Application of a sorbent trap system to gas-phase elemental and oxidized mercury analysis

Zishuo Zhang [a,1], Yujin Eom [a], Michelle J. Lee [a,b], Tai Gyu Lee [a,c,*]

[a] Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul, 03722, South Korea
[b] Tenafly High School, 19 Columbus Drive, Tenafly, NJ, 07670, USA
[c] Department of Earth and Environmental Engineering, Columbia University, 500 W. 120th Street, New York, NY, 10027, USA

HIGHLIGHTS

- A sorbent trap that utilizes activated carbon was investigated.
- Pure AC was impregnated with 5% aqua regia to increase its Hg adsorption capacity.
- The Hg-spiked trap was found to be reproducible in terms of preparation and highly stable.
- The sorbent trap was successfully tested at a combustion facility.

ARTICLE INFO

ABSTRACT

A sorbent trap that utilizes activated carbon (AC) as the solid trapping medium is a new technology for measuring total mercury (Hg) emissions from combustion facilities. In this study, sorbent trap technology was further developed, improved and evaluated at the laboratory scale. AC was impregnated with 5% aqua regia to enhance its Hg adsorption capacity. Sorbent traps spiked with an Hg standard solution were found to be reproducibly prepared and highly stable. The effect of the Hg concentration on the spiking efficiency was further investigated. The adsorption of elemental and oxidized Hg by the sorbent trap was studied under various experimental conditions (temperature, flow rate and inlet Hg concentration). The Hg concentration of the flue gas effluent from the sorbent trap was measured. In addition, the concentration of Hg adsorbed on the AC was determined by digesting the used AC with an acid according to US EPA method 3052 and then analyzing it with cold vapor atomic absorption spectrometry. Furthermore, the gas-phase Hg emissions from a combustion source were measured using the sorbent trap according to US EPA method 30B. The results showed that the sorbent trap could be used for Hg concentrations between 10.0 and 40.0 μg m^{-3} and flow rates between 0.5 and 1.0 lpm with adsorption efficiencies greater than 90%.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Mercury (Hg) emissions into natural cycles are increasing worldwide and causing considerable damage to human beings and the living environment. Combustion facilities, such as coal-fired power plants and cement and waste incineration plants, are important anthropogenic Hg emission sources. Accurate, convenient, and inexpensive Hg measurement and removal technologies must be developed, and emission limits should be precisely defined (López-Antón et al., 2012; Pirrone et al., 2010).

For gas-phase Hg analysis, two flue gas sampling methods are available. One method utilizes devices that can continuously analyze Hg emissions, such as the relatively new Hg continuous emission monitoring system (Hg CEMS) technology. Although this type of system allows Hg concentrations to be monitored in real time, the high purchase and maintenance costs associated with real-time monitoring prohibit the wide use of this method in research. In addition, calibration tests must be conducted periodically (Won et al., 2013; Zamzow et al., 2003).

The other method involves the use of a trapping medium, which

is based on wet chemistry (solution chemistry) or consists of a dry solid sorbent such as activated carbon (AC). Wet chemistry methods, such as the ASTM D6784-02 standard test (ASTM International, 2008), allow different forms of Hg (Hg^p, Hg^0, and Hg^{2+}) to be measured separately. However, the preparation, recovery and pretreatment of the gas sample are highly complex, and Hg loss occurs during the preparation and transportation processes (Kellie et al., 2004; US EPA, 2008). In contrast, dry chemistry-based methods, with their advantages of facile catalyst preparation and instrument settings, convenient transport, a convenient pretreatment procedure, low cost and high analytical accuracy, are being widely used and promoted for the measurement of Hg emissions in combustion facilities. A sorbent trap, which is based on dry chemistry, can trap and retain gas-phase Hg, even when other compounds are present, and the collected compounds can be easily desorbed and extracted for analysis.

A sorbent trap is a type of Hg adsorption reactor that utilizes AC as the trapping medium. In this study, pure AC was impregnated with 5% aqua regia to increase its adsorption capacity. Each sorbent trap contained two 0.3-g sections of AC separated by glass wool at the end of a tube, which was aligned along the direction of the flue gas flow. The first section lying in the front adsorbed most of the Hg in the flue gas, and the second section, called the breakthrough section, was used to determine the amount of Hg remaining. When conducting field tests, paired traps are required for sorbent trap sampling. The first section of one of the traps, the spiked trap, was spiked with a specific amount of Hg. No Hg was added to either section of the other trap (the unspiked trap) (Schmid and DeRosier, 2011).

To ensure the accuracy of experimental results obtained by the sorbent trap method, a series of regulated experiments called a relative accuracy test audit (RATA) must be completed. The US EPA has developed a sorbent trap reference method called US EPA method 30B for performing a RATA. The US EPA requires that the spike recovery of the spiked section be between 85 and 150%, and the amount of Hg spiked in the spiked section must be between 50 and 150% of the amount of Hg captured from the flue gas (US EPA, 2007). Vapor spiking is the main spiking technique applied to products for commercial use, but a more simple and convenient method for preparing spiked samples must be developed. In analytical bias tests, the average sample recovery must be between 90 and 110% (Laudal, 2009). In this study, AC samples were spiked with Hg standard solutions, and the gas-phase Hg^0 and Hg^{2+} adsorption recovery of the sorbent trap was evaluated at different concentrations, flow rates and temperatures at the laboratory scale.

2. Experimental

2.1. Preparation of AC impregnated with 5% aqua regia

A crystalline, granular activated carbon with a 4−30 US mesh size (Kayacarbon, Korea) was used in this study. The activated carbon was impregnated with 5% aqua regia to increase its adsorption efficiency. The aqua regia reagent was prepared by mixing concentrated HCl and HNO$_3$ in a 3:1 ratio. Then, 2 mL of the 5% aqua regia solution were diluted with deionized (DI) water to a final volume of 40 mL. The resulting solution was then added dropwise to 2.0 g of pure AC in a 50-mL polypropylene tube (DigiTUBE, SCP Science, Canada). The AC was soaked in a 5% aqua regia solution for 30 min at 90 °C. This temperature was maintained using a heating block (SCP Science, Canada). The mixture was then cooled to 20 °C, filtered through a 0.45-μm membrane filter and dried in an oven at 110 °C for 24 h. The impregnated AC was carefully stored in a dry, sealed environment.

2.2. Preparation of Hg-spiked AC using an Hg standard solution

First, an Hg standard solution (1000 mg L^{-1} HgCl$_2$) was prepared from certified reference material 3133 (Hg, NIST, Gaithersburg, USA) and 2% HNO$_3$. Next, the Hg standard solution was added to the 5% aqua regia-impregnated AC in a glass bottle. The mixture was then stirred gently and dried at 20 °C for one week. The Hg concentration of the Hg-spiked AC was calculated as follows:

$$C_{\text{spiked-Hg, theoretical}} = \frac{C_{\text{sol, std}} \times V_{\text{sol, std}}}{W_{\text{AC}}} \tag{1}$$

where $C_{\text{spiked-Hg, theoretical}}$ is the theoretical Hg concentration of the spiked AC (ng g^{-1}) and W_{AC} is the weight of the unspiked, chlorine-impregnated AC (g). $C_{\text{sol, std}}$ and $V_{\text{sol, std}}$ are the concentration and volume of the Hg standard solution (1000 μg L^{-1}), respectively.

2.3. Reproducibility and stability of the Hg-spiked AC

To complete the RATA, the Hg-spiked AC must be prepared reproducibly, and its stability must be evaluated. For the sorbent to be used in a sorbent trap system, the sorbent preparation must be adequately reproducible as demonstrated by the Hg concentrations of samples randomly selected from a large batch of Hg-spiked ACs, which must be the same. In addition, Hg-spiked AC must exhibit good stability for use in practical applications, i.e., the Hg concentration in the spiked AC cannot change dramatically over time. In this study, Hg-spiked AC with an Hg concentration of 1.67 μg g^{-1} was prepared and divided equally into three bottles. The short-term stability of the in-lab prepared Hg-spiked AC samples was investigated following confirmation of their homogeneity. The Hg concentration of the Hg-spiked AC was evaluated by digesting the AC with acid according to US EPA method 3052 and analyzing the sample with a cold vapor atomic absorption (CVAA)-type Hg analyzer (RA-915$^+$/RP-91, Lumex Ltd., St. Petersburg, Russia).

2.4. Comparison of actual and theoretical spiked Hg concentrations

Due to molecular Hg volatilization and moisture on the AC surface, the actual Hg concentration of the Hg-spiked AC was lower than the Hg concentration of the spiking solution (theoretical concentration). Thus, to determine the relationship between the theoretical and actual Hg concentrations in the AC with a focus on accurately manufacturing spiked samples with a given concentration, spiking efficiency tests were performed using different Hg concentrations.

In this study, 0.3 g of Hg-spiked AC was tested with theoretical Hg concentrations of 0.67, 1.33, 2.00, 2.67, 3.33, 4.00, 4.67, 5.33, and 6.00 μg g^{-1}. For each Hg concentration, three individual batches were prepared. Then, they were digested according to US EPA method 3052 and analyzed with a CVAA-type Hg analyzer.

2.5. Elemental Hg capture by the sorbent trap

As shown in Fig. 1(a), an Hg^0 calibration unit (Model 3310, Tekran Instruments Corporation, Toronto, Canada) was used to generate a flue gas with a highly precise specific Hg^0 concentration. The flue gas was controlled by a flow meter to a desired flow rate and then passed through a sorbent trap that had been pre-heated by a heating box for adsorption. Finally, the flue gas was discharged to a continuous, real-time, on-line gas-phase Hg^0 analyzer (VM-3000, Mercury Instruments, Karlsfeld, Germany).

Hg^0 adsorption experiments were conducted to determine the ability of the sorbent trap to capture Hg^0 and to measure the average sample recovery at different inlet Hg^0 concentrations (10,