

# The method of determination of mercury adsorption from flue gases

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**Abstract.** For several recent years Faculty of Energy and Fuels of the AGH University of Science and Technology in Krakow conduct intensive studies on the occurrence of mercury contained in thermal and coking coals, as well as on the possible reduction of fossil-fuel mercury emissions. This research focuses, among others, on application of sorbents for removal of mercury from flue gases. In this paper we present the methodology for testing mercury adsorption using various types of sorbents, in laboratory conditions. Our model assumes burning a coal sample, with a specific mercury content, in a strictly determined time period and temperature conditions, oxygen or air flow rates, and the flow of flue gases through sorbent in a specific temperature. It was developed for particular projects concerning the possibilities of applying different sorbents to remove mercury from flue gases. Test stand itself is composed of a vertical pipe furnace inside which a quartz tube was mounted for sample burning purposes. At the furnace outlet, there is a heated glass vessel with a sorbent sample through which flue gases are passing. Furnace allows burning at a defined temperature. The exhaust gas flow path is heated to prevent condensation of the mercury vapor prior to contact with a sorbent. The sorbent container is positioned in the heating element, with controlled and stabilized temperature, which allows for testing mercury sorption in various temperatures. Determination of mercury content is determined before (coal and sorbent), as well as after the process (sorbent and ash). The mercury balance is calculated based on the Hg content determination results. This testing method allows to study sorbent efficiency, depending on sorption temperature, sorbent grain size, and flue-gas rates.

## 1 Introduction

Thermal coal combustion is one of the major sources of anthropogenic mercury emission to the atmosphere. In Poland, this is the dominant source with annual share of approximately 56% [1], which amounts to 5 700 kg of emitted mercury per year. In Polish power plants flue gases leaving boiler are treated in a following manner. Fly ash is removed using electrostatic precipitators (ESPs), fabric filters, or in a lesser extent, cyclone separators. Sulfur oxides are

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removed using wet and semi-dry installations. Nitrous oxides are removed either by catalytic or by non-catalytic reduction [2]. Depending on mercury content in coal, its chemical composition, type of boiler, combustion conditions, and flue gases treatment installation, the mercury content in gases released to the atmosphere varies from 1 µg/Nm<sup>3</sup> to even 30 µg/Nm<sup>3</sup> [1, 3]. Combination of high mercury content in coal, unfavorable elemental composition (low chlorine, bromine and iron content, high calcium content), requires, in addition to passive methods, usage of additional technologies reducing mercury emission (so called ‘active methods’) [4, 5]. Potentially the Best Available Techniques (BATs) include: injection of pulverized activated coal into flue gases, adsorption on immobilized activated carbon bead, and usage of sulfur-impregnated sorbents. Reduction of mercury emission can be achieved by selection of coals to be combusted, its physical enrichment, mild pyrolysis, as well as combustion in fluidized bed [5].

One of the methods with highest efficiency, which is widely used in USA, is an injection of pulverized activated carbons into flue gases. These activated carbons are often modified to facilitate mercury removal [5, 6]. Although adsorptive methods are highly efficient, their cost is very high, reaching from 40 to 90 thousand USD per 1 kg of mercury removed. This cost can be decreased by usage of cheaper sorbents like selected fractions of coke dust, especially those acquired from coke dry cooling installations [7]. The first step to determine if a given sorbent is suitable for mercury removal from flue gases, is a laboratory test. This enables precise evaluation of efficiency of mercury removal from specified flue gases by a given sorbent. Such evaluation can be achieved by measuring mercury content in gases before and after sorbent treatment. However, such measurements on laboratory scale encounter several problems, which can significantly reduce reliability of the results. Because of that, the mercury balance for measuring system is more reliable method of mercury removal assessment in laboratory scale experiments.

For recent years Faculty of Energy & Fuels is performing research on mercury occurrence in coals as well as on technologies reducing mercury emission to the atmosphere. Within this research lot of effort is made to use pulverized and granulated cheap sorbents to remove mercury from gaseous phase. In this paper, several methods of laboratory scale mercury adsorption measurements were presented. Calculations of efficiency of mercury removal were based on mercury balance and not on direct measurements conducted before and after adsorption.

## 2 Experimental

### 2.1 Sorbents

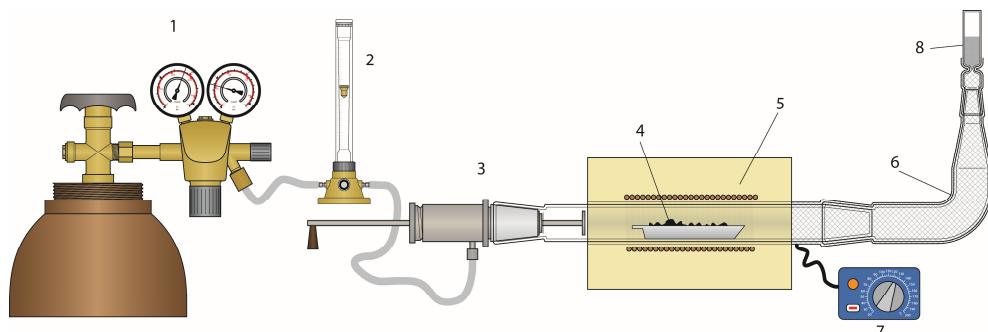
Within the scope of research three types of sorbents were analyzed: mineral (A), organic-waste product from energo-chemical coal processing (B), and organic-produced during waste pyrolysis (C). Properties of these sorbents were presented in Table 1.

**Table 1.** Properties of studied sorbents.

Parameter	Unit	Sorbent		
		A	B	C
Carbon content	%	0.1	87.2	78.0
Sulfur content	%	< LOQ	0.59	2.64
Specific Surface area SBET	m <sup>2</sup> /g	34.5	16.5	74.7
Total pore volume (<300 nm)	cm <sup>3</sup> /g	0.135	0.018	0.0239
Density	g/cm <sup>3</sup>	2.16	1.99	no data

## 2.2 Measuring system

Figure 1 presents scheme of a test stand for measuring mercury sorption from flue gases from solid fuel combustion. It consists of tube furnace with temperature regulation, quartz combustion pipe, gas cylinder, flowmeter and sorbent containing container. Temperature of flue gases can be controlled between quartz tube outlet and combustion pipe. The fuel sample is combusted in flow of air or oxygen, and flue gases are directed through the sorbent container. Subsequently, the amount of absorbed mercury is measured. Analysis is performed in defined, controlled conditions which include: temperature and time of combustion, temperature of flue gases going through the sorbent, and flow rate. The fuel sample is inserted in a small ceramic container, which is gradually transferred into the area of highest temperature. Combustion time in this area is 10 min. Single fuel sample input is around 1 g. During single experiment it is possible to combust several portions of fuel, the amount of which depends on mercury content. The sorbent container is located inside a heating element, which allows stabilization of sorbents temperature during the measurement. This allows simulation of industrial conditions as well as analyzing mercury sorption in different temperatures. Sorbent mass, which is determined mainly by its density and granulation, varies between 1 g and 4 g. Before the procedure, mercury content is measured in both fuel and sorbent according to methods described in section 2.3. After the procedure, mercury content is analyzed in ash as well as in sorbent.



**Fig. 1.** Scheme of a test stand. 1- source of oxidizer, 2- rotameter, 3- oxidizer supply system, 4 – coal sample, 5 – tube furnace, 6 – heated flue gases stream, 7 – temperature regulator, 8 – sorbent bed.

In all instances experimental conditions and the coal used were the same (see table 2).

**Table 2.** Experimental conditions.

Parameter	Description
Fuel	lignite
Combustion temperature	850°C
Flue gases flow rate	5 cm <sup>3</sup> /s
Combustion time	10 min
Mass of the sorbent	1 g

## 2.3 Mercury content analysis

The content of mercury in samples of coal, sorbent and ash was measured using atomic absorption spectrometry with cold vapor atomization (CV-AAS) method on automatic

mercury analyzer MA-3000 (Nippon Instruments Corporation). Sample mass was between 50.0 and 52.5 mg, with analytical granulation of 0.2 mm. Program for subbituminous coal samples was used. Briefly, sample was heated for 2 min at 180°C, then heated for 7 minutes at 850°C. Subsequently, mercury vapors were reduced to elemental form ( $Hg^0$ ), which was captured in amalgam by gold covered sand bed. After the sample was decomposed the amalgam was heated to approximately 700°C. Released mercury vapors were directed into cuvette and measured with UV light at 253.7 nm. The final result was a mean from three to five analysis for the same samples. When standard deviation exceeded 10%, additional measurements were performed.

## 2.4 Comparison with other methods

Other analytical methods for mercury content determination are presented in many publications [8-19]. They are based on the following detection methods:

- atomic absorption spectrometry (AAS) – this method draws upon a high vapour pressure of Hg at relatively low temperatures. A very often used technique is cold-vapour atomic absorption spectrometry,
- atomic fluorescence spectrometry (AFS) – initially, atomic fluorescence spectrometry with flame atomization was used, further modifications included electrothermal atomization and cold-vapour method,
- atomic emission spectrometry (AES) – traditional induction methods such as flame induction or arc discharge are replaced with DC-induced plasma, radio frequency-induced plasma and microwave-induced plasma,
- mass spectrometry (MS) – first applications of MS for determining the mercury content appeared as a variation of method based on spark ionization (Spark Source – SS-MS). Coupling MS with inductively-coupled-plasma (ICP-MS) found a much more applications,
- UV-visible spectrophotometry (Colorimetry) – this had been a popular method of total mercury determination until 1960s when the AAS method was introduced,
- neutron activation analysis (NAA) – main advantages of this method are short analysis time, non-destructive analysis, large sensitivity and precision,
- X-ray fluorescence spectrometry (XRD) – the main advantages are the same as in case of NAA. Additionally it allows for testing many elements simultaneously,
- electron-capture detection spectrometry (ECD) – this method is widely used for determining organic mercury compounds. Its main advantage is a possibility of methylmercury immediate determination without need of turning it into volatile form.

Table 3 presents detection limit of selected methods of the mercury determination.

**Table 3.** Detection limit of selected methods of the mercury determination. [9, 12, 14, 15, 17, 18]

Methods	Detection limit ng
Atomic absorption spectrometry	0.1
Atomic emission spectrometry	0.005
Mass spectrometry	0.005
Colorimetry	100
Neutron activation analysis	0.01
X-ray fluorescence spectrometry	~25
Electron-capture detection spectrometry	0.5

## 2.5 Calculating the balance

The above mentioned method allows for preparation of mercury balance through analysis of mercury distribution between combustion products and sorbent. The following data is required for calculating the balance:

- mass of mercury in fuel ( $C$ ),
- mass of mercury in sorbent before analysis ( $S_B$ ),
- mass of mercury in sorbent after analysis ( $S_A$ ),
- mass of mercury in ash ( $A$ ).

Thus the efficiency of mercury removal using given sorbent was calculated according to formula (1):

$$\eta = \frac{S_A - S_B}{C - A} \cdot 100\% \quad (1)$$

## 3 Results and discussion

### 3.1 Validation of mercury content determination

Table 4 presents results of validation of method in terms of CV-AAS method accuracy. Table 5 presents summary of validation of mercury content determination method in terms of repeatability and reproducibility for coal samples.

**Table 4.** Results of validation of mercury content determination accuracy.

Parameter	Certified Reference Material (CRM)		
	SRM 2693	LECO 502-680	SRM 2692c
Nominal value [ppb]	37.3	110	179.0
Extended uncertainty [ppb]	7.7	11	6.9
Number of repetition CRM	6	6	6
Mean value [ppb]	38.7	112.3	185.8
Standard deviation SD [ppb]	3.5	3.3	4.7
Variation coefficient CV [%]	9.0	2.9	2.5
Range of results [ppb]	8.0	6.8	10.8
Methods accurate	YES	YES	YES

**Table 5.** Summary of validation of mercury content determination method in terms of repeatability and reproducibility for coal samples (number of repetitions = 6).

Sample number	Mean [ppb]	SD <sub>r</sub> [ppb]	CV <sub>r</sub> [%]	SD <sub>R</sub> [ppb]	CV <sub>R</sub> [%]
1	28.7	3.3	11.4	4.1	14.3
2	41.0	2.1	5.1	2.7	6.6
3	49.9	2.3	4.6	2.9	5.8
4	67.2	2.9	4.3	3.7	5.5
5	106.2	7.3	6.9	9.1	8.6
6	138.8	3.6	20.6	5.2	3.7
7	153.6	8.0	5.2	10.7	7.0
8	195.5	16.6	8.5	26.6	13.6
9	330.3	11.5	3.5	15.2	4.6

Where: SD – standard deviation, CV – variation coefficient, indexes: r – repeatability, R – reproducibility.

Table 6 presents additional parameters of mercury determination method acquired during validation.

**Table 6.** Parameters of mercury content determination method.

Parameter	Value
Detection limit [ng]	0.002
Quantification limit [ng]	0.006
Range of application [ng]	0.006–20
Linearity ( <i>r</i> coefficient)	0.9999
Extended uncertainty (relative) [%]; depending on range	3.0–10.0

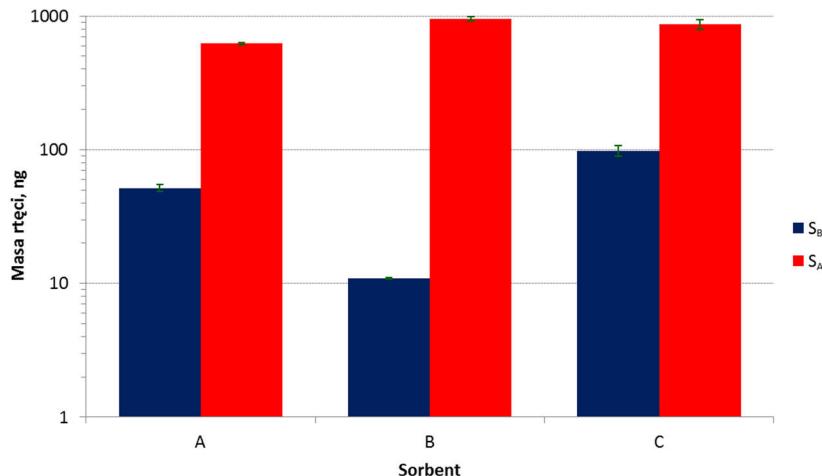
The full validation performed for CV-AAS method showed that:

- (i) method is accurate for coal samples with mercury content between 30 and 330 ppb,
- (ii) repeatability and reproducibility of the method are acceptable,
- (iii) method extended uncertainty fits between 3 and 10%, depending on range,
- (iv) method quantification limit is 0.006 ng of mercury,
- (v) method is highly linear.

To sum up, performed validation confirmed that the CV-AAS method using MA-3000 automated mercury analyzer is useful for determining mercury content in coal samples.

### 3.2 Sorbents analysis

Figure 2 presents mercury content in sorbent before and after experiment.



**Fig. 2.** Mass of mercury in sorbents before ( $S_B$ ), and after ( $S_A$ ) experiment

For calculations it was assumed that all mercury in coal is transferred to combustion products (ash and flue gases), and subsequently it is transferred to sorbents bed. This assumption is fulfilled because of tightness of installation and forced flow of oxidizer and flue gases. Values of mercury removal efficiency are presented in Table 7.

**Table 7.** Efficiency of mercury removal for tested sorbents. [%]

Sorbent	Mercury efficiency removal
A	43.5
B	85.1
C	68.3

## 4 Conclusions

During presented study the main challenge was determination of mercury content in analyzed samples. Most of presently used methods use different variants of atomic spectrometry, mass spectrometry, or fluorescence spectroscopy [19]. In presented system scope of analysis was reduced to mercury content in solid matrix (coal sample, ash, and sorbent). Determination of mercury content in solid phase is easier than in gaseous phase, because it lacks complications resulting from condensation during flue gases cooling, mercury speciation, and high dust level present in industrial installations.

Presented laboratory test stand for studying mercury sorption enables:

- (i) analysis of mercury distribution between fuel, combustion products and ash, without need for troublesome measurements of mercury content in gaseous phase,
- (ii) analysis of sorbents efficiency based on mercury balance,
- (iii) analysis of influence of sorbents temperature on mercury sorption,
- (iv) analysis of sorbents granulation on mercury sorption,
- (v) analysis of gas flow rate on mercury sorption.

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## References

1. P. Burmistrz, K. Kogut, M. Marczak, J. Zwoździak, Fuel Process. Technol. **152** 250-258 (2016).
2. J. Zyśk, A. Wyrwa, M. Pluta, Atmos. Environ. **45** 605-610 (2011).
3. S.X. Wang, L. Zhang, G.H. Li, Y. Wu, J.M. Hao, N. Pirrone, F. Sprovieri, M.P. Ancora, Atmos. Chem. Phys. **10** 1183-1192 (2010).
4. J.H. Pavlish, L.L. Hamre, Y. Zhuang, Fuel **89** 838-847 (2010).
5. H. Clack: *Methods for reducing mercury emission from coal combustion.* [in:] *Mercury as a coal combustion pollutant*, 105-120, (Oficyna Drukarska Jacek Chmielewski, Warszawa, 2014).
6. E.S. Olson, A. Azenkeng, J.D. Laumb, R.R. Jensen, S.A. Benson, M.R. Hoffmann, Fuel Process. Technol. **90** 1360-1363 (2009).
7. P. Burmistrz, L. Czepirski, K. Kogut, A. Strugała, Przem. Chem. **93** No. 12 (2015), 1-6.
8. B. Welz, M. Schubert-Jacobs, Frasenius J Anal. Chem. **331** 324-329 (1988).
9. A. Urba, K. Kvietkus, J. Sakalys, Z. Xiao, O. Lindqvist, Water, Air, Soil Pollut. **80** 1305-1309 (1995).
10. R.L. Lancione, D.M. Drew, Spectrochim. Acta B **40** 107-113 (1985).
11. R.I. Pereiro, C.A. Diaz, Anal. Bioanal. Chem. **372** 74-90 (2002).
12. C. Dietz, Y. Madrid, C. Camara, J. Anal. At. Spectrom. **16** 1397-1402 (2001).
13. E. Björn, T. Larsson, L. Lambertsson, U. Skyllberg, W. Frech, Ambio **36** 443-451 (2007).
14. National Institute for Minamata Disease, *Research on Mercury. Development in Mercury Analysis*, [http://www.nimd.go.jp/archives/english/tenji/c\\_corner/c07.html](http://www.nimd.go.jp/archives/english/tenji/c_corner/c07.html) (access at: 2016.09.26).
15. P. Jones, S. Hardy, J. Chromatogr. A **765** 345-352 (1997).
16. Annual Report of Institute of High Energy Physics, *Study of Chemical Species with Nuclear Analytical Techniques*, Chinese Academy of Sciences 109-122, (2001).
17. I.N. Aretaki, P. Koulouridakis, N. Kallithrakas-Kontos, Anal. Chim. Acta **562** 252-257 (2006).
18. A.M. Caricchia, G. Minervini, P. Soldati, S. Chiavarini, C. Ubaldi, R. Morabito, Microchem. J. **55** 44-55 (1997).
19. M. Macherzyński, J. Górecki, K. Styszko: *Chemical analysis of mercury and its compounds.* [in:] *Mercury as a coal combustion pollutant*, 105-120, (Oficyna Drukarska Jacek Chmielewski, Warszawa, 2014).