

## LECTURE

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## Determination of different oxidation states of arsenic and selenium by inductively coupled plasma-atomic emission spectrometry with ion chromatography

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**Abstract** Recent regulation in Japan requires more sensitive trace analysis methods for the determination of arsenic and selenium and their oxidation states As(III) and (V), Se(IV) and (VI). The hydride generation (HG) technique is usually used in combination with AAS and ICP-AES to increase sensitivity. However, hydrochloric acid is mostly used to acidify the sample solution in HG. Isobaric interferences due to chlorine-related species cause mass spectral problems when the same solution is used for the determination of these elements by ICP-MS. In this study, different oxidation states of As and Se were determined by coupling ion chromatography (IC) to an ICP-AES instrument. An HG technique was used to introduce test samples into the ICP. Nitric acid was employed to acidify the samples for HG. The concentrations of acid and base were kept as low as possible to reduce contamination. The formation of As and Se hydrides could be achieved without HCl, if the concentrations of acid and alkaline solutions were optimized. However, HCl was necessary for additional reduction of Se(VI) to Se(IV).

### Introduction

The requirement for the determination of trace metals in the environment has tightened since the environmental standard for water was amended in Japan in March 1993. The limit for As is now 10 ng/ml, which is one fifth of the old standard, and Se is limited for the first time to 10 ng/ml. Although the standard regulates only the total amount of As and Se, it is well known that the toxicity is dependent on the chemical form [1]. Therefore, the determination of the chemical form is important [2, 3]; but at present a speciation analysis is not required from a legal point of view. HG has been used in combination with AAS,

ICP-AES, and ICP-MS to increase the sensitivity for these elements [4–8]. When HG is used, As(V) and Se(VI) are reduced to As(III) and Se(IV), respectively, by the reducing reagents for the generation of hydrides. In order to determine As and Se precisely, the oxidation states of these elements should be preserved. In this study, As(III) and As(V) and Se(IV) and Se(VI) were separated by IC and then detected by ICP-AES. To improve the sensitivity, an HG technique was used to introduce the sample into the ICP. Sodium tetrahydroborate was used as the reducing reagent. The alkaline concentration of the NaBH<sub>4</sub> solution and the acid concentration of the sample were optimized. Hydrochloric acid has often been used for HG [9], but in this work nitric acid was used whenever possible. We also explored the possibility of a change of oxidation states and volatilization loss of analytes during acid digestion procedures.

### Experimental

**Instrumentation.** For IC, a Dionex 2000i system (Dionex, Sunnyvale, CA, USA) equipped with a conductivity detector in series was applied. For separation of the ionic species, an anion-exchange column HPIC AS4A, 250 × 4 mm (Dionex) was used. The mobile phase (pH 8.98) consisted of 1.7 mmol/l of sodium hydrogencarbonate and 1.8 mmol/l of sodium carbonate. Arsenic(III), arsenic(V), selenium(IV), and selenium(VI) exist in the chemical forms of AsO<sub>3</sub><sup>3-</sup>, AsO<sub>4</sub><sup>3-</sup>, SeO<sub>3</sub><sup>2-</sup>, and SeO<sub>4</sub><sup>2-</sup>; therefore, these ionic species can be separated by an anion-exchange column. As a suppressor, a solution of 25 mmol/l sulfuric acid was used to convert NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> to carbonic acid (pH 4.75) before the mobile phase was transferred to the conductivity detector. The flow rate was 1.0 and 1.2 ml/min, respectively, when a Meinhard pneumatic nebulizer and the HG was used. The sample volume injected into the IC was 50 µl. Element-specific detection was performed by an ICP-AES system (Model JY24 of Jobin-Yvon, Longjumeau Cedex, France) under the operating conditions listed in Table 1.

**Chemicals.** Distilled and de-ionized water was purified by passing through a Milli-Q system (Model SP Low TOC of Millipore, Bedford, MA, USA, 18.3 MΩ). Arsenic(III) solution was prepared from a standard solution (1000 µg/ml) of Kanto Chemical (Tokyo, Japan), prepared by dissolving As<sub>2</sub>O<sub>3</sub> and sodium chloride (0.05%) in 1 mol/l HCl. Arsenic(V) solution was prepared from a standard solution (1000 µg/ml) of SPEX Chemical (Edison, NJ, USA), pre-

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**Table 1** Operating conditions for Ar ICP-AES

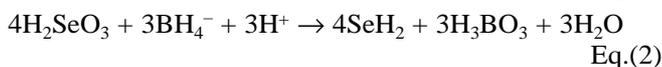
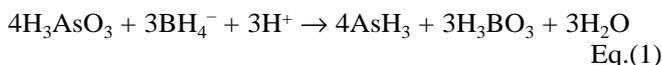
Plasma conditions	For pneumatic nebulizer	For hydride generation
Forward power	1000 W	1000 W
Outer gas flow rate	13 l/min	13 l/min
Sheath gas flow rate	0.2 l/min	0.4 l/min
Auxiliary gas flow rate	0.0 l/min	0.0 l/min
Injector gas flow rate	0.3 l/min	0.6 l/min
Analytical lines		
Arsenic	193.76 nm	
Selenium	196.09 nm	

pared by dissolving  $\text{H}_3\text{AsO}_4 \cdot 0.5 \text{H}_2\text{O}$  in 0.5 mol/l  $\text{HNO}_3$ . Selenium(IV) solution was prepared from a standard solution (1000  $\mu\text{g}/\text{ml}$ ) of SPEX Chemical, prepared by dissolving Se in 0.5 mol/l  $\text{HNO}_3$ . Selenium(VI) solution was prepared by dissolving sodium selenate in 0.1 mol/l  $\text{HNO}_3$ . Sodium tetrahydroborate solutions were prepared by dissolving  $\text{NaBH}_4$  (Merck, Darmstadt, FRG) in sodium hydroxide solutions. Sodium hydrogencarbonate and sodium carbonate for the mobile phase were of analytical-reagent grade (Kanto Chemical). The mobile phase was deaerated by aspiration prior to use. Nitric acid and sodium hydroxide used in this experiment were of ultrapure grade obtained from Cica-Merck (Kanto Chemical and Merck). Perchloric acid, hydrogen peroxide, and hydrofluoric acid used for acid digestions were from Tamapure-AA-100 (Tama Chemical, Tokyo, Japan).

## Results and discussion

### Hydride generation

The HG technique was used to introduce the sample into the ICP and to increase the sensitivity. An ultrasonic nebulizer (USN) was also employed for improving the sensitivity. However when an USN is used, concomitants are also concentrated together with the analyte and then matrix effects cause a problem. The detection limits ( $3\sigma$ ) for As(III) and Se(IV) were 78 ng/ml and 110 ng/ml, respectively, when using a pneumatic nebulizer. The detection limits were improved to 0.42 ng/ml and 0.65 ng/ml when using the HG technique. Reaction equations for As(III) and Se(IV) are as follows:



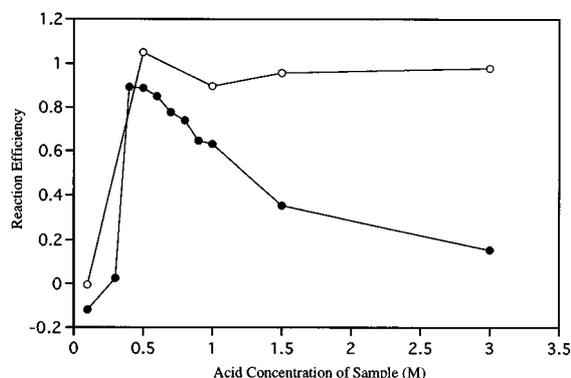
In these reactions, tetrahydroborate ( $\text{BH}_4^-$ ) acts as a reductant. It is unstable and is decomposed in an acid solution, and has therefore to be stabilized in an alkaline solution. Acidic conditions are clearly necessary to generate the hydrides of As and Se. Usually, HCl is employed to acidify a sample [9]. However, in this experiment,  $\text{HNO}_3$  was applied to reduce isobaric interferences and to improve the detection limits when using ICP-MS. The concentrations of alkaline and acid solutions were optimized. The relative reaction efficiencies of As(III) and Se(IV)

were obtained by changing the  $\text{HNO}_3$  concentration from 0.1 to 3 mol/l and the NaOH concentration from 0 to 1 mol/l. The results are shown in Table 2 for As and Se. The relative reaction efficiency was calculated with respect to that obtained under the conventional conditions of 3 mol/l HCl and 1 mol/l NaOH. These data indicate that the comparative reaction efficiency can be obtained when the combination of acid and alkaline concentrations was 0.5 and 0.1 mol/l or 0.5 and 0.5 mol/l, respectively. However, with a NaOH concentration of 0.1 mol/l,  $\text{NaBH}_4$  was decomposed rather rapidly and the reaction efficiency of Se(IV) decreased to 65% within three days. Therefore, the NaOH concentration was fixed to 0.5 mol/l, and the reaction efficiency was obtained by changing the concentration of  $\text{HNO}_3$  for As and Se (Fig. 1). From this figure it is clear that As hydride can be generated when the acid concentration is more than 0.5 mol/l and there is no major

**Table 2** Relative reaction efficiency of As(III) and Se(IV) obtained by  $\text{HNO}_3$ 

Arsenic(III)					
Alkaline concentration of $\text{NaBH}_4$ solution (mol/l)	Acid concentration of sample solution (mol/l)				
	0.1	0.5	1	1.5	3 <sup>a</sup>
0	0.33	0.61	0.65	0.52	0.65
0.1	0.46	1.1	1.1	1.1	1.2
0.5	0.00	1.1	0.90	0.96	1.0
1 <sup>a</sup>	0.00	0.00	1.2	1.1	1.1
Selenium(IV)					
Alkaline concentration of $\text{NaBH}_4$ solution (mol/l)	Acid concentration of sample solution (mol/l)				
	0.1	0.5	1	1.5	3 <sup>a</sup>
0	0.20	0.35	0.26	0.22	0.22
0.1	0.18	0.82	0.53	0.42	0.44
0.5	0.00	0.89	0.63	0.35	0.16
1 <sup>a</sup>	0.10	0.10	0.54	0.45	0.38

<sup>a</sup>Conventional conditions are the combination of 3 mol/l HCl and 1 mol/l NaOH

**Fig. 1** Relationship between  $\text{HNO}_3$  concentration and relative reaction efficiency of (○)As(III) and (●)Se(IV) at 0.5 mol/l NaOH concentration

difference between HCl and HNO<sub>3</sub>. From the analytical point of view the concentration of acid should be kept as low as possible to reduce contamination. On the contrary, the reaction efficiency of Se(IV) decreased with an increase in acid concentration (Fig. 1). Apparently, the formation of Se hydride requires a more reducing atmosphere than that of As hydride. Considering that HCl is a reducing acid and HNO<sub>3</sub> is an oxidizing acid, NaBH<sub>4</sub> is decomposed and the reducing power is deteriorated when the concentration of HNO<sub>3</sub> is high. The optimum concentration of HNO<sub>3</sub> was 0.5 mol/l for Se, i.e., the optimum concentration of HNO<sub>3</sub> is 0.5 mol/l for both As and Se.

#### Coupling IC with ICP-AES by using pneumatic nebulization

In order to check the separation conditions, the IC eluent was transferred to the ICP by using pneumatic nebulization after passing through a conductivity detector. At first, As and Se standard solutions were prepared by using a mixed solution of NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> (pH 8.98), similar to the mobile phase of the IC. An alkaline solution was not suitable for standard solutions of As because As(III) was converted to As(V) in this solution. An acid solution should be used to stabilize the signals for As(III). However, in this case, the As and Se species could not be recognized by a conductivity detector due to considerable interference by nitrate. In contrast, the As and Se species could be measured by ICP-AES without any interference. That is a clear advantage of ICP-AES as against a conductivity detector.

#### Coupling IC with ICP-AES by using HG

Under the optimum conditions determined for HG, the determination of As and Se was performed by an on-line system (Fig. 2). To adjust the acid concentration to 0.5 mol/l, 1 mol/l HNO<sub>3</sub> was merged with the eluent before the HG step. The chromatograms of ICP-AES are shown in Fig. 3 for As and Se. In each case, the chromatogram obtained

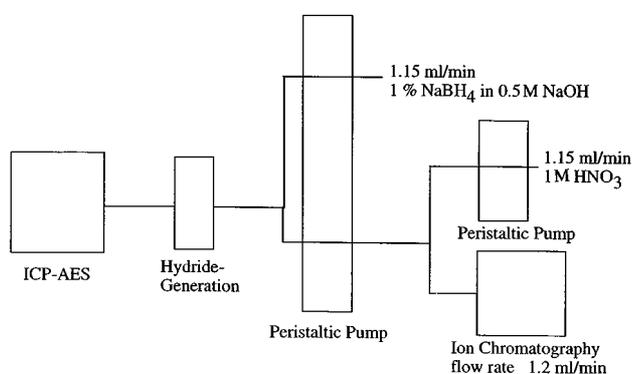


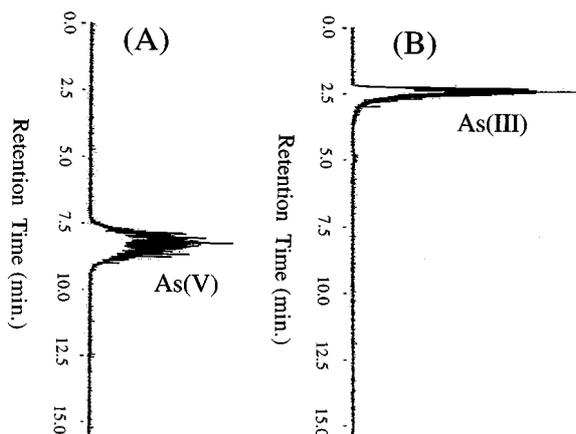
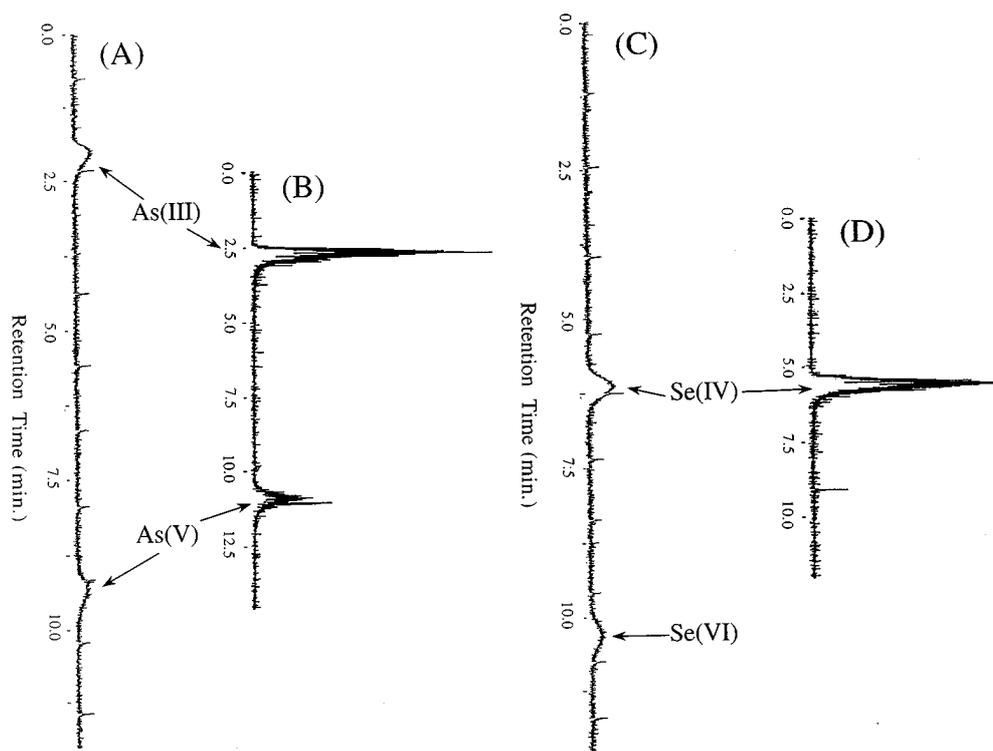
Fig. 2 On-line system of IC/HG/ICP-AES

by pneumatic nebulization is also shown for comparison. The concentration of As and Se is 5 µg/ml for pneumatic nebulization and 1 µg/ml for HG. The detection limits ( $3\sigma$ ) for As(III), As(V), and Se(IV) were 1.3 µg/ml, 2.3 µg/ml, and 0.94 µg/ml, respectively, by IC/ICP-AES using a pneumatic nebulizer. With HG, the detection limits for As(III), As(V), and Se(IV) were improved to 70 ng/ml, 170 ng/ml, and 57 ng/ml, respectively. In this case, the improvement was by one order of magnitude. The reaction efficiency of As(V) was lower than that of As(III). For Se(VI), the detection limit of 1.9 µg/ml could be obtained by IC/ICP-AES with a pneumatic nebulizer. However, Se(VI) could not be measured by IC/ICP-AES with HG, because the reduction of Se(VI) to the hydride form was not achieved. Therefore, an additional reduction of Se(VI) to Se(IV) is necessary before. This could be achieved by heating for 6 min at 70°C in a 6 mol/l HCl solution [10]. If the sample is kept at 6 mol/l HCl for more than one day, Se(VI) is quantitatively reduced to Se(VI) without heating.

#### Investigation of the acid digestion

Acid digestion is necessary to decompose organic and inorganic compounds and to convert solid samples into the liquid state. The sample is heated with high concentrations of acid at high temperature (160–230°C). During the digestion procedures, there is a possibility that oxidation states might be changed and analytes might be volatilized. To check this possibility, test samples containing Se(IV) and Se(VI) at a concentration of 5 µg/ml were prepared separately. The samples were digested by using HNO<sub>3</sub>, HClO<sub>4</sub> and HF, and Se(IV) was measured without using IC. The Se(IV) signal was compared with that of the non-digested samples. It was found that the conversion from Se(VI) to Se(IV) did not occur, and there was no loss of analytes during the digestion procedures. It has been reported that Se(VI) is converted to Se(IV) when HCl is present in high concentration [10, 11] and Se is volatilized when the sample is heated with sulfuric acid [12]. Apparently, a reducing atmosphere is necessary with the use of HCl to convert Se(VI) to Se(IV) [10, 11]. For As, the same experiment was performed, and in this case As(III) and As(V) were measured separately by an on-line system with IC. The chromatogram obtained for the digested sample is shown in Fig. 4. Again, it was confirmed that the oxidation states did not change and there was no loss of analytes during the digestion procedures. Even if perchloric acid was replaced by hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) for acid digestion, the oxidation states of As and Se were not changed, neither was a loss of analytes observed. The oxidization power of H<sub>2</sub>O<sub>2</sub> is lower than that of HClO<sub>4</sub>, but if H<sub>2</sub>O<sub>2</sub> is sufficient to digest the required samples, it is better because it is safer to handle and moreover chlorine is not contained in the digested samples.

**Fig. 3 A–D** Chromatogram of **A** pneumatic nebulization/ICP-AES for As, **B** HG/ICP-AES for As, **C** pneumatic nebulization/ICP-AES for Se, and **D** HG/ICP-AES for Se



**Fig. 4 A, B** Effect of digestion procedures on the determination of different oxidation states for As. **A** 5  $\mu\text{g/ml}$  solution of As(V). **B** 5  $\mu\text{g/ml}$  solution of As(III)

## Conclusions

The oxidation states of arsenic could be determined without using HCl in all analytical procedures. The determination of As(III) and As(V) was possible by an on-line method of IC/HG/ICP-AES, but the reaction efficiency of As(V) was lower than that of As(III). The detection limits for As(III) and As(V) were 70 ng/ml and 170 ng/ml, respectively.

For selenium, HCl was necessary for additional reduction of Se(VI) to Se(IV). It is more favourable to determine Se(VI) and Se(IV) without using IC. At first Se(IV)

is measured by HG/ICP-AES and after additional reduction Se(IV) is measured again by HG/ICP-AES. The concentration of Se(VI) can be calculated from the difference of the two measurements. The detection limit for Se(IV) was 0.65 ng/ml.

If oxidizing acids ( $\text{HNO}_3$ ,  $\text{HClO}_4$ , and  $\text{H}_2\text{O}_2$ ) were used for sample digestion, a change of oxidation state and loss of analytes could not be observed for both As and Se.

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