



Determination of total arsenic in coal and wood using oxygen flask combustion method followed by hydride generation atomic absorption spectrometry

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ABSTRACT

A simple and sensitive procedure for the determination of total arsenic in coal and wood was conducted by use of oxygen flask combustion (OFC) followed by hydride generation atomic absorption spectrometry (HGAAS). The effect of various items (composition of absorbent, standing time between the combustion and filtration, particle size and mass of sample) was investigated. Under the optimized conditions of the OFC method, nine certified reference materials were analyzed, and the values of arsenic concentration obtained by this method were in good accordance with the certified values. The limit of detection (LOD) and relative standard deviation (RSD) of the method were $0.29 \mu\text{g g}^{-1}$ and less than 8%, respectively. In addition, eight kinds of coals and four chromated copper arsenate (CCA)-treated wood wastes were analyzed by the present method, and the data were compared to those from the microwave-acid digestion (MW-AD) method. The determination of arsenic in solid samples was discussed in terms of applicable scope and concentration range of arsenic.

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1. Introduction

Arsenic is widespread in the environment at low concentrations. However, even in low concentrations, arsenic can cause serious health problems such as skin ailments, cardiovascular and neurological damage, fatal cancers, organ failure, as well as death [1,2]. In the environment, arsenic occurs from both natural and anthropogenic sources. Some organisms (especially marine organisms) naturally contain trace (but not negligible) amounts of arsenic [3]. Coal contains a trace amount of arsenic, which will be usually concentrated in ash when coal is burned [4,5]. Chromated copper arsenate (CCA) is the most common preservative chemical for woods in decks, fence posts, docks, and foundations. These CCA-treated woods have been a problem due to the toxic elements, especially arsenic, which must be managed regardless of the disposal methods [6–9]. Thus, it is very important to develop a simple method for the determination of total arsenic in these solid environmental and biological samples.

Except for a few instrumental methods, such as instrumental neutron activation analysis, the quantitative determination of trace arsenic in a solid material has been usually carried

out after the dissolution to make an aqueous solution by use of Eschka method [10,11] or microwave-acid digestion (MW-AD) [12–17]. The solution containing arsenic is analyzed by highly arsenic-sensitive analytical methods, such as graphite furnace atomic absorption spectrometry (GFAAS), hydride generation atomic absorption spectrometry (HGAAS), and inductively coupled plasma-mass spectrometry (ICP-MS). However, the Eschka method has a disadvantage of complex and time-consuming procedure. The MW-AD and related methods involve a high instrumental cost and some limitations such as the necessity of high temperatures for complete mineralization [18] and the effect of residual gaseous nitrogen oxides in digests which may decrease the arsenic signal when HGAAS is used [19]. Recently, a microwave-induced combustion method was used to digest seafood samples for arsenic analysis, but the method still involves a high instrumental cost [20].

Oxygen flask combustion (OFC) method has been popularly used to decompose organic compounds for the determination of volatile elements, such as sulfur, phosphorus, and halogens [21]. In our previous papers, we have applied the OFC method to the trace analysis of fluorine [22] and mercury [23,24] in coal, ash, and soil. The OFC method has an advantage in terms of low initial cost and easy operation compared to the Eschka method and MW-AD.

Several studies have been reported about the determination of arsenic in organic compounds, such as Arsenazo III, by use of the OFC method [25–28]. However, there have been only a few studies on the use of the OFC method for the trace analysis of arsenic. Puttemans et al. [29] reported the determination of arsenic in sam-

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Table 1
Certified reference materials.

CRMs	Certified values of arsenic ($\mu\text{g g}^{-1}$)
NIST1632c (coal)	6.18 ± 0.26^a
SARM19 (coal)	$7.0 (6.0\text{--}8.0)^b$
SARM20 (coal)	$4.7 (4.6\text{--}6.0)^b$
BCR180 (coal)	4.23 ± 0.19^c
BCR181 (coal)	27.7 ± 1.2^c
NCS DC 73348 (bush branches and leaves)	0.95 ± 0.12^c
NCS DC 73349 (bush branches and leaves)	1.25 ± 0.15^c
DOLT-3 (dogfish liver)	10.2 ± 0.5^c
TORT-2 (lobster hepatopancreas)	21.6 ± 1.8^c

^a Reference value (provided by the supplier but not certified) and standard deviation.

^b Certified value and confidence interval in parentheses.

^c Certified value and standard deviation.

ples using the OFC method followed by GFAAS; they used only one certified reference material (CRM) (orchard leaves). Consequently, for the determination of total arsenic in environmental and biological samples, application study on the utilization of OFC method is utterly inadequate.

In this study, we attempted to apply the OFC method followed by HGAAS to the trace analysis of arsenic in various solid samples. Environmental and biological samples, which include coal and CCA-treated wood, are tested. The determination of arsenic by the OFC method is discussed in terms of applicable scope and concentration range of arsenic.

2. Experimental

2.1. Samples

Nine CRMs (five coal samples, two plant samples, and two fish samples) used in this study are from National Institute of Standards & Technology, USA (NIST1632c), Community Bureau of Reference, EC (BCR: 180 and 181), SA Bureau of Standards, Republic of South Africa (SARM: 19 and 20), China National Analysis Center for Iron and Steel (NCS DC: 73348 and 73349), and National Research Council, Canada (DOLT-3 and TORT-2). The certified values of arsenic in these materials are listed in Table 1. The certified value of arsenic for NIST1632c is not provided by CRM supplier. However, the supplier gives a reference value in their information. So, we indicated the reference value in Table 1. Also, eight kinds of coals and four CCA-treated woods were tested for the arsenic determination.

2.2. Reagents

All solutions were prepared in ultra-pure water, which had been further purified from distilled water by a Milli-Q system. Hydrochloric acid (HCl) was of arsenic analysis grade (Wako, Osaka, Japan). Other chemicals were of analytical grade quality. The calibration solutions for arsenic in the range of $1.0\text{--}15.0 \mu\text{g l}^{-1}$ were prepared daily by sequential dilution of a 1000 mg l^{-1} stock solution

Table 2
Detailed conditions of HGAAS.

Hydride generation	
NaBH ₄ solution concentration	2.5% in 0.5% NaOH
NaBH ₄ solution flow rate	2.0 ml min^{-1}
KI solution concentration	30%
KI solution flow rate	2.0 ml min^{-1}
HCl solution concentration	6 mol l^{-1}
HCl solution flow rate	5 ml min^{-1}
Carrier gas flow rate	Argon, 250 ml min^{-1}
Pre-reduction	On
Atomic absorption spectrometer	
Wavelength	197.3 nm
Lamp current	12 mA
Slit	1.0 nm
Quartz tube atomizer temperature	1000°C

of arsenic(III) from sodium arsenite (NaAsO_2). The oxygen flask as well as all the containers and materials used for the arsenic determination were soaked in a solution of 3 mol l^{-1} HCl solution for at least 12 h, and then rinsed for three times with ultra-pure water prior to use. After a combustion step, the oxygen flask was cleaned in the HCl solution with ultrasonic bath for 15 min.

2.3. Procedure of OFC method and measurement

Unless otherwise indicated, the determination of total arsenic in samples was performed as follows. The procedure of OFC was essentially the same as that described in our previous papers [22–24]. A portion of sample (0.04 g) was precisely weighed, and transferred on a $40 \text{ mm} \times 40 \text{ mm}$ ash-free filter paper (Advantec, 5C). After folded into a cylindrical shape, the paper with the sample was inserted into a platinum cage attached to the flask plug, and combusted in a usual way in a 500 ml oxygen flask, in which 5 ml of an absorbent solution of 1:1 HCl had been placed and oxygen had been filled. After the combustion, the flask was shaken for 2 min and allowed to stand for 30 min. The resulting solution was filtered, and the filtrate was diluted to a fixed volume (25 ml) and analyzed for the total arsenic concentration in the solution by HGAAS (Nippon Jarrel Ash AA-890 with a flow-injection type hydride generator HYD-10) via on-line pre-reduction of arsenic(V) to arsenic(III) with a KI/HCl solution. The detailed conditions of HGAAS were shown in Table 2.

For each run, samples were prepared by the OFC method at least in triplicate, and the HGAAS of each sample was carried out twice. From these more than six measurements, the mean value and standard deviation (SD) for the arsenic concentration were obtained. A blank experiment for the OFC method was done, and it was confirmed that both the absorbent (1:1 HCl) and the combustion with the filter paper gave some response of $1.2\text{--}1.4 \mu\text{g l}^{-1}$ in the resulting solution, and the arsenic concentration in the blank solution was subtracted from the measured values.

Table 3
Microwave digestion program.

Step	Stage 1			Stage 2		
	Time (min)	Power (W)	Temp. ^a ($^\circ\text{C}$)	Time (min)	Power (W)	Temp. ^a ($^\circ\text{C}$)
1	2	250	110	5	250	130
2	1	0	110	5	400	130
3	5	250	110	5	500	130
4	5	400	110	5	600	130
5	5	500	110	15	400	130
6	20	400	110			

^a Temperature at the sleeve (outer vessel).

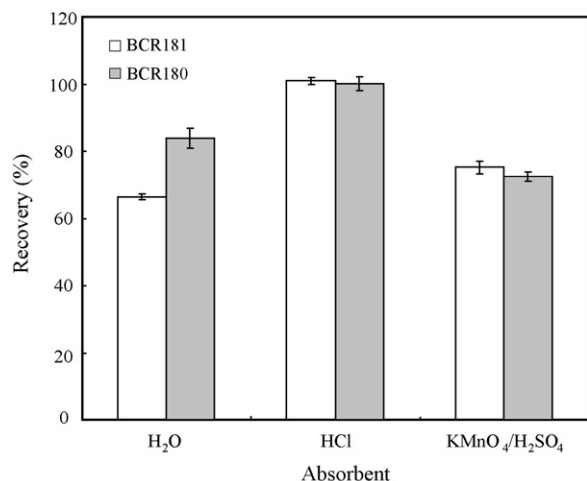


Fig. 1. Effect of the kind of absorbent upon the recovery of arsenic (BCR180 and BCR181).

2.4. Microwave-acid digestion (MW-AD)

For comparison with the data obtained from the OFC method for real coals and CCA-treated wood wastes, the MW-AD method was also carried out according to our previous papers [23,24]. The digestion program was set as listed in Table 3. Powdered sample (ca. 0.1 g) was precisely weighed and acid-digested with HNO₃ + H₂O₂ (5 + 3 ml) using a microwave processor (Milestone ETHOS1600) (Stage 1). After cooling and further addition of HNO₃ + H₂O₂ (2 + 1 ml), microwave processing was performed again (Stage 2). After cooling and filtration, the filtrate was diluted to a fixed volume (25 ml) and was subjected to HGAAS for the measurement of arsenic concentration.

3. Results and discussion

3.1. Optimization of the conditions of OFC method

Firstly, the effect of the composition of absorbent species used in the OFC method upon the recovery of arsenic was examined. Three kinds of absorbents (5 ml) were applied to the OFC method for two CRMs, BCR180 and BCR181. As shown in Fig. 1, the recoveries of arsenic for water, 1:1 HCl solution, and 0.01 M KMnO₄ solution (with 3% H₂SO₄) by the OFC method were 66–90%, ca. 100%, and 71–77%, respectively. Thus, it is confirmed that the 1:1 HCl solution is the best absorbent for the determination of arsenic.

Based on the absorbent of 5 ml 1:1 HCl solution, the effect of the standing time between the combustion and filtration upon the recovery of arsenic was examined, when a CRM, BCR180, was subjected to the OFC method. The results are presented in Fig. 2, and the standing time with the range of 5–50 min was studied. It was found that the recovery of arsenic increased with an increase in the standing time and reached to ca. 100% after 30 min, which is considered that most of arsenic in coal is set out and absorbed in the HCl solution after the OFC combustion, while a little is absorbed on the surface of the coal ash during the combustion and produces some insoluble compounds, and the dissolution of these compounds in the HCl solution would take some time. Thus, the standing time of 30 min is required for the determination of total arsenic by the OFC method.

Two CRMs, BCR180 and BCR181, whose original particle sizes were 63–212 μm (230–70 mesh), were sieved and examined for the effect of the particle size upon the recovery of arsenic. As shown in Fig. 3, when the OFC method was carried out, the particle size of less than 150 μm (100 mesh) gave a good recovery of arsenic. Thus, the particle size of less than 150 μm was used in the study.

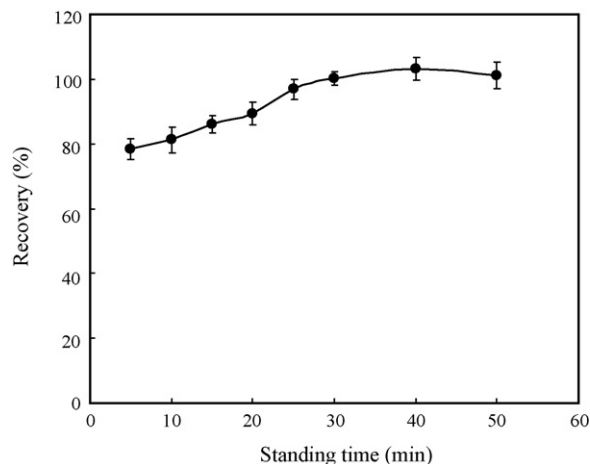


Fig. 2. Effect of the standing time between the combustion and filtration upon the recovery of arsenic (BCR180).

The effect of the mass of coal upon the recovery of arsenic was assessed, when the OFC method was carried out for a CRM, NIST1632c. It was found that the masses of 0.02–0.08 g were suitable for the determination of arsenic in coal by the OFC method in terms of the recovery and standard deviation. The somewhat low recovery observed in the case of a big mass of sample may be ascribed to the incomplete combustion of coal in the OFC method. In addition, compared with the other methods, the limited sample mass of the present method may cause the problem of heterogeneity, and thus averaging the data from multiple sampling is needed.

In conclusion, the optimum conditions of OFC method for the determination of total arsenic in a sample are as follows. A mass of sample (0.02–0.08 g) with the particle size of less than 150 μm is combusted in a 500 ml oxygen flask, in which 5 ml of 1:1 HCl solution is placed as an absorbent. Before the filtration, the standing time of 30 min is required, and the total arsenic in the solution is measured by HGAAS.

3.2. Application of OFC method to the determination of arsenic in various CRMs

By use of the optimum conditions for the OFC method followed by HGAAS, nine CRMs (NIST1632c, SARM19, SARM20, BCR180, BCR181, NCS DC 73348, NCS DC 73349, DOLT-3, and TORT-2), which

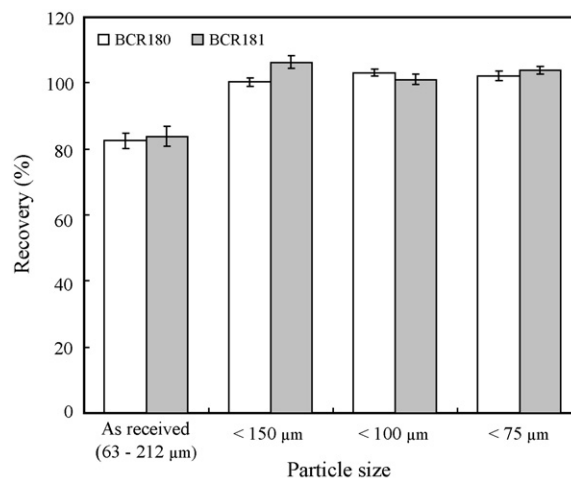


Fig. 3. Effect of the particle size of coal upon the recovery of arsenic (BCR180 and BCR181).

Table 4
Determination of arsenic in various CRMs by the OFC method.

CRMs	Measured ($\mu\text{g g}^{-1}$)	Recovery (%)	RSD (%)
NIST1632c	6.15 \pm 0.14	99.5	2.3
SARM19	6.80 \pm 0.40	97.2	5.8
SARM20	4.69 \pm 0.06	99.8	1.3
BCR180	4.24 \pm 0.09	100.2	2.1
BCR181	28.0 \pm 0.5	101.1	1.8
NCS DC 73348	0.97 \pm 0.07	102.1	7.2
NCS DC 73349	1.28 \pm 0.10	102.4	7.8
DOLT-3	10.5 \pm 0.5	102.9	4.8
TORT-2	20.8 \pm 0.9	96.3	4.3

include coals, plants, and marine organisms (Table 1), were tested for the determination of arsenic. Table 4 presents the arsenic concentration and the recovery for these CRMs obtained by the present method, which were in good agreement with the certified values. The limit of detection (LOD) was calculated as the concentration equal to three times the standard deviation of the background signal (the signal obtained by blank experiments). The relative standard deviation (RSD) was less than 8%. It is proved that the OFC method can be favorably applied to the determination of total arsenic in solid environmental and biological samples.

3.3. Application of OFC method to the determination of arsenic in various coals and CCA-treated woods

Real coal samples, which are used in power plants and industries in Japan, were tested. Eight kinds of coals were subjected to the OFC method followed by HGAAS, and the arsenic concentrations obtained are indicated in Table 5. The arsenic concentrations in these coal samples varied from 0.49 to 3.61 $\mu\text{g g}^{-1}$. The same samples were subjected to the MW-AD method followed by HGAAS, and the results are also recorded in Table 5. The values of arsenic concentration obtained from the OFC method are very consistent with those measured by the MW-AD method, and it is proved that the present method can give the same accuracy compared with the MW-AD method for coal samples.

Consequently, it has been proved that the OFC method is useful for environmental and biological samples, which contain trace amount of arsenic (0.5–28 $\mu\text{g g}^{-1}$). Sometimes, environmental and biological samples contain high amount of arsenic, which is mainly by artificial cause. CCA-treated wood wastes are the typical example for this. Therefore, we attempted to apply the OFC method to the samples of CCA-treated wood waste. Table 5 also shows the results, which are compatible with those obtained by the MW-AD method. Therefore, it is evident that the OFC method works well not only for trace amount of arsenic but also for relatively high amount of arsenic (over 12 mg g^{-1}).

Table 5
Determination of arsenic in various coals and CCA-treated woods by the OFC method and MW-AD method.

Sample	Arsenic concentration ($\mu\text{g g}^{-1}$)	
	OFC	MW-AD
Coal1	0.66 \pm 0.05	0.70 \pm 0.07
Coal2	0.49 \pm 0.03	0.45 \pm 0.04
Coal3	2.05 \pm 0.10	1.99 \pm 0.08
Coal4	3.61 \pm 0.18	3.53 \pm 0.23
Coal5	1.63 \pm 0.07	1.68 \pm 0.05
Coal6	0.54 \pm 0.05	0.56 \pm 0.04
Coal7	1.55 \pm 0.06	1.66 \pm 0.09
Coal8	0.62 \pm 0.07	0.59 \pm 0.10
Wood1	1150 \pm 30	1200 \pm 30
Wood2	1080 \pm 50	1100 \pm 10
Wood3	2280 \pm 40	2220 \pm 30
Wood4	12400 \pm 100	12500 \pm 200

4. Conclusion

The OFC method followed by HGAAS was investigated for the determination of total arsenic in coal and CCA-treated wood. The effect of various items (composition of absorbent, standing time between the combustion and filtration, particle size and mass of sample) was examined, and the optimized conditions for the OFC method were established. It has been proved that the OFC method can give satisfied results in terms of the recovery of arsenic by use of CRMs as well as real samples for which the MW-AD method was also done. The present method can be applied to coal, CCA-treated wood, and other biological samples, such as plants and marine organisms. The limit of detection (LOD) and relative standard deviation (RSD) of the method were 0.29 $\mu\text{g g}^{-1}$ and less than 8%, respectively. The applicable range of arsenic contained in a sample for the present method was 0.5–12,000 $\mu\text{g g}^{-1}$.

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