



Determination of mercury thermospecies in coal



Nikolay R. Mashyanov^{a,*}, Sergey E. Pogarev^a, Elena G. Panova^a, Nikolay Panichev^b, Vladimir Ryzhov^c

^a St. Petersburg University, St. Petersburg 199034, Russia

^b Tshwane University of Technology, Pretoria 0001, South Africa

^c Lumex Analytics GmbH, Wakendorf II, 24558, Germany

HIGHLIGHTS

- A technique for mercury thermospeciation study is proposed.
- Coals can be divided into three groups by prevailing of low-, mid-, and high-temperature Hg species.
- The technique can identify mercury bond by sorption and to sulfides lattice.
- Points of mercury accumulation in coal matrix and inclusions were revealed.

ARTICLE INFO

Article history:

Received 12 October 2016

Received in revised form 23 March 2017

Accepted 28 March 2017

Available online 5 April 2017

Keywords:

Coal

Mercury

Thermoscanning

ABSTRACT

The mercury concentration in coal varies in a wide range with the world average (the Clarke value) of 100 ppb. Mercury in coal can be represented by various forms having different matrix binding energy that govern different properties and behavior both in geochemical cycling and in technological processing. The technique of gradual heating (thermoscanning) of samples based on standard available equipment was developed to reveal and study the dynamic behavior of mercury release from coals. Analyses of coals of different types from deposits in Russia, Ukraine, and South Africa revealed the presence of various mercury thermospecies, part of which can be attributed to adsorbed elemental mercury and mercury bound to pyrites. Microprobe analysis exhibited points of mercury accumulation up to tenths of percent by weight within coal organic matrix and mineral inclusions. The thermoscanning technique gives additional information about mercury speciation in coal for better understanding of mercury geochemistry in fossil fuels and also for enhancement of the coal pre-treatment technology before combustion or gasification to reduce mercury emission to environment.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The latest UNEP Mercury Assessment of 2013 indicates that the coal combustion is the second largest (after artisanal and small-scale gold mining) source of the anthropogenic mercury contributing 24% of global mercury emissions to the atmosphere [1]. The mercury (Hg) concentration in coal varies in a wide range of more than five orders of magnitude, from values less than 1 ppb up to 300 ppm with the world's average of 100 ppb [2]. Generally, the mercury content in coal is governed by geological position of the coal deposit and syngenetic or subsequent geochemical processes rather than by the coal type [3]. Geological transformation, such as metamorphism and subsequent hydrothermal activity, generates various Hg species in coal and bearing strata. Mercury in coal

can be represented by syngenetic mercury initially bound to organic matrix; by sorbed and occluded elemental mercury; isomorphous in sulfides; and bound to silica (mainly clays) minerals. These Hg species show different properties and behavior both in geochemical cycling and in technological processing, including coal preparation, burning, or gasification. However, commonly only the total mercury concentration in coal is studied.

At present, atomic absorption spectroscopy (AAS) is the main method of the total Hg determination in coal using four standard methods of sample preparation [4]. They differ from each other mainly in the way of sample preparation: by bomb combustion (ASTM D3684, ISO 15237); by acid extraction (ASTM D6414, EPA 7471); by wet oxidation (ASTM D6414), and by thermal decomposition (EPA 7473, ASTM D6722). The most important disadvantage of the first three methods is the extremely difficult procedure of sample preparation arising from the necessary decomposition of the solid coal samples. The method of direct combustion of solid samples of coal does not require any chemical treatment; hence,

* Corresponding author.

E-mail address: nrm@lumex.ru (N.R. Mashyanov).

the total time of analysis is drastically reduced to less than 5 min [5]. Direct combustion is also used in the USEPA 30B method to analyze mercury collected at charcoal traps.

The study of Hg speciation in coals is important for better understanding of mercury geochemistry, in particular, its migration and accumulation in coal. Along with the information about total mercury concentration in coal samples, the knowledge of the mercury portions releasing within definite temperature intervals can be useful for implementation of effective and low-cost reduction of mercury in pre-combustion and pre-gasification coal treatment [6–9]. The mercury species have different matrix binding energy and can be determined by the so-called thermoscaning technique based on the real-time detection of mercury release from a sample during its gradual heating. The method of thermal decomposition, or thermoscaning, has been used for studies of thermospectra of mercury in ores, rocks, and soils [10–12]. Most of these data have been obtained with laboratory experimental setups using mixtures of pure chemical Hg compounds as samples or these with simple matrices [13–16]. The data on the temperature of the mercury species decomposition show significant uncertainty even for pure chemical compounds, because various parameters of the instrumental setups and measurement procedures used in the experiments did not ensure acquisition of comparable data. Even much more limited data are obtained for coals, for which main studies were focused on evaluation of the percentage of mercury released at definite temperature intervals [17–19] or involved complicated time-consuming procedures [20]. In this study, we used a set of a standard RA-915M Zeeman mercury atomic absorption spectrometer coupled with a PYRO-915 pyrolysis attachment (Lumex Instruments) [21], which enables gradual heating of the sample and continuous monitoring of the releasing mercury and value of non-selective absorbance. The measurement procedure was optimized to study the Hg thermospecies in coal and other solid samples.

2. Materials and methods

2.1. Experimental set

The set of the standard RA-915M mercury analyzer and PYRO-915+ attachment (Lumex Instruments) was used for thermoscaning of samples. The PYRO-915+ attachment consists of the double-chamber atomizing system combined with the heated analytical cell (Fig. 1).

The temperature inside the first section of the atomizer (Programmable evaporator) is varied under control of the dedicated RAPID software. The second section (Catalytic converter) and the optical analytical cell are constantly heated at 750 °C to avoid atomic mercury recombination with chlorine and other oxidants.

A sample is placed into a quartz boat, which is inserted into the evaporator, where temperature is varied from ambient to 850 °C. The released mercury and other volatile compounds are transferred through the catalytic converter (where complete combustion of remaining volatile organic compounds occurs) to analytical cell.

The Zeeman background correction provides high selectivity of the mercury determination in samples with complex matrices [21]. Real-time measurement enables real-time record of the process of the Hg release from a sample with a response time of 1 s. Concurrently, the optical density of the background absorption D is also measured in real time. As it is known, $D = \ln(I_0/I)$, where I_0 and I are the intensities of the analytical radiation at the inlet and outlet of the optical cell, respectively. Due to the high selectivity of the Zeeman background correction, an increase in the optical density in the analytical cell up to the value of $D = 2$ does not lead to a false signal. The real-time record of D makes it possible to qualitatively control processes of the matrix decomposition, such as organic matrix burning and SO_2 release during destruction of sulfide minerals (see Section 3.3).

The set was calibrated with NIST-traceable stock mercury solution covering the whole range of the mercury content in samples (from 10 ppb to 10 ppm). Precision and accuracy were determined using coal standard reference materials SARM-19 (200 ppb) and SARM-20 (250 ppb), both are bituminous South African coal. Periodic control shows long-term (for months) stability of the calibration. Absolute limit of detection (LOD) of total Hg determination in coal, defined as 3 s (standard deviation) from ten blank measurements, was found to be 0.2 ng. For typical mass (200 mg) of coal, used for the analysis, the LOD of Hg determination in concentration unit was 1 ppb; measuring range is 1–10,000 ppb; precision is 4%; accuracy is 7%; analysis throughput is 15–20 samples per hour.

Experiments with various types of coals and other solid matrices made in four involved laboratories show good reproducibility of mercury thermospectra (see part 2.2), and the optimized measurement procedure can be used to obtain the comparable data in any laboratory having this standard equipment.

For this study, 90 samples from 44 coal deposits in Russia, South Africa, and Ukraine were collected and analyzed for total mercury; mercury thermospeciation was studied in 30 samples. In addition, 40 samples were analyzed with a TESCAN VEGA II LMU scanning electron microscope coupled with Energy Dispersive Spectroscopy (EDS) Analyzer Oxford INCA ENERGY 450/XT at St. Petersburg State University's Resource Centre "Geomodel".

2.2. Optimization of the thermoscaning procedure

The thermoscaning procedure is similar to a standard one for total mercury described in 2.1, differing only by gradual

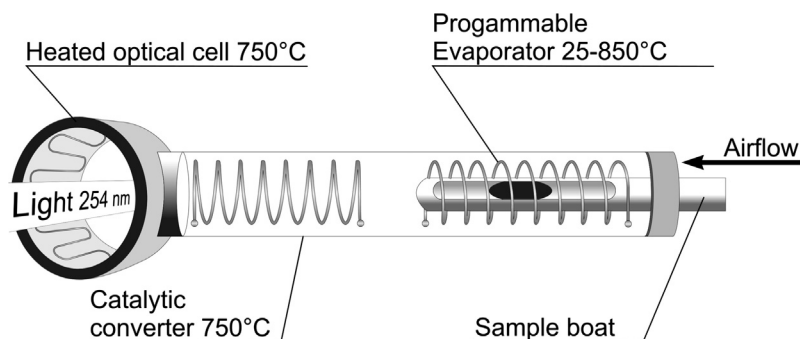


Fig. 1. Thermoscaning system: PYRO-915 + double-section atomizer and heated analytical cell.

Download English Version:

<https://daneshyari.com/en/article/6474511>

Download Persian Version:

<https://daneshyari.com/article/6474511>

[Daneshyari.com](https://daneshyari.com)