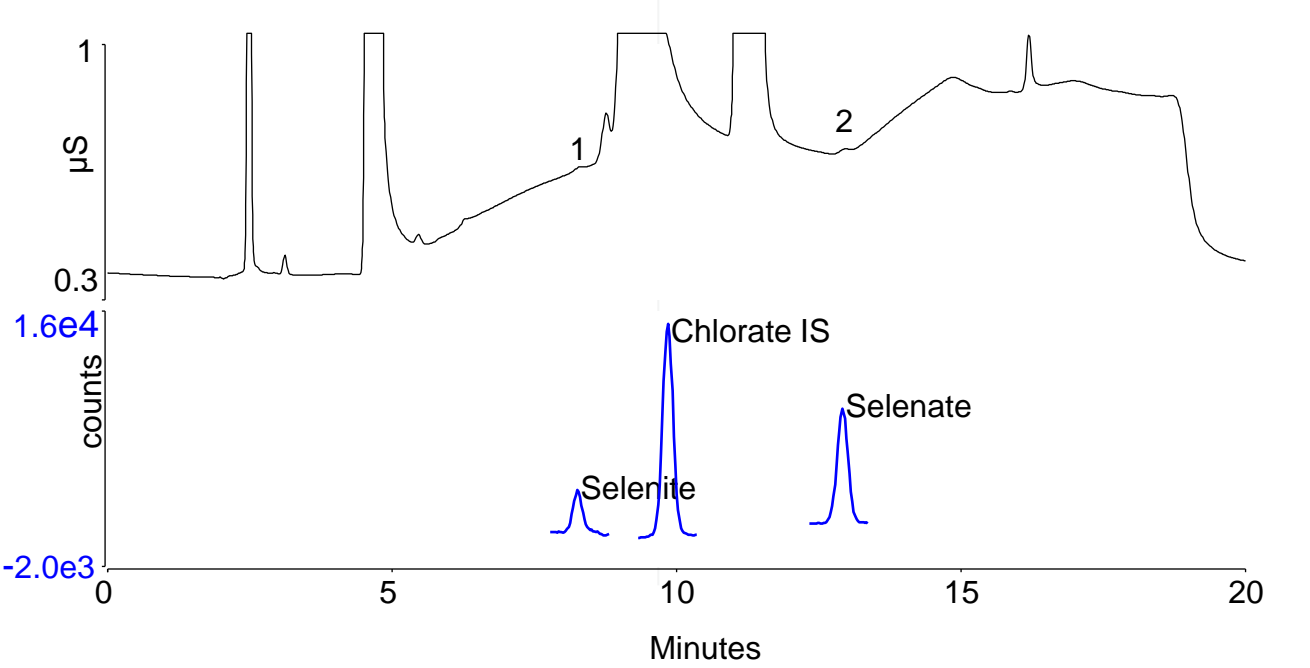
Conclusions

- An IC-MS method that allows the determination of selenium species in simulated contaminated environmental waters was developed.

- The reagent-free ion chromatography system provides excellent reproducibility, thereby yielding excellent quantification accuracy and consistently reliable results.

- The method can be applicable to screen whether the environmental water has been contaminated with selenium species.

References

1. EPA National Primary Drinking water regulations. https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations#one

2. Markus Lenz , Arne Gmerek & Piet N. L. Lens (2006) Selenium speciation in anaerobic granular sludge, International Journal of Environmental Analytical Chemistry, 86:9, 615-627, DOI: 10.1080/03067310600585902

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