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Isotope Dilution Analysis of Selenite and Selenate in Natural Water Using Microwave-Induced Nitrogen Plasma Mass Spectrometry

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Isotope dilution analysis of the sub-μg l^{-1} levels of selenite and selenate in natural water samples by microwave-induced nitrogen plasma mass spectrometry (MIP-MS) was performed. An appropriate amount of a spike solution containing ^{78}Se-selenite and ^{78}Se-selenate was added to the natural water sample to be analyzed. Both analytes in the water were then concentrated simultaneously by passing the sample through a column that was filled with an anionic exchange resin. After the concentration process, all of the selenite and some of the selenate on the resin were eluted by 0.03 M nitric acid. The residual selenate was eluted by 0.13 M nitric acid. The eluted sample solutions were injected into MIP-MS, and isotope dilution analyses were carried out. Selenite and selenate concentrations as low as 0.01 μg l^{-1} in the natural water sample were successfully determined by the proposed method.

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Introduction

Selenium is one of the essential elements for biological organs.[1,2] However, it is known that selenium compounds react as toxins when their concentration is too high. The toxicity of selenium also depends on its chemical form.[3-5] Selenium is generally taken into the body through water and foods, such as vegetables and meats. The concentration of selenium in foods may depend on the concentration of selenium in natural water, such as river water and ground water in the area where the foods were grown and/or produced. For an assessment of the natural effects of selenium, and also for nutritional and toxicological purposes, the accurate concentration of selenium compounds in the natural water must be known.

On the other hand, the total concentration of selenium species in natural water is usually at a trace level, such as the sub-μg l^{-1} level.[6] Therefore, highly sensitive, selective and accurate analytical methods are required for the determination of selenite and selenate in natural water samples; selenite and selenate are known to be major selenium species in natural water.

Many studies have been conducted regarding the determination of sub-μg l^{-1} levels of selenite and selenate in natural water by preconcentration and separation with ion exchangers,[7-12] activated carbon,[13] chelating resin,[14] sorbent resin,[15] and coprecipitation,[16] or by hydride generation–atomic absorption spectrometry (HG-AAS)[17] and HG-atomic fluorescence spectrometry,[18] or by fluorometry using 2,3-diaminonaphthalene.[19-22] The accuracy of these methods was, however, influenced by the variation in the recovery of analytes during the preconcentration, the separation, the chemical reaction processes, *etc*. Therefore, a more accurate calibration method, whose accuracy was not affected by the variation of the recovery of analytes, such as an isotope dilution (ID) method, was necessary.

Tao *et al*. reported on hydride generation inductively coupled plasma mass spectrometry (HG-ICP-MS) with an ID method for the determination of 50 ng l^{-1} levels of total selenium, not selenite nor selenate, in a seawater-certified reference material.[23] Tanzer and Heumann reported on the determination of selenite and selenate in natural water samples by negative thermal ionization mass spectrometry (NTI-MS) using an ID method.[24] Their analytical method was, however, time-consuming because the preparation of solid samples as selenium salts that were obtained by the evaporation of the sample solution to dryness, or as elemental selenium that was obtained by the reduction process, was required prior to the NTI-MS measurement. Gallus and Heumann reported on the determination of selenite and selenate in certified reference water samples by gas chromatography inductively coupled plasma mass spectrometry (GC-ICP-MS) with an ID method.[25] However, selenite must be converted into a volatile piazselenol prior to the determination. On the other hand, selenate was determined after being converted into selenite, and then into piazselenol. Therefore, the procedure of the latter researchers was complicated.

A microwave-induced plasma mass spectrometer (MIP-MS) was developed and placed on the market by Hitachi Ltd. (Japan) in the early 1990s. Oishi *et al*.[26] and Okamoto[27] reported on the characteristic behavior of nitrogen MIP-MS. The most important characteristic of nitrogen MIP-MS for selenium analysis is that the nitrogen plasma does not produce any spectroscopic interfering molecular ions containing an argon atom, such as $^{38}Ar^{40}Ar^{+}$ (= $^{78}Se^{+}$), $^{40}Ar^{40}Ar^{+}$ (= $^{80}Se^{+}$), *etc*. Therefore, nitrogen MIP-MS had highly sensitive selenium detection, higher than that of an inductively coupled plasma

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mass spectrometer (ICP-MS), because the most abundant isotope, ^{80}Se, could be measured. Moreover, nitrogen MIP-MS provided accurate analysis of the selenium isotopic ratio, also for the reason mentioned above. Therefore, MIP-MS was thought to be suitable for a selenium analysis, especially with the ID method.

Yoshinaga *et al*.[28] and Shirasaki *et al*.[29] reported the determination of selenium in biological samples by ID-MIP-MS. Ohata *et al*. reported the determination of the total concentration of selenium in human blood serum by ID-MIP-MS with a hydride generation technique.[30] However, no study has been reported for the determination of sub-μg l^{-1} levels of selenite and selenate in natural water samples by ID-MIP-MS.

In this study, in order to achieve both accuracy and high sensitivity in the determination of selenite and selenate in water samples, an ID-MIP-MS analysis was attempted with a preconcentration and chromatographic separation process performed by an anionic exchange resin. The proposed method was applied to the analysis of selenite and selenate in natural water and commercially available mineral water samples, and was shown to provide an accurate and highly sensitive analysis.

Experimental

Apparatuses

A Hitachi P-7000 MIP-MS was used to measure the selenium isotopic ratio (^{80}Se/^{78}Se) to carry out an ID analysis of selenite and selenate. Typical operating conditions for MIP-MS are given in Table 1.

A Hitachi Z-8000 polarized Zeeman graphite furnace atomic absorption spectrometer (GF-AAS) was used to measure selenium absorbances to fix the conditions for the concentration and separation of selenite and selenate with the anionic exchange resin used in this study. The operating conditions for GF-AAS were as follows: drying, 80 – 120˚C (ramp mode), 30 s; pyrolysis, 700˚C, 30 s; atomization, 2700˚C, 5 s; cleaning, 2800˚C, 3 s. Palladium was used as a chemical modifier for selenium measurements by GF-AAS.

Reagents

A selenite standard solution was prepared by diluting a commercially available selenium standard solution (1000 mg l^{-1}, SeO_2 in 0.1 M nitric acid, Wako Pure Chemical Co., Japan). A selenate solution was prepared by dissolving Na_2SeO_4 (Wako Pure Chemical Co.) in high-purity water. A ^{78}Se(IV) spike solution was prepared by dissolving a ^{78}Se stable isotope (metal powder form, ^{78}Se: 98.80%, Oak Ridge National Laboratory, USA) in a high purity nitric acid (Tama Pure AA, Tama Chemical Co., Japan); a 25 mg portion of ^{78}Se was dissolved with nitric acid (1 + 3) and then diluted to 200 μg l^{-1} with high-purity water. A ^{78}Se(VI) spike solution was prepared by the oxidation of a ^{78}Se(IV) solution with potassium bromide. The accurate selenium concentration of the solution mentioned above was determined against the commercially available selenium standard solution.

Bio-Rad AG1-X8 anionic exchange resin was used for the concentration and separation of selenite and selenate after washing the resin with 0.13 M nitric acid to remove selenium contamination in the resin. The high-purity water used in this study was made by a Milli-Q ultra pure water system (Milli-Q gradient purity system equipped with an Elix pure water system, Millipore Co., Japan).

Concentration and separation of selenite and selenate by anionic exchange resin

All of the operations described below were carried out in a class-10 clean bench placed in a class-1000 clean room. An appropriate amount of a spike solution containing ^{78}Se-selenite and ^{78}Se-selenate was added to a 1000 ml water sample in a Teflon bottle to be analyzed. The sample solution was heated on a hot plate at *ca*. 80˚C over night to achieve isotopic equilibrium. After cooling down to room temperature, the pH of the sample was measured by a pH meter, and was adjusted to pH = 8 – 10 if necessary by the addition of a sodium hydroxide solution. The water sample was then dropped on the anionic exchange resin, which was packed (10 mm height) in a Teflon column (8 mm × 10 cm) using a peristaltic pump. The flow rate of the sample water into the column was 15 ml min^{-1}. Afterward, all of the sample solution, *ca*. 10 ml of pure water, was dropped on the resin to wash it.

The elution procedure was as follows: all of the selenite and some of the selenate were eluted by a 10 ml portion of 0.03 M nitric acid. After that, the residual selenate on the resin was eluted by 10 ml of 0.13 M nitric acid. The flow rate of the nitric acid in the elution procedure was 2 ml min^{-1}. These eluted solutions were measured individually by MIP-MS.

Measurement of the isotopic ratio of ^{78}Se and ^{80}Se to determine the concentration of selenite and selenate

First, 0.14 M nitric acid was introduced to wash the inside the tube, spray chamber, *etc*. for a few minutes before the measurement of the sample solution. Then, the ion counts at m/z = 78 and 80, the spike and reference isotopes, respectively, of the analytical blank were measured. ^{80}Se/^{78}Se in a sample solution containing ^{78}Se spike was obtained after subtracting the ion counts of the analytical blank obtained just before the sample measurement. The selenium concentration in the sample water was calculated by an equation described by Yoshinaga *et al*.,[28] as follows:

$$C = w_n M_s(A_s - RB_s)/w_s W(RB_n - A_n),$$

where R is the obtained isotopic ratio (^{80}Se/^{78}Se), C is the concentration of selenium in the sample (in ng ml^{-1}), w_n is the atomic weight of natural selenium (78.96), w_s is the atomic weight of spike selenium (78.02), M_s is the amount of added spiked selenium (in ng), A_s is the abundance of ^{80}Se in the spike (0.0077), B_s is the abundance of ^{78}Se in the spike (0.9880), A_n is the abundance of ^{80}Se in natural selenium (0.4961),[31] B_n is the abundance of ^{78}Se in natural selenium (0.2377),[31] and W is the volume of the sample (in ml).

Table 1 Typical operating conditions for MIP-MS

Microwave power	1.3 kW
Plasma gas flow (nitrogen)	14 L min^{-1}
Nebulizer gas flow (nitrogen)	1.3 L min^{-1}
Sampling cone (Pt)	0.8 mm orifice
Skimmer cone (Cu)	0.4 mm orifice
Temp. of spray chamber	4˚C

Results and Discussion

Optimization of measurement conditions

This study used the ID method to determine selenite and selenate concentrations in natural water, because it is thought to be the most accurate and reliable technique for plasma mass

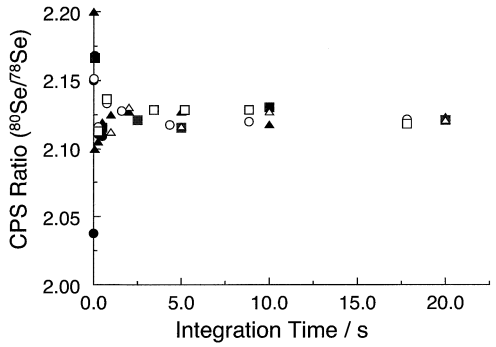

Fig. 1 Relationship between the accuracy of the ^{80}Se/^{78}Se isotopic ratio and the integration time. Dwell time: ●, 50 μs; ▲, 5 ms; ■, 50 ms. Number of scans: ○, 20; △, 200; □, 2000. Sample: 100 μg l^{-1} standard solution.

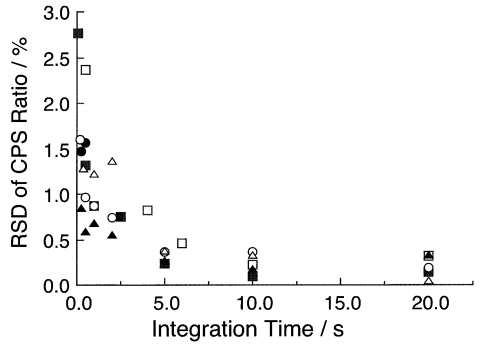

Fig. 2 Relationship between the integration time and RSD of CPS ratio. Dwell time: ●, 50 μs; ▲, 5 ms; ■, 50 ms. Number of scans: ○, 20; △, 200; □, 2000. Sample: 100 μg l^{-1} standard solution. Number of measurements, 5.

spectrometry tasks, such as MIP-MS. In order to optimize the measurement conditions for ID-MIP-MS, we investigated the accuracy and precision with which the selenium isotopic ratio was measured. Figure 1 shows the relationship between the accuracy of the ^{80}Se/^{78}Se isotopic ratio and the integration time obtained by various combinations of dwell times (0.05 – 50 ms) and numbers of scans (1 – 4000), *e.g.*, 0.05 ms times 1 scan or 5.0 ms times 4000 scans gives an integration time of 0.05 ms or 20 s, respectively. It was confirmed that the accuracy of the isotopic ratios obtained by the measurements depended on neither the dwell time nor the number of scans, but only on the integration time. It was also found that an integration time of at least 2 s was required to obtain an accurate isotopic ratio. Therefore, 5 s was selected.

Figure 2 shows the relationship between the integration time (obtained by various combinations of dwell times and numbers of scans, as mentioned in Fig. 1) and the precision as a relative standard deviation (RSD) of the isotopic ratio obtained by 5 sequential measurements. It was confirmed that the precision of the isotopic ratio obtained by the measurements depended on neither the dwell time nor the number of scans, but rather on the integration time, and that an integration time of at least 5 s was necessary to reach 0.5% RSD of the isotopic ratio measurements. Therefore, the following measurement and data acquisition conditions were found to be optimal: dwell time, 25 ms; number of scans, 200 times (equaling 5 s integration time); and number of measurements, 5 times.

Concentration and separation of selenite and selenate

(i) Selection of eluent. The requirements of the eluent used in this study were that: (1) it could elute both selenite and selenate from the anionic exchange resin used, (2) spectroscopic interfering molecular ions on ^{78}Se and ^{80}Se must not be produced from the eluent and (3) a high-purity reagent containing negligible levels of selenium was commercially available. In order to select the eluent, preliminary experiments were performed by using nitric acid, citric acid, ammonium citrate and ammonium nitrate. It was found that all of these reagents were able to elute both selenite and selenate from the anionic exchange resin. No spectroscopic interference and no contamination from those reagents were observed from the reagent mentioned above. Therefore, nitric acid was selected as the eluent in this study.

(ii) pH of water sample. In order to concentrate selenite and selenate onto the anionic exchange resin from an aqueous sample solution, the relationship between the pH of the sample

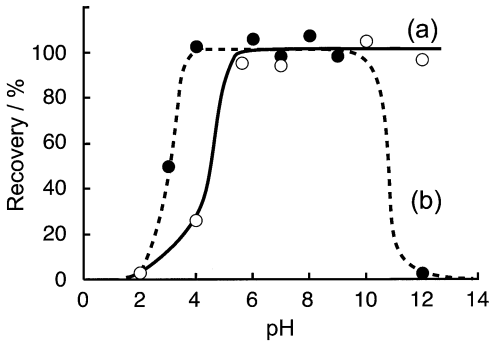

Fig. 3 Relationship between the pH of the sample and the recovery of selenite or selenate. (a) selenate, (b) selenite. Sample, 10 μg l^{-1} selenite standard solution or 10 μg l^{-1} selenate standard solution. Both selenite and selenate standard solutions were concentrated 25 times, respectively, by the proposed method.

before the concentration process and the recovery of the analytes from the resin was investigated using selenite and selenate standard solutions. Although quantitative recovery was not necessary in this study, since the concentration of selenite and selenate would be determined by the ID method, the recovery of selenite and selenate was used to characterize the behavior and performance of the resin in concentrating and separating the analytes.

In order to separate selenite from selenate using the anionic resin, the following two methods were thought to be candidates: methods based on the differences in the conditions in (1) the concentration process onto the resin and (2) the elution process from the resin. As shown in Fig. 3, selenite was recovered quantitatively when the pH of the sample solution was between pH = 4 and 10. On the other hand, selenate was recovered when pH = 6 – 12. Therefore, if the pH of the sample solution was 12, only selenate would be concentrated. However, there was no appropriate pH condition under which selenite alone would be concentrated from the sample. This finding meant that the quantitative separation of selenite from selenate in the concentration process was difficult. Therefore, the separation of selenite from selenate was attempted in the elution process from the resin.

(iii) Concentration of nitric acid to elute selenite and selenate. In order to separate selenite from selenate in the elution process from the anionic exchange resin, the relationship between the concentration of nitric acid and the recovery of the analytes was

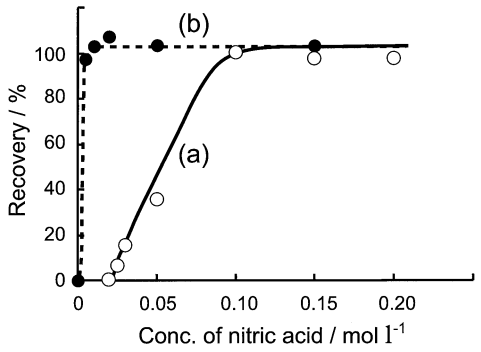

Fig. 4 Relationship between the concentration of nitric acid and the recovery of selenite or selenate. (a) selenate, (b) selenite. Sample, 10 μg l^{-1} selenite standard solution or 10 μg l^{-1} selenate standard solution. Both selenite and selenate standard solutions were concentrated 25 times, respectively, by the proposed method.

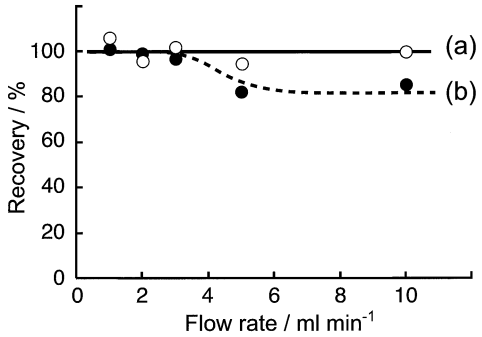

Fig. 5 Relationship between the flow rate of nitric acid and the recovery of selenite or selenate. (a) selenate, (b) selenite. Sample, 10 μg l^{-1} selenite standard solution or 10 μg l^{-1} selenate standard solution. Both selenite and selenate standard solutions were concentrated 25 times, respectively, by the proposed method. Concentration of nitric acid: (a) 0.13 M, (b) 0.01 M.

examined by using a selenium standard solution containing selenite and selenate. As shown in Fig. 4, selenite and selenate were quantitatively eluted from the resin by using nitric acid whose concentrations were 0.005 and 0.10 M, respectively. In addition, selenate was not eluted by nitric acid, whose concentration was under 0.02 M. Therefore, it was considered that the quantitative separation and recovery of selenite and selenate could be achieved by using 0.005 and 0.10 M nitric acid, respectively.

However, when selenite and selenate in the natural water sample were concentrated onto the anionic exchange resin, at least 0.03 M nitric acid was required for 100% elution of selenite; *ca*. 20% selenite still remained after the elution, even by 0.02 M nitric acid. This phenomenon was not observed at all when the selenite standard solution was used, but was observed when the natural water sample was used. This phenomenon was thought to be due to some matrix effect of natural water. Therefore, 0.03 M nitric acid was selected to elute all of the selenite at once. However, Fig. 4 indicates that *ca*. 10% of selenate was also eluted by 0.03 M nitric acid, *i.e*., (i) all of the selenite and some of the selenate and (ii) the residual selenate was eluted by using (i) 0.03 and (ii) 0.13 M nitric acid, respectively. It was not preferable because it meant that the complete separation of selenite from selenate could not be achieved. Although these eluted solutions give seriously inaccurate results for both selenite and selenate if the external calibration is used, accurate results are expected to be achieved by the ID method. The analytical result to be obtained by measuring 0.03 M nitric acid elution is the total concentration of selenite and selenate. Also, the concentration of selenate is obtained by measuring 0.13 M nitric acid elution. Therefore, the concentration of selenite will be obtained by subtracting the selenate concentration from the total selenium concentration.

(iv) Flow rate for concentration and elution process. The relationship between the flow rate (5, 8, 10, 15 and 25 ml min^{-1}) of the sample solution to the concentration and the recovery of the analytes was investigated. A flow rate of 15 ml min^{-1} was selected, since a quantitative and constant recovery was obtained at all of the flow rates that we studied (figure not shown).

In order to optimize the flow rate of nitric acid to elute selenite and selenate from the resin, the relationship between the flow rate, between 1 and 10 ml min^{-1}, and the recovery of the analytes was investigated. As shown in Fig. 5, both selenite and selenate were eluted quantitatively by nitric acid with a flow rate under 3 ml min^{-1}. Although a quantitative recovery was not required for ID-MIP-MS, a flow rate of 2 ml min^{-1}, at which the quantitative recovery was achieved, was selected.

Determination of selenite and selenate by ID-MIP-MS

In order to confirm the accuracy of the proposed method, selenite in a standard solution containing 0.10 μg l^{-1} selenite and selenite and selenate in a mixed standard solution containing 0.05 μg l^{-1} selenite and 0.05 μg l^{-1} selenate were concentrated/separated by the proposed method, and were then analyzed by ID-MIP-MS. Table 2 shows that the analytical values for both selenite and selenate, as determined by the proposed method, are in good agreement with the concentrations of the standard solutions. This means that the recovery of the analytes by the proposed method is quantitative.

On the other hand, selenite and selenate in commercially available mineral water samples with and without the addition of selenite and selenate standard solution were also concentrated/separated by the proposed method, and were analyzed as shown in Table 3. The added analytes were 0.5 μg l^{-1} selenite and 0.5 μg l^{-1} selenate. As a result, the recoveries of selenite and selenate were 100% and 103%, respectively, and the accuracy of the proposed method was confirmed. Therefore, the proposed method was applied to various natural water samples. Table 4 shows that the analytical results for selenite and selenate in water samples were as determined by the proposed method. Selenite and selenate concentrations as low as 0.01 μg l^{-1} in water samples were successfully determined by the proposed method. The analytical results for the total concentration of selenite and selenate in the ground water were obtained by using a sample solution that was eluted at once by 0.13 M nitric acid. The results were in good agreement with the sum of the selenite and selenate concentrations, which were obtained by the ID-MIP-MS analysis, respectively. On the other hand, the analytical results obtained by MIP-MS using the calibration curve prepared by a selenite standard solution containing gallium as the internal standard element were about 60% lower than that of the ID-MIP-MS analysis. This phenomenon was thought to be due to some matrix effect of natural water.

The detection limit of ^{80}Se was calculated from the slope of the calibration curve and the standard deviation of the background counts. It was 0.09 μg l^{-1} when the 3σ definition was used, and the value was comparable to that which had been

Table 2 Recovery of selenite and selenate in a standard solution by ID-MIP-MS[a]

	Selenite/μg l^{-1}	Selenate/μg l^{-1}
Added	0.10	—
Found	$0.10 \pm 0.00_4$ (n = 4)	—
Recovery	100% ± 4%	—
Added	0.05	0.05
Found	0.05	0.05
Recovery	100%	100%

a. The sample solutions were concentrated 100 times by the proposed method.

Table 3 Recovery of selenite and selenate in a water sample by ID-MIP-MS[a]

Mineral water A[b]	Selenite/μg l^{-1}	Selenate/μg l^{-1}
Added	0.00	0.00
Found	0.09 ± 0.01 (n = 3)	0.11 ± 0.01 (n = 3)
Added	0.50	0.50
Found	0.59 ± 0.01 (n = 3)	0.63 ± 0.06 (n = 3)
Recovery	100% ± 2%	103% ± 9%

a. The sample solutions were concentrated 100 times by the proposed method.
b. Mineral water A is commercially available in Japan.

Table 4 Analytical results for selenite and selenate in water samples by ID-MIP-MS[a]

	Selenite/μg l^{-1}	Selenate/μg l^{-1}
Mineral water B[b]	0.02	0.02
Tap water[c]	0.01	0.01
Ground water[d]	0.03	0.02
Ground water[e]	$0.05 \pm 0.00_3$ (n = 4)	
Ground water[f]	$0.02 \pm 0.00_2$ (n = 5)	

a. The sample solutions were concentrated 100 times by the proposed method.
b. Mineral water B is commercially available in Japan.
c. Tap water of Kitami city.
d. Ground water was taken in Kitami Institute of Technology.
e. The sample used was the same as (d). The elution process was carried out by 0.13 M nitric acid. Analytical values shown are the total concentration of selenite and selenate.
f. The sample used was the same as (d). Analytical values shown are the total concentration of selenite and selenate. Analytical results were not obtained by ID-MIP-MS but were obtained by MIP-MS using the calibration curve prepared by a selenite standard solution containing gallium as the internal standard.

reported.[28] Therefore, 0.9 ng l^{-1} of ^{80}Se was detectable when the sample solution was concentrated 100 times. The relative standard deviation of the proposed method for the determination of 0.1 μg l^{-1} levels of selenite and selenate was 2 – 9%.

The use of ID-MIP-MS with the anionic exchange concentration and separation can greatly enhance the capacity of the technique for the determination of selenite and selenate in natural water samples, because it provides improvements in the accuracy, in the detection limit and in the elimination of potentially interfering polyatomic species that were observed during a measurement based on nitrogen-ID-MIP-MS with preconcentration. Full advantage of the proposed method can be realized and used to determine sub-μg l^{-1} levels of selenite and selenate in natural water.

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