

Determination of mercury in ash and soil samples by oxygen flask combustion method–Cold vapor atomic fluorescence spectrometry (CVAFS)

Wenhua Geng, Tsunenori Nakajima, Hirokazu Takanashi, Akira Ohki*

Department of Bioengineering, Faculty of Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

Received 12 July 2007; received in revised form 10 September 2007; accepted 9 October 2007

Available online 13 October 2007

Abstract

A simple method was developed for the determination of mercury (Hg) in coal fly ash (CFA), waste incineration ash (WIA), and soil by use of oxygen flask combustion (OFC) followed by cold vapor atomic fluorescence spectrometry (CVAFS). A KMnO_4 solution was used as an absorbent in the OFC method, and the sample containing a combustion agent and an ash or soil sample was combusted by the OFC method. By use of Hg-free graphite as the combustion agent, the determination of Hg in ash and soil was successfully carried out; the Hg-free graphite was prepared by use of a mild pyrolysis procedure at 500 °C. For six certified reference materials (three CFA samples and three soil samples), the values of Hg obtained by this method were in good agreement with the certified or reference values. In addition, real samples including nine CFAs collected from some coal-fired power plants, five WIAs collected from waste incineration plants, and two soils were analyzed by the present method, and the data were compared to those from microwave-acid digestion (MW-AD) method.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Oxygen flask combustion; Determination; Mercury in ash and soil

1. Introduction

Mercury (Hg) is a major concern among hazardous heavy metals because of its high volatility and high toxicity, especially due to its neurological health impacts [1,2]. In environmental matrices, Hg usually occurs in very low contents, so that highly sensitive analytical methods are needed for the determination of the element [3]. Cold vapor atomic absorption spectrophotometry (CVAAS) or cold vapor atomic fluorescence spectrophotometry (CVAFS) is most frequently used, and recently the isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICPMS) method is also applied [4]. For solid samples, the analyte needs to be recovered from the solid matrices and introduced into the analytical instrument. The difficulties include loss of the analyte due to inadequate extraction and/or volatilization as well as the contamination during complex recovery procedures.

In recent years, there has been growing interest about the release of Hg into atmosphere due to the combustion of fossil fuel (especially coal) and the incineration of waste. In such combustion and incineration, a considerable portion of Hg in coal and waste is transferred into ash. Thus, it is important to develop a simple and precise method for the determination of Hg in ash.

Two methods are now routinely used for the recovery of Hg from solid samples [5]: (i) heat-vaporization method which usually involves trapping of Hg by gold amalgamation (EPA Method 7473) and (ii) acid digestion aided by microwave heating (ASTM Method D5513, etc.). However, these methods involve complex and time-consuming procedures and/or result in high instrumental cost.

Oxygen flask combustion (OFC) method has been used routinely to decompose organic compounds, especially medicines, for the determination of volatile elements, such as sulfur [6] and halogens [7]; it has been adopted in some official methods, the Japanese Pharmacopoeia, etc. In our previous papers, we have applied the OFC method to the determination of F [8], Hg [9] and S [9] in coal. The OFC method has a big advantage in terms of low initial cost and easy operation compared to the above-mentioned two methods.

* Corresponding author. Tel.: +81 99 285 8335; fax: +81 99 285 8339.
E-mail address: ohki@be.kagoshima-u.ac.jp (A. Ohki).

Table 1
Certified reference materials

Certified reference material	Certified value of Hg ($\mu\text{g g}^{-1}$)
GBW08401 (CFA)	0.039 ^a
BCR038 (CFA)	2.1 ± 0.15
NIST1633b (CFA)	0.1431 ± 0.0018
NIST2709 (soil)	1.4 ± 0.08
NIST2710 (soil)	32.6 ± 1.8
NIST2711 (soil)	6.25 ± 0.19

^a Reference value.

For non-combustible inorganic matter, such as ash, addition of a combustion agent is necessary to perform the OFC method. There have been some studies about the determination of Hg in soil by use of the OFC method in which cellulose acetate [10] or cellulose [11] was used as a combustion agent. It has been reported that the determination of trace elements in coal fly ash (CFA) is difficult because the elements tend to be trapped inside the matrix [12]. To our knowledge, there have been no studies about the application of OFC to ash samples.

In this study, we developed a simple and precise determination of Hg in coal fly ash (CFA) by use of the OFC method followed by CVAFS. A novel combustion agent, Hg-free graphite, which had been subjected to Hg removal procedure, was used. This method was subsequently applied to a number of ash (waste incineration ash, WIA) and soil samples.

2. Experimental

2.1. Samples

Six certified reference materials (three CFA samples and three soil samples) used in this study are from National Institute of Standards & Technology, USA (NIST: 1633b, 2709, 2710, and 2711), Community Bureau of Reference, EC (BCR38), and National Research Center for Certified Reference Materials, China (GBW08401). The certified values (or reference values) of Hg in these materials are listed in Table 1. Also, real samples including nine CFAs, five WIAs, and two soils were tested. The CFAs were produced from different kinds of bituminous coals, and collected at electrostatic precipitators in some Japanese coal-fired power plants, while the WIAs were from municipal waste, and taken from bag filters in some Japanese incineration plants. The particle sizes of CFAs and WIAs were under 200 mesh ($74 \mu\text{m}$). The soils were collected near our building (Department of Bioengineering, Kagoshima University), and they were air-dried, milled and sieved (<100 mesh) before use.

2.2. Reagents

All solutions were prepared in ultra-pure water, obtained from a Milli-Q system (SIMS 700 0J). Potassium permanganate and sulfuric acid used as the absorbent solution for Hg were of mercury analysis grade (Kanto, Tokyo, Japan). Other chemicals were of analytical grade quality. The calibration solutions for Hg in the range of 0.05 – 1.5 ng ml^{-1} were prepared daily by sequential dilution of a 100 ng l^{-1} stock solution. The reduction

solution for CVAFS, 8% (m/v) tin(II) chloride (SnCl_2) in 12% (v/v) H_2SO_4 , was freshly prepared weekly.

The oxygen flask as well as all the containers and materials used for the Hg determination were soaked in a 3 M HCl solution. After washing with water, they were rinsed once with 0.01 M KMnO_4 (with 3% H_2SO_4), once with 20 g l^{-1} hydroxylammonium chloride (NH_3OHCl) solution to decompose KMnO_4 , and then three times with ultra-pure water prior to use.

2.3. Procedure of OFC and measurement

Unless otherwise indicated, the determination of Hg in CFA, WIA, and soil was performed as follows. The procedure of OFC was essentially the same as that described in our previous paper [9] except that a bag oblate (Kokko, Shizuoka, Japan) was used as the wrapping material instead of an ash-free filter paper. A combustion agent (0.05 g) and an ash or soil sample (0.01–0.03 g) were precisely weighed, mixed and transferred into two pieces of bag oblate. After folding into a cylindrical shape, the oblate with the sample mixture was combusted with the usual way in a 500 ml oxygen flask, in which 5 ml of an absorbent solution of 0.01 M KMnO_4 (with 3% H_2SO_4) had been placed and oxygen had been filled (see Fig. 1). After the combustion, the flask was shaken for 2 min and allowed to stand for 20 min. The remaining KMnO_4 was decomposed by the addition of an NH_3OHCl solution (20 g l^{-1}). The resulting solution was filtered, and the filtrate was diluted to a fixed volume (25 ml) and analyzed for the Hg^{2+} concentration in the solution by CVAFS using a PSA 10.025 Millennium Merlin instrument (PS Analytical Ltd., Orpington, Kent, UK). The detection limit of CVAFS is 0.1 ng l^{-1} .

Samples were prepared by the OFC method at least in triplicate, and the CVAFS analysis of each sample was carried out twice. A blank experiment for the OFC method was done, and it was confirmed that both the absorbent (0.01 M KMnO_4 with 3% H_2SO_4 , etc.) and the combustion with wrapping material and combustion agent gave some response in the resulting solution, and the Hg concentration in the blank solution was subtracted from the measured values. The recovery (%) in the determination of Hg in ash or soil was defined as $([\text{mean measured value}]/[\text{certified value}]) \times 100$.

2.4. Mild pyrolysis

For the removal of Hg from a combustion agent (graphite), mild pyrolysis was carried out according to a literature [13]. Powdered graphite (0.5 g) was placed in an alumina boat and heated by a horizontal tubular furnace at a rate of 1 K s^{-1} up to 300 – $500 \text{ }^\circ\text{C}$ under nitrogen flow (100 ml min^{-1}) and the temperature was maintained for 1 h. The resulting graphite was analyzed for the Hg content.

2.5. Microwave-acid digestion

For comparing with the data obtained from the OFC method for real samples, a microwave-acid digestion (MW-AD) was also carried out [14]. Powdered ash or soil sample (ca. 0.1 g) was accurately weighed and transferred into a pressure-

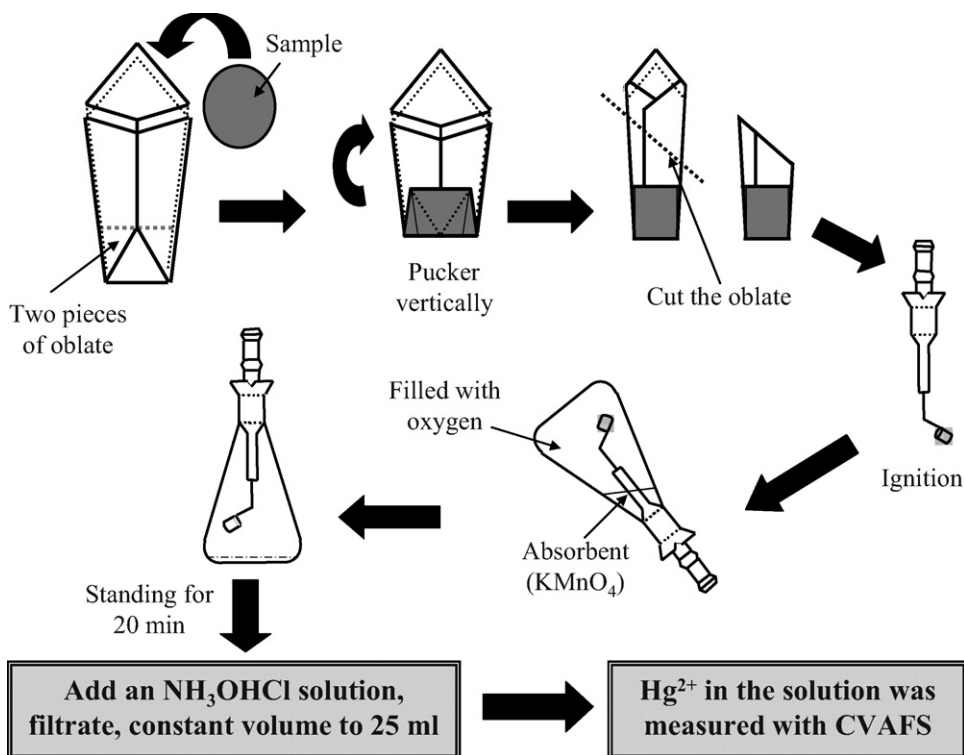


Fig. 1. Procedure of OFC method.

resistant PTFE vessel (100 ml), and acid-digested with HNO₃ + H₂O₂ (5 + 3 ml) using a microwave irradiation (Milestone ETHOS1600, Shelton, Connecticut, USA). After cooling and further addition of HNO₃ + H₂O₂ (2 + 1 ml), microwave processing was performed again. The detailed MW-AD conditions were described in the literature [14]. After cooling and filtration, the filtrate was diluted to a fixed volume (25 ml) and was subjected to CVAFS for the determination of Hg.

3. Results and discussion

3.1. Determination of Hg in CFA and soil by use of the developed method

Because of the incombustibility of inorganic matter, addition of combustion agents, generally organic matters, is indispensable to the determination of Hg in ash and soil by use of the OFC method. Four combustion agents, naphthalene, phenanthrene, cellulose acetate, and graphite, were tested. First, the contents of Hg in these agents were examined by the OFC method followed by CVAFS, which has been successfully used for the decomposition of organic matters [15,16] and coal [9] to determine total Hg. Except phenanthrene, the other three agents have high Hg contents, 0.034 μg g⁻¹ for naphthalene, 0.032 μg g⁻¹ for cellulose acetate, and 0.125 μg g⁻¹ for graphite, which will cause errors in the accurate determination of total Hg in ash and soil, especially for those with low Hg contents. In fact, the Hg content in a certified reference material of CFA, GBW08401, is only 0.039 μg g⁻¹. In order to reduce the errors caused by the presence of Hg in the combustion agents, it is thus necessary to remove Hg from the agents. It has been recently reported that the

pyrolysis at a relatively low temperature (mild pyrolysis) effectively worked for the removal of Hg from some coals [13,17]. For graphite, the removal of Hg was achieved by use of the mild pyrolysis, and the results are shown in Fig. 2. The Hg content in the treated graphite was very low (0.011 μg g⁻¹) when the mild pyrolysis even at 300 °C was carried out, and the content further decreased as the pyrolysis temperature was elevated; the Hg content in the 500 °C-treated graphite was 0.004 μg g⁻¹. We used the 500 °C-treated graphite as an Hg-free combustion agent.

The determination of Hg in a certified reference material of CFA, BCR38, was performed by the OFC method with a combustion agent followed by CVAFS. As shown in Fig. 3,

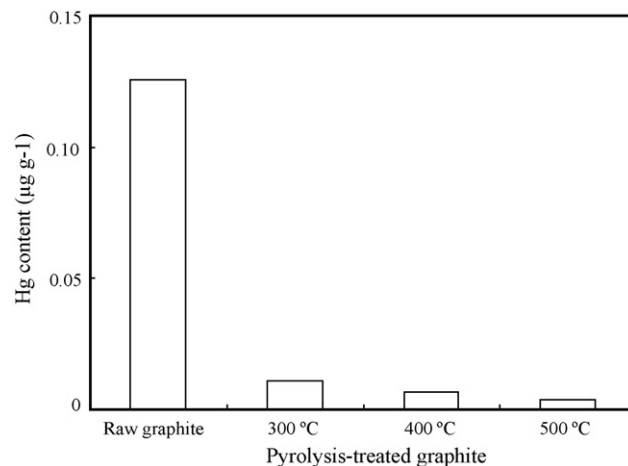


Fig. 2. Hg contents in raw graphite and treated graphites (mild pyrolysis at 300–500 °C).

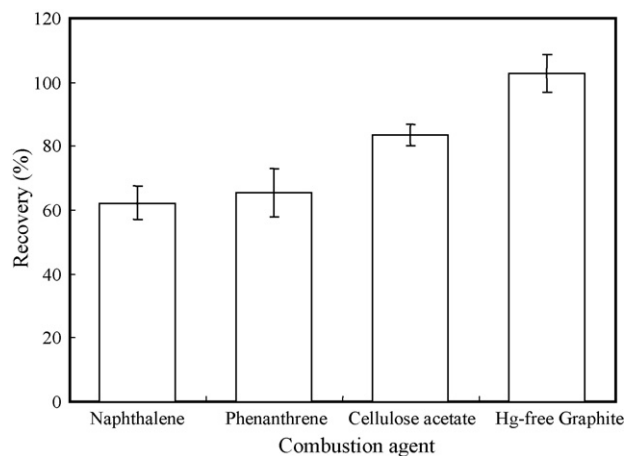


Fig. 3. Effect of the kind of combustion agent upon the recovery of Hg (BCR38).

the recoveries of Hg for naphthalene, phenanthrene, cellulose acetate, and the Hg-free graphite were 62%, 66%, 84%, and ca. 100%, respectively. It is found that the Hg-free graphite is the best combustion agent for the determination of Hg in CFA by the OFC method. There may be several reasons why the Hg-free graphite favorably works as the combustion agent in the OFC method: (i) the absence (or remarkably low content) of Hg in the agent has an advantage in the lowering of error, (ii) graphite can attain a mild combustion resulting in the effective transfer of Hg from the sample to the absorbent, and (iii) graphite is in a fine powder form, leading to thorough mixing with the ash sample.

The effect of the absorbent used in the OFC method followed by CVAFS upon the recovery of Hg was examined. Three kinds of absorbents, water, 0.01 M $K_2Cr_2O_7$ solution (with 3% H_2SO_4) and 0.01 M $KMnO_4$ solution (with 3% H_2SO_4) were applied to the OFC method for two certified reference materials, NIST1633b and NIST2709. As shown in Fig. 4, when the two materials with the Hg-free graphite were combusted in the flask, less than 10% of Hg in the CFA of NIST1633b was changed to Hg^{2+} , whereas about 40% of Hg in the soil of NIST2709 was changed to Hg^{2+} , which can be dissolved in the water. It is proposed that the occurrence of Hg in CFA is different from that in

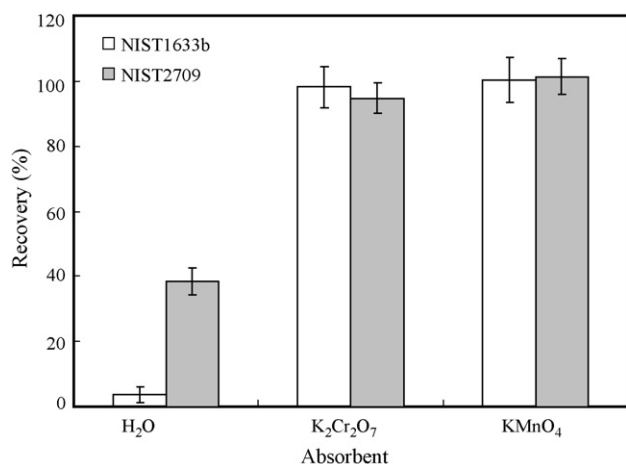


Fig. 4. Effect of the kind of absorbent upon the recovery of Hg.

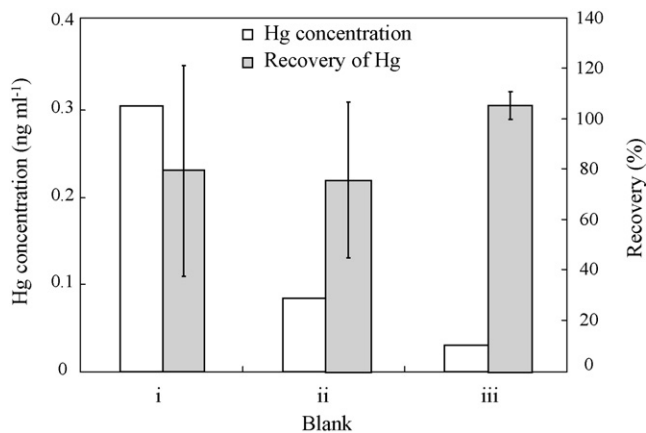


Fig. 5. Hg concentrations in blank solutions resulted from the absorbent and the combustion of: (i) raw graphite + ash-free filter paper; (ii) Hg-free graphite + ash-free filter paper; (iii) Hg-free graphite + two pieces of bag oblate, and the recoveries of Hg in GBW08401 corresponding to the blank solutions.

soil, and thus the ratio of Hg^0 and Hg^{2+} in the resulting gas after the combustion is different in the CFA and soil samples. All of the Hg^0 can be oxidized and absorbed by $K_2Cr_2O_7$ and $KMnO_4$ solution. Thus, it is confirmed that $K_2Cr_2O_7$ and $KMnO_4$ solutions are the suitable absorbents for the determination of Hg in CFA and soil by the OFC method, and the $KMnO_4$ solution is adopted as the absorbent in this research.

The Hg concentration in the blank solution mentioned above, besides from the absorbent solution (0.01 M $KMnO_4$ with 3% H_2SO_4) and the combustion of combustion agent, the Hg^{2+} ion in the blank solution can also be from the combustion of the wrapping material. In general, an ash-free filter paper was used as the wrapping material for the OFC method. However, the Hg in the paper caused a relatively high Hg concentration in the blank solution, which affected the determination of Hg in the samples with a low Hg content (see Fig. 5). In this experiment, a bag oblate (Kokko, Shizuoka, Japan), which was made from starch and soybean lecithin and used for taking powdery medicine, was attempted as the wrapping material for the OFC combustion, and resulted in a low Hg blank. As shown in Fig. 5, the Hg concentrations in the blank solutions resulted from the absorbent solution (0.01 M $KMnO_4$ with 3% H_2SO_4) and the combustion of: (i) raw graphite + ash-free filter paper (Advantec, 7), (ii) Hg-free graphite + ash-free filter paper, and (iii) Hg-free graphite + two pieces of bag oblate, were 0.31 ng ml^{-1} , 0.08 ng ml^{-1} , and 0.03 ng ml^{-1} , respectively. When those combustion systems were used, the recovery of Hg was examined for a certified reference material, GBW08401, which has a low Hg content. The results are also seen in Fig. 5, and the combination of Hg-free graphite and bag oblate gave a satisfactory recovery; in this paper, satisfactory recoveries mean 90–110% recoveries.

The effect of the mass of CFA upon the recovery of Hg based on 5 ml of $KMnO_4$ and H_2SO_4 solution was assessed, when the OFC method was carried out for BCR38 and NIST1633b. The results are shown in Fig. 6. It was found that the masses of 0.01–0.03 g based on 0.05 g Hg-free graphite were suitable for the determination of Hg in CFA by the OFC method in terms of the recovery. A somewhat low recovery observed in the case of

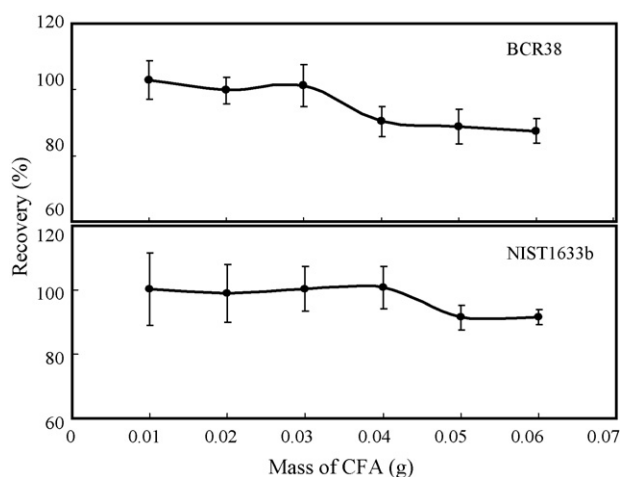


Fig. 6. Effect of the mass of CFA upon the recovery of Hg.

a large mass of CFA sample may be ascribed to the shortage of combustion agent and oxygen.

In conclusion, the optimum conditions are as follows. Powdered ash or soil (0.01–0.03 g) with 0.05 g Hg-free graphite is mixed and transferred into two pieces of bag oblate, and combusted in a 500 ml oxygen flask, in which 5 ml of KMnO_4 and H_2SO_4 solution is placed as an absorbent. The Hg^{2+} ion in the resulting solution after the OFC combustion is measured by CVAFS.

3.2. Application of OFC method to the determination of Hg in CFA, WIA, and soil

By use of the optimum conditions described above, six certified reference materials of CFA and soil (GBW08401, BCR38, NIST1633b, NIST2709, NIST2710, and NIST2711) were tested to determine Hg using the OFC method followed by CVAFS. As shown in Fig. 7, satisfactory recoveries are obtained for all of the six certified reference materials. It is proved that the OFC method can be favorably applied to the determination of Hg in CFA and soil samples.

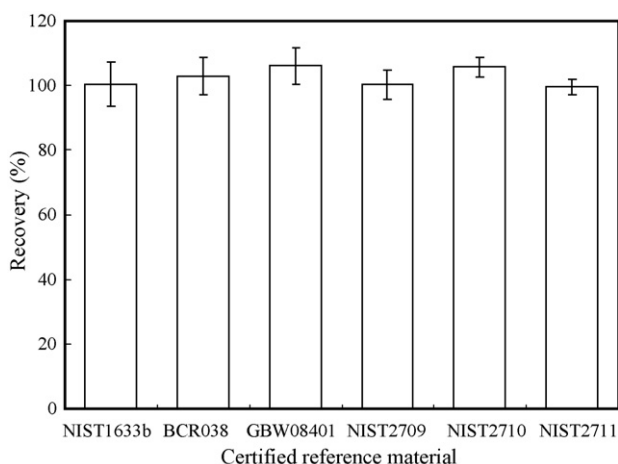


Fig. 7. Determination of Hg in certified reference materials of CFA and soil.

Table 2

Determination of Hg in real samples (CFA, WIA, and soil) by the OFC method and the MW-AD method

Sample	Hg content ($\mu\text{g g}^{-1}$)	
	OFC method	MW-AD method
CFA1	0.146 ± 0.011	0.142 ± 0.015
CFA2	0.484 ± 0.016	0.502 ± 0.025
CFA3	0.454 ± 0.022	0.443 ± 0.034
CFA4	0.615 ± 0.031	0.630 ± 0.042
CFA5	1.60 ± 0.07	1.58 ± 0.09
CFA6	0.204 ± 0.015	0.187 ± 0.017
CFA7	0.284 ± 0.018	0.292 ± 0.016
CFA8	0.531 ± 0.021	0.516 ± 0.027
CFA9	0.913 ± 0.054	0.892 ± 0.043
WIA1	0.117 ± 0.004	0.110 ± 0.003
WIA2	1.20 ± 0.05	1.28 ± 0.07
WIA3	4.21 ± 0.21	4.23 ± 0.35
WIA4	1.46 ± 0.11	1.41 ± 0.07
WIA5	3.51 ± 0.20	3.63 ± 0.25
Soil 1	0.149 ± 0.005	0.152 ± 0.009
Soil 2	0.104 ± 0.004	0.102 ± 0.012

In addition, real samples including nine CFAs, five WIAs, and two soils were analyzed by the OFC method followed by CVAFS. For those samples, the determination of Hg was also done by the authentic MW-AD method followed by CVAFS. The results are listed in Table 2. The Hg contents in the samples obtained by the two methods are about the same, suggesting that the OFC method can be favorably applied to the real samples. Also, it is demonstrated that the OFC method effectively works not only for CFA and soil samples but also for WIA samples.

4. Conclusion

A simple method of the OFC method followed by CVAFS was investigated for the determination of Hg in ash and soil samples. The Hg concentration in blank solution was successfully reduced by use of Hg-free graphite (combustion agent) and a bag oblate (wrapping material). By use of six certified reference materials, it was proved that the proposed method was favorably applied to the determination of Hg in CFA and soil. In addition, the comparison between the OFC method and the authentic MW-AD method provided a good agreement in the values of Hg contents in real samples including CFA and WIA.

References

- [1] L.B. Clarke, L.L. Sloss, Trace Elements-emissions From Coal Combustion and Gasification, IEACR/49, IEA Coal Research, London, 1992.
- [2] Y.E. Yudovich, M.P. Ketris, Mercury in coal: a review. Part 2. Coal use and environmental problems, *Int. J. Coal Geol.* 62 (2005) 135–165.
- [3] C.T. Costley, K.F. Mossop, J.R. Dean, L.M. Gargen, J. Marshall, J. Carroll, Determination of mercury in environmental and biological samples using pyrolysis atomic absorption spectrometry with gold amalgamation, *Anal. Chim. Acta* 405 (2000) 179–183.
- [4] S.J. Christopher, Development of isotope dilution cold vapor inductively coupled plasma mass spectrometry and its application to the certification of mercury in NIST standard reference materials, *Anal. Chem.* 73 (2001) 2190–2199.
- [5] S. Melaku, I. Gelaude, F. Vanhaecke, L. Moens, R. Dams, Comparison of pyrolysis and microwave acid digestion techniques for the determination of

- mercury in biological and environmental materials, *Microchim. Acta* 142 (2003) 7–12.
- [6] P. Borda, Determination of sulphur in organometallic compounds by the oxygen flask method, *Anal. Chim. Acta* 196 (1987) 355–357.
- [7] T. Miyahara, F. Ogai, H. Kitamura, K. Narita, Y. Takino, T. Toyooka, Determination of fluorine in organic compounds by potentiometric titration with aluminum chloride solution combined with oxygen flask combustion, *Anal. Sci.* 14 (1998) 1145–1147.
- [8] W. Geng, T. Nakajima, H. Takanashi, A. Ohki, Determination of total fluorine in coal by use of oxygen flask combustion method with catalyst, *Fuel* 86 (2007) 715–721.
- [9] W. Geng, T. Nakajima, H. Takanashi, A. Ohki, Utilization of oxygen flask combustion method for the determination of mercury and sulfur in coal, *Fuel*, in press.
- [10] M.N. White, D.J. Lisk, Note on the determination of mercury in soil by oxygen flask combustion, *J. Assoc. Off. Anal. Chem.* 53 (1970) 530–537.
- [11] A.M. Ure, C.A. Shand, The determination of mercury in soils and related materials by cold-vapor atomic absorption spectrometry, *Anal. Chim. Acta* 72 (1974) 63–77.
- [12] A. Iwashita, T. Nakajima, H. Takanashi, A. Ohki, Y. Fujita, T. Yamashita, Effect of pretreatment conditions on the determination of major and trace elements in coal fly ash using ICP-AES, *Fuel* 85 (2006) 257–263.
- [13] A. Iwashita, S. Tanamachi, T. Nakajima, H. Takanashi, A. Ohki, Removal of mercury from coal by mild pyrolysis and leaching behavior of mercury, *Fuel* 83 (2004) 631–638.
- [14] A. Iwashita, T. Nakajima, H. Takanashi, A. Ohki, Determination of trace elements in coal and coal fly ash by joint-use of ICP-AES and atomic absorption spectrometry, *Talanta* 71 (2007) 251–257.
- [15] P. Gouverneur, W. Hoedeman, The determination of mercury in organic compounds, *Anal. Chim. Acta* 30 (1964) 519–523.
- [16] S.A. Rahim, S.W. Bishara, D. Amin, Titrimetric microdetermination of inorganic and organic mercury by amplification reactions, *Talanta* 24 (1977) 681–682.
- [17] A.C. Merdes, T.C. Keener, S.J. Khang, R.G. Jenkins, Investigation into the fate of mercury in bituminous coal during mild pyrolysis, *Fuel* 77 (1998) 1783–1792.