Short communication

ISSN 2658-3518

LIMNOLOGY FRESHWATER BIOLOGY

www.limnolfwbiol.com

Standard test method for mercury content evaluation in solid mineral fuels

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ABSTRACT. In addition to carbon, oxygen, hydrogen and nitrogen, fossil fuels contain other chemical elements, some of which may be hazardous to human health and the environment. Mercury and its compounds are one of the most dangerous among them. Therefore, information about mercury contents in coals and products of their processing is extremely important for both mining and processing enterprises and consumers. Mercury compounds may be accumulated in coal mining and processing wastes, and if they transfer into water-soluble forms, may lead to damaging of the environment. In the view of above, a standard method for the determination of mercury content has been developed, which is applicable not only to coals and products of their processing, but also to coal mining and combustion wastes. Also, to control the correctness of measurements by the developed method, reference samples with a certified mercury contents were developed.

Keywords: coal, mercury contents, wastes of coal mining and processing, instrumental methods

1. Introduction

Fossil coals are characterized by various quality indicators. These include ones allowing characterization of coals applicability for energy and coke production; their behavior during processing. Also, there exist indicators allowing for evaluation of environmental safety of coals extraction and utilization.

Mercury contents in coals is one of the indicators of their processing safety. Mercury is one of the most dangerous elements in coals. In this regard, the mercury content in coals is regulated in many countries, including the People's Republic of China. The latter determines the assessment of the mercury content during export of Russian coals.

Mercury can be found in coals in various forms: mineral (silicate and pyrite) and organic (Duan et al., 2017). The form of mercury in coal determines its redistribution during processing (sorting, benefication, combustion, cokemaking, etc.). When coal is burned, mercury compounds can either escape into the atmosphere with flue gases, or concentrate in slags (Boron and Wan, 1990; Streets et al., 2018).

When mercury is concentrated in waste products from combustion and coal mining, there is a risk of its emission into the environment in water-soluble forms. This increases the risks of adverse effects of mercury compounds due to bioaccumulation (Koval et al., 2000).

2. Materials and methods

In the Russian Federation, the determination of mercury content in fossil coals is regulated by the standard method GOST 32980-2014 "Solid mineral fuel. Determination of total mercury content". The essence of this method consists of burning a sample of solid fuel in a calorimetric bomb in an oxygen atmosphere in the presence of a solution of nitric acid. The mercury compounds formed during combustion are absorbed by the nitric acid solution. The bomb is thoroughly washed with water, after which the nitric acid solution from the bomb and the washings are combined and then filtered. The mercury compounds that have been recovered from the sample of fuel are reduced with tin chloride. Mercury is determined by cold vapour atomic absorption spectrometry with a mercury lamp (wavelength of 253.7 nm).

However, the practical implementation of this standard has shown a rather low reproducibility of results when testing high-ash fuels, which is due to the lack of completeness of mercury extraction. Also, the scope of this standard does not include solid waste from the mining and processing of fossil coals. In this regard, a method was developed for determining the mercury content in coal mining and processing wastes, subsequently approved in the form of a national

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Received: August 18, 2022; ***Accepted:*** August 18, 2022;
Available online: August 22, 2022

standard GOST R 59176-2020 “Solid mineral fuels. Determination of mercury by direct combustion”.

3. Results and discussion

The method is based on the thermal decomposition of the sample. This decomposition is accompanied by atomization of mercury, the transfer of atomic mercury into the analytical cuvette of the analyzer by air flow and the measurement of atomic absorption of mercury at a resonant wavelength of 253.7 nm. The mass fraction of mercury in the sample is determined automatically by the peak area (analytical signal) on the basis of a pre-set calibration characteristic using the apparatus software.

This standard method was developed taking into account the main provisions of the standard ASTM D6722-11 “Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis”. The key advantage of the method is the possibility of its implementation on modern domestic equipment - an atomic absorption spectrometer with a module for generating “cold vapor”. When testing the method, an analyzer of the mass concentration of mercury vapor RA-915M (LUMEX-AHK, St. Petersburg, Russia) was used. This device provides high performance analysis and allows analyzing up to 20 samples per hour (when including parallel samples - up to 10 ones). The use of the PA-915M analyzer and similar devices makes it possible to introduce an instrumental express method for determining the mass fraction of mercury into the practice of testing laboratories. Its implementation minimizes the influence of the operator on the testing process, and, as a result, the magnitude of the operator’s error. The high throughput of the equipment makes it possible to apply the method at those stages of the life cycle of coal products, where the speed of results is extremely important. E.g., in the operational management of the flow of mined coal or when coal products pass through the borders of states.

To ensure the quality control of measurements in the implementation of this method, work was also initiated to create reference samples of mercury content in coal and rocks. At the moment, the reference samples are undergoing the certification procedure. Table shows their preliminary characteristics.

The implementation of the standard makes it possible to determine the mercury content in coal, overburden rocks, tailings and coal combustion wastes in the range from 0.010 to 4.000 g/t, which fully covers the ranges of mercury content in these objects. E.g., the average content of mercury in coals varies in the range of 0.05-0.3 g/t (Krylov, 2016), and in solid fuel combustion wastes it can reach 3.5 g/t (Yudovich and Zolotova, 1994).

Table. Characteristics of reference samples of fossil coals, rocks and wastes from coal mining and processing.

RS	Material for the manufacturing of a reference sample	Hg^d, ng/g average
IRS-1	Hard coal	8.4
IRS-2	Hard coal concentrate	265.0
IRS-3	Hard coal	1834.3
IRS-4	Waste of brown coal combustion	2.0
IRS-5	Waste of coal concentrate combustion	287.9
IRS-6	Sandstone	9.3
IRS-7	Claystone roof of coal seam	26.4

4. Conclusions

Standard method was developed for determination (by direct combustion) of mercury contents in solid fossil fuels and wastes of their mining and combustion. The materials have been proposed for manufacturing of the reference samples of mercury contents in coals and wastes from coal mining and combustion.

Acknowledgements

The work was carried out within the framework of the Strategic Academic Leadership Program “Priority 2030”.

Conflict of interest

Authors declare no conflict of interest.

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