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Determination of mercury in various coals from different countries by heat-vaporization atomic absorption spectrometry: Influence of particle size distribution of coal

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ABSTRACT

Fifty-one kinds of coals, which are practically used in Japanese power plants and industries, were analyzed for Hg by an automatic mercury analyzer (AMA) based on an official method (heat vaporization atomic absorption spectrometry). Almost all coals were imported coals from various countries. These coals are supplied in a powdery form as standard samples by a Japanese organization and called "SS-coals". Since the sample amount of coal used in the AMA measurement is usually small, the particle size of coal may greatly affect the measurement, however there have been no systematic studies on the matter. Some of the SS-coals, which were much finer than frequently-used certified reference materials (NIST SRM coals), showed a great deviation in data (relative standard deviation (RSD) is high) in the determination of Hg. The SS-coals were ground further into fine powder, and the resulting coals (ground SS-coals) gave lower RSD values. The mean values of Hg content when the as-received SS-coals were measured many times (more than six runs) became about the same as those for the ground SS-coals. The deviation in data in the Hg determination was discussed with the possibility of localization of Hg in coal body at a microscopic level. The content of Hg in coal (bituminous coals) correlated not with that of sulfur (or pyritic sulfur) but with that of ash. Also, it was found that the coals of high inherent moisture exclusively had low Hg contents.

1. Introduction

Mercury (Hg) is a very toxic element, and hence its water quality standard for drinking water is the lowest among toxic heavy metals (0.5 ng/L in Japan). Recently, there has been growing interest in the presence of Hg in coal because of its high toxicity as well as high volatility. A significant portion of Hg in coal is released into the atmosphere during combustion, which is recognized as the main anthropogenic source of the element. Therefore, there have been many studies on the presence of Hg in coal in terms of analysis, emission behavior, and the control of emission [1–8].

For the determination of Hg in coal, there are some official methods, such as ISO 15237:2003, JIS M 8821:2002, and US EPA 7473:2007. Nowadays, the use of automatic mercury analyzer (AMA) based on heat vaporization method, which is described in the official methods (JIS and US EPA), is the most popular [5]. Many researchers have determined Hg in coal with the aid of AMA [9–14]. The AMA measurement has a great advantage compared to the conventional manual-type methods especially in terms of easiness. For the AMA measurement, a small sample amount (50–100 mg) is recommended, mainly due to the elimination of contamination for Hg and coexisting other elements, such as sulfur, in the instruments.

It has been reported that the determination of Hg in coal sometimes involves a certain deviation in data, which is not dependent on the kind of analytical method [15,16]. Probably, such a deviation is caused by the localization of Hg in coal at a microscopic level. Especially for the AMA measurement, the localization of Hg in coal will greatly affect the accuracy of data, because the sample amount is small. It is difficult to sufficiently pulverize coals, and the ease of pulverization is greatly dependent on the kind of coals, especially when coals are varied worldwide. So far, there have been no systematic studies on the influence of the particle size of coal on the accuracy of data when the AMA measurement is performed.

Japan is the world's leading importer of coal, and the percentage of world trade for coal concerning Japan is ca. 20%. Japan mainly imports bituminous coals with relatively low sulfur content from various countries in the world (Australia, China, Indonesia, USA, Canada, South Africa, etc.) and therefore various coals from different countries are used in Japanese power plants and industries. The Japan Coal Energy Center (JCOAL) and the National Institute of Advanced Industrial Sciences and Technology (AIST) are in charge of supplying standard samples of more than a hundred kinds of coals consumed in Japan with data on proximate analysis (JIS M 8812), ultimate analysis (JIS M

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8813), and the analyses of ash components (JIS M 8815), although those samples do not have data about trace elements, such as Hg. This system is called the "Coal Sample Bank", and the standard samples are named "SS-coals" with a sequential number, such as SS001. The coal samples are prepared by the same grinding process and supplied as a fine powder, which are placed in a laminate package filled with nitrogen. The homogeneity of samples is guaranteed by the suppliers as far as the analytical data provided from the suppliers above-mentioned are concerned. This kind of sample bank system should be the first attempt for various coals from different countries.

In this study, fifty-one kinds of SS-coals (SS020–070), which vary according to the producing country, were analyzed for Hg by AMA. Although it is difficult to collect many kinds of coals from different countries, the sample bank system (SS-coals) enables us to analyze such coals in the same laboratory. Since it was found that some of the coals showed a remarkable deviation in data in the determination of Hg, the influence of the particle size of coal upon the accuracy of data was investigated. Moreover, the relationship between the Hg content in coal and various coal properties was investigated.

2. Experimental

2.1. Samples and reagents

Four certified reference materials of coal, NIST SRM 1632c and 1632d (National Institute of Standards and Technology, USA), SARM 19 (SA Bureau of Standards, Republic of South Africa), and BCR 181 (Community Bureau of Reference, EC) were used. Fifty-one kinds of SS coals were obtained from the AIST. The SS coals were supplied with the data of proximate analysis (JIS M 8812) and ultimate analysis (JIS M 8813), and those data are listed in Table 1. The contents of some major inorganic

Table 1
Proximate analysis and ultimate analysis of SS coals.

Coal (country)	Proximate analysis (wt.%, as-received)				Ultimate analysis (wt.%, dry)				
	Inherent moisture	Ash	Volatile matter	Fixed carbon	C	H	N	S	O
SS020 (ZAF)	3.5	12.9	30.9	52.7	71.1	4.2	1.8	0.7	8.9
SS021 (ZAF)	2.4	14.4	24.1	59.1	71.9	4.0	1.7	0.4	7.3
SS022 (ZAF)	2.8	13.7	26.4	57.1	71.6	4.1	1.7	0.5	7.9
SS023 (USA)	4.2	6.8	41.5	47.5	73.5	5.3	1.5	0.4	12.2
SS024 (USA)	4.7	7.1	38.1	50.1	72.7	5.4	1.6	0.4	12.5
SS025 (USA)	4.7	7.9	37.8	49.7	72.0	5.4	1.6	0.6	12.3
SS026 (USA)	10.1	12.5	34.7	42.6	66.2	5.0	1.2	0.3	13.5
SS027 (CHN)	5.2	10.2	27.7	56.9	71.9	4.4	0.9	0.6	11.4
SS028 (AUS)	5.2	8.0	26.8	60.1	74.0	4.4	1.7	0.3	11.2
SS029 (JPN)	5.6	11.4	43.4	39.7	67.3	5.6	1.1	0.1	13.9
SS030 (JPN)	1.7	19.4	37.3	41.5	64.8	5.0	1.1	2.0	7.5
SS031 (CAN)	5.6	10.8	32.2	51.4	68.6	4.9	0.9	0.1	14.0
SS032 (AUS)	2.7	11.8	30.8	54.7	72.1	5.4	1.6	0.4	8.4
SS033 (IDN)	10.8	0.9	43.6	44.7	72.0	5.3	1.0	0.1	20.6
SS034 (IDN)	2.9	8.7	43.3	45.2	71.3	6.2	1.2	0.7	11.7
SS035 (AUS)	1.2	14.5	18.3	65.9	75.3	4.4	1.4	0.4	3.8
SS036 (AUS)	1.2	22.2	19.2	57.8	67.5	4.2	1.3	0.4	4.3
SS037 (CHN)	1.6	16.5	8.5	73.4	75.4	3.5	1.1	0.3	2.9
SS038 (COL)	4.6	0.9	39.0	55.5	80.2	5.7	1.6	0.5	11.1
SS039 (CAN)	9.2	12.0	35.1	43.7	64.8	4.8	1.4	0.2	15.5
SS040 (IDN)	5.5	7.5	43.6	43.5	71.0	5.8	1.2	0.6	13.5
SS041 (IDN)	5.0	1.4	41.3	52.3	76.9	5.7	1.6	0.4	13.9
SS042 (AUS)	2.6	10.9	31.5	55.0	73.3	4.8	1.7	0.6	8.5
SS043 (USA)	7.8	6.1	35.9	50.3	71.0	5.0	1.4	0.3	15.8
SS044 (JPN)	2.3	22.9	34.3	40.6	61.5	4.9	1.1	0.5	8.5
SS045 (JPN)	2.7	37.7	28.5	31.2	48.6	4.0	0.9	0.8	7.1
SS046 (ZAF)	2.4	10.3	31.2	56.2	73.0	4.5	1.8	0.4	9.7
SS047 (USA)	2.0	8.9	40.2	48.9	72.8	5.4	1.4	0.2	11.2
SS048 (AUS)	1.4	15.7	29.0	53.9	70.6	4.6	1.6	0.6	6.6
SS049 (ZAF)	2.0	13.2	25.0	59.8	71.2	4.0	1.8	0.3	9.2
SS050 (AUS)	1.9	14.2	29.9	54.0	70.8	4.6	1.6	0.5	8.1
SS051 (USA)	2.7	9.2	39.5	48.6	73.4	5.4	1.4	0.6	9.8
SS052 (AUS)	3.6	10.5	33.5	52.5	73.0	4.9	2.0	0.4	8.9
SS053 (AUS)	2.2	12.1	33.7	51.9	73.5	5.1	1.7	0.5	6.8
SS054 (AUS)	2.2	11.1	32.5	54.2	74.2	4.9	1.6	0.4	7.6
SS055 (IDN)	6.0	4.2	41.8	48.0	74.4	5.5	1.6	0.8	13.3
SS056 (CHN)	0.9	18.3	10.5	70.2	73.3	3.4	1.2	0.3	3.2
SS057 (CHN)	2.3	10.9	32.9	53.9	74.1	4.8	1.4	0.5	8.0
SS058 (CHN)	2.6	10.8	33.1	53.6	73.6	4.8	1.4	0.4	8.8
SS059 (AUS)	3.6	11.1	26.5	58.7	74.8	4.4	1.7	0.6	6.9
SS060 (AUS)	2.3	12.3	29.2	56.2	74.0	4.7	1.6	0.4	6.7
SS061 (USA)	5.7	7.0	40.6	46.7	74.2	5.2	1.3	0.2	11.6
SS062 (CHN)	8.7	4.9	33.5	52.8	76.2	4.7	0.9	0.2	12.6
SS063 (AUS)	1.6	13.0	27.3	58.1	73.7	4.6	1.6	0.3	6.7
SS064 (CHN)	1.5	14.3	18.3	65.9	75.5	4.0	1.3	0.3	4.5
SS065 (CHN)	9.2	5.9	31.4	53.5	75.7	4.4	1.0	0.2	12.3
SS066 (IDN)	6.0	1.8	42.4	49.9	78.4	5.6	1.7	0.3	12.2
SS067 (CHN)	1.7	14.3	16.1	67.9	76.5	3.9	1.3	0.1	3.6
SS068 (VYN)	1.4	4.6	6.4	87.6	89.2	3.2	1.0	0.5	1.5
SS069 (IDN)	16.9	4.0	39.7	39.5	71.3	5.3	1.1	0.6	17.0
SS070 (IDN)	13.6	5.3	39.9	41.2	69.9	5.0	1.4	0.1	17.5