MERCURY OCCURRENCE IN SHUNGITE AND COAL

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Mercury cycling in the environment

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Introduction

Shungite is a mineraloid consisting of up to 99 % of carbon.

Shungite matter is considered as a specific allotrope of carbon having complex globular supramolecular structure including up to 0.001 % of natural fullerenes.

Deposits of shungites are located within the Paleoproterozoic host rocks in Karelia (NW of Russia) and represent the greatest accumulations of carbon with reserves of up to one billion ton.

Surprisingly high mercury concentration with an average of 2200 (median 1100) ppb was found in the studied shungite samples that is much higher as compared to the coal mercury clarke value of 100 ppb.

We made comparative study of total mercury and mercury thermospeciation in the Karelian shungites and mercury-containing hard coals from Donbass basin.

Shungite and Coal

Total mercury and mercury thermospeciation were studied in 19 shungite samples from Karelian deposits and 20 hard coal samples from Donbass coal mines (Ukraine)

Shungite, Zazhogino deposit, Karelia

C content 98%, total Hg 1100 ppb

Anthracite, Gukovskaya mine, Donbass

C content 92%, total Hg 390 ppb

Experimental

1 - RA-915M spectrometer

2 - PYRO optical cell

3 - PYRO atomizer

4 – sample boat

5 - PYRO controller

The set of the standard RA-915M mercury analyzer and PYRO-915+ attachment (Lumex) was used for total mercury and mercury thermospecies determination*.

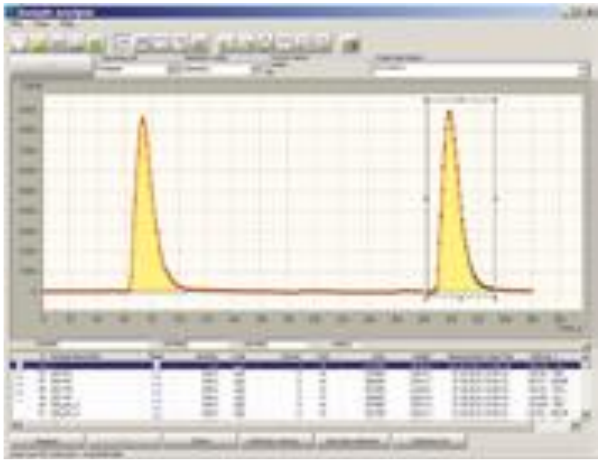
** Fuel (2007), V.203, 973-980. https://doi.org/10.1016/j.fuel.2017.03.085*

Total mercury determination

1. Weighing

2. Sample introducing

3.Measurement & calculation



Direct pyrolysis Sample: 100 – 300 mg

Overall time for analysis: 1 – 3 min

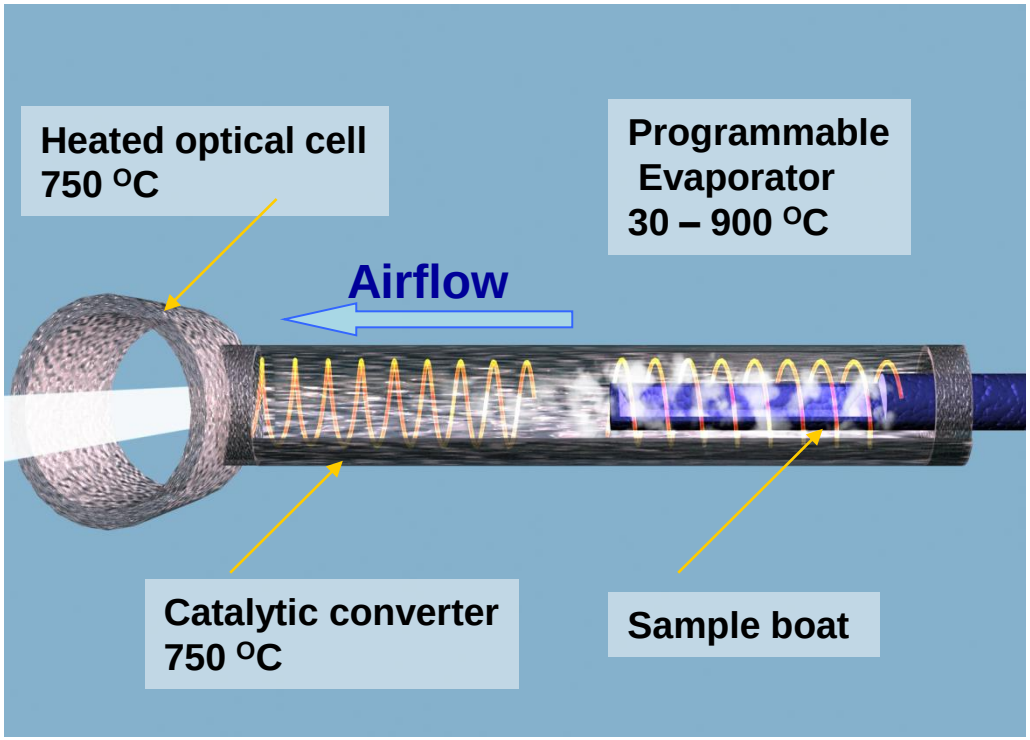
Limit of Detection: 1 – 2 ppb

Calibration with NIST-traceable stock mercury solution

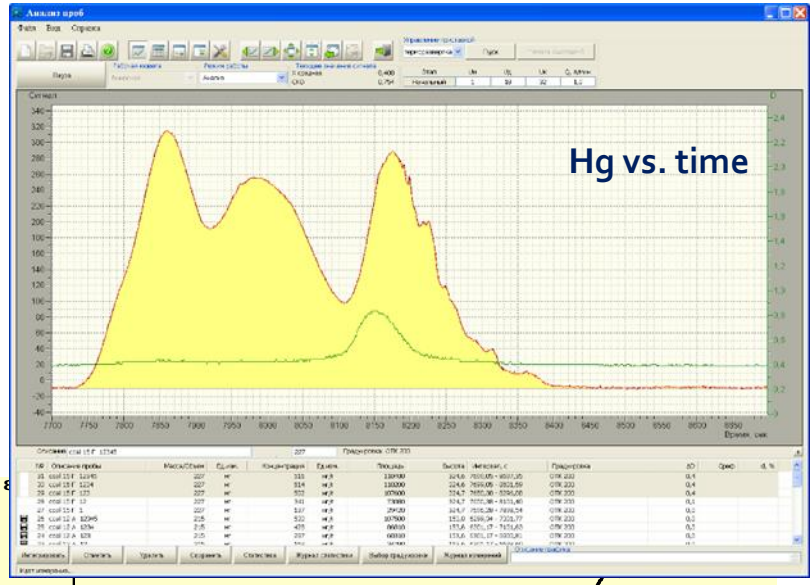
Validation with coal SRMs: SARM-19 and SARM-20

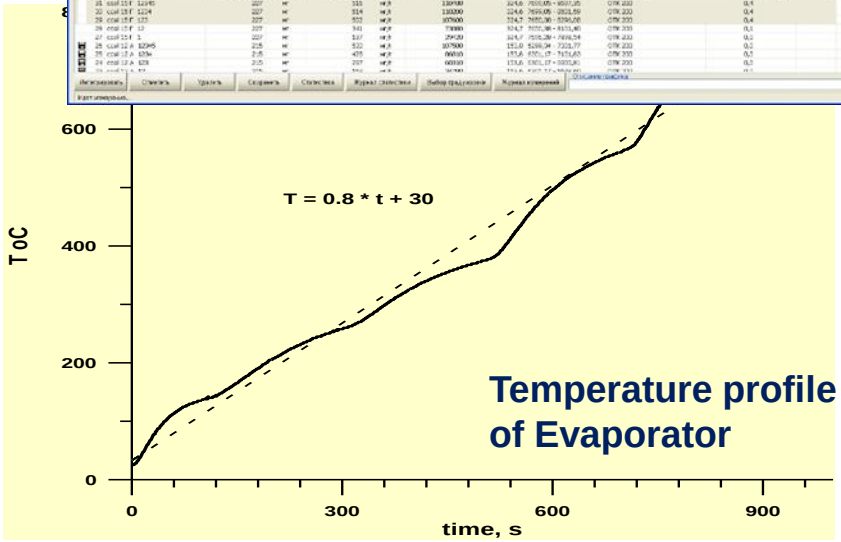
Precision 4% Accuracy 7%

Thermoscanning: linear heating of the samples



PYRO-915 Atomizer and Analytical cell

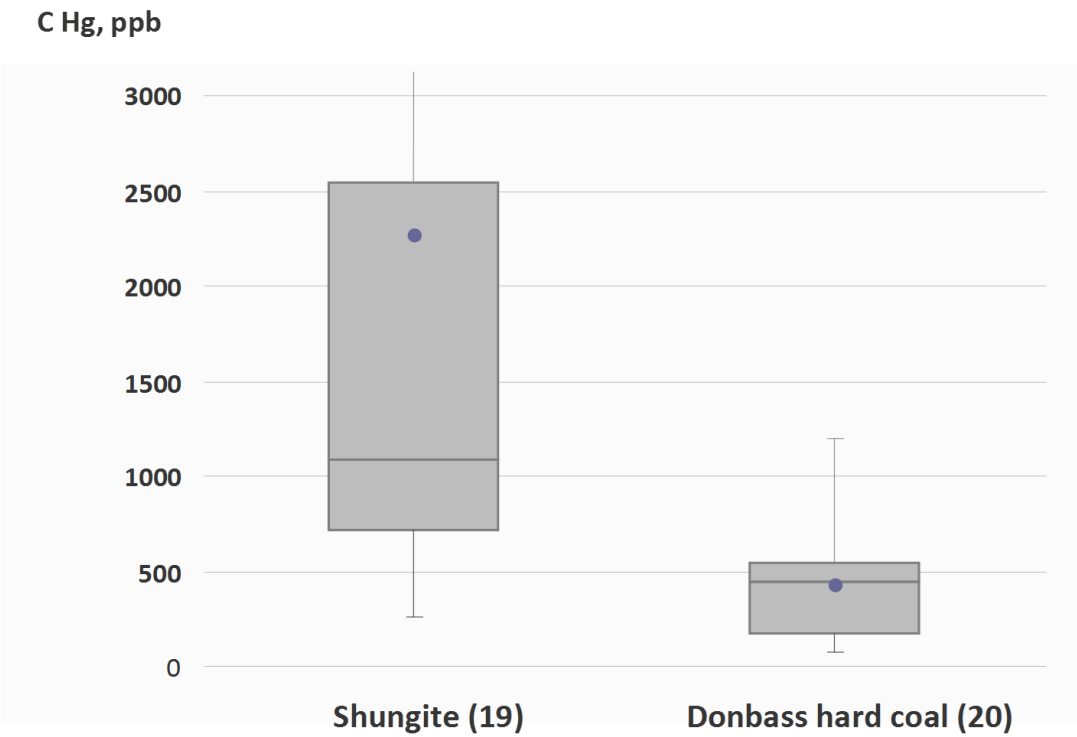




Linear heating: from ambient to 900 °C; rate: 45 °C/min;

Hg release detection: real time, continuous (1 s).

Total mercury in shungite and Donbass coal

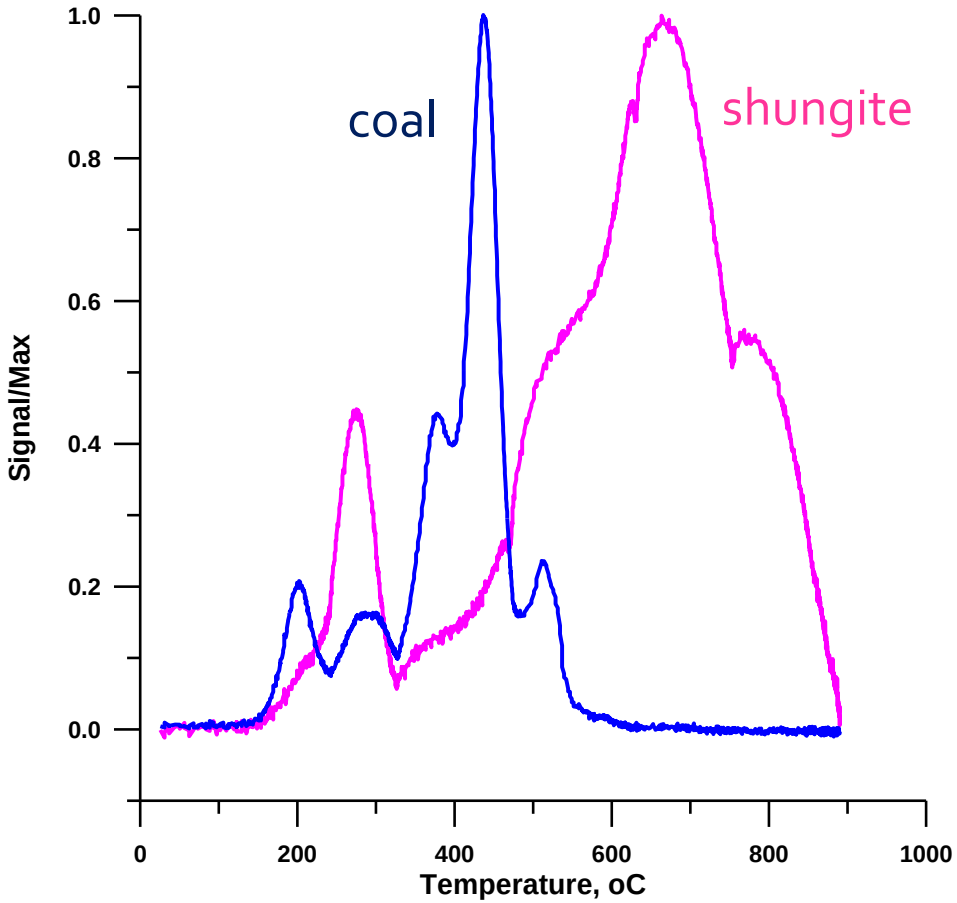


Box-and-whisker plot:

- median (midline),
- average (dot),
- 25th and 75th percentiles (box edges),
- 5th and 95th percentiles (whiskers).
- In brackets – number of samples

The Hg concentration in shungites from Karelia is significantly greater than in mercury-enriched hard coals from Donbass.
Donbass coal mines are located within Karpinski mercury belt; no mercury-bearing structures and deposits in Karelia are known.

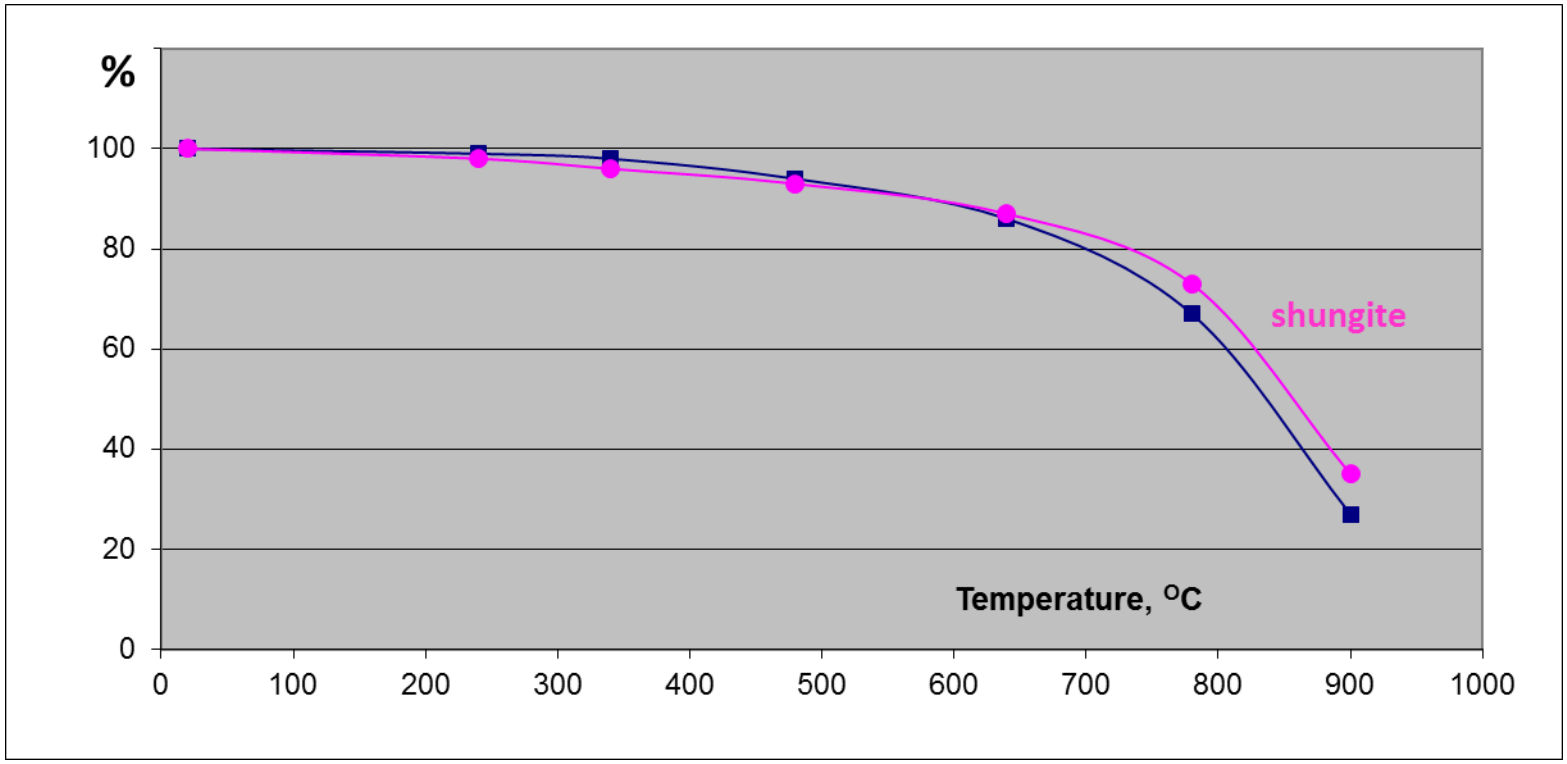
Mercury thermospectra of shungite and coal



Thermoscanning technique reveals occurrence of high-temperature form of mercury in Karelian shungites releasing at temperature > 640 ^{o}C and comprising 39-45% of total Hg.

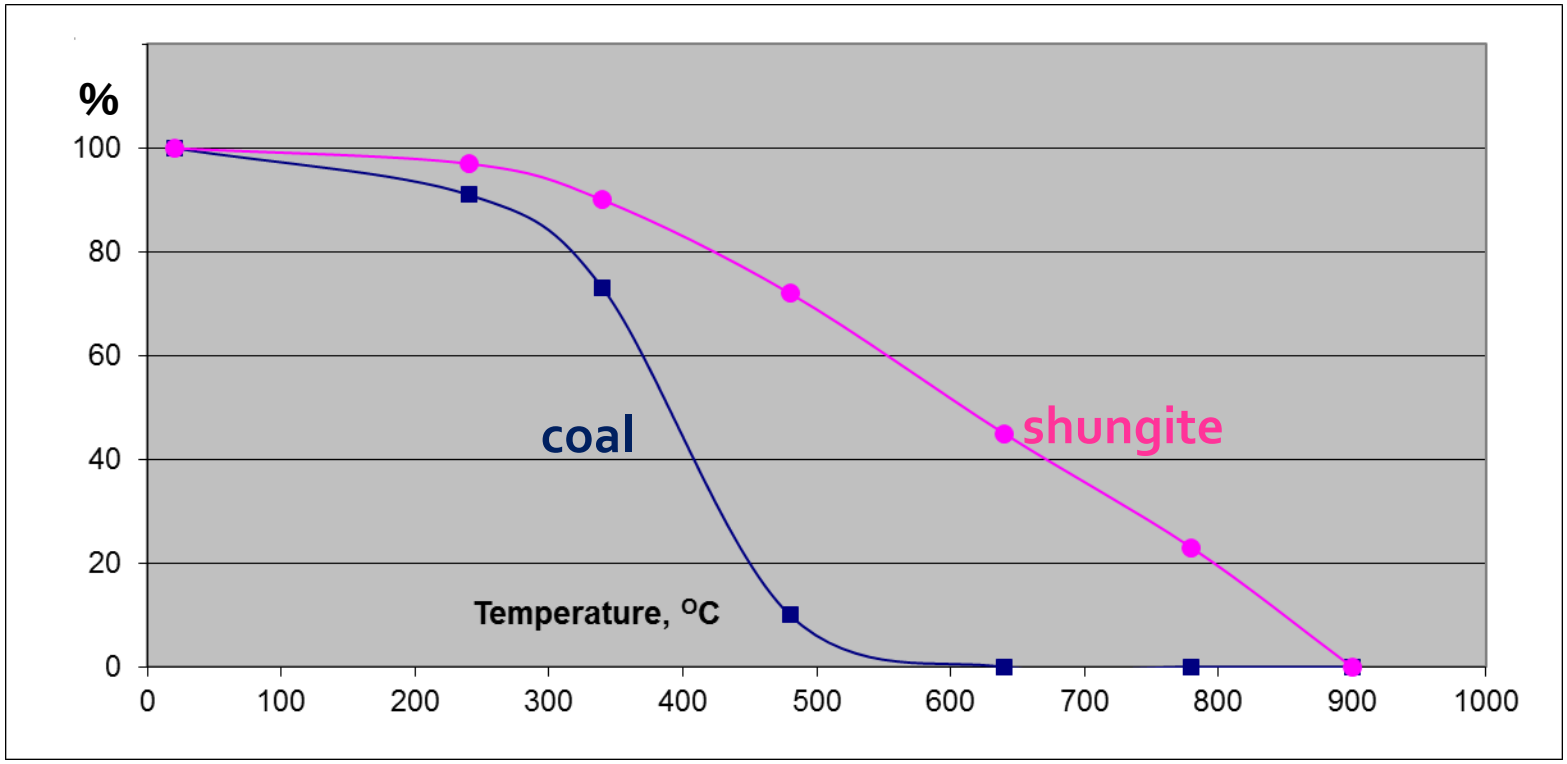
It drastically differs from thermospectra of Hg-enriched Donbass coals, where main portion of mercury is released in a temperature range below 640 ^{o}C.

Shungite vs coal: loss of mass



Loss of mass upon heating is similar for shungite and coal

Shungite vs coal: loss of mercury



Loss of mercury upon heating is much faster in coal than that in shungite

Mercury sorption by shungite matter

High sorption capacity of shungite is well known. Two potential mechanisms of the shungite mercury enrichment were tested: from gaseous phase with atomic Hg(0) and from “hydrothermal” solution with ionic Hg^{2+}.

The shungite sample with the initial total mercury content of 730 ppb and grain size < 0.5 mm divided it two parts was exposed for 30 days to a high mercury concentration: to saturated Hg vapour and to solution with $Hg(NO_3)_2$ concentration of 10 mg/L.

Both experiments showed total mercury 53- and 22-fold increase after Hg(0) and $Hg(NO_3)_2$ exposures, respectively.

In both cases, no noticeable change in portion of the high-temperature species (above 640 ^{O}C) was observed.

Conclusion

A high mercury concentration up to 12,000 ppb with 2200 average and 1100 ppb median was found in all shungite samples, which is much higher than the Hg concentration in the Hg-enriched coal from Donbass mercury belt having average 460 and median 440 ppb of total mercury.

For the first time, the thermoscanning technique revealed firmly bound, high-temperature form of mercury in shungites releasing at temperature > 640 ^{O}C. It drastically differs from coals, where main portion of mercury is released in a temperature range below 640 ^{O}C.

Exposure to both Hg vapour and ionic mercury does not increase the content of the high-temperature form of mercury specific for shungite.

The occurrence of unusual, high-temperature form of mercury can be explained within a hypothesis of the shungite genesis due to the mercury-rich mantle methane jets pyrolysis that brings about the presence of fullerenes in the shungite matter.