

# Application News

## No. A495

### Spectrophotometric Analysis

## Measurement of Arsenic and Selenium in White Rice and River Water by Hydride Generation-Atomic Absorption Spectrometry (HG-AAS) with Electric Cell Heating

### ■ Introduction

The hydride generation method is known as a technique for high-sensitivity measurement of elements such as arsenic (As) and selenium (Se), based on the fact that at ambient temperature such elements react with newly generated active hydrogen to generate hydrogen gas compounds. Because it is not easily affected by alkaline metals, alkaline earth metals, and other elements coexisting in samples, it is often used for high-sensitivity measurement of As, Se, and other elements in the environment, foods, and other samples, not only in atomic absorption spectrometry, but also in ICP atomic emission spectrometry, ICP mass spectrometry, and other methods.

The method commonly used for atomic absorption spectrometry involves sending the hydrogen compound gas ( $\text{AsH}_3$  and  $\text{H}_2\text{Se}$ ) generated in a hydride vapor generator into a quartz absorption cell and atomizing the elements by thermal decomposition. Then either a flame or electric heating (furnace) is used to heat the absorption cell.

Electric heating avoids the need for gas supplies required for the flame method (acetylene and air) and offers about 1.5 times higher sensitivity than the flame method for As and Se measurements.

In this example, hydride generation-atomic absorption spectrometry (HG-AAS) with an electric cell heater for heating the absorption cell was used to measure arsenic and selenium in certified white rice reference material (NMIJ CRM 7502-a) and certified river water reference materials (JSAC 0301 with nothing added and JSAC 0302 with As and Se added).

### ■ Pretreatment

#### (1) White Rice

About 1 g of the sample was weighed into a beaker, moistened with a small amount of water, 10 mL of nitric acid was added, and then the sample was thermally decomposed on a hot plate. After the vigorous reaction was finished, 5 mL of nitric acid and 1 mL of perchloric acid were added and thermal decomposition was further continued. After white smoke appeared, the sample was heated to almost dryness and allowed to cool. Then 5 mL of hydrochloric acid (1 + 1) was added to dissolve soluble salts. The result was transferred to a separate container and pure water was added to make 25 mL of the sample stock solution.

Then 10 mL of this sample stock solution was pre-reduced to create 20 mL of the measurement sample. Arsenic was pre-reduced by adding hydrochloric acid, potassium iodide and ascorbic acid and selenium by adding hydrochloric acid to make 20 mL of the measurement solutions.

#### (2) River Water

10 mL was pre-reduced to create 20 mL of the measurement sample, in the same manner as for the white rice.

### ■ System Configuration and Measurement Conditions

The system was configured from an AA-7000 atomic absorption spectrophotometer connected to an HVG-1 hydride vapor generator and SARF-16C atomic muffle furnace (electric cell heater). The cell heater is shown in Fig. 1.

Major measurement conditions are indicated in Table 1.

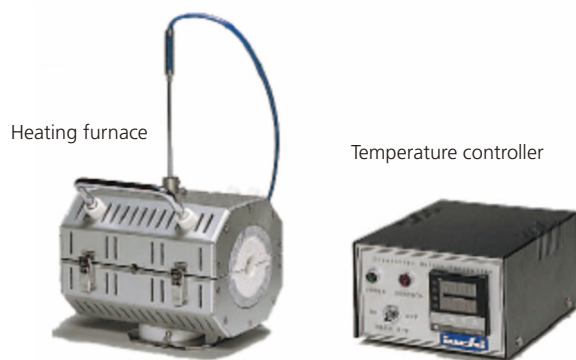


Fig. 1 SARF-16C Atomic Muffle Furnace (Electric Cell Heater)

Table 1 Measurement Conditions

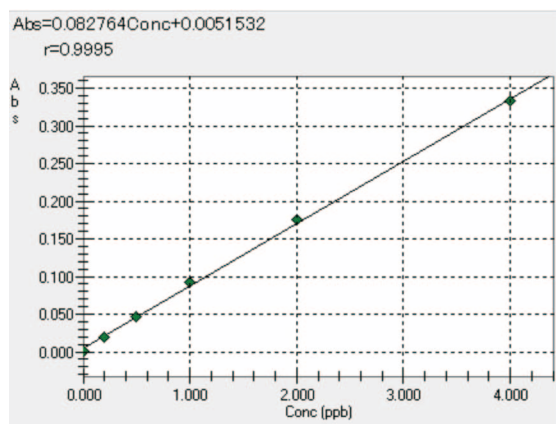
	As	Se
Analytical wavelength	193.7 nm	196.0 nm
Slit width	0.7 nm	
Background correction	Deuterium lamp method (D2 method)	
Absorption cell heating system	Electric heating (800 °C)*	
Carrier gas	Ar (about 0.1 L/min)	
Integration time (number of times repeated)	5 sec (n = 5)	
Reagent concentration	NaBH <sub>4</sub> 0.4 % (NaOH 0.4 %)	
	5 mol/L hydrochloric acid	
Sample delivery rate	4 mL/min (0 to 7 mL/min variable)	
Reagent delivery rate	1.5 mL/min (0 to 2.5 mL/min variable)	

\* The electric cell heater cannot be installed as a dual-purpose (flame and furnace) unit for the AA-7000 system.

**Analytical Results**

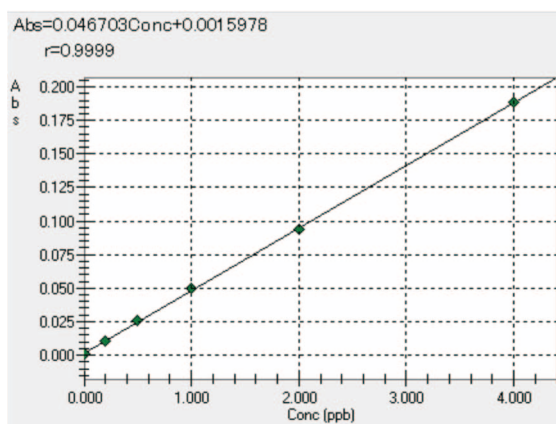
**Calibration Curve and Sensitivity**

Calibration curves for As and Se are shown in Figs. 2 and 3, respectively. As a guideline for the lower limit of detection, a 1 % absorption value (0.0043 Abs) was achieved at a concentration of 0.05 ppb for As and 0.09 ppb for Se in the measurement solution.



Operation	Sample ID	Concentration Setting (ppb)	Absorbance	%RSD
STD-AV	Blank	0.0000	0.0010	134.72
STD-AV	0.2ppb	0.2000	0.0196	2.65
STD-AV	0.5ppb	0.5000	0.0470	2.39
STD-AV	1ppb	1.0000	0.0929	1.87
STD-AV	2ppb	2.0000	0.1747	1.23
STD-AV	4ppb	4.0000	0.3330	1.79

Fig. 2 Calibration Curve for As



Operation	Sample ID	Concentration Setting (ppb)	Absorbance	%RSD
STD-AV	Blank	0.0000	0.0011	78.53
STD-AV	0.2ppb	0.2000	0.0103	17.81
STD-AV	0.5ppb	0.5000	0.0257	4.26
STD-AV	1ppb	1.0000	0.0495	3.12
STD-AV	2ppb	2.0000	0.0941	1.30
STD-AV	4ppb	4.0000	0.1885	2.12

Fig. 3 Calibration Curve for Se

**Analytical Results**

Measurement results for white rice are indicated in Table 2 and for river water in Table 3. Results from both samples closely matched respective certified values.

**Table 2 Measurement Results of As and Se in White Rice**

White Rice (NMIJ CRM 7502-a)

Element	As	Se
Certified Value (mg/kg)	0.109	–
Measured Value (mg/kg)	0.101	0.010
%RSD (n = 5)	1.7 %	8.5 %

**Table 3 Measurement Results of As and Se in River Water**

River Water (JSAC 0301-3 unspiked)

Element	As	Se
Certified Value (µg/L)	0.20	(0.08)*
Measured Value (µg/L)	0.21	< 0.2
%RSD (n = 5)	7.4 %	–

\* Reference value

River Water (JSAC 0302-3 spiked)

Element	As	Se
Certified Value (µg/L)	5.2	5.0
Measured Value (µg/L)	5.1	5.3
%RSD (n = 5)	1.5 %	1.0 %

**Conclusion**

This example shows how an AA-7000 system with electrically heated hydride generation can be used to analyze the arsenic and selenium in food and environmental water with high sensitivity, without the need for gas supplies (acetylene and air) required by flame methods.