Automated determinations of selenium in thermal power plant wastewater by sequential hydride generation and chemiluminescence detection

Kentaro Ezoe [a], Seiichi Ohyama [b], Md. Abul Hashem [a], Shin-Ichi Ohira [a], Kei Toda [a,*]

[a] Department of Chemistry, Kumamoto University, 2-39-1 Kurokami, Kumamoto 869-8555, Japan
[b] Environmental Science Research Laboratory, Central Research Institute of Electric Power Industry, 1646 Abiko, Abiko 270-1194, Japan

A B S T R A C T

After the Fukushima disaster, power generation from nuclear power plants in Japan was completely stopped and old coal-based power plants were re-commissioned to compensate for the decrease in power generation capacity. Although coal is a relatively inexpensive fuel for power generation, it contains high levels (mg kg^{-1}) of selenium, which could contaminate the wastewater from thermal power plants. In this work, an automated selenium monitoring system was developed based on sequential hydride generation and chemiluminescence detection. This method could be applied to control of wastewater contamination. In this method, selenium is vaporized as H_2Se, which reacts with ozone to produce chemiluminescence. However, interference from arsenic is of concern because the ozone-induced chemiluminescence intensity of H_2Se is much lower than that of AsH_3. This problem was successfully addressed by vaporizing arsenic and selenium individually in a sequential procedure using a syringe pump equipped with an eight-port selection valve and hot and cold reactors. Oxidative decomposition of organoselenium compounds and pre-reduction of the selenium were performed in the hot reactor, and vapor generation of arsenic and selenium were performed separately in the cold reactor. Sample transfers between the reactors were carried out by a pneumatic air operation by switching with three-way solenoid valves. The detection limit for selenium was 0.008 mg L^{-1} and calibration curve was linear up to 1.0 mg L^{-1}, which provided suitable performance for controlling selenium in wastewater to around the allowable limit (0.1 mg L^{-1}). This system consumes few chemicals and is stable for more than a month without any maintenance. Wastewater samples from thermal power plants were collected, and data obtained by the proposed method were compared with those from batchwise water treatment followed by hydride generation-atomic fluorescence spectrometry.

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1. Introduction

After the Fukushima disaster in 2011, power generation from all Japanese nuclear power plants was stopped, which reduced the contribution to power generation from nuclear power plants from 30% before the accident to zero [1]. To account for this loss in power generation, thermal power generation was increased to 90% in 2013 [2]. Among the fuels used for power generation, coal is inexpensive, and old coal-burning power stations were re-commissioned after the disaster. However, coal usually contains selenium at levels of several milligrams per kilogram [3,4], which means that wastewater from the treatment systems for exhaust gas and fly ash may be contaminated with selenium [5–7].

Selenium is an essential trace element for production of selenium containing proteins and enzymes [8], and the adult recommended daily intake of selenium is > 45 µg [9]. The antioxidant glutathione peroxidase contains selenocysteine in its active center [10] and acts to protect human health by preventing cancer [11]. However, intake of too much selenium is not healthy, and the safe upper limit is 400 µg a day for an adult [12]. Both organic and inorganic selenium can damage neuronal cell lines [13]. Because the difference between the recommended daily intake and safe upper limit is small [14], treatment of wastewater to remove selenium is important [15]. To prevent selenium pollution, an allowable limit for selenium in wastewater has been established at 0.1 mg L^{-1}[16].

Selenium in wastewater and drinking water has been detected by ICP-MS [17,18], ICP-OES [19], hydride generation–atomic fluorescence spectrometry (HG–AFS) [20–22], HG–AAS [23], and GF–AAS [24]. However, the instruments required for these

techniques are large, expensive to purchase, expensive to run because of their requirements for argon gas, and are not suitable for on-site long-term monitoring. One of the authors previously attempted selenium detection using hydride generation and an electrochemical gas sensor, but the co-generated matrix damaged the gas sensor within a few days. The developed instrument was effective at measuring selenium but showed issues on application to wastewater monitoring [25] and also the developed instrument was large.

As an alternative to electrochemical detection, chemiluminescence has been investigated for selenium monitoring. Chemiluminescence is a very sensitive and dry method for heavy metal hydride vapors [26–29]. Previously we have applied chemiluminescence detection to a portable device for measuring arsenic in drinking water that did not need purified water [30], and to a device for detection of dimethyl sulfide at nanomolar levels in environmental water samples [31]. To date, chemiluminescence has not been applied to detection of selenium in water, except for by Ye and Chen [32]. In their study, Se was preconcentrated using a complexation and extraction to organic solvent in a batchwise protocol. The H_2Se produced in the flow system was preconcentrated again in a liquid nitrogen cryotrap to determine trace levels of selenium. However, the response signals of the analytical system were not shown in the paper.

The aim of the present study was to develop a compact and durable analysis system for automated long-term monitoring of selenium in wastewater from thermal power plants. Chemiluminescence detection was used as an alternative to the electrochemical gas sensor used in our earlier work. The system was applied to analysis of authentic wastewater samples. Before analysis, the wastewater samples were treated with potassium permanganate ($KMnO_4$) to decompose any organoselenium compounds. The selenium in the sample was then separated from arsenic so that it did not interfere with the selenium signal. These steps were performed sequentially using a syringe pump. Therefore, this method is termed sequential injection analysis–chemiluminescence (SIA–CL).

2. Experimental

2.1. Reagents

Selenium stock solutions ($1 g L^{-1}$) were prepared from sodium selenite and sodium selenate (Nacalai Tesque, Kyoto, Japan), and arsenic stock solutions were prepared from sodium arsenite (Wako Pure Chemical Industries, Osaka, Japan). The stock solutions were prepared by dissolving the reagents in pure water, and working solutions were prepared by diluting the stock solutions with pure water. The decomposition of organoselenium compounds and selenium reduction were performed using $2 g L^{-1}$ $KMnO_4$ (Wako Pure Chemical Industries) in 3 M sulfuric acid and 5% potassium bromide (Nacalai Tesque) in 7.5 M HCl, respectively. Hydride generation was performed with 0.6 M sodium borohydride ($NaBH_4$) dissolved in 0.06 M NaOH for stabilization. The chemicals used were all reagent grade, and deionized water was used in all experiments.

2.2. Analytical system

The analytical system is shown in Fig. 1. It consisted of a syringe pump (VersaPump 6, Kloehn, Las Vegas, NV) with an eight-port switching valve (V6 rotary valve, 17620, Kloehn) with a 10 mL Hamilton syringe, two reactors (hot and cold) and a chemiluminescence (CL) detector. The eight-port valve of the syringe pump was connected to reagent bottles containing $KMnO_4$, KBr, $NaBH_4$,
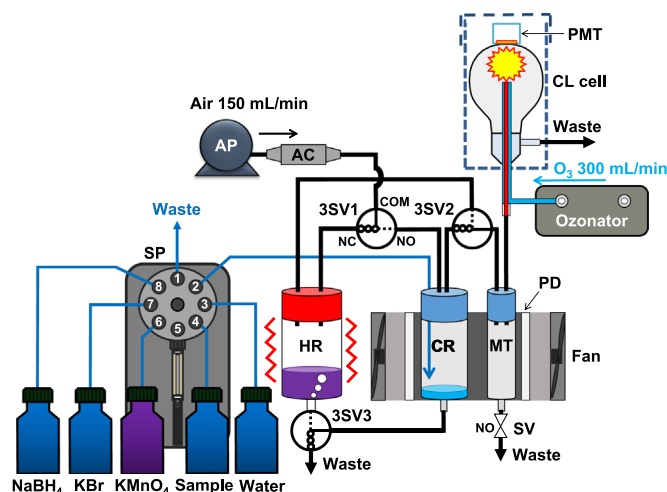

Fig. 1. SIA–CL system for measurement of selenium. SP: syringe pump, HR: hot reactor, CR: cold reactor, MT: mist trap, PD: Peltier device, 3SV1-3: three-way solenoid valves, SV: solenoid valve, CL cell: chemiluminescence cell, PMT: photomultiplier, AP: miniature airpump, AC: activated carbon column. The COM, NO and NC on 3SV represent common, normal open, and normal closed ports of the solenoid valve.

sample, pure water, a waste line, and the cold reactor. The first reactor (hot reactor) was a glass tube (28 mm outer diameter (o. d.) × 24 mm inner diameter (i.d.), 80 mm length) with a drain tube (3.0 mm o.d. × 1.8 mm i.d., 15 mm length) welded in the bottom. The hot reactor was heated using a heating tape (1 m, max 60 W 200 V ac) to 110 °C (no thermo control) by applying 100 V ac. The top of the glass tube was conically tapered to a ground glass joint that was plugged with a glass cap. The cold reactor was a 50 mL plastic sample tube inserted in an aluminum block (40 mm × 25 mm × 80 mm), which was cooled by a pair of Peltier devices (40 mm × 80 mm, powered by 12 V dc) coupled with a pair of aluminum heat sinks (70 mm square, CEP420151B, TaiSol Electronics, Taipei, Taiwan). The temperature of the aluminum block was approximately 5 °C. The cold reactor was sealed with a silicone plug. Both the glass cap on the hot reactor and the silicone plug on the cold reactor contained air inlet and outlet tubes. Air was introduced at 150 mL min^{-1} by a miniature airpump (L-3T-S-10, Techno Takatsuki, Osaka, Japan) via a couple of three-way solenoid valves (3SV1 and 3SV2, MTV-3-1/4UFH-3, Takasago Electric, Nagoya, Japan). The airflow switching is shown in Fig. 1. On/off of solenoid valves for the 3SV1, 3SV2 and normal-open type solenoid valve SV (MTV-02-1/4UNF, Takasago Electric) were synchronized with each other. An additional three-way valve (3SV3) was attached at the bottom of the hot reactor as a drain, and was controlled separately from the other valves.

The cold reactor was connected to the CL detector via a mist trap (2.5 mL polyethylene tube), which was also placed in the cooled aluminum block. The CL cell was similar to that previously developed for dimethyl sulfide detection [31]. The CL cell was prepared by chromium plating a 100 mL round bottomed flask, except for an optical window at the bottom (ø 22 mm), by RF sputtering to allow for reflection of the chemiluminescence. A miniature airpump (CM-15-12, Enomoto Micro Pump, Tokyo, Japan) was used to produce a flow of ozone (300 mL min^{-1}), which was controlled by a needle valve equipped flow meter (RK200-V-B-1/4-Air-0.5 L/min, KOFLOC, Kyoto, Japan). Ozone (approximately 3000 ppmv) was produced by an ozone generator (1000BT-12, Enaly, Shanghai, China) from silica-gel dried air. The ozone was introduced to the CL cell through the space between an outer glass tube (6 mm o.d. × 3 mm i.d.) and a smaller Teflon® tube (1/16″ × 0.33 mm i.d.) that was placed inside it. A photomultiplier tube (PMT, R3550A ASSY, Hamamatsu Photonics, Hamamatsu, Japan)