

# Development of Simplified Determination Method for Selenium in Aqueous Solution

## Background

The Japanese national effluent standard for selenium (Se) has been set at 0.1 mg/L since June 1994. In coal-fired power plants, Se is detected in flue gas desulfurization (FGD) wastewater because a trace amount of Se is contained in coal. The concentration of Se in wastewater largely varies depending on the coals employed. Thus, there is a high need for process monitoring for controlling Se concentration in wastewater.

## Objectives

This study aims to propose a simplified determination method for Se that can be applied to the process monitoring, and to optimize various operating parameters for accurate Se determination. In addition, it aims to demonstrate its applicability to FGD wastewater.

## Principal Results

### 1. Development of simplified Se determination method using a selenium hydride gas sensor

A simple and rapid determination method for Se (IV)<sup>\*1</sup> in aqueous solutions was proposed. The method employs an amperometric gas sensor, which is used as a gas leak detector for selenium hydride (H<sub>2</sub>Se) in the working environment. The analytical procedure is as follows: an HCl solution is added to a sample containing Se (IV), and the subsequent addition of a NaBH<sub>4</sub> solution generates H<sub>2</sub>Se, which is measured by the sensor. With a simple experimental apparatus (Fig. 1), we confirmed that in principle, the proposed method can determine Se (IV) in aqueous solution.

### 2. Optimization of operating parameters

To improve the analytical accuracy of this method, we built up a new experimental system that offers precise control on various operating parameters. A highly linear calibration curve was obtained for Se (IV) standard solution by optimizing the operating parameters (Fig. 2). The optimized parameters were carrier gas flow rate, NaBH<sub>4</sub> flow rate, concentration of NaBH<sub>4</sub>, and concentration of HCl. The stability of the signal at low concentrations region was improved in this system (Table 1). This is because resolution of the signal profile was improved by optimizing the operating parameters and using high sensitivity H<sub>2</sub>Se gas sensor (Fig. 3).

### 3. Application to FGD wastewater

The proposed method was applied to FGD wastewater in coal-fired power plants. The Se (IV) concentrations were not determined due to two interferences, one of which was inhibition of H<sub>2</sub>Se generation caused by organic compounds in the samples. The other is a large negative interference caused by I<sup>-</sup> contained in the wastewaters. These two interferences were removed by the sample pretreatment, which was thermal decomposition in a mixed solution of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> (Fig. 4). The measured values with our method were in good agreement with those obtained with ICP-AES when the FGD wastewater samples are taken after pretreatment. This pretreatment is effective for the removal of interferences, but takes 4-5 hours for completion. Therefore, the pretreatment method should be largely shortened and simplified.

## Future Developments

To build up a Se process monitor, a rapid pretreatment and a simple reduction method of Se (VI) to Se (IV) will be established.

**Main Researcher:** Hiroyuki Masaki, Ph.D.,

Research Scientist, Environmental Chemistry Sector, Environmental Science Research Laboratory

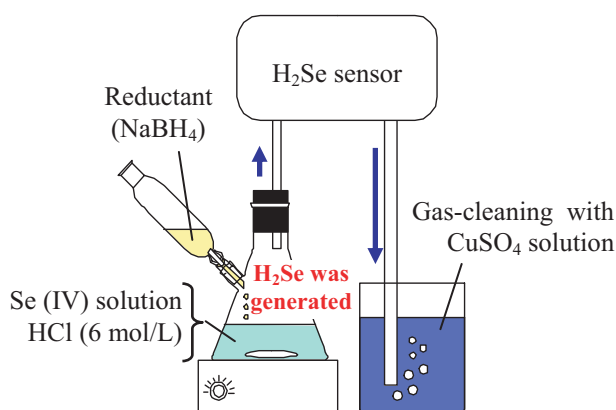
## Reference

H. Masaki, et al, 2007, "Development of simplified monitor for selenium in aqueous solution (Part 1) - Review and applicability evaluation of simple determination method -", CRIEPI Report V06014 (in Japanese).

H. Masaki, et al, 2008, "Development of simplified monitor for selenium in aqueous solution (Part 2) - Optimization of the analysis parameters and applicability to desulfurization wastewaters -", CRIEPI Report V07006 (in Japanese).

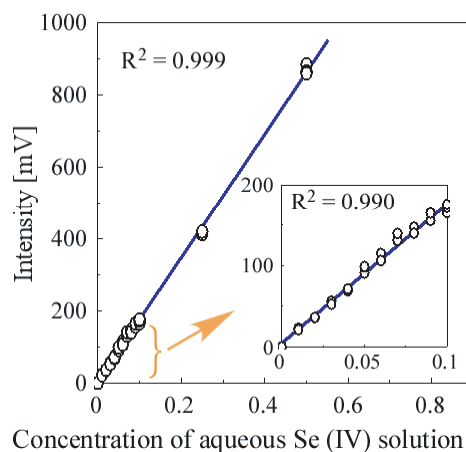
---

\* 1 : Se mainly exists in wastewater as oxyanion of Se (IV) and Se (VI). Se (VI) is generally reduced to Se (IV) for the determination.



**Fig.1** The simple apparatus for Se measurement.

A  $\text{NaBH}_4$  solution is added to a mixed solution of Se (IV) and HCl solution, which generates  $\text{H}_2\text{Se}$ . The generated  $\text{H}_2\text{Se}$  gas is measured with an amperometric gas sensor.



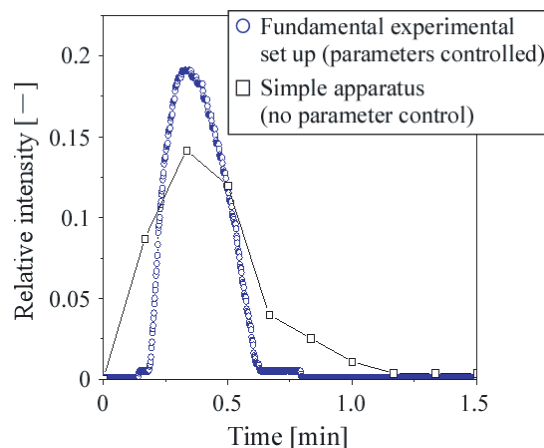
**Fig.2** A calibration curve for Se (IV) standard solution.

A highly linear calibration curve was obtained in the proposed method by optimizing the operating parameters; the carrier gas flow rate of 500 mL/min, the  $\text{NaBH}_4$  flow rate of 30 mL/min, the  $\text{NaBH}_4$  concentration of 3.0 g/L, and the HCl concentration of 6.0 mol/L. A simple and rapid determination method from aqueous Se (IV) with a detection limit of 0.002 mg/L and a quantitative limit of 0.005 mg/L

**Table 1** Stability of  $\text{H}_2\text{Se}$  signal

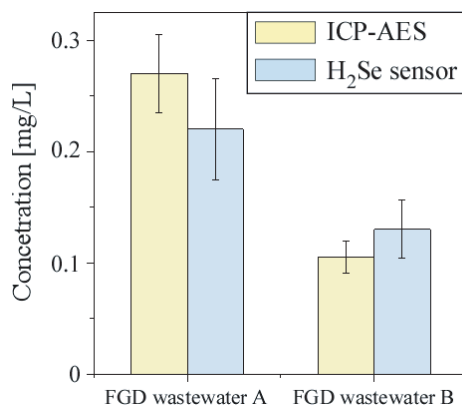
Concentration of Se [mg/L]	Relative standard deviation [%]	
	Simple apparatus (no parameter control)	Fundamental experiment set up (parameters controlled)
0.01	14.0	4.6
0.05	5.6	4.6
0.1	3.9	3.2
0.5	3.9	1.5

A relative standard deviation of the signal intensity was used as an index for the stability of the signal. At low concentrations region, the signal intensity was stabilized by optimizing operating parameters on a  $\text{H}_2\text{Se}$  gas sensor with a high resolution.



**Fig.3** Comparison of signal profiles of  $\text{H}_2\text{Se}$  for 0.1 mg/L Se solution.

The resolution of the signal profile was improved by optimizing operating parameters and using high sensitivity  $\text{H}_2\text{Se}$  gas sensor



**Fig.4** Se (IV) concentration in FGD wastewater after pretreatment of thermal decomposition.

The measured values with our method were in good agreement with those obtained with ICP-AES when the samples were thermally pretreated. Since the thermal pretreatment takes 4-5 hours, it should be largely shortened and simplified.